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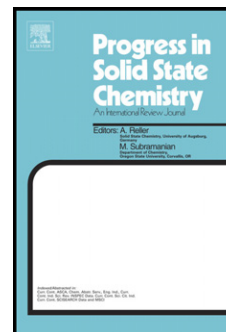
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Role of structural defects in olivine cathodes

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Abstract

The high rate capability and structural stability of the olivine phosphates attracted a lot of interest as promising cathode materials for high energy density batteries. Alteration on these cathode materials, for instance, reducing particle size, conductive coating and metal ion doping were performed in order to improve the conductivity and to obtain high specific capacity. Wide range of transition metal ions with range of valences (M^{1+} to M^{5+}) was successfully doped both in M_1 site (Li) and M_2 site (M) of olivine $LiMPO_4$ ($M = Fe, Mn, Co$ and Ni) cathode. The large charge difference between the doped supervalent ions and M cations at the M_2 site, limited the use of supervalent cations in the olivines. However, the supervalent dopants (namely; Cr^{3+} , Ti^{4+} , Nb^{5+}) are reported to be successfully substituted in the olivine with an improvement in electrical and ionic conductivity. The amount of defect can be reduced by low concentration of dopants, choosing suitable synthesis method and optimized reaction conditions. Charge compensation vacancies accomplished through aliovalent doping reduces the grain size and widens the Li^+ migration path resulting in faster Li^+ diffusion. However, the drastic improvement in electrical conductivity for the aliovalent doping is still unclear. Rather writing a lengthy standard review, this manuscript intends to describe briefly the lattice defects owing to metal ion doping and its influence in improving the cathode performance of the olivine phosphates. This gives a new approach in this field.

Keywords: Olivine phosphates; structural defect; isovalent doping; supervalent doping.

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Introduction

Crystalline LiMnPO_4 was originally synthesized by Zambonini and Malossi in 1931 [1], since then olivine phosphates containing iron and manganese as transition metal cations were started evolving. Later, in 1960's, many investigations were made on these olivine phosphates but all are limited to crystallographic studies and then determining their magnetic properties to a greater extent [2-4]. In 1997, Padhi et al. demonstrated the electrochemical energy storage capability on these olivine phosphates for the first time on using LiFePO_4 as a cathode for rechargeable battery applications [5]. The high rate of discharge capacity, excellent columbic efficiency and high structural stability (strong P – O covalent bond in the orthorhombic lattice) has made the olivine – type compounds as attractive cathode materials than the layered (or) spinel oxides for high energy rechargeable batteries [5]. The olivine crystal structure has an orthorhombic lattice with hexagonally closed packed (hcp) oxygen atoms, corner-shared MO_6 octahedra, edge-shared LiO_6 and tetrahedrally coordinated PO_4 polyanions

Since 1997, heaps of work has been performed to establish this olivine-type cathode LiMPO_4 with different transition metal cation substitutions, such as $M = \text{Fe, Mn, Co}$ and Ni [6-9] for energy storage applications. It is well known that the conventionally available non-aqueous electrolyte falls within the voltage stability window ranging between 3.5 and 4.5 V. This limits the high operating voltage cells containing Co or Ni as transition metal cations, for instance, LiNiPO_4 as cathode [7] has the redox potential ($\text{Ni}^{2+/3+}$) over 5.1 V. While in the case of LiCoPO_4 cell tested under the distinct electrolyte LiPF_6 in EC:DEC, the material exhibited a voltage plateau at 4.8 V but the cyclability and cell capacity (167 mAh/g) are reported to be quite marginal [9]. These issues hindered the potential use of LiCoPO_4 and LiNiPO_4 as cathodes for lithium batteries widely. On the other hand, LiMnPO_4 is an eco-friendly and convincing candidate of the olivine family as it has a compatible redox couple

(4.1 V), ensuring a high energy density at a potential within the safe voltage window of the commercial electrolytes. Unfortunately, this material suffers from lattice distortions due to Jahn-Teller effect of Mn^{3+} ions that resulting in low capacity and low electronic conductivity [9]. Further, the unstable nature of the charged MnPO_4 makes this material less cycleable and not suitable for high performance cathode. In this context, LiFePO_4 gains more attention among the family of the olivine-type cathode. This is mainly due to its low cost, non toxicity, high stability, high deliverable capacity (170 mAh/g) and compatible operating voltage (3.45 V versus Li) with the available commercial electrolytes [9].

The conventional non-aqueous electrolytes commonly used are with LiPF_6 salt in the mixture of propylene carbonate (PC), ethylene carbonate (EC) and dimethyl carbonate (DMC) [10]. Similar to non-aqueous (organic solvents) electrolytes, many aqueous electrolytes with Li salts are also demonstrated for high voltage battery applications [11]. This approach has several merits over organic solvent as electrolyte in lithium batteries, including greater safety and low cost [12-13]. The important features include high rate operation, better reversibility and longer cycle life. Also, the non reactive electrolyte and low ohmic electrode-electrolyte interface of aqueous battery provides good capacity retention and fast Li^+ diffusion. Recently, we had shown the redox behavior of the olivine cathodes in LiOH aqueous electrolyte and its electrochemical performance after multiple cycling [12 - 15]. The mechanism through which electron transfer reactions occur in the presence of aqueous LiOH electrolytes is reported by us to be identical to the known behavior of these olivine phosphates in non-aqueous electrolytes.

Another serious setback of the olivine phosphate is low electrical and ionic conductivity. To increase the conductivity, various efforts were made by synthesizing the olivine with enhanced properties such as nanostructured material, reduced particle size, conductive coatings and doping. These factors are proved to be useful with increasing active

material utilisation and a better cyclability. Materials science paves the way that the improvement in conductivity of olivine cathode material can be achieved through the crystal defects nucleated while tailoring one of the above said factors [16-17]. Defects are defined as slight deviation in the crystal lattice from its perfect atomic arrangement, and few to be listed are; volume defect leads to porous nanostructure, lattice confinement leads to reduced particles, conductive carbon or metal ion coating nucleates surface defect and the metal atom doping results in point and line defects.

The major goal of this review is to highlight the structural defects owing to doping and formation of metal ion complex in M_1 and M_2 site of the olivine LiMPO_4 crystal system. Theoretical and experimental determinations of the changes in lattice parameters owing to these alterations are discussed in this review. The change in Li^+ ion mobility and specific capacity are correlated with the concentration of the structural defects.

Discussions

(a) Structure of phase pure LiMPO_4

The olivine structure LiMPO_4 (Fig. 1) exhibits orthorhombic structure with Pnma space group, wherein it consists of a PO_4 tetrahedral unit sharing the corners with M^{2+} ions and edges with Li^+ ions on octahedral positions and forms a linear chain running along the b axis [6]. Vadivel Murugan et al., [7] have synthesised single-crystalline LiMPO_4 with different transition metal cations, such as $M = \text{Mn, Fe, Co, Ni}$ via microwave assisted sol-gel route. These metal cations are mostly preferred to synthesize in olivine structure invariably as the size of the ionic radius for the Fe, Mn, Co and Ni are quite similar. Figure 2 shows the XRD patterns of the olivine phosphate LiMPO_4 with $M = \text{Mn, Fe, Co, Ni}$, synthesized by identical reaction conditions and the $(h k l)$ indices corresponding to the peaks are also indexed.

(b) Defects due to doping in *M* site

Prior discussing the metal atom doping in *M* site of LiMPO_4 , a short overview on the structural and electrochemical behaviour of LiMPO_4 ($M = \text{Mn, Fe, Co, Ni}$) is given here. All the samples with different metal atom substitutions maintained the parent olivine structure, as displayed in the XRD pattern in Fig. 2 [7]. All the patterns are in single phase, however, a small peak shift was observed towards higher 2θ value and slight decrease in lattice parameters (Table 1) across the series Mn, Fe, Co, Ni [7, 9, 18] is also noticed. This observation is in accordance with Vegard's law and concedes with the theoretical value calculated by Fisher et al., [18-20] in Table 1. Although the ionic radius of Mn, Fe, Co, Ni are quite comparable, the binding energy between the metal ions and the electrostatic interaction varies, thus leads to this peak shift and change in lattice parameters. This change in interaction energy between *M* and O (or) Li also reflects in the redox voltage and specific capacity of the material (Table 1). For an interest, the above said transition metal cations were also substituted in the olivine and investigated extensively in aqueous batteries by the author's [12-15].

As discussed earlier, because of the unavailability of suitable electrolytes that can withstand the potential range of 5 V, cathodes including LiCoPO_4 and LiNiPO_4 have not gained much attention for high power battery applications comparing to their LiFePO_4 and LiMnPO_4 counterparts. However, given the higher voltage of Ni and Co cations, researchers have substituted these transition cations “doping” into LiFePO_4 and LiMnPO_4 cathodes with a general formula $\text{Li}(M'_xM_{1-x})\text{PO}_4$ ($M' = \text{Ni or Co}$ and $M = \text{Mn or Fe}$) to improve the overall cell voltage [9, 21-30]. A series of point defect such as vacancy and interstitial defects can be favored in the structure as a result of doping with different metal cations. This leads to change in binding energy between the transition metals and lithium ion in the structure, due to change in the ionic radius ($\text{Mn} = 0.83 \text{ \AA}$, $\text{Fe} = 0.78 \text{ \AA}$, $\text{Co} = 0.75 \text{ \AA}$, $\text{Ni} = 0.69 \text{ \AA}$). Gardiner

and Islam [21] estimated that Mn will have higher binding energy with Li than Fe. The change in lattice parameter upon metal atom doping was in agreement with the Vegard's law implying that the theoretical estimation is nicely coincided with the experimental values. The change in binding energy leads to Frenkel and Schottky defects in the system and hence the change in lattice parameter. It is understandable that the lattice constant is increased and decreased while increasing the concentration of Mn and Co in LiFePO_4 [9, 28], thus substantiating the fact that binding energy and lattice constant rely on ionic radius of the metal ion.

The increase in the concentration of dopants and its effect on the specific capacity of the olivine cathode was shown in Fig. 3a [9]. The changes in cell voltage and capacity of LiFePO_4 on substitutions with various concentrations of cations i.e. Mn, Co, Ni are displayed in Fig. 3b [9, 27-30]. The decrease in capacity of LiFePO_4 upon increasing the doping concentration of cations is due to formation of defect cluster in the system while the cell voltage increased from 3.5 to 4.7 V. Thus the interstitial defect induces electrostatic interactions between the defect regions that lead to agglomerated defect clusters, which restrict the Li^+ mobility resulting in poor capacity retention [21].

Apart from the above discussed transition metals, many other dopants having wide range of valences (1^+ to 5^+) are also been successfully substituted in the olivine structure and their change in electrochemical behavior was also investigated [16-18]. No change in charge concentration was found for isovalent doping i.e. Mg^{2+} , Zn^{2+} in M^{2+} sites of olivine structure [31-34]. The isovalent substitution shows little lower (intrinsic) energy with high specific capacity [18]. The dopants 1^+ and 3^+ were also found favorable in maintaining the olivine structure with small lattice defect that cannot be excluded. It's been reported that supervalent dopants (4^+ and 5^+) cannot be substituted in M^{2+} sites and were found unfavorable in maintaining the structural stability. This is due to the 4^+ and 5^+ substitutions in M^{2+} site of

LiMPO_4 that leads to high charge compensation due to the nucleation of structural defects (point defects) in the M_1 and M_2 sites [16-18]. Nevertheless, Fisher et al. [18] reported that small concentration ($\sim 3\%$) of the supervalent dopants can be successfully substituted into the olivine lattice, which facilitates the Li path wider that gives faster Li mobility. A small amount of Nb^{5+} doping in LiFePO_4 increases the conductivity from $\sim 10^{-8}$ S/cm to $\sim 10^{-6}$ S/cm [35]. However, it's an open question, how this supervalent doping and point defects can improve the electrical and ionic conductivity [18].

(c) Role of defects and synthesis conditions

Later, Meethong et al. [17] reported the optimal value of supervalent dopants that can be substituted into olivine lattice are about 10 % without any structural destruction and the amount of defects can be controlled by choosing suitable synthesis procedures and reaction conditions. To investigate the role of synthesis in forming structural defects, we synthesized our cathode ($\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{PO}_4$) by sol-gel synthesis using different chelating agents. The x-ray diffraction patterns (XRD) of triethanolamine (TEA) and polyvinylpyrrolidone (PVP) [36] assisted sol-gel synthesized materials are shown in Fig. 4. The obtained x-ray diffractograms for these two chelating agents were well aligned with the JCPDS pattern of parent olivine structures. However, in the PVP assisted sample (Fig. 4), a small peak split was seen for all the observed peaks although a single phase olivine compound was obtained. The metal complex formation mechanism with PVP polymer ligand depends on various factors like; oxidation state, electronic structure and radius of the metal ion. In the chosen $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{PO}_4$ cathode, Co and Ni ions have smaller ionic radius (135pm) than the Mn ion (140pm). The smaller ionic radius interacts faster with polymer to form complex matrix. Hence, smaller ionic radii of Co and Ni ions complex first with PVP and then the Mn bonding starts to initiate. Thus, due to the difference in ionic radii, complex formation

mechanism for Mn is delayed and resulted in a separate LiMnPO_4 phase. The existence of olivine phase compounds has two different lattice parameters due to different chelating agents (TEA and PVP). Consequently, this leads to a lattice mismatch and peak splitting. Hence, the role of synthesis, chelating agents and reaction temperature influences the amount of defects.

(d) Defects due to doping in Li site

Islam et al. [19] have simulated a module and calculated the possible diffusion path of Li ion (listed in Table 2) and required migration energy to reach the surface of LiMPO_4 . In the three possible orientations of diffusion path, Li migration was faster along (010) direction. This is due to shorter Li-Li separation distance that requires lower Li hopping energy. Fig. 5 shows the Li path along (010) direction, where Li ions diffusion is in one-dimensional path with non-linear curved trajectory between adjacent Li sites. Substitution of larger atom in Li site will inhibit the Li migration and trap down the Li mobility in the olivine cathode material [19].

XianHua and SheJun [37] reported that, while Na^{1+} or Be^{2+} have been doped in the M_1 (Li) site with the general formula $(\text{Li}_{1-x}\text{M}_x)\text{FePO}_4$, Na-doped LiFePO_4 showed higher electronic conductivity as well as local structural stability than the Be-doped LiFePO_4 . These authors have concluded that doping in Li-site with a partially filled light metal was found to have better performance than with the completely filled light metal ions. Moreover, doping of high valence cations nucleate cation vacancies and lattice tilt, to compensate the charge difference in the structure. Islam et al. [18] optimized that the defect created in Li site through doping (until ~3%) can enhance the electrical conductivity without affecting the crystal structure. Sung-yoon chung, et al. [38] doped series of metal cations ranging from valence 1+ to 5+ in low concentration (~ 1%) and showed the stability in olivine structure while achieving an improvement in capacity. The supervalent (3^+ to 5^+) dopants like Cr, Y, Ti, Zr

and Nb have been successfully doped in the olivine structure in low concentration without affecting the structural stability [38-43]. These dopant decreases the grain size due to cation vacancies created during charge compensation and also the presence of the dopant increases the size of channel for Li^+ diffusion. This feature has resulted in improving the electrical and ionic conductivity of the olivine cathode [38-43].

Similar defects can also be created by non-stoichiometric reactants i.e. excess or deficient Li ions [44 - 45] in the M_1 (Li) site of olivine. Synthesis of non-stoichiometric LiMPO_4 with excess and deficient Li leads to a formation of Li_3PO_4 and $M_3(\text{PO}_4)_2$ impurities respectively. Increase in the percentage of $M_3(\text{PO}_4)_2$ reduces the specific capacity of the olivine cathode than the Li_3PO_4 impurity. This is because Li_3PO_4 acts just as inert mass of the material during the electrochemical reaction [44 - 45]. The defects and lattice disordering due to the presence of M^{2+} in Li site or vice versa can be reduced by increasing the reaction conditions and its synthesis temperature. Fang et al. [46] reduced the defects of Mn^{2+} disorder by ~7% in synthesizing LiMnPO_4 while increasing the heating temperature from 120°C to 200°C in hydrothermal method. This decline in defects (Mn^{2+} disordering) influences an improved specific capacity of the material from 37 mAh/g (at 120°C) to 70 mAh/g (at 200°C) [46].

Summary and overview

The possible defects due to metal ion substitution on Li^+ and M^{2+} sites of LiMPO_4 were discussed and the influence of these defects in electrochemistry of the material are also correlated. The substitution of isovalent as well as polyvalent dopant cations on both Li and M site without affecting the olivine structure is feasible given that the optimized low concentration (~3%) of dopant, suitable synthesis method and reaction conditions are chosen appropriately. In the mixed dopants, metal ion formation depends on the oxidation state and the ionic radii of the metal ions. The defects and cation valences help in reducing the grain

size and increasing the Li migration channel size while giving high Li^+ mobility. However, the drastic change in electrical conductivity due to the lattice vacancy and defects created by supervalent doping is still unclear.

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Figure Captions

Fig. 1 Atomic arrangement of perfect LiMPO_4 olivine structure.

Fig. 2 X-ray diffraction of LiMPO_4 ($M = \text{Mn, Fe, Co and Ni}$) synthesised by Vadivel Murugan et al. [7].

Fig. 3 (a) Change in specific capacity upon increase in dopant concentration [9] and (b) Change in cell voltage and specific capacity on different metal ion complex [9, 28-29].

Fig. 4 X-ray diffraction pattern of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{PO}_4$ synthesized by TEA and PVP assisted Sol-gel and standard JCPDS patterns of olivine structures [36].

Fig. 5 Li diffusion along (010) direction in LiMPO_4 olivine [19].

Table 1 Change in lattice constant and electrochemical behavior for different metal ion substitution LiMPO_4 ($M = \text{Mn, Fe, Co and Ni}$).

Table 2 Possible Li^+ diffusion paths and Li^+ migration energy in olivine phosphates [20-21].

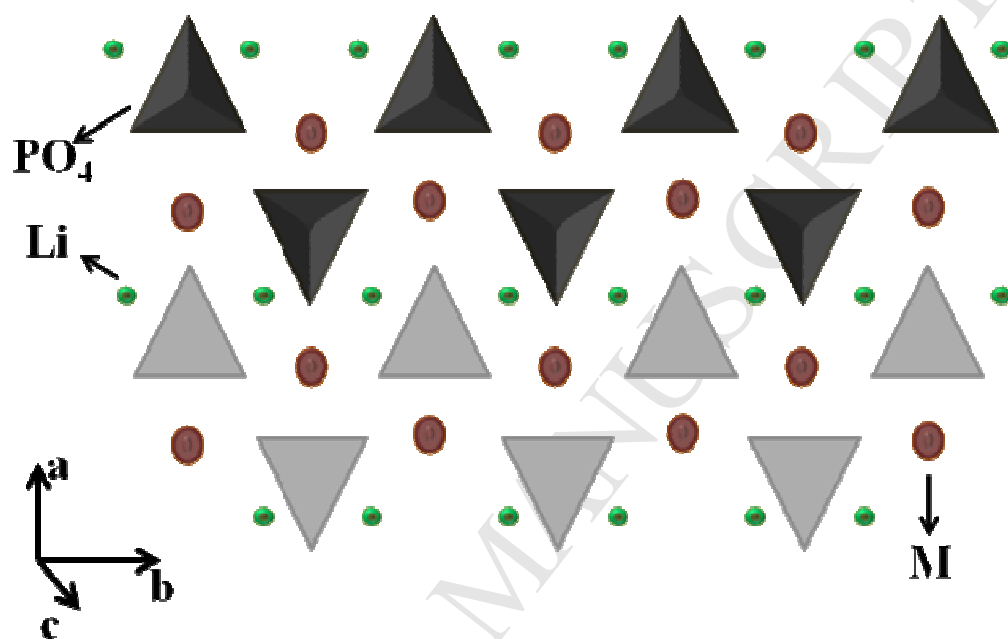


Fig. 1 Atomic arrangement of perfect LiMPO₄ olivine structure (without any crystal defects)

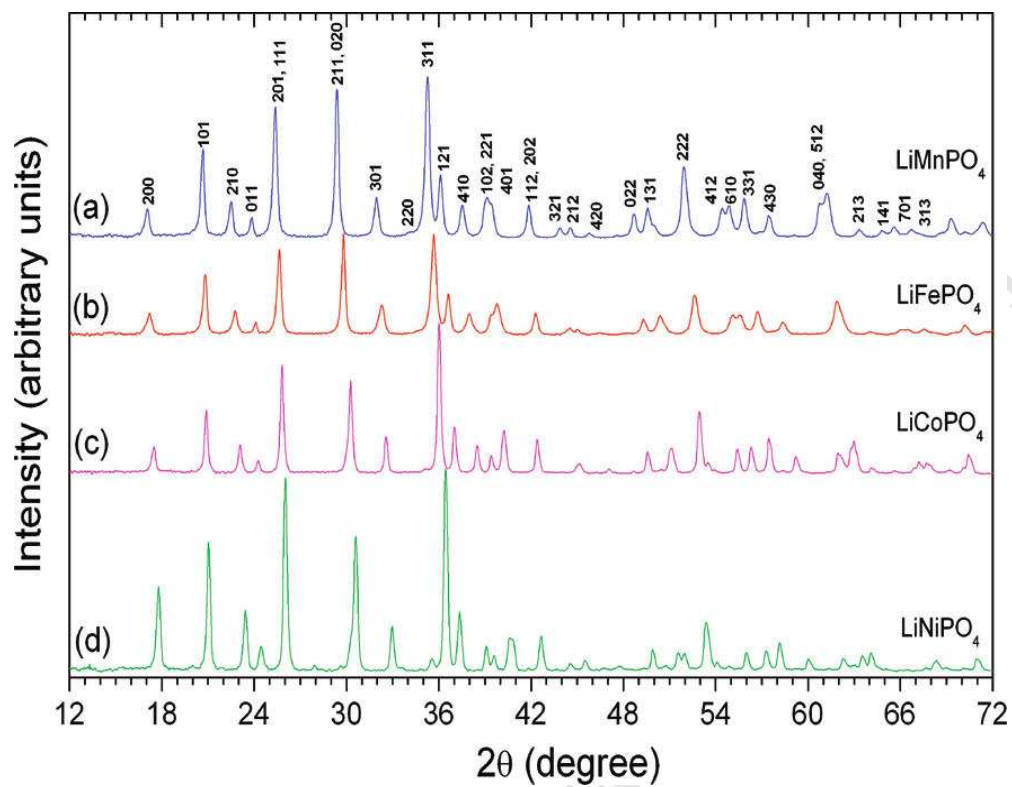


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Murugan et al. [7].

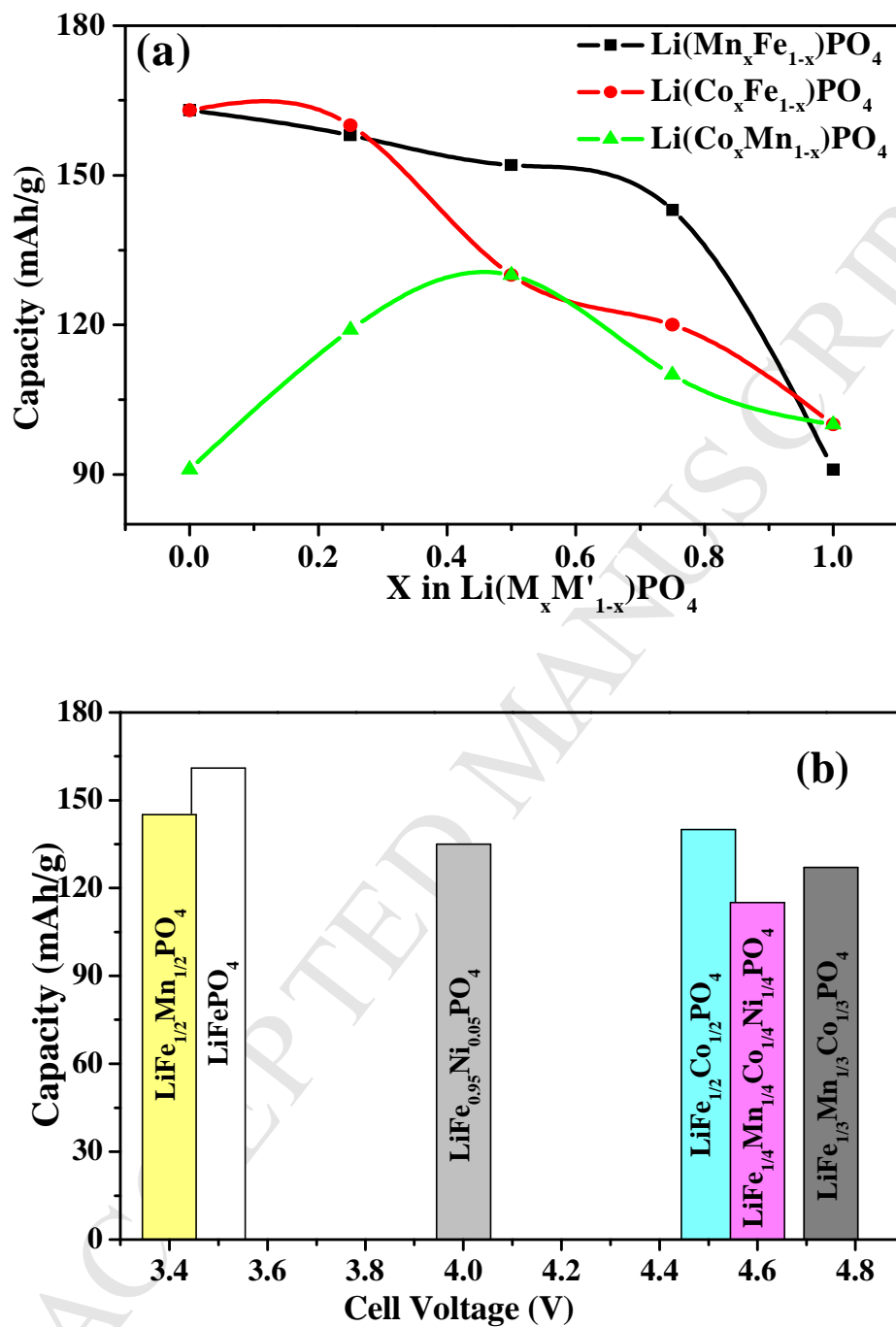


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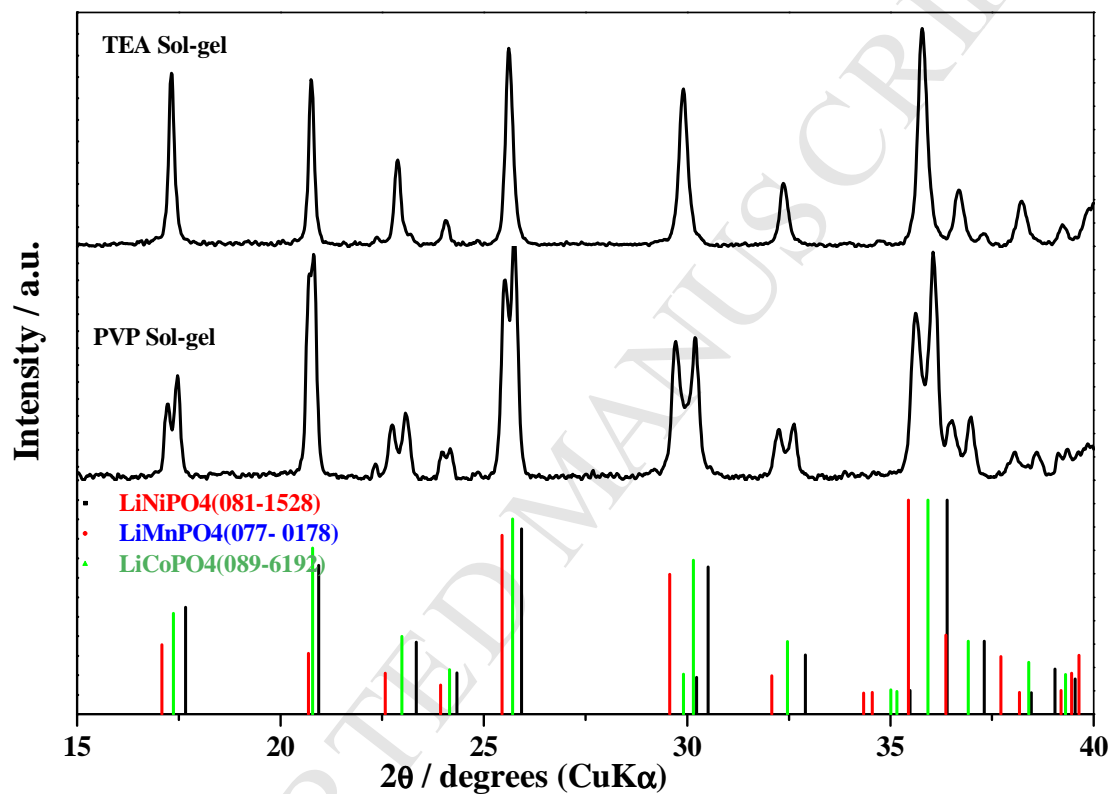


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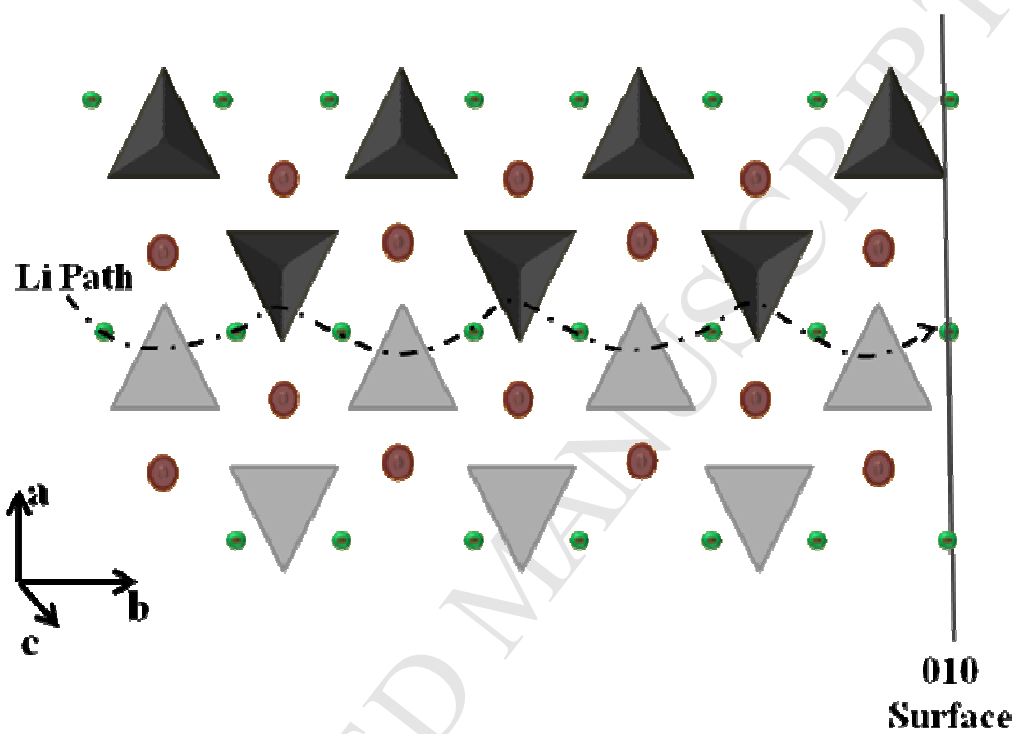


Fig. 5 Li diffusion along (010) direction in LiMPO₄ olivine [19].

Table 1 Change in lattice constant and electrochemical behavior for different metal ion substitution LiMPO_4 ($M = \text{Mn, Fe, Co and Ni}$)

LiMPO_4		Lattice parameters			Redox Voltage Vs. Li/Li^+ (V) [9]	Capacity in non-aqueous electrolyte (mAh/g) [7]
		a(Å)	b(Å)	c(Å)		
LiMnPO_4	Cal.	10.5401	6.0874	4.6878	4.1	45
	Exp.	10.446	6.106	4.746		
LiFePO_4	Cal.	10.3713	6.0216	4.6695	3.45	160
	Exp.	10.321	6.000	4.695		
LiCoPO_4	Cal.	10.2428	5.9093	4.6418	4.8	120
	Exp.	10.216	5.923	4.704		
LiNiPO_4	Cal.	10.1353	5.8432	4.6257	5.1	---
	Exp.	10.047	5.8621	4.681		

Based on references: Calculated [18] and Experimental [7]

Table 2 Possible Li^+ diffusion paths and Li^+ migration energy in olivine phosphates [20-21].

Diffusion Path	Li-Li Separation in LiFePO_4 (Å)	Li Migration energy (eV)		
		LiFePO_4	$\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$	LiMnPO_4
[010]	3.01	0.55	0.59	0.62
[001]	4.67	2.89	2.86	2.83
[101]	5.69	3.36	3.58	2.26