Density Functional Theory and Electrochemistry Studies on LiFe$_x$Mn$_{1-x}$PO$_4$ Solid Solutions

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(Dated: Received on April 10, 2019; Accepted on May 30, 2019)

The thermodynamic stability and lithiated/delithiated potentials of LiFe$_x$Mn$_{1-x}$PO$_4$ were studied with density functional theoretical calculations. The results show that the formation free energy of the LiFe$_x$Mn$_{1-x}$PO$_4$ solid solution is slightly higher than that of the phase-separated mixture of LiFePO$_4$ and LiMnPPO$_4$, and the two forms may co-exist in the actual LiFe$_x$Mn$_{1-x}$PO$_4$ materials. The calculation manifests that the lithiated/delithiated potentials of LiFe$_x$Mn$_{1-x}$PO$_4$ solid solutions vary via the Mn/Fe ratio and the spatial arrangements of the transition metal ions, and the result is used to explain the shape of capacity-voltage curves. Experimentally, we have synthesized the LiFe$_x$Mn$_{1-x}$PO$_4$ materials by solid-phase reaction method. The existence of the LiFe$_x$Mn$_{1-x}$PO$_4$ solid solution is thought to be responsible for the appearance of additional capacity-voltage plateau observed in the experiment.

Key words: LiFe$_x$Mn$_{1-x}$PO$_4$, Solid solution, Solid state synthesis, Density functional theory calculation, Electrochemical performance

I. INTRODUCTION

LiFe$_x$Mn$_{1-x}$PO$_4$ is considered to be an excellent cathode material sharing the merits of the good conductivity of LiFePO$_4$ and the high energy density of LiMnPPO$_4$ [1–3]. For this reason, enormous efforts have been made to improve the electrochemical performance of LiFe$_x$Mn$_{1-x}$PO$_4$ using various synthetic methods, including solid-phase, hydrothermal, and sol-gel methods [4–6]. As to its structure, whether LiFe$_x$Mn$_{1-x}$PO$_4$ is a solid solution or a mixture of LiFePO$_4$ and LiMnPPO$_4$ has not been well understood yet. It seemed to be held that LiFe$_x$Mn$_{1-x}$PO$_4$ is a solid solution [7], because its X-ray diffraction (XRD) patterns did not show two separated olivinal phases with different lattice parameters [8–13]. Instead, only one set of diffraction peaks that changed via the iron/manganese ratio were measured, reflecting the lattice parameters varying continuously between LiFePO$_4$ and LiMnPPO$_4$. On the other hand, two discrete plateaus, corresponding to the typical $\Psi_{Fe^{3+}/Fe^{2+}}$ of LiFePO$_4$ and $\Psi_{Mn^{3+}/Mn^{2+}}$ of LiMnPPO$_4$ respectively, have been measured in the charge/discharge curves of LiFe$_x$Mn$_{1-x}$PO$_4$ [14]. The discrete plateaus in charging/discharging curves hint that the LiFe$_x$Mn$_{1-x}$PO$_4$ solid may exist as phase-separated mixture of LiFePO$_4$ and LiMnPPO$_4$ [15]. The structures of the LiFe$_x$Mn$_{1-x}$PO$_4$ solid solution and the phase-separated mixture of LiFePO$_4$ and LiMnPPO$_4$ are illustrated in Scheme 1, where the green and black octahedrons represent the FeO$_6$ and MnO$_6$ groups.

DFT calculations have been widely used in the material science studies, and they also played an important role in the researches of lithium ion battery materials [16–18]. At present, the structural studies on LiFe$_x$Mn$_{1-x}$PO$_4$ mainly focus on the effect of different proportion of metal elements on its crystal lattices [19], the nuclear magnetic resonance (NMR) spectra [20–22], and the change of plateau potentials with the ratio of transition metal ions in Li$_x$Fe$_y$Mn$_{1-y}$PO$_4$ [23]. Whether it is a solid solution or a phase-separated mixture has not received much theoretical interest yet. Recognizing the extreme importance of the issue for understanding its electrochemistry mechanisms, we conducted this conjuncted study with DFT calculation and electrochemistry experiment for Li$_x$Fe$_y$Mn$_{1-y}$PO$_4$.

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DOI:10.1063/1674-0068/cjcp1904071 ©2019 Chinese Physical Society
of acetylene black for the secondary ball-milling for 6 h, 6 h at 350 °C for 1 h, 350 °C for 1 h, 450 °C for 2 h, 550 °C for 2 h, 650 °C for 12 h) to synthesize the samples. The XRD results of LiFe$_x$Mn$_{1-x}$PO$_4$/C samples are shown in FIG. S1 (supplementary materials). The obtained samples were ground with carbon black and PVDF (HSV900) with the weight ratio 8:1:1, then were stirred in NMP (1-methyl-2-pyrrolidinone) solvent in isolating from air. The slurry was coated on an Al foil to prepare the cathode for testing. The capacity-voltage curves were measured on a NEWARE battery testing system.

### II. Computational and Experimental Methods

The calculations were performed with the Cambridge Sequential Total Energy Package (CASTEP) module of the Material Studio program, using the Perdew-Burke-Ernzerhof (PBE) functional in conjunction with the projector augmented wave (PAW) [24, 25] and norm-conserving pseudopotentials (NCPPP). The plane wave energy cutoff was set as 900 eV. The valence 2s and 2p electrons of O, 3s and 3p electrons of P, 3d and 4s electrons of Fe/Mn were taken into calculation. Since Fe/Mn are paramagnetic, spin polarization should be considered in order to correctly describe the properties of the materials. The maximum spin number of crystals was set as the sum of the maximum spin numbers of all transition metal atoms. The distance between $k$ points in Monkhorst-Pack network was 0.04 Å$^{-1}$. The lattices and geometric structures of primitive cell were optimized till the total energy converged to $10^{-5}$ eV/atom, the force to 0.03 eV/Å, and the pressure to 0.05 GPa. In order to describe the strong correlation between the d electrons of Fe and Mn, Hubbard $U$ value is introduced to correct the quadratic term of PBE function [26, 27]. We set the $U$ values of d electrons of Mn and Fe to be 4.3 eV and 4.5 eV, respectively, by referring to the previous works [28].

The LiFe$_x$Mn$_{1-x}$PO$_4$ samples were synthesized with the solid phase method described as follows. Li$_2$CO$_3$, FeC$_2$O$_4$·2H$_2$O, MnCO$_3$ and NH$_4$H$_2$PO$_4$ were put onto the agate ball-milling pot, with the molar ratio 1.2:$(1-x):1$ ($x=0.2, 0.4, 0.8, 1$). The glucose was also added to the raw material as the carbon source with the quantity to be 6.5% of the total mass. The mixture was ball-milled for 6 h at rotation speed of 400 r/min, then the raw material was dried in air-circulating oven at 80 °C for 12 h. After drying, the raw material was transferred into an agate mortar to grind for 10 min. The precursors were heated in nitrogen atmosphere for 6 h at 350 °C, then it was mixed with 10% by weight of acetylene black for the secondary ball-milling for 6 h, with alcohol as dispersant. The precursors were heated in the tube furnace under N$_2$ atmosphere (200 °C for 1 h, 350 °C for 1 h, 450 °C for 2 h, 550 °C for 2 h, 650 °C for 12 h) to synthesize the samples. The XRD results of LiFe$_x$Mn$_{1-x}$PO$_4$/C samples are shown in FIG. S1 (supplementary materials). The obtained samples were ground with carbon black and PVDF (HSV900) with the weight ratio 8:1:1, then were stirred in NMP (1-methyl-2-pyrrolidinone) solvent in isolating from air. The slurry was coated on an Al foil to prepare the cathode for testing. The capacity-voltage curves were measured on a NEWARE battery testing system.

### III. Results and Discussion

#### A. Structures and thermodynamical stability

We have constructed the initial structural model of pure LiMPO$_4$ (M=Fe, Mn) olivine crystals based on the experimental lattice parameters [29, 30]. FIG. 1 displays the model projected along the [010], [001], and [100] directions, together with the sketch showing the Li$^+$ channel. For the LiFe$_x$Mn$_{1-x}$PO$_4$ ($x=0.75, 0.50, 0.25$) solid solutions, the transition metal atoms are distributed in the cell according to different Fe/Mn ratios. The fractional coordinates of the transition metal atoms in LiFe$_x$Mn$_{1-x}$PO$_4$ are provided in the supplementary materials (Table S1).

Geometric optimizations were carried out based on the initial constructed models, followed with property calculations at the optimized structures. Table I lists the calculated lattice parameters and the formation free energies (in eV per unit cell) of LiFe$_x$Mn$_{1-x}$PO$_4$ with different Mn/Fe ratios.

The free energy differences between the LiFe$_x$Mn$_{1-x}$PO$_4$ solid solutions and the phase separated mixtures can be evaluated according to the following equation:

$$
\Delta G_{s.s.} = G_{\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4} - xG_{\text{LiMnPO}_4} - (1-x)G_{\text{LiFePO}_4}
$$

(1)
DFT and electrochemistry studies on LiFe$_x$Mn$_{1-x}$PO$_4$

FIG. 1 Projections of olivine LiMPO$_4$ along (a) [010], (b) [001], and (c) [100]. (d) The Li$^+$ channel along [010]. M=Fe or Mn.

TABLE I The cell parameters $a$, $b$, $c$ and formation free energy $G$ of LiFePO$_4$/LiMnPO$_4$ single crystals and LiFe$_x$Mn$_{1-x}$PO$_4$ solid solutions.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>$G$/eV</th>
<th>$a$/Å</th>
<th>$b$/Å</th>
<th>$c$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFePO$_4$</td>
<td>-11947.021</td>
<td>10.3256</td>
<td>6.0046</td>
<td>4.6891</td>
</tr>
<tr>
<td>Li$<em>{0.75}$Fe$</em>{0.25}$MnPO$_4$</td>
<td>-11736.812</td>
<td>10.5385</td>
<td>6.1310</td>
<td>4.7717</td>
</tr>
<tr>
<td>Li$<em>{0.5}$Fe$</em>{0.5}$MnPO$_4$</td>
<td>-11526.614</td>
<td>10.6131</td>
<td>6.1620</td>
<td>4.7851</td>
</tr>
<tr>
<td>Li$<em>{0.25}$Fe$</em>{0.75}$MnPO$_4$</td>
<td>-11317.458</td>
<td>10.6575</td>
<td>6.2027</td>
<td>4.8056</td>
</tr>
<tr>
<td>LiMnPO$_4$</td>
<td>-11104.140</td>
<td>10.3294</td>
<td>6.0086</td>
<td>4.6948</td>
</tr>
</tbody>
</table>

This gives rise to the $\Delta G_{s.s.}$ values to be 2.25, 2.24, and 1.25 eV, respectively, when $x$ equals to 0.25, 0.50, and 0.75. The formation energies of LiFe$_x$Mn$_{1-x}$PO$_4$ solid solutions are slightly higher than the sum of the formation energy of pure LiMnPO$_4$ and LiFePO$_4$, implying that the phase-separated mixture, at a certain extent, is thermodynamically more stable than the solid solutions.

Several points can be manifested based on our calculations. Firstly, the formation energy differences between the solid solutions and the phase-separated mixtures are small, roughly in the range of 0–57.8 kJ/mol. Moreover, the free energy calculated here only includes the entropy due to the electron arrangement in the ground state, without taking into account the entropy caused by the disorder of atoms (including the transition metal ions, lithium ions, and vacancies). The formation energy differences between the solid solutions and the phase-separated mixtures would be even smaller if the disorder entropy was included. The crystalline temperature of LiMPO$_4$ olivine is estimated to be several hundred degree centigrade. At such high temperature, the solid solutions can exist as a considerably large portion according to the Boltzmann distribution. If cooling fast enough, the solid solutions can co-exist with the phase-separated LiFePO$_4$/LiMnPO$_4$ mixture at room temperature. Unlike the Li$^+$ ions, the mobilities of transition metal ions are very low at room temperature. Thus the structure of solid solutions, once formed, is not easy to destroyed, even after several electrochemical cycles.

Secondly, our calculations demonstrate that the change of lattice parameters with the increase of Fe/Mn ratio is small. Therefore, it seems to be difficult to distinguish difference phases with X-ray diffraction or EDX element distribution, as being observed in Refs.[13, 31]. Especially, the samples in most of the reported studies were prepared as small particles, and the XRD patterns can be broadened by size-effect or masked by poor crystallization.

Third, while it is difficult to be directly observed by X-ray diffraction or EDX element distribution, the co-existence of solid solutions and the phase-separated mixture can be identified by electrochemical methods. This is because the transferring of Li$^+$ sensitively depends on the local environment around it.

B. Lithiated/delithiated potential of LiFe$_x$Mn$_{1-x}$PO$_4$

In a crystal of olivine type LiMnPO$_4$, the intercalation/deintercalation potential of a single lithium ion is determined by its local environment. The six nearest transition metal ions surrounding the lithium
ion (FIG. 2) are the most important factor influencing lithium migration, although the out-side transition metal atoms and lithium ions/vacancies also play a role for sure. The effect of lithium intercalation/deintercalation can be reflected in the valence state change of the nearest surrounding six transition metal ions.

To calculate the intercalation/de-intercalation potential of a lithium ion, we build 2×2×2 supercells of LiMnPO_4 with or without removing a single lithium ion. The supercells of LiMPO_4 and Li_3MPO_4 (x<1) are shown in FIG. 3. This structure is capable of simulating the embedded/disengagement of lithium ion, as the deintercalation of a lithium ion only affects the atoms nearby it and won’t change the symmetry of whole crystal or cause collapse of the lattice. In order to simplify the calculation, all atoms beyond 6 Å from the lithium cavity were fixed during geometry optimization.

The formation free energies of the Li_8M_4P_8O_32 and Li_7M_3P_8O_32 supercells were calculated at the optimized structures. The lithiated/delithiated potential of LiMPO_4 can be evaluated by subtracting the formation energy of Li_8M_4P_8O_32 to that of the Li_7M_3P_8O_32 and the lithium ion:

E_{Li,MPO_4/LiMPO_4} = G_{LiMPO_4} - G_{Li,MPO_4} - xG_{Li} / xF (2)

In the above formula, F is the Faraday constant (96485.3329 C/mol), and E_{Li,MPO_4/LiMPO_4} is the lithiated/delithiated potential. Table II lists the calculated lithiated/delithiated potentials of LiFe_2Mn_{1-x}PO_4 with different Mn/Fe ratios (x=0.00, 0.50, 0.67, 0.83, 1.00). For comparison, the experimental values from Ref. [3] and the present work (LiFe_0.5Mn_0.5PO_4/C synthesized by solid-phase method) are also provided in the table. As shown in Table II, with the increase of Mn content, the lithiated/delithiated potential of LiFe_2Mn_{1-x}PO_4 solid solution increases gradually, and the calculated values are in good agreement with results of our experiments and that from Ref. [3].

It should be mentioned that, due to the variation of the arrangements of transition metal ions, the potential E_{Li,MPO_4/LiMPO_4} in a practical material may not be a fixed value. For a specific lithium ion, the closest 6 transition metal ions surrounding it make up an asymmetric octahedron. Even if the ratio of Fe/Mn ions is fixed, the local environment of the lithium ion can vary with the spatial arrangement of Fe/Mn ions. Therefore, the capacity-voltage curve of intercalation/deintercalation of lithium ions in LiFe_{1-x}Mn_{1-x}PO_4 should be a slope made up of several sub-plateaus. In addition to the effects of the six closest transition metal ions, the potential of Li^+ intercalation can also be influenced by the secondary closest transition metal ions, the vacancies, and nearby lithium ions. This will cause the charge/discharge plateaus to split multiple times and form a continuous rising/declining curve ranging from 4.1 V to 3.4 V. This kind of charge/discharge curves have been observed experimentally [31–36].

### Table II: The lithiated/delithiated (E_{Li,MPO_4/LiMPO_4}) potentials depending on the Mn/Fe ratios.

<table>
<thead>
<tr>
<th>LiMnPO_4</th>
<th>LiFe_{0.25}Mn_{0.75}PO_4</th>
<th>LiFe_{0.5}Mn_{0.5}PO_4</th>
<th>LiFe_{0.75}Mn_{0.25}PO_4</th>
<th>LiFe_{0.8}Mn_{0.2}PO_4</th>
<th>LiFePO_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.15</td>
<td>3.78</td>
<td>3.54</td>
<td>3.45</td>
<td>3.62</td>
<td>3.42</td>
</tr>
<tr>
<td>4.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.45</td>
</tr>
</tbody>
</table>

### C. Experimental study on the capacity-voltage curves of LiMn_{x}Fe_{1-x}PO_4

As mentioned above, our DFT calculation suggests that the LiMn_{x}Fe_{1-x}PO_4 solid solution can co-exist with the phase-separated LiMnPO_4/LiFePO_4 mixture. Under suitable synthetic conditions, the LiMn_{x}Fe_{1-x}PO_4 solid solution may be produced with a quite high proportion in the whole sample. Because transition metal ions have higher charge and stronger chemical interation with the PO_4^{3-} groups, it is almost impossible for them to migrate in the materials like lithium ions at room temperature. Once successfully synthesized, this solid solution structure can exist stably in the electrochemical cycles. Recently, Xia et al. synthesized the LiMn_{x}Fe_{1-x}PO_4 samples by hydrothermal method and studied its electrochemical properties [3]. It was found that, besides the plateau at 3.4 V (due to Fe^{3+}/Fe^{2+}) and the plateau at 4.1 V (due to Mn^{3+}/Mn^{2+}), there is also the third plateau at 3.75 V. We synthesized a series of LiMn_{x}Fe_{1-x}PO_4 samples by solid-phase method. From one of these samples, LiFe_{0.5}Mn_{0.5}PO_4/C, we also observed a similar phenomenon as Ref. [3]. As shown in FIG. 4 (a, c, d), three plateaus can be well distinguished at 3.4 V, 3.62 V, and 4.1 V, respectively.

The additional plateau (the plateau at 3.62 V) can be...
FIG. 3 The $2 \times 2 \times 2$ supercrystal of LiMPO$_4$ (left) and Li$_x$MPO$_4$ (right). The selected Li ion (the bright-orange atom in green circle) was removed in the Li$_x$MPO$_4$ (right). $M$=Fe or Mn.

FIG. 4 Electrochemical properties of LiFe$_{0.8}$Mn$_{0.2}$PO$_4$ synthesized by solid-phase method. (a) the charge/discharge curves at the 1st and the 60th cycles, the charge/discharge rate is 0.05 C (1 C=170 mA/g), (b) CV curves at different electrochemical window, the scan rate is 0.1 mV/sec. (c) and (d) dV/dQ curves of the 1st and the 60th charge/discharge.

observed in the first circle and also in the sixtieth circle, so we can exclude the possibility that the plateau is due to a side reaction. It should be the inherent property of a phase in the lithium iron phosphate sample. As displayed in FIG. 4(b), the cyclic voltammetry (CV) curve also shows an additional reduction reaction at the potential about 3.6 V, depending on the electrochemical window. Thus the plateau at 3.62 V can be considered as the unique plateau of LiMn$_x$Fe$_{1-x}$PO$_4$ solid solution in the material.

It should be pointed out that the 3.62 V plateau does not always appear in every solid-state synthesized sample, which seems to hint that the formation of the solid solution phase is not a thermodynamic control process but a kinetic control one. This is fully in consistent with our DFT calculations, which show that the free energy of the solid solution is slightly higher than that of the phase-separated mixtures.

IV. CONCLUSION

In summary, the thermodynamic stability and electrochemical properties of LiFe$_{2-y}$Mn$_{1-y}$PO$_4$ have been studied with DFT calculations. The results show that the free energies of LiFe$_{2-y}$Mn$_{1-y}$PO$_4$ solid solutions are slightly higher than that of the phase-separated LiFePO$_4$/LiMnPO$_4$ mixture by 0–2.25 eV per cell. Because of their small difference in free energy, solid so-
olutions can coexist with the phase-separated mixtures at high temperature, and can be synthesized in considerable proportions if appropriate cooling procedures are adopted. The lithiated/delithiated potential of LiFe$_{3-x}$Mn$_x$PO$_4$ solid solution was studied with DFT calculation. The dependence of the potentials on the Fe/Mn ratio and the spatial arrangement of transition metal ions was discussed. Experimentally, we have synthesized LiFe$_{3-x}$Mn$_x$PO$_4$ using the solid-state reaction method and the existence of the LiFe$_{3-x}$Mn$_x$PO$_4$ solid solution was identified from the capacity-voltage curve measurements. Since the formation of solid solution LiFe$_2$Mn$_{1-x}$PO$_4$ is essentially a kinetically controlled process, it is necessary to control the synthesis conditions more precisely. Comparing with LiFePO$_4$ and LiMnPO$_4$, LiFe$_2$Mn$_{1-x}$PO$_4$ is expected to have higher electronic conductivity [4], and thus deserves further study.

**Supplementary materials:** DFT calculated fractional coordinates of the transition metal atoms in LiFe$_2$Mn$_{1-x}$PO$_4$ and the XRD results of the synthesized LiFe$_2$Mn$_{1-x}$PO$_4$/C are shown.

**V. ACKNOWLEGEMENTS**

This work was supported by the Science and Technology Foundation of Jiangsu Province (BK20151237), the special nano-technology of Suzhou (ZXG2013004), USTC-NSRL Association Funding, the Collaborative Innovation Centre of Suzhou Nano Science and Technology Foundation of Jiangsu Province (BK20151237), Nano Science and Technology of China, and the Supercomputer Center of USTC.