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Density Functional Theory Study of Redox Potential Shifts in \( \text{Li}_{x}\text{Mn}_{y}\text{Fe}_{1-y}\text{PO}_4 \) Battery Electrodes

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ABSTRACT: Olivine-structured \( \text{LiMPO}_4 \) materials (\( M = \text{Mn, Fe, Co, Ni or mixtures} \)) exhibit higher redox-potentials than their layer oxide counterparts. This is due to the so-called inductive effect in the former where the inner P–O bonds in the phosphate units make the M–O bond weaker than in the latter. A strategy to further increase the redox-potentials in the olivines is to mix two metals. Along these lines, Kobayashi et al. have shown experimentally that \( \text{Mn}^{2+}–\text{Mn}^{3+} \) and \( \text{Fe}^{2+}–\text{Fe}^{3+} \) redox potentials approximately shift 0.1 V upon full substitution of Fe by Mn in \( \text{Li}_{x}\text{Mn}_{y}\text{Fe}_{1-y}\text{PO}_4 \). Here, we found through Density Functional Theory calculations that the average metal–oxygen bond lengths (\( M = \text{Mn, Fe} \)) increases upon rising Mn content, resulting in a decrease in the covalency of the transition-metal–oxygen interaction. The decrease in the covalency can be linked with good qualitative agreement to the experimentally observed \( \text{M}^{2+}–\text{M}^{3+} \) voltage-plateau positive shift. Finally, the impact of the Mn-content-dependent voltage plateaus and unit-cell volume on the energy densities of the active compound is discussed.

1. INTRODUCTION

Lithium metal phosphates are attractive cathode materials due to their low cost, environmentally benign constituents and elevated redox potentials compared to their corresponding oxides. The improved potentials may be explained in crystal-field theory by the inductive effect exerted by phosphorus on oxygen within the phosphate group. This entails a lower crystal-field splitting of the transition-metal d orbitals and thus a shift away from the Li–Li\(^{+} \) level of the counter electrode. LiFePO\(_4\), in particular, has been widely studied due to its excellent stability, although its voltage is limited (~3.4V vs. Li/Li\(^{+}\)) when compared to other metal phosphates, such as LiMnPO\(_4\) (~4.1V vs. Li/Li\(^{+}\)). By contrast, the chemical stability of LiMnPO\(_4\) has been shown to be inferior to that of LiFePO\(_4\). Additionally, the kinetics of delithiation–lithiation reaction for LiMnPO\(_4\) is considerably slower than LiFePO\(_4\), possibly due to structural instabilities of the Jahn–Teller-active Mn\(^{3+} \) phase, lower intrinsic electronic and/or ionic conductivities, a larger lattice mismatch during the two-phase reactions and higher-lying surface states compared to the bulk energy states. In an attempt to combine the high energy density of the LiMnPO\(_4\) cathode with the high stability of the LiFePO\(_4\) cathode, several groups have investigated...
mixed systems, i.e., Li$_x$Mn$_y$Fe$_{1-y}$PO$_4$\textsuperscript{7-9}, which exhibit an Fe$^{2+}$–Fe$^{3+}$ voltage plateau when $x<y$ and a Mn$^{2+}$–Mn$^{3+}$ voltage plateau when $x>y$.

Interestingly, electrochemical charge–discharge experiments on Li$_x$Mn$_y$Fe$_{1-y}$PO$_4$ for $0 \leq x \leq 1$ (performed at a rate of C/20 at 30 °C) conducted by Kobayashi \textit{et al.}\textsuperscript{7} showed a systematic upshift of the Fe$^{2+}$–Fe$^{3+}$ redox potential as Fe in LiFePO$_4$ was Mn-substituted to form LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ and a systematic downshift of the Mn$^{2+}$–Mn$^{3+}$ redox potential as Mn in LiMnPO$_4$ was Fe-substituted to form LiMn$_{0.2}$Fe$_{0.8}$PO$_4$. Extrapolating their voltage-plateau data to the full Mn-content range, $0 \leq y \leq 1$, yields voltage shifts of 0.13 V and 0.16 V for the Fe$^{2+}$–Fe$^{3+}$ and a Mn$^{2+}$–Mn$^{3+}$ voltage plateaus, respectively.

In this paper, we seek to gain a deeper atomic-scale insight into the origin of these redox potential shifts and their practical implications on the cathode material.

The structure of this work is as follows. We first briefly introduce the basic structural properties of the olivine-structured lithium metal phosphates together with the computational methods used here, namely the density-functional theory (DFT). Thereafter, we present a DFT study of all possible configurations involving different Li/Mn/Fe and Li-valence electron arrangements in a Li$_x$Mn$_y$Fe$_{1-y}$PO$_4$ unit cell for $y = 0, 0.25, 0.5, 0.75, 1$, imposing the constrain that the Li valence electrons localize on available Mn ion when $x>y$ (the Mn$^{2+}$–Mn$^{3+}$ plateau) and on available Fe ions when $x<y$ (the Fe$^{2+}$–Fe$^{3+}$ plateau.) As such, we first show that the origin of the aforementioned experimentally observed voltage shift stems from a change in the metal–oxygen bond lengths which again alters the energy of the metal:3d–oxygen:2p antibonding state. These bond-length changes are shown to be correlated to the Mn/Fe ratio in the compound, and M–O bond-length changes of 0.01 Å in the LiMPO$_4$ phase are observed. Lastly, the predicted convex-hull diagram of Li$_x$Mn$_y$Fe$_{1-y}$PO$_4$ with the resulting predicted open-circuit voltage (OCV) profiles is presented as well as the predicted gravimetric energy density (specific energy) and the volumetric energy density.

2. METHODOLOGY

2.1 Crystal structure of lithium metal phosphates (Li$_x$Mn$_y$Fe$_{1-y}$PO$_4$). Olivine LiMPO$_4$ sets in the orthorhombic crystal system belonging to the Pnma space group (no. 60) and its unit cell contains four formula units of LiMPO$_4$. See Figure S1 in Supporting Information for the olivine LiMPO$_4$ structure with M = Fe. In this study, only Mn and Fe atoms are allowed to occupy the TM sites. The structure consists of sheets in the $bc$ plane of canted MO$_6$ octahedra which are sharing corners with each other, while edge-sharing LiO$_6$ octahedra run along the [010] direction. In this way, layers of LiO$_6$ and MO$_6$ octahedra each on a distorted 2D grid sequentially stack in the $a$ direction with a layer of PO$_4$ units in between each metal–oxygen complex. PO$_4$ units connect the LiO$_6$ octahedra and the MO$_6$ octahedra.
For the input structure for the DFT calculations, the structure of Padhi et al.\textsuperscript{1} with specifications given in Table 1 was used. For the calculations on Mn-containing phases, relevant Fe ions were substituted by Mn and the structure was let to fully relax to its equilibrium state.

**Table 1.** Fractional coordinates and site symmetry of species in LiFePO\textsubscript{4} in its Pnma space group\textsuperscript{10} used as the input structure for the DFT calculations. \(a = 10.334\ \text{Å}, \ b = 6.008\ \text{Å} \text{and} \ c = 4.693\ \text{Å}\) were used as lattice constants\textsuperscript{1}.

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>Site symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1 (4a)</td>
</tr>
<tr>
<td>Fe</td>
<td>0.28222</td>
<td>0.25</td>
<td>0.97472</td>
<td>m (4c)</td>
</tr>
<tr>
<td>P</td>
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<td>0.25</td>
<td>0.41820</td>
<td>m (4c)</td>
</tr>
<tr>
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<td>0.74279</td>
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<tr>
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<td>0.25</td>
<td>0.20602</td>
<td>m (4c)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.16558</td>
<td>0.25</td>
<td>0.28478</td>
<td>1 (8d)</td>
</tr>
</tbody>
</table>

**2.2 Computational methods.** The initial structures for geometry relaxation were created and analyzed using the Atomic Simulation Environment (ASE) software package\textsuperscript{11}. Subsequent optimization of ion positions and lattice parameters to their equilibrium state were achieved by solving the electronic-structure problem in density-functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP)\textsuperscript{12}. The Kohn–Sham one-electron valence states were expanded in a plane-wave basis using a kinetic-energy cutoff of 500 eV and solved self-consistently using Pulay mixing\textsuperscript{13} of the electronic densities. The projector-augmented-wave (PAW) method\textsuperscript{14} was utilized to describe the atomic cores. As such Li and O 1s, P 1s, 2s, 2p, Mn as well as Fe, 1s, 2s, 2p, 3s and 3p electrons were treated as core electrons. The effects from exchange and correlation were modeled within the generalized-gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) parametrization\textsuperscript{15}. Partial occupations were found by employing the Gaussian method, and the electronic levels were smeared by 10 meV. Due to the electronic self-interaction error, GGA results frequently give rise to noticeable deviations from experimental observations, especially of the band gap,\textsuperscript{16,17} which originates from the fact that the self-interaction tends to favor a delocalization of the electrons. This effect is particularly pronounced in systems with a strong localization of the d-orbital electrons, which is the case of the Mn and Fe 3d orbitals in Li\textsubscript{1-x}Mn\textsubscript{x}Fe\textsubscript{1-y}PO\textsubscript{4}. Here, as well in previous studies\textsuperscript{18–20}, this problem is solved by utilizing the Hubbard-\(U\) correction\textsuperscript{21}. Following Zhou et al.\textsuperscript{18} a \(U\) value of 4.5 eV was applied on the 3d orbitals of Mn and a \(U\) value of 4.3 eV was applied on the 3d orbitals of Fe. Ferromagnetic spin arrangements were initialized on each TM ion (Mn and Fe) and all calculations were carried out with spin polarization. The nominal oxidation states of the TMs were determined by their magnetic moments as well as via their Bader charges\textsuperscript{22}. The high-spin electronic configuration of Fe\textsuperscript{2+} yields a magnetic moment of 4 \(\mu_B\) (four unpaired electrons) and Fe\textsuperscript{3+} one of 5 \(\mu_B\) (five unpaired electrons), whereas Mn\textsuperscript{2+} and Mn\textsuperscript{3+} yield 5 \(\mu_B\) and 4 \(\mu_B\), respectively.
3. RESULTS AND DISCUSSION

3.1 Voltage-plateau upshift upon Mn substitution. In order to investigate the shifting of the voltage plateaus observed by Kobayashi et al.\textsuperscript{7}, we have used DFT calculations to determine the phase stability of Li\textsubscript{x}FePO\textsubscript{4} and Li\textsubscript{x}MnPPO\textsubscript{4} and their mixed-metal phases, Li\textsubscript{x}Mn\textsubscript{0.25}Fe\textsubscript{0.75}PO\textsubscript{4}, Li\textsubscript{x}Mn\textsubscript{0.5}Fe\textsubscript{0.5}PO\textsubscript{4} and Li\textsubscript{x}Mn\textsubscript{0.75}Fe\textsubscript{0.25}PO\textsubscript{4} by calculating their convex hull. A total of 106 symmetry-inequivalent structures using a Li\textsubscript{x}M\textsubscript{1}yM\textsubscript{2}1-yPO\textsubscript{4} (M1,M2 = Mn or Fe; 0 \leq x \leq 1) unit cell of four formula units (24 to 28 atoms) were investigated: 16 structures for LiFePO\textsubscript{4} and LiMnPPO\textsubscript{4} each, 20 structures for Li\textsubscript{x}Mn\textsubscript{0.25}Fe\textsubscript{0.75}PO\textsubscript{4}, 32 structures for Li\textsubscript{x}Mn\textsubscript{0.5}Fe\textsubscript{0.5}PO\textsubscript{4} and 22 structures for Li\textsubscript{x}Mn\textsubscript{0.75}Fe\textsubscript{0.25}PO\textsubscript{4}. These 106 configurations constitute the total number of possible symmetry-inequivalent configurations using the aforementioned unit cell of Li\textsubscript{x}M\textsubscript{y}Fe\textsubscript{1-y}PO\textsubscript{4} including all degrees of freedom of the system, which are the following three, i) which Li sites are occupied, ii) how the Mn and Fe ions are distributed in the unit cell, and iii) the specific transition-metal ions in the cell that become oxidized upon the removal of Li ions from the structure. Here, we have assumed that the Li valence electrons localize on Mn ions (if they are present) until all Mn sites have been exhausted before they start to localize on Fe ions. From the total energies of these structures, \( E_{\text{rel,i}}^{y} \), the relative energies were calculated using

\[
E_{\text{rel,i}}^{y}(x) \equiv E_{\text{Li,Mn,Fe1-y}PO4}(x) - x E_{\text{Li,Mn,Fe1-y}PO4} - (1-x)E_{\text{Mn,Fe1-y}PO4},
\]

Equation 1

where \( i \) runs over the symmetry-inequivalent configurations for fixed \( x \) and \( y \) values. Using the lowest of these relative energies for each Li concentration would yield the computationally predicted open-circuit voltage (OCV) of the system under strict equilibrium conditions at T = 0 K with respect to a Li-metal reference electrode,

\[
U_{OCV}^{y}(x) = \frac{E_{\text{rel}}^{y}(x) - E_{\text{rel}}^{y}(x)}{(x - x)} + \frac{E_{\text{rel}}^{y}(x) - (E_{\text{rel}}^{y}(x) + E_{\text{Li}}(x))}{e}, \quad x_1 \leq x \leq x_2,
\]

Equation 2

with \( e \) being the elementary charge. At finite temperatures, still under strict equilibrium, Equation 2 needs to be corrected using Boltzmann distribution to include the contributions from all the configurations at a given \( x \) and \( y \). \( E_{\text{Boltzmann rel}}^{y}(x) = \frac{\sum p_i e^{-\frac{E_{\text{rel}}^{y}(x)}{k_B T}}}{\sum p_i e^{-\frac{E_{\text{rel}}^{y}(x)}{k_B T}}},
\]

Equation 3
where $E_{\text{rel},i}^\gamma$ is the relative energy defined in Equation 1, $k_B$ is Boltzmann constant, $T$ is the temperature, and $n_i$ is the multiplicity of configuration $i$ (i.e. the number of symmetry-equivalent subconfigurations in configuration $i$).

The relative energies and OCV plots for the Li$_x$Mn$_y$Fe$_{1-y}$PO$_4$ system at $T=0$ K and $T=300$ K are shown in Figure 1. It should be noticed that the differences in the OCV plots at $T=0$ K and $T=300$ are negligible.

![Figure 1](image)

Figure 1. a) Phase-stability plots showing the relative energies and the convex hull using the lowest-lying energies with the associated open-circuit-voltage profiles for investigated ratios of Fe and Mn. b) Phase-stability plots showing the relative energies and the convex hull using the Boltzmann averaged ($T=300$ K) energies with the associated open-circuit-voltage profiles for investigated ratios of Fe and Mn.

For Li$_x$FePO$_4$, Li$_x$Mn$_{0.5}$Fe$_{0.5}$PO$_4$ and Li$_x$MnPO$_4$ the convex hull is correctly predicted. However, for the Li$_x$Mn$_{0.25}$Fe$_{0.75}$PO$_4$ and Li$_x$Mn$_{0.75}$Fe$_{0.25}$PO$_4$ phases the convex hulls are not commensurate with the ones observed by Kobayashi$^7$ and others, due to too stable configurations at half lithiation. Indeed, during operando conditions, kinetic effects will favor the presence of relative high-energy structures, whose contribution at equilibrium conditions would be otherwise insignificant. Estimating the likelihood of a given configuration including kinetic effects is not straightforward. To begin with, it would require to calculate all the transition state barriers between each possible couple of configurations at a given x and y, which is a cumbersome task. The simplest approximation, followed here, is to consider that all the configurations at a given x and y have the same probability of occurrence. This approach is justified by the tortuous one-dimensional nature of Li diffusion in olivines, with relative high barriers for Li...
diffusion (between 0.6 eV and 1.4 eV in LiFePO4, depending on the degree of lithiation\textsuperscript{23}). This tortuous Li diffusion in olivines suggests that in many cases the easiest way to move Li ions between two low energy configurations will be through a path that contains a relative high-energy configuration as an intermediate state. In this scenario, the transition state barriers, rather than the individual energy of each configuration determine the time that the system spends in each configuration. Therefore, we have calculated the average of the relative energies as each Li concentration for each Fe–Mn composition as follows,

\[
E_{\text{avg rel}}(x) = \frac{\sum_i n_i E_{\text{rel},i}(x)}{\sum_i n_i},
\]

Equation 4

An example of how these relative-energy averages are performed is found in the Supporting Information section S2. The associated OCV with respect to a Li-metal reference electrode is calculated using

\[
U_{\text{OCV, avg}}(x) = \frac{E_{\text{avg rel}}(x_2) - E_{\text{avg rel}}(x_1)}{(x_2 - x_1)e} + \frac{\langle E_{\text{LiMn,Fe1-yPO4}} \rangle - \langle E_{\text{Mn,Fe1-yPO4}} \rangle + E_{\text{Li(s)}}}{e}, \quad x_1 \leq x \leq x_2,
\]

Equation 5

where \( \langle E \rangle \) denotes an average over the possible energies (for most Mn concentration, there is only one relative energy for LiMn\textsubscript{x},Fe\textsubscript{1-x}PO\textsubscript{4} and Mn\textsubscript{x},Fe\textsubscript{1-x}PO\textsubscript{4}). The convex hull derived from these weighted relative energies is shown in Figure 2(a) with the associated OCV plot in (b).
Figure 2. (a) Convex hulls, represented by dashed lines, of investigated ratios of Fe and Mn in $E_{\text{Li,Mn,Fe}_{1-x}PO_4}$ and (b) the associated open-circuit voltage (OCV) showing how the redox couple plateaus increase upon Fe substitution by Mn. Equilibrium voltages are indicated by dashed horizontal lines.
As seen from the convex hull in Figure 2(a), there exist very stable phases at \( x = y \) for all alloys (the solid-solution behavior around this place observed in experiments are not captured in the present DFT study, since our Li-concentration resolution is too low). These results agree well with experimental results summarized by Trinh et al.\(^\text{35}\) in Figure 3, where a solid-solution region, represented by red bars along \( x = y \), separates the two-phase reactions (cyan bars) on both sides, one for the Mn\(^{2+}\)–Mn\(^{3+}\) reaction (\( x < y \)) and one for Fe\(^{2+}\)–Fe\(^{3+}\) reaction (\( x > y \)). As shown by Figure 2(b), the Fe\(^{2+}\)–Fe\(^{3+}\) voltage plateau (four bottommost OCV profiles) increases as the Fe ions are substituted by Mn ions with a total plateau increase going from Li\(_x\)FePO\(_4\) to Li\(_x\)Fe\(_{0.25}\)Mn\(_{0.75}\)PO\(_4\) of 0.23 V. Meanwhile, the Mn\(^{2+}\)–Mn\(^{3+}\) voltage plateau (topmost OCV profiles) decreases as the Mn ions are substituted by Fe ions with a total increase going from Li\(_x\)MnPO\(_4\) to Li\(_x\)Fe\(_{0.75}\)Mn\(_{0.25}\)PO\(_4\) of 0.26 V. Extrapolation of the voltage-plateau values, shown in Figure 4, to the full Mn-content range (0 \( \leq y \leq 1 \)) yields a total voltage shift of 0.34 V for the Mn\(^{2+}\)–Mn\(^{3+}\) couple and 0.31 V for the Fe\(^{2+}\)–Fe\(^{3+}\) couple. This agrees qualitatively well with the observations by Kobayashi \textit{et al.}\(^\text{7}\) who reported a voltage-plateau upshift of 0.13 V and 0.16 V for the Fe\(^{2+}\)–Fe\(^{3+}\) and Mn\(^{2+}\)–Mn\(^{3+}\) plateaus, respectively, upon Mn-substituting LiFePO\(_4\) to LiMnPO\(_4\). Our results therefore predict a Mn/Fe voltage upshift of 3.4/3.1 mV per percent Mn substituted for Fe. Kobayashi \textit{et al.}\(^\text{7}\) and Snydacker \textit{et al.}\(^\text{36}\) suggested that this voltage-plateau shift could be attributed to

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Overview of phases in Li\(_x\)Mn\(_y\)Fe\(_{1-y}\)PO\(_4\) from previous experimental studies\(^\text{2,8,24-34}\). The data was taken from Trinh\(^\text{35}\).}
\end{figure}
changes in the TM–O bond lengths, and we have therefore investigated the evolution of these bond lengths as the Mn/Fe ratio is changed.

Figure 4. Calculated TM$^{2+}$–TM$^{3+}$ voltage plateau dependence on the Mn content ($y$) in Li$_x$Mn$_y$Fe$_{1-y}$PO$_4$. The star data points are extrapolated from the dot data points obtained from the voltage plateaus in Figure 2(b).

3.2 Correlation of voltage-plateau shifts to structural changes. From Figure 5, a systematic small increase of 0.014 Å in the multiplicity-weighted average Fe$^{2+}$–O bond length in LiMn$_y$Fe$_{1-y}$PO$_4$ (using extrapolation up to $y = 1$) is obtained from the calculations as Fe ions are substituted by Mn ions. Due to the inductive effect this weakens the Fe–O bonding, which strengthens the ionic character of Fe, thereby lowering the Fe:3d–O:2p antibonding state, which results in a lowering of the Fe$^{2+}$–Fe$^{3+}$ redox energy leading to an increase in the OCV as suggested by Kobayashi et al. and illustrated in Figure 6. A similar argument holds for the downshift of the Mn$^{2+}$–Mn$^{3+}$ redox potential: A small decrease of 0.015 Å in the average Mn$^{2+}$–O bond lengths in LiMn$_y$Fe$_{1-y}$PO$_4$ (using extrapolation down to $y = 0$) is obtained from the calculations as Mn ions are substituted by Fe ions. Again, due to the inductive effect this strengthens the Mn–O bonding, which enhances the ionic character of Mn, thereby increasing the Mn:3d–O:2p antibonding state, which results in an increase of the Mn$^{2+}$–Mn$^{3+}$ redox energy leading to a decrease in the OCV of Li$_x$Mn$_y$Fe$_{1-y}$PO$_4$ upon Fe substitution. A similar, but significantly smaller increase (0.006 Å) in the average Mn$^{3+}$–O bond length upon increasing Mn concentrations is also seen, whereas the average Fe$^{3+}$–O bond length essentially remains constant.

It is well known that octahedral Mn$^{3+}$ complexes exhibit strong pseudo-Jahn–Teller (JT) distortions in Li$_x$MnPO$_4$ compounds and the Mn$^{3+}$Fe$_{1-y}$PO$_4$ configurations in this study were therefore examined by calculating the measure of the degree of the JT distortion defined by,
\[
    d_{\text{JT}} = \frac{\sum_i b_{\text{Mn}^{3+}}^i - 0}{2} - \frac{\sum_j b_{\text{Mn}^{3+}}^j - 0}{4},
\]

where the first sum \((i)\) is over the two longest Mn\(^{3+}\)–O bond lengths and the last sum \((j)\) in over the four shortest Mn\(^{3+}\)–O bond lengths. Hence, a high (low) \(d_{\text{JT}}\) value indicates a large (small) pseudo-JT distortion of the Mn\(^{3+}\)O\(_6\) complex. As seen by Figure 7, where the average of \(d_{\text{JT}}\) for each Mn concentration \((y = 0.5\) has three symmetry-inequivalent configurations\) has been plotted, the degree of the JT distortion becomes more pronounced with higher Mn concentrations. The origin of this trend comes from the shorter Fe\(^{3+}\)–O bond lengths compared to the Mn\(^{3+}\)–O bond lengths, which effectively apply a compressive strain on the Mn\(^{3+}\)–O bond lengths relative to the Mn\(^{3+}\)–O bond lengths in the all-Mn\(^{3+}\) phase (MnPO\(_4\)). Such a compressed Mn\(^{3+}\)O\(_6\) complex cannot reach the same degree of pseudo-JT distortion (i.e., \(d_{\text{JT}}\) is relatively small) as a complex in an all-Mn\(^{3+}\) compound. This pseudo-JT distortion of the Mn\(^{3+}\)O\(_6\) complexes constitutes a new mechanism which can alter the Mn\(^{2+}\)–Mn\(^{3+}\) voltage plateau, and through that the OCV, in addition to the aforementioned metal–oxygen bond-length changes. As the pseudo-JT distortion increases so does the elastic energy required by the system to accommodate it. When the Mn\(^{3+}\) gets reduced to Mn\(^{2+}\) the pseudo-JT distortion disappears, recovering the elastic energy paid by the system. Thus, the larger the pseudo-JT distortion is, the more elastic energy is recovered upon lithiation, increasing the OCV. Typically, the JT stabilizations energies (equivalent to the elastic energy to accommodate the distortion) in Mn\(^{3+}\)O\(_2\)\(_6\) complexes are around 0.25 eV.\(^{39}\) Assuming a linear relationship between the size of the distortion and the JT energies (i.e., following the harmonic approximation) passing from \(d_{\text{JT}} = 0.43\) Å to \(d_{\text{JT}} = 0.37\) Å would imply a change in the elastic energy of \(-0.03\) eV. Even though this energy is rather small, it could explain why the shift in the OCV for the Fe plateau (0.23 V) is slightly smaller than that of Mn (0.26 V), although the change in the average metal–oxygen bond length was practically the same (~1.5 pm) in both cases.
Figure 5. Average metal–oxygen bond lengths versus Mn concentration \( y \) for both oxidation states (2+ and 3+) of Mn and Fe.
Figure 6. Origin of Fe$^{2+}$–Fe$^{3+}$ voltage-plateau upshift upon increasing Mn concentration: As Fe is substituted for Mn, the Fe–O bond lengths increase (ultimately by 0.014 Å on average from our calculations), thereby weakening the Fe–O bonds. This lowers the antibonding state of the Fe:3d–O:2p mixing, lowering the redox potential and thereby increasing the OCV.

Figure 7. The average Jahn–Teller lattice distortion for each Mn concentration $y$ in Mn$_y$Fe$_{1-y}$PO$_4$ configuration.
3.3 Energy densities. In order to assess the influence of the voltage-plateau shifts on the energy densities, both the multiplicity-weighted averaged gravimetric energy density and the volumetric energy density of the active Li$_{x}$Mn$_{y}$Fe$_{1-y}$PO$_{4}$ material were calculated from our DFT results and these are plotted in Figure 8. A brief outline of how these energy densities are calculated is found in the Supporting Information section S3. Since the specific capacity of LiMnPO$_{4}$ and LiFePO$_{4}$ are very similar (170.9 mAh/g and 169.9 mAh/g, respectively), the main contribution to the associated gravimetric energy densities shown in Figure 8(a) stems from the linear TM$^{2+}$–TM$^{3+}$ redox voltage trends displayed in Figure 4, and since both the Mn and the Fe voltage plateaus increase by almost the same per Mn substituted for Fe (3.4 mV versus 3.1 mV per percent Mn substituted for Fe for Mn$^{2+}$–Mn$^{3+}$ and Fe$^{2+}$–Fe$^{3+}$ redox couples, respectively), the resulting gravimetric energy density also increases nearly linearly as a function of the Mn content $y$. A similar trend is seen for the volumetric energy density, defined as the total number of charges involved in the redox reactions in one unit cell multiplied by the voltage at which the reactions take place divided by the volume of the fully lithiated unit cell: A nearly linear increase in the energy density as the Mn content is increased. These values agree well with experiments (e.g., 2073 Wh/L for LiFePO$_{4}$ and 2413 Wh/L for LiMnPO$_{4}$)$^{7,40}$. However, the larger volume of the Mn-rich compounds compared to the Fe-rich compounds results in a slight negative curvature of the volumetric energy density versus the Mn content. In spite of the comparably smaller volume of the Fe-rich compounds combined with the upshift of the Fe$^{2+}$–Fe$^{3+}$ voltage plateaus (through Mn substitution), the volumetric energy density is still maximum for the Li$_{x}$MnPO$_{4}$ compound due to the significantly higher voltage of the Mn$^{2+}$–Mn$^{3+}$ redox process.
Figure 8. Gravimetric (a) and volumetric (b) energy densities versus the Mn content $y$. Both densities are for the active $\text{Li}_x\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4$ material. The volumetric density is calculated using the volume of the fully lithiated unit cells.

4. CONCLUSIONS

The benefits of the high average voltage from Mn, the excellent stability from Fe and the good rate capability of the mixed-metal compound\textsuperscript{9}, combined with the inexpensive PO\textsubscript{4} anionic framework of $\text{Li}_x\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4$ ($0 \leq x \leq 1$ and $0 \leq y \leq 1$) makes this material very attractive for use as a Li-ion cathode resulting in numerous studies of the lithiated mixed-metal olivine phosphates\textsuperscript{7–9}. However, this cathode material still raises some fundamental questions, one of them being why the voltage plateaus of the transition-metal (TM) redox couples change as a function of the Mn content ($y$) as observed in experiments\textsuperscript{7}. Through a careful density-functional-theory (DFT) study of each Li–TM arrangement and Li-valence-electron localization arrangement in one unit cell of $\text{Li}_x\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4$ (4 f.u.), we have...
found this voltage-plateau upshift upon increasing the Mn/Fe ratio to originate from the TM–O bond-length changes as the average TM–O bond lengths increases (by 0.015 Å for the Mn$^{2+}$–O bond lengths and 0.014 Å for the Fe$^{2+}$–O bond lengths). These bond-length changes alter the TM:3d–O:2p antibonding state such that this is lowered (raised) for Fe (Mn), thereby increasing (decreasing) the open-circuit voltage upon increasing (decreasing) Mn/Fe ratio. Additionally, we found that the strength of the pseudo-Jahn–Teller distortion in the Mn$^{3+}$O$_2$$^-$ complexes increased upon increasing Mn concentration, which we think could have an impact on the open-circuit voltage in addition to the above-mentioned TM–O bond-length effects.

Notably, we found that it was crucial to perform an averaging over the relative energies at each Li concentration and Mn concentration instead of following the conventional approach of using the lowest-lying relative energies at each $x$ and $y$. In this way, excellent agreement with experimental results were obtained. This points out the importance of including higher-energy configurations, which unavoidably will be present during the charge and discharge cycling of the cathode materials.

A consequence of the Mn-content-dependent voltage is a potential nontrivial dependence of the energy densities upon the Mn content, in particular regarding the volumetric energy density since the volume also depends on the Mn content. However, our studies found a nearly linear trend for both the gravimetric and the volumetric densities, favoring a Mn-rich compound if the energy densities were to be maximized.

ASSOCIATED CONTENT

Supporting Information

Crystal structure of LiFePO$_4$; weighted relative energies via symmetry-equivalent subconfigurations; energy densities.

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Notes

The authors declare no competing financial interest.

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**TOC Graphic**

Adding Mn
a) Phase-stability plots showing the relative energies and the convex hull using the lowest-lying energies with the associated open-circuit-voltage profiles for investigated ratios of Fe and Mn. b) Phase-stability plots showing the relative energies and the convex hull using the Boltzmann averaged (T=300 K) energies with the associated open-circuit-voltage profiles for investigated ratios of Fe and Mn.

181x101mm (150 x 150 DPI)
(a) Convex hulls, represented by dashed lines, of investigated ratios of Fe and Mn in $E_{\text{Li}_x \text{Mn}_y \text{Fe}_{1-y} \text{PO}_4}$ and (b) the associated open-circuit voltage (OCV) showing how the redox couple plateaus increase upon Fe substitution by Mn. Equilibrium voltages are indicated by dashed horizontal lines.
Figure 3. Overview of phases in Li$_x$Mn$_y$Fe$_{1-y}$PO$_4$ from previous experimental studies$^2,8,31-33,23-30$. Adapted from Trinh$^{34}$.
Figure 4. Calculated $\text{TM}^{2+}$-$\text{TM}^{3+}$ voltage plateau dependence on the Mn content ($y$) in $\text{Li}_x\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4$. The star points are extrapolated from the dot data points obtained from the voltage plateaus in Figure 2(b).
Figure 5. The average Jahn–Teller lattice distortion for each Mn concentration $y$ in Mn$_y$Fe$_{1-y}$PO$_4$ configuration.
Figure 6. Average metal–oxygen bond lengths versus Mn concentration \( y \) for both oxidation states (2+ and 3+) of Mn and Fe.
Figure 7. Origin of $\text{Fe}^{2+} - \text{Fe}^{3+}$ voltage-plateau upshift upon increasing Mn concentration: As Fe is substituted for Mn, the Fe–O bond lengths increase (ultimately by 0.014 Å on average from our calculations), thereby weakening the Fe–O bonds. This lowers the antibonding state of the Fe:3d–O:2p mixing, lowering the redox potential and thereby increasing the OCV.
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113x176mm (100 x 100 DPI)