Removing the Two-Phase Transition in Spinel LiMn$_2$O$_4$ through Cation Disorder

Tina Chen, Julia Yang, Luis Barroso-Luque, and Gerbrand Ceder*

Cite This: ACS Energy Lett. 2023, 8, 314–319

ABSTRACT: Resource constraints have become critical for the Li-ion industry. Spinel LiMn$_2$O$_4$ presents a cheaper, more sustainable alternative to traditional layered Li-ion cathodes, but its capacity is constrained by a two-phase transition at 3 V associated with large, inhomogeneous volume change leading to capacity loss. In this Letter, we argue that disorder can replace the two-phase region with solid-solution behavior to create high-capacity cathodes. By investigating the voltage curve and lithiation pathway of LiMn$_2$O$_4$ spinel with varying levels of Mn disorder, we find that disorder shortens the 3 V plateau by raising the energy landscape and stabilizing motifs found in solid-solution configurations. The plateau disappears completely with 25% Mn 16c occupancy. These results provide guidance on the optimal level of disorder in spinels to achieve both solid-solution behavior and good Li mobility and also highlight more generally how disorder can be utilized to reduce the effects of problematic phase transformations in ordered frameworks.

Rechargeable lithium-ion (Li-ion) batteries are used as the energy storage device of choice in electric vehicles. With the increasing electrification of transportation, demand for Li-ion batteries is expected to grow nearly 5-fold in the coming decade. Currently, the Li-ion cathode industry is dominated by well-ordered layered materials, such as Li(Ni,Mn,Co)O$_2$ (NMC) and Li(Ni,Ca,Al)O$_2$ (NCA). With their two-dimensional pathways enabling facile Li transport, these layered materials display impressive electrochemical performance but require Co or Ni to remain chemically stable in octahedral environments. As both Co and Ni are expensive and resource-scarce, it is imperative to develop high-energy-density cathodes with alternative structures that can utilize broader chemistries.

One prime example of such an alternative structure is spinel LiMn$_2$O$_4$, which uses earth-abundant Mn and also has excellent rate capability and thermal stability (of Mn$^{4+}$) in the charged state. While its theoretical capacity is 285 mAh g$^{-1}$, in commercial use its Li cycling has been restricted to the 4 V range between Mn$_2$O$_4$ and LiMn$_2$O$_4$ which provides only half the theoretical capacity. The remaining capacity cannot be accessed because cycling the additional Li between LiMn$_2$O$_4$ and Li$_2$Mn$_2$O$_4$ occurs at ~3 V through a strong two-phase reaction. Such first order transitions proceed with a strong compositional inhomogeneity in cathode particles leading to large stresses and concomitant capacity degradation. Guided by the general concept that disorder can disrupt the orderings, and thus reduce the strength, of two-phase reactions, recent experiments on heavily ball-milled cation-excess Li–Mn–O–F spinels confirm that disorder can indeed remove the 3 V plateau and lead to a high-rate, high-energy-density cathode material. While the most common type of disorder associated with spinel is inversion, in which the 16d transition metals (TM) swap with the 8a cations, experiments (in the Li–Mn–O–F systems and a Li–(Co,Al)$_2$O$_4$ system) indicate that TM occupancy of the 16c sites is crucial to disrupting the phase transition at the 3 V plateau. Li occupancy of 16d sites has also been shown to enable face-sharing environments seen in solid-solution-like configurations through the phase transition in spinel Li$_x$Ti$_3$O$_12$. In this paper, we model the complex structural arrangements that occur when a spinel is forced to undergo disorder of the 16d TM onto the 16c sites and investigate its electrochemical voltage profile and lithiation behavior. We demonstrate that even with modest amounts of disorder the solid-solution...
region of spinel can be extended, leading to a much smaller two-phase region. At larger levels of disorder, the two-phase region can be fully transformed into a solid-solution regime, consistent with experiments, pointing at cathode materials that can combine very high rate with very high capacity.

To investigate the complex configurational space that results with 16c/16d disorder, we build a cluster expansion (CE) model of the configurational energetics of the system, as described in section 1 in the Models and Methods section in the Supporting Information (SI). The model reproduces well the physical properties (i.e., phase diagram) of the DFT training data, as shown in Figure S2 in the SI. This model parametrizes the total energy of configurations in terms of site occupancies on the lattice and, when fitted to the interactions of clusters of sites, can be used in conjunction with Monte Carlo (MC) simulations (as described in the SI Model and Methods, section 2) to enable the calculation of finite-temperature thermodynamics with near ab initio precision. We fit the model to energies of configurations calculated using density functional theory (DFT) and verify the CE’s performance against the DFT data using physically relevant density functional theory (DFT) and verify the CE’s temperature thermodynamics with near ab initio precision. We fit the model to energies of configurations calculated using density functional theory (DFT) and verify the CE’s performance against the DFT data using physically relevant properties in the SI Model and Methods, section 3. Using semi-grand-canonical (sgc) MC, we calculate the voltage curves associated with topotactic (de)lithiation within spinel frameworks with varying levels of Mn 16c/16d disorder from the 16d sites onto the 16c sites, where d indicates the 16c Mn occupancy.

Figure 1 shows the calculated voltage profiles from sgc MC simulations of the disordered spinels, with increasing 16c/16d disorder visualized through color gradation from blue to red. The dark blue curve shows the voltage profile of the ordered spinel phase with \( d = 0.0 \), which includes the characteristic spinel plateaus at \( \sim 3 \text{ V} \) and \( \sim 4.3 \text{ V} \). The two-phase region at \( \sim 3 \text{ V} \) is evident by the large discontinuity in composition (\( x_{4/3} \)). Compared to experimental results of the ordered spinel \( \text{LiMn}_2\text{O}_4 \), the simulated voltage profile shows more steeply sloped behavior from \( \sim 3.8 \text{ V} \) to \( \sim 4.3 \text{ V} \) plateau due to the self-interaction of Mn in DFT, which is discussed further in SI Note 1. Additional comparisons of the average voltages of lithiation in ordered \( \text{LiMn}_2\text{O}_4 \) when using different DFT parameters (Li pseudopotential and DFT functional) are shown in Figures S1 and S3, and an additional comparison to the Monte Carlo simulation is shown in Figure S4. An additional small voltage step is also seen at around \( x = 0.7 \), which is consistent with experiments at temperatures slightly below room temperature.

As the Mn disorder onto the 16c sites increases, the \( \sim 3 \text{ V} \) plateau shortens starting from \( d = 0.05 \) and completely disappears when \( d = 0.25 \). The shortening of the \( \sim 3 \text{ V} \) plateau is a result of increased solubility on the \( x_{4/3} \) side. The \( \sim 4.3 \text{ V} \) plateau also disappears, and the more complex behavior around \( x_{4/3} = 0.5 \) is replaced with linearly sloping behavior. This is consistent with previous studies in \( \text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4 \) showing that the step at \( x_{4/3} = 0.5 \) in \( \text{LiMn}_2\text{O}_4 \) can be smoothed out by cation disorder on the 16d sites, as it originates mainly from interactions between 8a tetrahedral Li. The steeply sloping behavior of the highly disordered spinels is also consistent with that of the disordered rocksalts, which the disordered spinels approach when the Mn are fully disordered over the 16c and 16d octahedral sites \( (d \rightarrow 0.5) \). The higher voltages as \( x_{4/3} \rightarrow 0 \) for more disordered spinels, however, are not consistent and due to the lack of oxygen oxidation, which is not included as a redox mechanism in the CE model. Explicit DFT calculations in this regime, in which oxygen oxidation is allowed, are consistent with experiments on the partially disordered spinel, as described in SI Note 2 and shown in Figures S5 and S6. An overall increase in average voltage with disorder can also be observed, indicating that disorder raises the energy of the fully delithiated \( \text{Mn}_2\text{O}_4 \) more so than it does the fully lithiated \( \text{Li}_2\text{Mn}_2\text{O}_4 \).

We hypothesize that the mechanism by which 16c/16d disorder removes the two-phase region is through raising the energies of the stable phases (spinel \( \text{LiMn}_2\text{O}_4 \) and lithiated spinel \( \text{Li}_4\text{Mn}_2\text{O}_4 \)) and lowering the energies of the solid-solution configurations at intermediate Li composition. Disorder on 16c/16d increases the energy of the spinel phase because electrostatic repulsion when Mn occupies 16c raises the site energy of Li in the face-sharing 8a sites. Disorder on 16c/16d can also lower the energy of the solid-solution phase through Li occupancy of non-Mn-occupied 16d sites, which stabilizes face-sharing environments in spinel \( \text{Li}_4\text{Ti}_2\text{O}_12 \). Using the CE and MC simulations, we confirm our hypothesis and obtain an additional mechanistic understanding by sampling the configurations observed along the phase transition.

To confirm that the energies of the spinel and lithiated spinel increase with the addition of 16c/16d disorder, we use the CE to evaluate the configurational energies of 100 partially disordered configurations, generated as described in SI Note 3, at the compositions \( \text{LiMn}_2\text{O}_4 \) and \( \text{Li}_4\text{Mn}_2\text{O}_4 \). The energies of partially disordered \( \text{LiMn}_2\text{O}_4 \) (green) and \( \text{Li}_4\text{Mn}_2\text{O}_4 \) (red) are shown with respect to the ordered states in Figure 2. Both spinel and lithiated spinel energies increase with disorder, but the energy increase is most pronounced for the \( \text{LiMn}_2\text{O}_4 \) spinel due to the decrease in tetrahedral Li in \( \text{LiMn}_2\text{O}_4 \) with disorder (see Figure S7 in the SI). Thus, Figure 2 confirms that the endmember phases of the two-phase region in ordered spinel become less stable with disorder, but the effect is more pronounced in \( \text{LiMn}_2\text{O}_4 \).

To investigate how disorder stabilizes solid-solution configurations relative to the spinel and lithiated spinel, we analyze the configurations sampled by the MC within the \( x_{4/3} \) range of the two-phase region to understand how (de)-
lithiation occurs in the partially disordered spinel compared to the ordered spinel. Figure 3 shows the concentration of tetrahedral (tet) and octahedral (oct) Li environments (Figure 3a,b) and tet environments categorized by the presence of any face-sharing nearest neighbor cations (Figure 3c,d) in the ordered \((d = 0.0)\) system and a disordered \((d = 0.1)\) system. The concentrations of tet-occupied and oct-occupied Li are shown in green and red in Figure 3a,b, and the isolated (non-face-sharing) tet Li, Li-face-shared tet Li, Mn-face-shared tet Li, and both Li- and Mn-face-shared tet Li are shown in black, blue, purple, and orange, respectively, in Figure 3c,d.

The results in Figure 3a,c confirm that, in the ordered system \((d = 0.0)\), Li is inserted into isolated tet sites \((8a\) sites, left inset in Figure 3c) until they are fully occupied (transparent green regime). The sudden jump in \(x_{Li}\) indicates a phase transition (transparent blue regime) along with the shift from tet to oct occupancy (right inset in Figure 3c). Lithiation in the disordered system \((d = 0.1)\) initially proceeds as in the ordered system, with the insertion of isolated tet Li. From \(x_{Li} \approx 0.4\) to \(x_{Li} \approx 1.2\), Li begins to occupy oct sites (left inset in Figure 3d), as evidenced by the rise in oct Li concentration (red in Figure 3b), and Mn-face-sharing tet sites (right inset in Figure 3d), as evidenced by the rise in tet Li with Mn-face-sharing environments (purple in Figure 3d). While the lower electrostatics between face-sharing Li\(_{tet}\) and Li\(_{oct}\) than between face-sharing Li\(_{tet}\) and Mn\(_{oct}\) would suggest a predominance of Li\(_{−}\)Li face-sharing over Li\(_{−}\)Mn face-sharing, the vastly larger population of tetrahedral environments that have a singly face-sharing Mn compared to those face-sharing with only one Li (see Figure S8 in the SI) makes it more likely for Li to be inserted into Mn-face-sharing sites, creating the...
face-sharing Li–Mn seen in Figure 3d. Besides a flattening of the isolated tet occupancy, no particular change in site occupancies characterizes the typical LiMn$_2$O$_4$ spinel stoichiometry even for this moderate level of disorder. Instead, lithiation until $x_{Li} \approx 1.4$ involves Li occupying Li-face-sharing tet sites (blue in Figure 3d). The regime involving more complex solid-solution insertion of Li into oct sites and face-sharing tet sites is highlighted in transparent red. The two-phase region in the $d \approx 0.1$ disordered spinel is already significantly reduced and appears between $x_{Li} \approx 1.4$ and $x_{Li} \approx 2.0$.

At intermediate Li content, face-sharing tet sites and oct sites in the disordered system are not accessible in the ordered spinel but are energetically competitive enough to appear in the disordered system. Unlike the only doubly face-sharing oct environments available in the ordered spinel, the disordered system contains environments with only one face-sharing contact, creating less electrostatic repulsion. The additional occupation of oct sites and face-sharing tet sites allows solid-solution insertion of Li past the spinel composition ($x_{Li} = 1.0$) to $x_{Li} \approx 1.4$, shortening the two-phase region and voltage plateau from 1.0 Li/Mn$_2$O$_4$ to 0.6 Li/Mn$_2$O$_4$.

From the configurational energies of the disordered spinel and lithiated spinel (Figure 2) and the configurations sampled from MC (Figure 3), we find that disorder reduces the two-phase region by destabilizing the spinel and lithiated spinel phases and stabilizing solid-solution configurations. These two effects can be clearly observed in Figure 4 which shows the simulated voltage curves indicate that the two-phase region and $\sim 3$ V voltage plateau disappear at $d = 0.25$, corresponding to 25% Mn 16c occupancy. Spinel with higher levels of disorder also lack two-phase behavior, indicating that they would also display solid-solution behavior, but their spinel characteristics decrease with disorder. Because the Mn begin to occupy 16c sites, the 8a–16c network that enables 3-D Li migration in spinel LiMn$_2$O$_4$ becomes increasingly obstructed with disorder. While Li can percolate through other tet sites (8b and 48f) that become accessible by disorder, the excess loss of spinel character and its channels with facile Li migration impacts the overall Li mobility in, and thus the rate capability of, the highly disordered materials.

However, disordered spinels with slightly lower levels of disorder ($d = 0.15–0.20$) likely still maintain many of the advantages of the more disordered spinels. For example, disordered spinels with $d = 0.15–0.20$ show significantly shorter voltage plateaus (from $x_{Li} \approx 1.7$ to $x_{Li} \approx 2.0$ per O$_2$) compared to the ordered spinel ($x_{Li} = 1.0$ to $x_{Li} = 2.0$). Thus, most of the Li inserted through a two-phase region in the disordered spinel can lithiate through solid solution in the $d = 0.15–0.20$ disordered spinels. Such lithiation through solid solution rather than two-phase behavior is expected to be more facile, as the system does not need to overcome barriers associated with nucleation and growth of a secondary phase. Disorder over 16c/16d sites also breaks the 16d Mn ordering that is responsible for the collective Jahn–Teller distortion in the ordered spinel. Thus, partially disordered spinels with 15–20% 16c Mn or TM occupancy are likely to show mostly solid-solution behavior without collective Jahn–Teller distortion as well as good rate capability due to high spinel character.

Our work shows that it may be possible to create a high-capacity earth-abundant spinel cathode material using partial 16c/16d disorder. Using ab initio modeling, we find that Mn disorder between the 16d and 16c sites in spinel LiMn$_2$O$_4$ shortens the two-phase region and 3 V plateau between LiMn$_2$O$_4$ and Li$_2$Mn$_3$O$_8$ even eliminating it with 25% Mn 16c occupancy. Our analysis indicates that the shortened plateau is due to disorder elevating the overall energy landscape and making higher-energy solid-solution configurations more accessible. The use of disorder to reduce and even remove two-phase regions by raising the overall energy landscape can be extended to other systems with problematic phase transformations within ordered frameworks. The suppression of the rate- and cyclability-limiting two-phase region of the spinel through disorder provides an avenue by which to optimize partially disordered spinels, bringing us another step closer to cheaper high-rate, energy-dense Li-ion cathodes.
Model and methods; details on the discrepancy between the experimental and simulated voltage curves of the ordered spinel LiMn$_2$O$_4$; analysis of the effect of oxygen oxidation on the disordered spinel voltage curves; details on the generation of the disordered LiMn$_2$O$_4$ and Li$_2$MnO$_4$; details on sampling of the solid-solution configurations in the two-phase region of the ordered system; and analysis between cluster expansion-evaluated energy of disordered LiMn$_2$O$_4$ configurations and fraction of tetrahedral Li (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Gerbrand Ceder — Department of Materials Science and Engineering, University of California Berkeley, Berkeley, California 94720, United States; Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States; orcid.org/0000-0001-9275-3605; Email: gceder@berkeley.edu

**Authors**

Tina Chen — Department of Materials Science and Engineering, University of California Berkeley, Berkeley, California 94720, United States; Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States; orcid.org/0000-0003-0254-8339

Julia Yang — Department of Materials Science and Engineering, University of California Berkeley, Berkeley, California 94720, United States; Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Luis Barroso-Luque — Department of Materials Science and Engineering, University of California Berkeley, Berkeley, California 94720, United States; Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States; orcid.org/0000-0002-6453-9545

Complete contact information is available at: https://pubs.acs.org/10.1021/acsnanolett.2c02141

**Author Contributions**

G.C. conceived and supervised the project. T.C. built the model, performed the computations and analysis, and wrote the manuscript. J.Y. and L.B.-L. developed and implemented the methods to fit the model and perform the Monte Carlo calculations. All authors discussed, reviewed, and edited the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Financial support is acknowledged from the Assistant Secretary for Energy Efficiency and Renewable Energy, Vehicle Technologies Office, under the Applied Battery Materials Program, of the U.S. Department of Energy (DOE) under Contract No. DE-AC02-05CH11231. The research was performed using computational resources sponsored by the DOE Office of Energy Efficiency and Renewable Energy and located at the National Renewable Energy Laboratory and from the Center for Functional Nanomaterials (CFN), which is a U.S. DOE Office of Science User Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704.

**REFERENCES**


(22) Gao, Y.; Reimers, J.; Dahn, J. Changes in the Voltage Profile of Li/Li$_{1-x}$Mn$_2$O$_4$ Cells as a Function of x. *Phys. Rev. B* 1996, 54 (6), 3878.


