

Short-range charge ordering in Mn-doped LiFePO₄

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This paper explores the impact of Mn doping in the battery electrode material Li(Mn)FePO₄ by computational methods. Structures are generated at up to 6.25% Li and 3.125% Mn content with varying Li, Fe, and Mn configurations. The oxidation state of the Fe and Mn ions are explicitly set using occupation matrix control, while the structures are optimized using DFT + U. Although Mn is redox active and can exist in both the +III and +II states, there is a strong preference for the latter. We show that the charge-compensating electrons prefer to occupy the Mn sites rather than the Fe sites during Li insertion. This results in Mn(II) and Fe(II) ions that interact electrostatically with the positively charged Li ions. The DFT + U data are consequently used to parametrize a Coulomb potential, incorporating short-range two-body corrections, and utilized within a Monte Carlo approach. The short-range order between the atomic species are then quantified by their coordination numbers at varying temperatures. The Monte Carlo sampling demonstrates lower Li-Li clustering in the Li(Mn)FePO₄ system at temperatures below 500 K and thus more disorder as compared to the undoped system. On average, this results in less cluster formation, which correlates with the enlarged solid solution region found in the LiMnFePO₄ phase diagram.

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I. INTRODUCTION

The LiFePO₄ (LFP) intercalation battery electrode is predicted to dominate parts of the global Li-ion battery market in the coming years [1]. For example, LFP is composed of more abundant elements [2], it is associated with cheaper production costs [3], and shows a more stable electrochemical performance when compared to many competing electrode formulations [4]. Since its proposal as an electrode material in 1997 by Padhi *et al.* [5], LFP has undergone extensive research leading to commercial viability, though several performance related challenges still persist [6].

At the atomistic level, incorporation of Li⁺-electron pairs into the crystal structure of FePO₄ induces a phase transition into a Li-rich LFP phase and a Li-poor FP phase [5]. The phase transition is characterized by an ordering of Li⁺ and Fe(II) with respect to vacancies and Fe(III). Full (dis)charge of the (LFP)FP electrode particles therefore proceeds through a sluggish movement of an FP/LFP interface within the bulk [7]. This behavior has unwanted effects at the meso- and microscale, where it induces coherency strain that affects the mechanical stability of the electrode particles [8].

A promising way to enhance the electrochemical performance of the LFP electrode is to make modifications that stabilize the solid solution phase of the LFP system. For the bulk system, a solid solution phase is present in the high-temperature region of the equilibrium phase diagram [9,10].

One way to influence the phase transformation is through size reduction of the LFP particles. In fact, charge/discharge experiments on nanosized LFP particles have shown higher (dis)charge rates compared to larger particles [11]. The improved performance was linked to the easier formation of a solid solution phase at the nanoscale [11,12].

Besides reducing the particle size, one of the more popular strategies to further enhance the capacity and the electrochemical rate performance of the LFP electrode is through doping, where Mn has been pointed out as one of the most promising dopants [13–17]. The addition of low amounts of Mn has been shown to improve mechanical properties [18] and kinetics, both with respect to electron conductivity and Li ion diffusion [13,19,20]. These improvements are attributed to an expansion of the unit cell owing to the higher ionic radii of Mn, which in turn mitigates the coherency strain between the FP/LFP phases while also enlarging the Li-ion diffusion channels. Mn doping has also been reported to influence the FP/LFP phase transition itself by stabilizing the solid solution phase, thereby making it accessible at lower temperatures [13,21].

The stability of the solid solution phase is in turn strongly correlated with the short-range order (SRO) between the Li⁺ and Fe(II) ions, where an increased Li⁺-Fe(II) SRO indicate a more favoured phase separation between LFP and FP. The SRO is thereby also related to the Li⁺-Fe(II) and vacancy-Fe(III) interactions. Thus, from a fundamental point of view, the solid solution phase implies an increased activity of Fe(II), as has also been discussed by Ellis *et al.* [22].

The mechanistic picture that emerges during Li intercalation in redox-active materials such as LFP, is that when the electron that is introduced together with the Li-ion reduces an Fe(III) into Fe(II), it is localized into a so-called small polaron [23]. Within this picture, the increased activity of Fe(II) leads

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to an increased electron mobility. Accurately capturing the Li^+ -Fe(II) interaction and considering the configurational arrangements of both species in simulations is, therefore, crucial when reproducing the experimentally derived phase diagram for the LFP system [24]. In a previous work, we developed an interaction model and performed simulations to quantify the Fe(II) activity and SRO in LFP at low and high Li contents [25]. Through these simulations, we showed that a significant amount of isolated Fe(II) exist in the high-temperature solid solution regime. At lower temperatures, a high degree of SRO was determined and several different cluster configurations were found in the system, consisting of chainlike structures formed by alternating Fe(II)- Li^+ pairs.

In this work, we extend on the previous investigation and develop an interaction model for $\text{Li}_x\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4$ (LMFP, $y = 0.03125$) based on density functional theory (DFT) data to investigate the configurational effects of Mn doping through canonical Monte Carlo simulations. More specifically, we use this model framework to address (i) whether the Mn site is redox active during the intercalation, i.e., whether the polaron prefers to localize on Fe or Mn, and (ii) whether the addition of Mn affects the Fe(II) activity and SRO.

II. METHODOLOGY

Electronic structure calculations were conducted using spin-polarized density functional theory (DFT) with a plane-wave basis set and pseudopotentials [26]. The Perdew-Burke-Ernzerhof density functional [27] was utilized with the Hubbard correction of Dudarev *et al.* [28], with a U-J value of 4.0 for Fe and 3.9 for Mn [29]. The procedure is further explained in an earlier paper on a diluted LFP system [25].

To enforce the localization of the polaron, occupation matrix control (OMC) was used in combination with DFT + U [30]. This allows explicit control of both ionic and electronic degrees of freedom in the $\text{Li}_x\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4$ system. Values of $x = 0.03125$ and $x = 0.0625$ with $y = 0.03125$ % were used. Supercells of size $2 \times 2 \times 2$ were employed, with one Fe exchanged to Mn. Addition of one Mn yields a concentration of 3.125%, which is the lowest amount possible in the $2 \times 2 \times 2$ supercell used. This is also within the range of Mn dopant concentrations that exhibits the best electrochemical performance [15,16].

The crystal structure of LFP is presented in Fig. 1(a). One of the Fe-sites is exchanged with an Mn, as shown in Fig. 1(b). Structures were generated with different charge ordering in the sublattices [Li,Va], and [Fe(II),Fe(III),Mn] where Mn has the oxidation state of either +II or +III. A detailed view of the structure including key Li-Li distances are given in Fig. 1(c) and 1(d). Note that these structures are not relaxed and that the distances correspond to the pure LFP structure, with no Mn. Two-body parameters ($C_{a_i a_j}^r$) describing the interactions between Li-Li, Li-Fe(II), Fe(II)-Fe(II), Li-Mn(II), and Fe(II)-Mn(II) were fitted to the total DFT + U energies according to Eq. (1).

$$E = \sum_{\langle i,j \rangle} \left[C_{a_i a_j}^r + \frac{q_{a_i} q_{a_j}}{r_{ij}} \right] + \text{const.}, \quad (1)$$

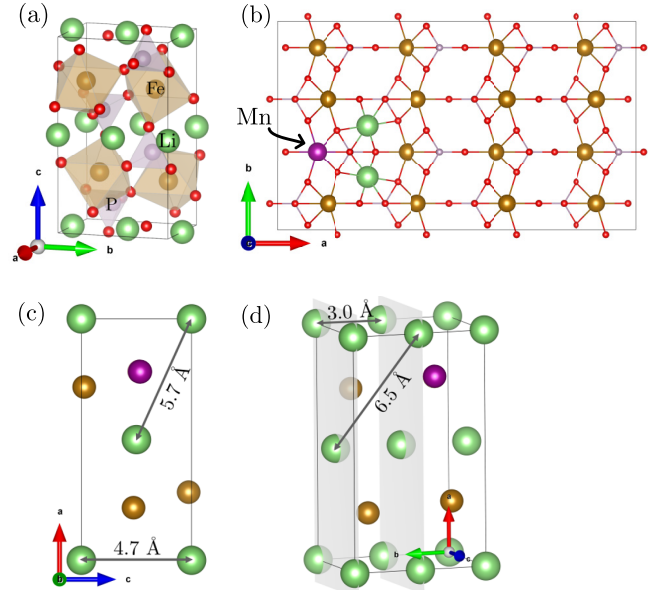


FIG. 1. The crystal structure of (a) LiFePO_4 , (b) a $2 \times 2 \times 2$ supercell of Li(Mn)FePO_4 with two Li ions where one Fe-site has been exchanged with one Mn, (c) the ac plane excluding oxygen and phosphorous for visualization purposes, and (d) a three-dimensional rendering of multiple such ac planes. The structures show the unrelaxed framework used as input for the DFT + U calculations, and is the framework used during the statistical sampling procedure. The labels show the respective chemical species: lithium (green), iron (brown), manganese (magenta), phosphorous (purple), and oxygen (red).

where a denotes the ion type [Li, Fe(II), or Mn]. The long-range electrostatic interactions are defined by the atomic charges q_{a_i} and q_{a_j} , for each atomic pair (i, j) and the distance between them denoted as r_{ij} . To ensure charge neutrality we require that, $Q = q_{\text{Li}} = -q_{\text{Fe(II)}} = -q_{\text{Mn(II)}}$ where Q is the charge scaling factor. Note that the constant term depends on the composition of the configuration, but is otherwise independent from the distribution of species on the lattices.

The parameters of the interaction model were fitted using the software package ccs [31] and used as an input to GULP for thermodynamic sampling [32]. This enables fast energy predictions during the Monte Carlo sampling procedure, in which all systems were equilibrated for 2×10^6 steps and data produced in the following 200 000 steps. Sampling was performed using supercells of dimensions $4 \times 8 \times 8$, comprising a total of 1984 Li sites.

Simulations were conducted across a temperature range of 200–1000 K. The high-temperature behavior of LFP is particularly interesting due to the three-phase coexistence described by the phase diagram that showcases an eutectoid point at 500 K and 60% Li [9,10]. This three-phase coexistence persists up to 600 K in the experimental phase diagram [10] and up to 900 K in the theoretical one [24]. The third intermediate phase appears to be metastable and has been observed in room temperature [33–35], thereby requiring the investigation of temperatures exceeding typical battery operating conditions. The code used in this paper can be found at Ref. [36].

III. RESULTS AND DISCUSSION

A. Data sets

To isolate and systematically analyze the interactions between individual chemical species, structures at low Li concentrations are generated. The $2 \times 2 \times 2$ supercell of LFP presented in Fig. 1(b) can accommodate 32 Li ions. First, one Li-Fe(II) pair is added to reach 3.125% lithiation. Within this system, there exists 16 symmetrically nonequivalent configurations of different Li-Fe(II) distances. By exchanging one Fe site with one Mn, a larger number of configurations can be obtained. Another Li-Fe(II) pair is subsequently added to create structures of 6.5% lithiation at a constant Mn-concentration of 3.125%.

Mn ions are known to exhibit multiple oxidation states, including +II, +III, and occasionally +IV. The +IV state typically emerges near the electrode/electrolyte interface during disproportionation, following the reaction $2\text{Mn(III)} \rightarrow \text{Mn(IV)} + \text{Mn(II)}$ [37]. Since our focus is on ordering phenomena within the bulk material, we restrict our analysis to the Mn(II)/Mn(III) redox couple.

To limit the number of DFT-calculations, the amount of systems is reduced as follows: $2 \times 2 \times 2$ supercells at 6.5% lithiation are generated with different Li configurations. These systems are first categorized into five groups based on their respective Li-Li distances, which are then subsequently categorized into five groups based on their Mn(II)/Fe(II)-Fe(II) distances. Choosing one system from each group, results in 25 configurations, uniformly covering the space of possible Li-Li distances and Mn(II)/Fe(II)-Fe(II) distances.

In addition, to determine whether the Mn site hosts the charge compensating electron, two datasets are initially generated with +II or +III oxidation number respectively. In the data set with Mn(III), its location is chosen randomly from all possible sites that are not occupied by an Fe(II) atom. For the system with 3.125% lithiation with one Mn(III) and one Fe(II), clustering is done based on the Li-Fe(II) distances and the Mn(III)-Fe(II) distances. The energies of all four data sets are given in Fig. 2.

Thus the approach allows us to reach 6.5% lithiation, leading to a total of 2×16 plus 2×25 number of structures, with varying Li-Li, Li-Fe(II), Li-Mn(II/III), and Fe(II)-Mn(II/III) distances. The lowest energies in the LMFP system are obtained when the Mn has an oxidation number of +II. This is attributed to the electronic configuration of the different oxidation states. Mn(II) has an electronic configuration of $3d^5$, similar to Fe(III). In turn, Mn(III) is $3d^4$ and has two unpaired electrons, making it less stable. Mn(III) is also known to display strong Jahn-Teller distortions [38,39].

Figure 3 presents the distances between the Mn ion and the closest oxygen atoms in the structures. In this context, it is evident that Mn(III) causes a more significant distortion in the crystal lattice as compared to Mn(II). Given this, along with the increased energetics, we can conclude that the Mn dopants will stay in the +II oxidation state unless the system undergoes complete delithiation. From this point forward, we will therefore use the data containing Mn in the +II state.

Figure 4 showcases the energy change in the LFP and LMFP systems as the polaron is placed on two transition metal (TM) ions, either on the Mn(II) site or the Fe(II) site. There is

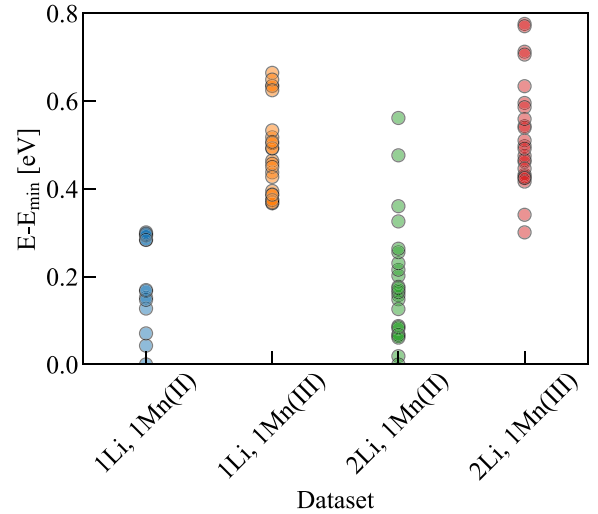


FIG. 2. Scatter plot comparing the DFT + U energies of systems with 1 Li and 1 Mn(II), 1 Li and 1 Mn(III), 2 Li and 1 Mn(II), and 2 Li and 1 Mn(III). In the case of Mn(III), the electron is located on an Fe site. Lowest energies are obtained when the Mn has a +II oxidation number. The 1 Li and 2 Li data sets are normalized separately.

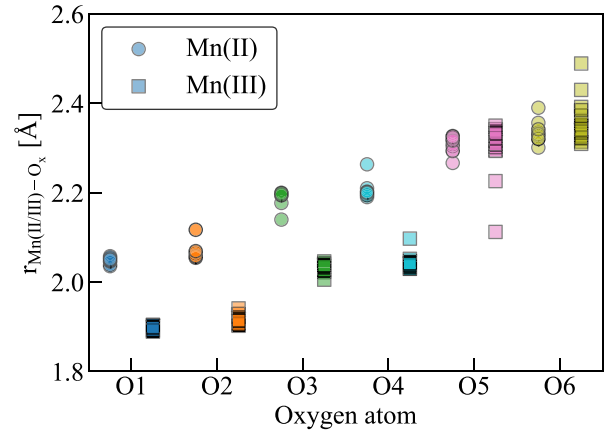


FIG. 3. Mn(II)-O and Mn(III)-O bond lengths for the different datasets presented in Fig. 2. Longer distance between O1 and O6 indicates a higher distortion in the crystal structure.

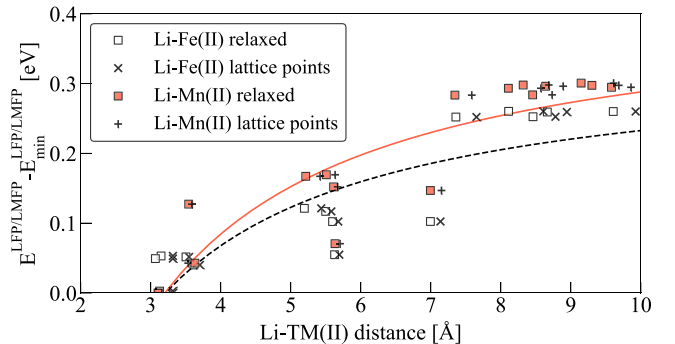


FIG. 4. The change in energy with Li-polaron separation in which the polaron is either located on an Mn site ($k = 1.36$, $c = 0.42$) or the polaron is located on an Fe site ($k = 1.1$, $c = 0.34$) [25]. Coulomb potentials parametrized by $E = -(k/r) + c$, where r is the distance between Li and the TM(II), are applied to the lattice points to guide the eye. Note that this fitting does not account for the periodicity of the supercell.

TABLE I. Fitted parameters in the interaction model described by equation 1 for the Mn doped LMFP and the undoped LFP [25].

r_{aij} [Å]	a_i	a_j	C [eV]	
			LMFP	LFP
3.05	Li	Li	−0.01	0.01
3.92	Fe(II)	Fe(II)	0.00	0.19
3.92	Mn(II)	Mn(II)	0.00	—
3.92	Fe(II)	Mn(II)	0.00	—
3.32	Li	Fe(II)	0.05	−0.01
3.55	Li	Fe(II)	0.07	0.04
3.70	Li	Fe(II)	0.05	0.10
3.32	Li	Mn(II)	−0.01	—
3.55	Li	Mn(II)	0.09	—
3.70	Li	Mn(II)	0.03	—
$Q = q_{Li} = -q_{Fe(II)} (= -q_{Mn(II)})$			0.31e	0.26e

a higher-energy increase as the Li-Mn(II) distance increases as compared to Li-Fe(II), indicating a preference for shorter Li-Mn(II) separations within the LMFP structure.

B. Fitting an interaction model

The two-body terms in equation 1 are parameterized using all structure-energy data containing Mn(II), with and without Fe(II). Additionally, we also use the data from our previous work for the Li-Fe(II) system without any dopants [25]. The electrostatic term, Q , is an effective average of all interactions between the three charged species.

For comparison, two interaction models are shown in Table I. One for the doped LMFP system defined in this study and one for the pure undoped system presented previously [25]. The mean-square error of the parameter fitting is 0.5 meV, much lower than the 2.3 meV that we obtained when fitting the pure LFP data. This is most likely due to the larger data set.

The Li-Fe(II) interaction terms are similar between the two systems. However, there is quite a pronounced difference for the Li-Li and Fe(II)-Fe(II) parameters. This difference is likely counterbalanced by the Li-Mn(II) parameters as well as the electrostatic term. No data exists when Fe(II) and Mn(II) are within the closest neighbors, which is why the interaction terms of this two-body cluster is zero. This is also the case for the Mn(II)-Mn(II) term. Since this is solely a fitting procedure, we anticipate variations in the terms that should not be given too much physical significance.

C. Statistical sampling

The generated interaction model is used in a sampling procedure to obtain statistical data on the clustering behavior of the different species in the system with 3.125% Mn at a 6.25% degree of lithiation. Initial structures of $4 \times 8 \times 8$ supercells are made by randomly distributing the Mn(II) species within the [Fe(II), Fe(III), Mn(II)] sublattice. The Monte Carlo simulations are conducted at a temperature range of 200–1000 K and compared to data at the same lithiation level obtained for the undoped LFP system from our previous work [25].

The process of Li insertion and extraction can cause cation migration and mixing, which can affect the distribution of dopant elements during battery cycling [40]. Two scenarios are therefore investigated: one in which the Mn(II) ions are fixed in their initial positions and one where they are allowed to change their position within the [Fe(II), Fe(III), Mn(II)] sublattice.

The first scenario, in which the Mn(II) are fixed in a disordered manner is presented in Fig. 5. The Li-Li coordination of the system, within a cutoff radius of 7 Å, is shown in Fig. 5(a) and Fig. 5(b). The coordination within the LMFP structure is virtually the same as in the undoped LFP at temperatures above 500 K. However, below 500 K we see an increase in the fraction of both isolated Li ions and those coordinating one other Li ion [see Fig. 5(a)]. At the same time we see a decreasing fraction of Li ions coordinating two or more other Li ions. There is therefore overall less Li ions within a radius of 7 Å.

The Mn doping also results in a difference in coordination between Li and the +II transition metals (TM), Mn and Fe, as can be seen from Fig. 5(c) and Fig. 5(d). At temperatures of 200 and 300 K, the number of isolated TM(II) remains the same as in the undoped system, but there is a decrease of the 1 coordinated Li-TM(II) pairs while there is an increase those coordinating to 2 TM(II)s. By studying the coordination of the individual TM(II)s, Mn(II), and Fe(II), around the Li ions, it appears that a slightly higher amount of Mn(II) coordinate to Li compared to Fe(II). The preference for Mn(II) is fully consistent with the DFT + U results presented in Fig. 4 where larger Li-Mn(II) separations are higher in energy as compared to the Li-Fe(II) case.

Next, we analyze the size of Li clusters in the system as a function of temperature. We consider clusters where Li ions are linked by TM(II) species following the analysis in Ref. [25]. The average size of linked clusters are presented in Fig. 6 showing reduced clustering in the Mn-doped system as compared to the undoped one. The clusters containing either only Li-Fe(II) or only Li-Mn(II) are similar in size.

In the LMFP case, long-range electrostatic interactions are more pronounced compared to the undoped LFP, leading to increased repulsion between Mn(II) ions and a preference for a disordered Mn arrangement. However, this increased electrostatic interaction alone does not fully explain the reduced clustering. Comparing this to the Va-Fe(III) case from our previous study, which also displayed enhanced electrostatic interactions with $Q = 0.33e$ [25], we observed even higher clustering tendencies than in the Li-Fe(II) case. This suggests that short-range interactions also play a role. If there is a preference for Li-Mn(II), Mn will act as a scavenger for Li, resulting in Li distributing across all Mn(II) and thus preventing the formation of large TM(II)-Li-TM(II) clusters.

We have thus far considered the case where the Mn(II) is fixed in randomly distributed positions. The polaron occupying the Fe sites are allowed to change positions within the sublattices [Fe(II), Fe(III)] to simulate electron hopping. The assumption that the Mn remains fixed in its lattice sites is open to debate. At the low temperatures of battery cycling, the probability of Mn diffusing into another site is likely low. However, theoretical studies suggest that Li insertion and extraction can significantly alter the microstructure of bulk

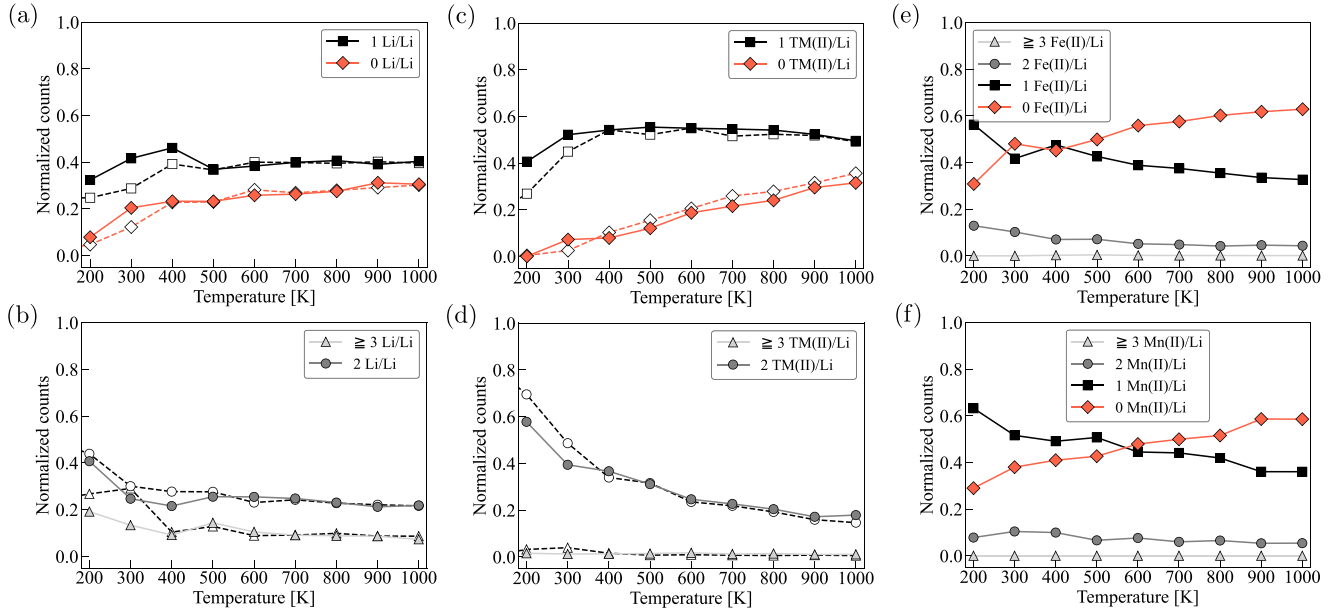


FIG. 5. Coordination plots from the Monte Carlo simulations of $4 \times 8 \times 8$ supercells at 6.25% Li, 3.125% Mn(II), and 3.125% Fe(II). The Mn atoms are fixed in a disordered arrangement and elements are allowed to change position within the sublattices [Li,Va], and [Fe(II), Fe(III)]. (a)–(b) coordination between every Li-Li at 7 Å cutoff distance, (c)–(d) Coordination between every Li-TM(II) at 4 Å cutoff distance, (e) coordination between every Fe(II)-Li at 4 Å cutoff distance, and (f) coordination between every Mn(II)-Li at 4 Å cutoff distance. Dashed lines and uncoloured markers represent the undoped LFP data previously presented in Ref. [25].

electrode particles, for example through grain boundary migration [41]. The distribution of dopant elements might then be entirely different in an aged battery electrode.

Another set of simulations are therefore conducted where the Mn(II) ions are freely sampled within the [Fe(II), Fe(III), Mn(II)] sublattices. No substantial difference were found in these simulated systems as compared to the case when the Mn(II) were fixed in their initial positions. The trend remains the same, of lower Li-TM(II)-Li clusters. In both doping

scenarios investigated, with Mn in fixed random position or where Mn is free to move, we observe that linked clusters within the system become smaller as compared to the undoped case. This tendency is more pronounced at lower temperatures and almost completely diminishes at temperatures above 500 K.

For the doped LMFP, less pronounced clustering at lower temperatures implies a more stable solid solution. This correlates well with both experimental and theoretical studies presented in literature [13,21]. For example, the theoretically derived phase-diagram of LMFP with 10% Mn content shows all three phases (LFP, FP, and solid solution) at room temperature [21]. This demonstrates that a simplified model incorporating electrostatic effects and two-body interactions can effectively capture key aspects of the thermodynamic landscape and provide insight into the SRO.

The electrostatic interactions in the simulated system are defined by a single effective charge factor, $Q = \pm q_{a_i} = \pm q_{a_j}$. As a result, the electrostatic interactions for Li-Li repulsion, Li-Fe(II)/Li-Mn(II) attraction and Fe(II)-Fe(II)/Mn(II)-Mn(II) repulsion are treated identically. In this model, Q assumes a higher value of 0.31e, compared to 0.26e in the undoped system. That the electrostatic interaction is identical between Li-Fe(II) and Li-Mn(II) is clearly not represented by DFT + U data shown in Fig. 4, where larger separations between Li-Mn(II) results in larger energy variations. This discrepancy is not important for the short-range two-body clusters, since their energies are corrected using the short-range two-body terms $C_{a_i a_j}$. The issue arises in configurations where Fe(II) and Mn(II) ions are positioned at intermediate distances from a Li ion. In such cases, the model treats Fe(II) and Mn(II) equivalently, despite the fact that the interaction energy is higher for Mn(II).

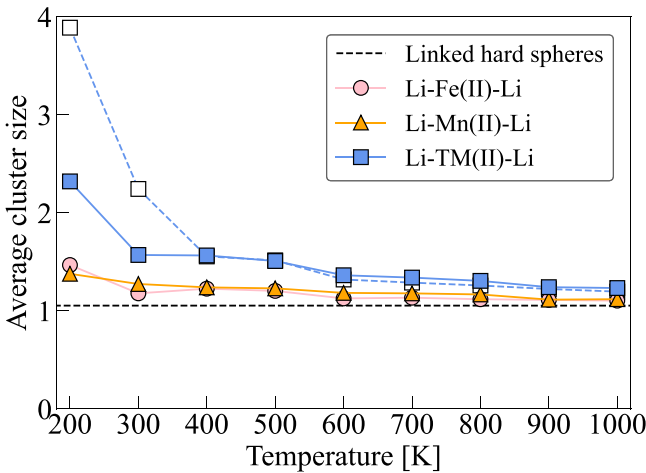


FIG. 6. The change in average cluster size of linked Li-TM(II)-Li clusters with temperature in LMFP and LFP. The uncoloured square markers represent the LFP system. The reference line represents a hard sphere model where there are no interaction between the species.

This simplification may obscure the SRO within the system. The question is then, if we had a more complex interaction model that can resolve the Li-Fe(II) and Li-Mn(II) at intermediate distances how would this effect the captured Li-Li ordering? Two factors are already clear, (i) the preference for Li-Mn(II) over Li-Fe(II) would be more apparent, (ii) we would see clusters containing more Mn(II) than Fe(II). While more Li-Mn(II) clustering would lead to more Li-Li order, the adjusted Mn(II)-Fe(II) repulsive interaction might compensate resulting in similar trends seen in the SRO.

Addressing this limitation in the interaction model is particularly important when simulating systems at higher Mn concentrations. For example, systems up to 80% Mn, which is currently the subject of extensive research [42]. The preference for Mn(II)-Li clustering might be enhanced at at higher Mn concentration leading to the to charge segregation observed experimentally [43–45]. Another compelling topic is the investigation of additional codopants that can further enhance the electrochemical performance of LFP [46–48]. Improving the interaction model requires incorporation of additional long-range correction terms that consider three-body clusters and/or unique charge scaling parameters for each unique ionic pair. These improvements would better capture the subtle energetic contributions that influence phase behavior and SRO.

Nonetheless, our simulation results align qualitatively with both theoretical and experimental observations suggesting solid solution stabilization [13,21,45]. Direct validation through comparison with SRO remains challenging. Existing Raman spectroscopy studies show little [49,50] to no change [51] in peak intensity, potentially reflecting local structural changes, but lack the resolution required for quantitative comparison. Similarly, pair distribution function analysis [52] show a decrease of peak intensity between Fe-O and Mn-O and thereby indicates a decrease in order but cannot say anything about the order between Li-Li or Li-TM. We therefore emphasize the need for future experimental work to provide more definitive insights into the SRO in these systems.

IV. CONCLUSION

We have investigated the temperature-dependent short-range charge ordering in LMFP with 3.125% Mn and a degree

of lithiation corresponding to 6.25% Li. This was done by parametrizing an interaction model based on DFT + U data of different Li, Fe(II), and Mn(II) configurations, where the long-range interactions are treated with a Coulomb potential and the short-range interactions are described by two-body interaction terms up to 4 Å. The DFT + U data show a higher stability of the Mn(II) oxidation state as compared to the Mn(III). It has therefore been assumed that the Mn remains in its +II charged state during the statistical sampling procedure.

Two scenarios were considered, one where the Mn site configuration within the structure remains fixed in its initially disordered state and one where the Mn is allowed to change its position within the sublattice [Fe(II), Fe(III), Mn(II)]. These scenarios converge to the same coordination between the Li-Li, Li-Fe(II), and Li-Mn(II) species, which ultimately results in similar cluster sizes. In both cases, less Li clustering was observed as compared to the undoped case. This effect is more pronounced at temperatures below 500 K. This implies a higher level of disorder within the system compared to pure LFP, which correlates well with the predicted higher stability of a solid solution phase in LMFP as compared to LFP. The clusters that can be found in the system are so-called linked clusters of Li-Fe(II)-Li. A direct consequence of less Li-Fe(II) coordinated pairs is a lower cluster size on average.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [36], embargo periods may apply.

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