Phase diagram and electrochemical properties of mixed olivines from first-principles calculations

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Using first-principles calculations, we study the effect of cation substitution on the transition-metal sublattice in phospho-olivines, with special attention given to the Li$_x$(Fe$_{1-y}$Mn$_y$)PO$_4$ system. We use a cluster expansion model derived from first-principles with Monte Carlo simulations to calculate finite-T phase diagrams, voltage curves, and solubility limits of the system. The phase diagram of Li$_x$(Fe$_{1-y}$Mn$_y$)PO$_4$ shows two low-temperature miscibility gaps separated by a solid solution phase centered at Li composition $x = y$, which corresponds to a state where most Fe ions are oxidized and most Mn are not. This intermediate low-T solid solution is stabilized by the dilution of phase-separating interactions caused by the disorder of redox potentials on the transition-metal sites. The calculated voltage curves show two plateaus at around 4.0–4.2 V and 3.5–3.7 V, corresponding to the Mn$^{3+}$/Mn$^{2+}$ and Fe$^{3+}$/Fe$^{2+}$ redox couples, respectively, with an extended sloping region in between corresponding to the low-T solid solution phase. In agreement with experiment, we find that the Mn$^{3+}$/Mn$^{2+}$ (Fe$^{3+}$/Fe$^{2+}$) voltage is decreased (increased) by Fe (Mn) substitution. We explain this by considering the energy of the solid solution which is the discharged (charged) state for these redox couples and argue that such changes are generic to all mixed olivine systems. We also find reduced phase transformation polarization on both plateaus which we attribute to the decreased composition difference between the oxidized and reduced state for each redox couple.

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I. INTRODUCTION

With the emergence of LiFePO$_4$ as a viable battery cathode material for large format batteries, cation-substituted phospho-olivine systems of the form Li$_x$(Fe$^{3+}$)$_{1-y}$Mn$^y$PO$_4$ (M = Mn or Co) have gained the interest of battery researchers.1–15 Specifically, the prospect of improved energy density over LiFePO$_4$ due to the higher redox potential of Mn$^{3+}$/Mn$^{2+}$ compared to Fe$^{3+}$/Fe$^{2+}$ [~4.1 V compared to ~3.4 V vs Li/Li$^+$ (Ref. 16)] has fuelled research into Li(Fe$_{1-y}$Mn$_y$)PO$_4$.13–7,11 Several questions in particular arise for mixed cation systems: LiFePO$_4$ is delithiated in a two-phase reaction forming FePO$_4$, and both phases tolerate only a small amount of off-stoichiometry.17 Zhou et al. showed that this two-phase reaction is unusual and driven by the strong electron-Li$^+$ interaction.18 Dilution of the Fe sites by Mn may modify the phase behavior upon delithiation. In particular, Yamada et al. observed that the reduction of Fe$^{3+}$ to Fe$^{2+}$ shifts from two-phase to single-phase upon Li insertion for samples with $0.2 \leq y \leq 0.6$ (samples with $y = 0, 0.2, 0.4, 0.6, 0.8,$ and 1.0 were tested, but those with $y \geq 0.8$ were unstable and did not completely retain the olivine structure in the delithiated state) while the Mn reaction remains entirely two-phase for $y \leq 0.8$.1

Our approach is to use first-principles calculation to study the temperature-composition phase diagram of Li$_x$(Fe$_{1-y}$Mn$_y$)PO$_4$ for different Mn-Fe compositions. In the case of LiFePO$_4$, both first-principles investigations and experiments have helped explain the observed low-temperature phase separation,16–20 diffusion path of Li$^+$,21–23 and high-rate capability.24 Of particular interest, first-principles calculations by Zhou et al.18 which take into account both lithium/vacancy (Li$^+$/V) and electron/hole ($e^-/h^+$) configurational entropy have proven accurate in predicting the finite-T phase behavior of the Li$_x$FePO$_4$ system. In this work, a modification to that model has been incorporated to take into account Mn substitution of Fe. The resulting phase diagram of Li$_x$(Fe$_{1-y}$Mn$_y$)PO$_4$, voltage curves, and solubility limits are reported and compared to experiment. We also study the change in polarization and hysteresis associated with the first-order phase transition as Mn is substituted for Fe.

II. METHODS

The model used in this work builds on the approach proposed by Zhou et al.18 which was used to determine the phase diagram of Li$_x$FePO$_4$. In that work, a coupled cluster expansion taking into account both ionic and electronic degrees of freedom was parametrized from generalized gradient approximation + U (GGA+U) ab initio calculations16 and then used as a Hamiltonian in Monte Carlo (MC) simulations. By thermalizing both the Li$^+$/V and $e^-/h^+$ distributions, the free energy can be obtained for any temperature and Li concentration. In essence, a cluster expansion is a representation of the energy of the system in the phase space of all Li$^+$/V and $e^-/h^+$ distributions. The typical form of the energy model is a polynomial expansion in the occupation variables at each site,

$$E[\lambda, \epsilon] = J_a + J_1 \lambda_i + J_2 \lambda_i \lambda_j + J_{ab} \lambda_i \epsilon_a + J_{ab} \epsilon_a \epsilon_b + \cdots$$  \hspace{1cm} (1)$$

In Eq. (1), $\lambda_i$ represents occupancy of Li$^+$ site $i$, where $\lambda_i = 1$ represents Li$^+$ occupation and $\lambda_i = -1$ represents vacancy occupation. Similarly, $\epsilon_a$ represents occupancy of iron site $a$, where $\epsilon_a = 1$ represents electron (Fe$^{2+}$) occupation and $\epsilon_a = -1$ represents hole (Fe$^{3+}$) occupation. The $J$ coefficients are
the effective cluster interactions (ECIs), which reflect the aggregate effect of several physical factors such as electrostatics, screening, relaxation, covalency, etc. Because the Fe$^{3+}$/Fe$^{2+}$ sublattice and the Li$^+/V$ sublattice do not coincide, this is a coupled cluster expansion rather than a quaternary model.\textsuperscript{25}

In this work, the same cluster expansion by Zhou et al.\textsuperscript{18} was used, apart from one modification. In order to simulate the Li$_{x}$(Fe$_{1-y}$Mn$_{y}$)PO$_4$ system, we replace the transition-metal point term by

$$\Delta E = \sum_{a \in \text{Mn Sites}} J_{\text{Mn}} e_{a} + \sum_{a \in \text{Fe Sites}} J_{\text{Fe}} e_{a},$$

where $J_{\text{Mn}}$ = -4.2 eV/2 and $J_{\text{Fe}}$ = -3.5 eV/2. This represents the electron energy on the transition-metal site shifted down by 0.7 eV/2 on a fixed set of randomly chosen metal sites to account for Mn substitution. The factor of 1/2 is due to the fact that in our formulation, the redox reaction of hole to electron state is represented by the change in occupation variable $e_{a}$ from -1 to 1. It is well documented in both experiments and first-principles calculations that the difference between redox voltages of LiMnPO$_4$ and LiFePO$_4$ with respect to Li is ~ -0.7 V.\textsuperscript{16,26,27} Since the point term ECI roughly corresponds to the chemical potential (i.e., the voltage), the model used in this work approximately takes into account the difference in redox potential associated with Mn versus Fe. Since in our model Mn only modifies the interactions in Li$_{x}$FePO$_4$ by the $e^{2}/h^{4}$ site energy on the Mn position, higher-order Mn-specific interactions such as Jahn-Teller distortion are not taken into account. We will discuss the implications of this later.

Monte Carlo simulations were performed at different temperatures and degrees of Mn substitution in 6×12×12 and 12×12×12 supercells (50 000 MC steps and 10 000 equilibration steps), where one cell corresponds to four Li$_{x}$(Fe$_{1-y}$Mn$_{y}$)PO$_4$ formula units. The free energy at each composition was obtained by integrating the relation between $\mu_{\text{Li}}$ and $x_{\text{Li}}$.

### III. RESULTS

To observe the effect of Mn on the voltage profile (Li content on x axis, voltage on y axis), Monte Carlo simulations were performed as a function of $\mu_{\text{Li}}$ at constant temperature for several Mn compositions. A typical calculated voltage profile output is shown in Fig. 1 for $y$ = 0.6, showing noticeable hysteresis between charge (decreasing $\mu_{\text{Li}}$) and discharge (increasing $\mu_{\text{Li}}$). Free-energy integration\textsuperscript{28} is employed to obtain the equilibrium voltage profile and thus remove the hysteresis, the result of which is shown in Fig. 2 for several Mn compositions. The voltage curves show two plateaus at ~-4.4 V and ~-3.5 V, corresponding to the Mn$^{3+}$/Mn$^{2+}$ and Fe$^{3+}$/Fe$^{2+}$ redox couples, respectively. This can be readily seen since the widths of the plateaus in the Li composition are roughly equal to the Mn/Fe compositions. The slight discrepancy of the calculated voltages as compared to experiments is typical for the GGA+$U$ approximation to obtain energies.\textsuperscript{16} Constant voltage (chemical-potential) regions correspond to first-order phase transitions and thus phase-separated regions in Li composition, and regions with varying voltage correspond to single-phase regions. Between the Mn$^{3+}$/Mn$^{2+}$ and Fe$^{3+}$/Fe$^{2+}$ plateaus is an extended single-phase region in which most Fe is oxidized while most Mn is not.

The information determined from the voltage curves shown in Fig. 2 can be summarized by plotting the composition at the phase boundaries as shown in Fig. 3 with Li content (x) along the x axis and Mn content (y) along the y axis. Region (a) is phase-separated corresponding to the Mn$^{3+}$/Mn$^{2+}$ couple; region (b) is single-phase corresponding to Mn$^{3+}$/Mn$^{2+}$ (shaded region) and Fe$^{3+}$/Fe$^{2+}$ (unshaded region); and region (c) is phase-separated corresponding to Fe$^{3+}$/Fe$^{2+}$. The dashed line corresponds to the experimentally determined boundary between single-phase Fe$^{3+}$/Fe$^{2+}$ and phase-separated Fe$^{3+}$/Fe$^{2+}$ by Yamada et al.\textsuperscript{1}

The results from free-energy integrations at different temperatures can be used to construct phase diagrams [liithium content (x) along the x axis and temperature along the y axis] as shown in Fig. 4. The phase diagram of Li$_{x}$FePO$_4$ (0 ≤ x ≤ 1), determined by both experiment\textsuperscript{19,20} and first-principles calculations,\textsuperscript{18} shows a low-temperature miscibility gap between FePO$_4$ and LiFePO$_4$ and a eutectoid transition to a solid solution (SS) phase. By substituting Mn on the Fe sublattice, the solid solution phase is stabilized at low tempera-
ture, and the phase diagram consists of two miscibility gaps at low temperature, the first between \(\text{Fe}^{3+}/\text{Fe}^{2+}\) couple; Region (b) corresponds to a single-phase region associated with the \(\text{Mn}^{3+}/\text{Mn}^{2+}\) couple (shaded region) and the \(\text{Fe}^{3+}/\text{Fe}^{2+}\) couple (unshaded); Region (c) corresponds to a two-phase region associated with the \(\text{Fe}^{3+}/\text{Fe}^{2+}\) couple. Circles correspond to the boundary between the two-phase and single-phase regions associated with the \(\text{Fe}^{3+}/\text{Fe}^{2+}\) couple as determined experimentally by Yamada et al. (Ref. 1). The dashed line denotes the experimentally determined boundary between single-phase \(\text{Fe}^{3+}/\text{Fe}^{2+}\) and phase-separated \(\text{Fe}^{3+}/\text{Fe}^{2+}\) as determined by Yamada et al. (Ref. 1).

**Figure 2** clearly shows that the voltage at which the phase transition occurs (hereafter referred to as the transition voltage) for both \(\text{Fe}^{3+}/\text{Fe}^{2+}\) and \(\text{Mn}^{3+}/\text{Mn}^{2+}\) couples increases as Mn content increases. The values of the transition voltage at 300 K for both couples as a function of Mn composition are cataloged in Fig. 5. The voltage for both redox couples steadily increases with Mn composition. It is also shown that the phase transition shifts from first order to second order with increasing Mn substitution for the \(\text{Fe}^{3+}/\text{Fe}^{2+}\) couple, and the opposite is seen for the \(\text{Mn}^{3+}/\text{Mn}^{2+}\) couple.

**Figure 6** shows the voltage of the \(\text{Fe}^{3+}/\text{Fe}^{2+}\) first-order phase transition upon both charge and discharge in the Monte Carlo simulation at different degrees of Mn substitution and a comparison to the experiments performed by Nakamura et al.10 on the \(\text{Li}_{x}\text{Fe}_{1-y}\text{Mn}_{y}\text{PO}_{4}\) system. Similarly, **Fig. 7** shows the transition voltages upon charge and discharge of the \(\text{Mn}^{3+}/\text{Mn}^{2+}\) first-order phase transition with increasing Mn

**FIG. 4.** Calculated phase diagrams of \(\text{Li}_{x}\text{(Fe}_{1-y}\text{Mn}_{y})\text{PO}_{4}\) for (a) \(y=0.1\), (b) \(y=0.3\), (c) \(y=0.5\), (d) \(y=0.7\), and (e) \(y=0.9\). Dashed line is speculative.
Fig. 5. Equilibrium phase-transition voltages at 300 K for Fe$^{3+}$/Fe$^{2+}$ and Mn$^{3+}$/Mn$^{2+}$.

substitution. In both Figs. 6 and 7, the same trend of increasing transition voltage with Mn substitution is observed. Also, the difference between the transition voltage determined upon charge and discharge (as discussed earlier and shown as the hysteresis in Fig. 1) decreases with increasing Mn substitution for the Fe$^{3+}$/Fe$^{2+}$ couple and increases for the Mn$^{3+}$/Mn$^{2+}$ couple. This effect is shown clearly in Fig. 8, which shows the polarization, defined as the difference between the charge and discharge transition voltages, at different degrees of Mn substitution for both the Fe$^{3+}$/Fe$^{2+}$ and Mn$^{3+}$/Mn$^{2+}$ couples.

IV. DISCUSSION

Most of the trends we find compare well to the available experimental work. In experimentally determined charge-discharge curves and open-circuit voltage (OCV) measurements of the Li$_x$(Fe$_{1-}$Mn$_{1-y}$)PO$_4$ system, two plateaus at $\sim 3.5$ and $\sim 4.1$ V are observed with a sloping (single-phase) region in between connecting the two, which shows good qualitative agreement with the data presented in Fig. 2. Also, the experimentally obtained voltage curves show similar variation in the plateau width with increasing Mn composition as observed in Fig. 2. The trends observed in Figs. 5–8, of increasing transition voltage and reduced polarization of the Fe$^{3+}$/Fe$^{2+}$ transition with increasing Mn composition, are similarly reflected in experimental data. Experimental polarization and transition voltage data of the Mn$^{3+}$/Mn$^{2+}$ transition is unavailable, but experimental data in the Li$_x$(Fe$_{1-}$Co$_{1}$)PO$_4$ system reflects a similar trend of increasing polarization and transition voltage of the Co$^{3+}$/Co$^{2+}$ transition with increasing Co content. While this is a different system, it serves to illustrate how a higher redox couple is modified by the presence of the Fe$^{3+}$/Fe$^{2+}$ couple.

Experiments performed by Yamada et al. do not produce a single-phase Mn$^{3+}$/Mn$^{2+}$ region when the Mn couple is diluted by Fe as we find in the shaded portion of Fig. 3. We believe that this difference between the calculations and experiments is due to the specific Jahn-Teller nature of Mn$^{3+}$. The Jahn-Teller distortion around Mn$^{3+}$ leads to a large lattice distortion. Typically, when large elastic effects are present around impurities, solid solution regions are small, and a first-order phase is preferred because a collective distortion of the unit cell results in less elastic strain energy than the combined elastic distortions around single impurities. The model used in this work represents Mn only by modifying the point term in the coupled cluster expansion determined for the Li$_x$FePO$_4$ system, leaving all higher-order ECIs unchanged. Thus, Mn-specific higher-order interactions are neglected in the model. These findings support the widely held opinion that the underlying physics of the LiMnPO$_4$

![Fig. 6](Color online) Phase-transition voltages of the Fe$^{3+}$/Fe$^{2+}$ couple as determined by Monte Carlo (12 $\times$ 12 cell size) simulation upon charge and discharge compared to experiments by Nakamura et al. (Ref. 10).

![Fig. 7](Color online) First-order phase-transition voltages of the Mn$^{3+}$/Mn$^{2+}$ couple as determined by Monte Carlo (12 $\times$ 12 cell size) simulation upon charge and discharge.

![Fig. 8](Color online) Polarization, defined as the difference between charge and discharge voltages, for Fe$^{3+}$/Fe$^{2+}$ and Mn$^{3+}$/Mn$^{2+}$ couples as determined by Monte Carlo (12 $\times$ 12 cell size) simulation compared to experiments by Nakamura et al. (Ref. 10).
system are different compared to the LiFePO$_4$ system.$^{1,30}$ Hence, while the phase diagram of the pure Li$_{x}$MnPO$_4$ system has not been investigated, it seems likely that the temperature at which solid solution occurs is higher than in Li$_{x}$FePO$_4$ due to the stronger phase-separation interaction caused by the Mn$^{3+}$ Jahn-Teller distortion.

A. Existence of single-phase region

To understand the phase behavior in Li$_{(1-x,y)}$(Fe$_{1-y/2}$,Mn$_{y/2}$)PO$_4$, we recollect the physical mechanism that is responsible for the two-phase region in Li$_{x}$FePO$_4$.$^{18}$ Both the $e^-$-$h^+$ and the Li$^+$-$V$ interactions by themselves are of the ordering type and do not promote phase separation, but in Li$_{x}$FePO$_4$ the $e^-$-$Li^+$ interaction is unusually strong due to the localized Fe$^{3+}$/Fe$^{2+}$ states. As this interaction dominates, Li$^+$ strongly attracts Fe$^{2+}$ which in turn attracts more Li$^+$, leading to a two-phase state. The Fe$^{2+}$-$Li^+$ (or Fe$^{3+}$-$V$) interaction is strong and favorable enough to overcome the Li$^+$-$Li^+$ (V-$V$) and Fe$^{3+}$-$Fe^{2+}$ (Fe$^{3+}$-$Fe^{2+}$) repulsion when all Li is brought together. This allows us to understand the trends observed in this paper. It is important to realize that in a mixed cation system such as Li$_{(1-x,y)}$(Fe$_{1-y/2}$,Mn$_{y/2}$)PO$_4$, the plateau voltages are not between fully lithiated (β) and delithiated (α) states, but between α and the SS phase (for Mn$^{3+}$/Mn$^{2+}$) and between SS and β (for Fe$^{3+}$/Fe$^{2+}$). As the Fe sites are diluted by Mn, the driving force for phase separation is decreased. In the SS where Fe is largely 3+ and most Mn is 2+, some Li$^+$ will have Mn$^{2+}$ neighbors, and some will have Fe$^{3+}$ neighbors. This unfavorable interaction raises the energy of the end member of each two-phase region and lowers the transition temperature to form solid solution as observed in Fig. 4. One can also make a mean-field argument to understand the tendency toward solid solution. In Li$_{(1-x,y)}$(Fe$_{1-y/2}$,Mn$_{y/2}$)PO$_4$, the Fe$^{3+}$-$V$ pairs that form are diluted by Mn$^{2+}$-$Li^+$ pairs, and hence their effective interaction energy (which is attractive) is diluted, leading to a lower transition temperature. The effect of random bond disorder in lattice models has been well studied in model systems and has been shown to transform first-order transitions into second-order ones and ultimately into glassy disordered states in agreement with our results.$^{31-34}$ The disorder in the low-T single phase which we find between the two miscibility gaps for $y=x$ in Li$_{(1-x,y)}$(Fe$_{1-y/2}$,Mn$_{y/2}$)PO$_4$ should be thought thereby as a glassy state rather than a high-T solid solution.

B. Increasing transition voltage

The variation in voltage of each redox couple with Mn/Fe concentration can be understood by considering the energy of the intermediate solid solution phase. The voltage in a two-phase reaction from $\alpha \rightarrow \beta$ is related to the energy of the two phases,$^{35}$

$$\phi = - \frac{E_{Li_{x}(Fe,Mn)PO_4} - E_{Li_{x-y}(Fe,Mn)PO_4} - (x_{\beta} - x_{\alpha})E_{Li}}{x_{\beta} - x_{\alpha}}.$$  \hspace{1cm} (3)

For the sake of argument, we neglect the small solubility in the fully lithiated and delithiated phase so that the plateau voltages for Mn and Fe are the following:

\begin{align*}
\phi_{Mn} & = - \frac{E_{Li_{y}(Fe,Mn)PO_4} - E_{Li_{(1-y)}(Fe,Mn)PO_4} - yE_{Li}}{y} \hspace{1cm} (4) \\
\phi_{Fe} & = - \frac{E_{Li_{y}(Fe,Mn)PO_4} - E_{Li_{(1-y)}(Fe,Mn)PO_4} - (1-y)E_{Li}}{1-y} \hspace{1cm} (5)
\end{align*}

Consider, for example, the Mn redox voltage. In the delithiated state, all lithium vacancies are surrounded by hole states (Mn$^{3+}$ or Fe$^{3+}$) just as in pure MnPO$_4$ as drawn schematically in Fig. 9. Lithiation of pure MnPO$_4$ labeled as (a) in Fig. 9] leads to a state [Li$_{1-y}$MnPO$_4$ denoted as (b) in Fig. 9], where all Li$^+$ are surrounded by electron states (Mn$^{2+}$). This is different in the case of Li$_{(1-x,y)}$(Fe$_{1-y/2}$,Mn$_{y/2}$)PO$_4$. Lithiation on the Mn plateaus leads to the intermediate phase [=Li$_{1-y}$(Fe$_{1-y/2}$,Mn$_{y/2}$)PO$_4$ labeled as (c) in Fig. 9] where Li$^+$ will be surrounded by some Mn$^{2+}$ and some Fe$^{3+}$. The unfavorable Li$^+$-Fe$^{3+}$ interaction (denoted by the dashed line in Fig. 9) leads to a higher average energy per Li inserted than in the pure case, hence a lower voltage. This is shown in more detail in the Appendix. Hence, it is the increased energy of the intermediate disordered state which decreases the voltage of the high redox couple (Mn) and increases the energy of the low redox couple (Fe).

C. Reduced polarization

The trend observed in Fig. 8, that the polarization of the Fe$^{3+}$/Fe$^{2+}$ transition reduces as Mn substitution increases, and vice versa for the Mn$^{3+}$/Mn$^{2+}$ transition, can be understood considering the composition difference between phases. Reduced polarization implies a reduced activation barrier to phase transition. At fixed temperature, the concentration difference (of Li) in the two-phase region between Fe$_{1-y}$Mn$_{y}$PO$_4$ (α) and Li$_{1-y}$Fe$_{1-y}$Mn$_{y}$PO$_4$ (SS) monotonically decreases as the Mn composition y is increased. Similarly, the concentration difference in the two-phase region between Li$_{1-y}$Fe$_{1-y}$Mn$_{y}$PO$_4$ (SS) and LiFe$_{1-y}$Mn$_{y}$PO$_4$ (β) monotonically increases with increasing y. For the Fe$^{3+}$/Fe$^{2+}$ transition, systems with increased y must undergo less extreme fluctuations in Li concentration, so a higher number of MC moves are accepted at lower overpotential. For the Mn$^{3+}$/Mn$^{2+}$ transition, the same occurs as y is decreased. Hence, the decrease in plateau voltage polarization is a fairly straightforward consequence of a reduction in the composi-
tion difference between the initial and final state along the first-order phase transition. We should point out that the polarization captured by a Monte Carlo simulation is only part of the polarization in a real electrode. Contributions from electronic resistance, surface charge transfer, strain accommodation, or interface velocity limitations cannot be modeled with our approach.

V. CONCLUSIONS

In this work, we present a framework based on first-principles calculation to model the phase behavior and electrochemical trends of mixed olivine systems, with specific emphasis on Li$_i$(Fe$_{1−x}$Mn$_x$)PO$_4$. Monte Carlo simulations using a Hamiltonian based on a modified coupled cluster expansion parametrized from GGA+$U$ ab initio calculations of Li$_i$FePO$_4$ were used to determine the phase diagram, voltage curves, and solubility limits of Li$_i$(Fe$_{1−x}$Mn$_x$)PO$_4$ with significant experimental agreement. Also, experimental trends in the transition voltage and polarization are mirrored in the calculations.

Given the efficacy of the model used in this work, several insights regarding the origin of the phase behavior and electrochemical trends observed in Li$_i$(Fe$_{1−x}$Mn$_x$)PO$_4$ can be made. The formation of the intermediate single-phase region (SS) centered at Li$_i$(Fe$_{1−x}$Mn$_x$)PO$_4$ and the lowered transition temperature to form solid solution are the result of the dilution of phase-separating interactions. The attractive interaction between Mn$^{2+}$ and Li$^+$ is diluted by Fe$^{3+}$ in the SS and vice versa. Similarly, the observed changes in plateau voltages can be explained by the change in energy of the intermediate solid solution. Due to the unfavorable Li$^+$ coordination, the Fe$^{3+}$ and Mn$^{2+}$ states in the SS have higher energy than in their pure FePO$_4$ or LiMnPO$_4$ phases leading to higher and lower plateau voltages for Fe$^{3+}$/Fe$^{2+}$ and Mn$^{3+}$/Mn$^{2+}$, respectively. While we have focused on the Li$_i$(Fe$_{1−x}$Mn$_x$)PO$_4$ system, our model to explain the variation in redox plateau voltage is likely valid for other transition-metal combinations as well, as all will have SS phases with unfavorable Li$^+$-M$^{3+}$ (or V-M$^{2+}$) pairs separating the voltage plateaus. The trends in polarization arise as a result of the composition difference in Li between the intermediate solid solution and end-member phases.

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APPENDIX

Neglecting triplet interactions and the small solubility in the fully lithiated and delithiated phases, the shift in the transition voltage of the Mn$^{3+}$/Mn$^{2+}$ and Fe$^{3+}$/Fe$^{2+}$ redox couples is shown to be independent of the point energies ($J_{Fe}$ and $J_{Mn}$) and depends entirely on the Mn content $y$ and the difference in the pair interaction energies between the completely delithiated/lithiated phase and the intermediate phase Li$_i$(Fe$_{1−y}$Mn$_y$)PO$_4$.

Subtracting Eq. (3) from Eq. (4) yields $\Delta \phi_{Mn}$:

$$\Delta \phi_{Mn} = \frac{-(E_{Li(Fe_{1−x}Mn_{x})PO_4} - E_{(Fe_{1−y}Mn_{y})PO_4})}{y} + E_{LiMnPO_4} - E_{MnPO_4}. \quad (A1)$$

Substituting Eqs. (1) and (2) into Eq. (A1), where $PI$ denotes the pair interaction energies,

$$\Delta \phi_{Mn} = -\frac{[J_o - J_{Fe}(1 - y) + J_{Mn} + PI_{Li(Fe_{1−x}Mn_{x})PO_4}] - [J_o - J_{Fe}(1 - y) - J_{Mn} + PI_{(Fe_{1−y}Mn_{y})PO_4}]}{y} + 2J_{Mn}$$

$$= \frac{PI_{Fe_{1−y}Mn_{y}PO_4} - PI_{LiFe_{1−y}Mn_{y}PO_4}}{y}. \quad (A2)$$

It should be noted that $PI_{Fe_{1−y}Mn_{y}PO_4} = PI_{LiMnPO_4} = PI_{MnPO_4}$ since all represent states where either all Li and Fe sites are occupied, or all are unoccupied, hence equivalent pair interactions. Because of unfavorable Li$^+$-Fe$^{3+}$ interactions, $PI_{LiFe_{1−y}Mn_{y}PO_4}$ $> PI_{Fe_{1−y}Mn_{y}PO_4}$, which explains the negative shift in the Mn$^{3+}$/Mn$^{2+}$ transition voltage in Li$_i$(Fe$_{1−y}$Mn$_y$)PO$_4$. A similar line of reasoning can be used to explain the positive shift in the Fe$^{3+}$/Fe$^{2+}$ transition voltage in Li$_i$(Fe$_{1−y}$Mn$_y$)PO$_4$.
