

The Effect of Cation Disorder on the Average Li Intercalation Voltage of Transition-Metal Oxides

Aziz Abdellahi,^{†,||} Alexander Urban,^{‡,||} Stephen Dacek,[†] and Gerbrand Ceder^{*,‡,§}

[†]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02141, United States

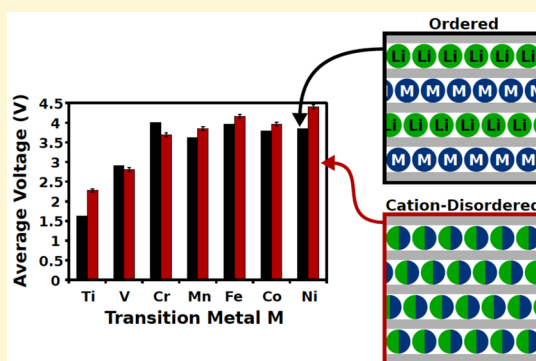
[‡]Department of Materials Science and Engineering, UC Berkeley, Berkeley, California 94720, United States

[§]Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

S Supporting Information

ABSTRACT: Cation disorder is a phenomenon that is becoming increasingly important for the design of high-energy lithium transition-metal oxide positive electrodes (LiMO₂) for Li-ion batteries. Disordered Li-excess rocksalts have recently been shown to achieve high reversible capacity, and *in operando* cation disorder (i.e., disorder induced by electrochemical cycling) has been observed in a large class of ordered materials. Despite the growing importance of cation disorder in the Li-ion battery field, very little is known about the effect of cation disorder on the average voltage (i.e., energy density) of lithium transition metal oxides. In this study, we use first-principles methods to demonstrate that, depending on the transition metal species, cation disorder can lead to an increase or a decrease of the average voltage of lithium transition metal oxides. We further demonstrate that the Ni^{3+/4+} redox can be high in disordered compounds, so that it may be preceded by oxygen activity.

Finally, we establish rules for the voltage evolution of compounds that experience *in operando* disorder.



INTRODUCTION

Cation disorder (defined as cation mixing between the lithium and transition-metal sublattices) is a phenomenon that is becoming increasingly important in the field of Li-ion batteries. As-synthesized disordered Li-excess rocksalts (Li_{1+x}Nb_yM_zO₂, [M = Mn, Fe, Co, Ni],^{1,2} Li_{1.2}Ni_{0.33}Ti_{0.33}Mo_{0.14}O₂,³ Li_{1+x}Ti_{2x}Fe_{1-3x}O₂,⁴ Li_{4/3}Ni_{1/3}Mo_{1/3}O₂⁵) were recently shown to achieve high reversible capacity, paving the way toward a new design space of high-capacity Li-ion battery cathodes. These high capacities are enabled by macroscopic Li transport through percolating zero-transition-metal pathways, which remain active upon disorder.^{6,7} *In operando* cation disorder (i.e., disorder induced by electrochemical cycling) also occurs in a large class of ordered materials, resulting in the formation of disordered bulk phases (Li_{1.211}Mo_{0.467}Cr_{0.3}O₂,⁶ Li₂VO₃,⁸ LiCrO₂,^{9,10} Li_{0.96}VO₂,¹¹ rutile TiO₂^{12,13}). Furthermore, *in operando* cation disorder can also occur at the surface of ordered compounds as a result of oxygen loss and transition metal migration, such as is the case for the NCA (LiNi_{0.8}Co_{0.2}Al_{0.05}O₂)¹⁴ and Li-excess NMC (Li_{1+y}Ni_wCo_zMn_{2-y-w-z}O₂) compounds.¹⁵⁻¹⁷

Cation disorder can have a strong impact on the lithium intercalation voltage of transition metal oxides, as is evidenced by the change in voltage profiles in materials that undergo *in operando* disorder.^{6,8,12} Surface disorder can also significantly affect the measured voltage if surface transport properties are poor. Disordered surfaces with an increased TM/Li ratio¹⁶ are

likely to exhibit poor transport properties, as Li excess is required to sustain macroscopic diffusion in disordered materials.^{6,7} As a result, the measured voltage profile in the particle may be greatly influenced by the redox processes occurring in the disordered surface region, where Li insertion/extraction occurs.

Understanding the effect of cation disorder on the voltage profile of transition metal oxides is therefore critical, both to rationally designing high-capacity disordered Li-excess rocksalts as well as to predicting the voltage evolution of ordered materials subject to *in operando* bulk or surface cation disorder. Despite the growing importance of cation disorder in the Li-ion battery field, however, little work has been done on quantitatively understanding its effect on the Li-intercalation voltage of transition-metal oxides. To our knowledge, the only work on this topic was conducted by Saubanere et al.¹⁸ Using a simplified voltage model based on chemically intuitive quantities, the authors argued that the average voltage of LiMO₂ cation-disordered rocksalts must be higher than their ordered homologues.

In general, cation disorder can have two important effects on the Li-intercalation voltage profile of transition metal oxides: (i) a change in the average voltage and (ii) an increase in the slope

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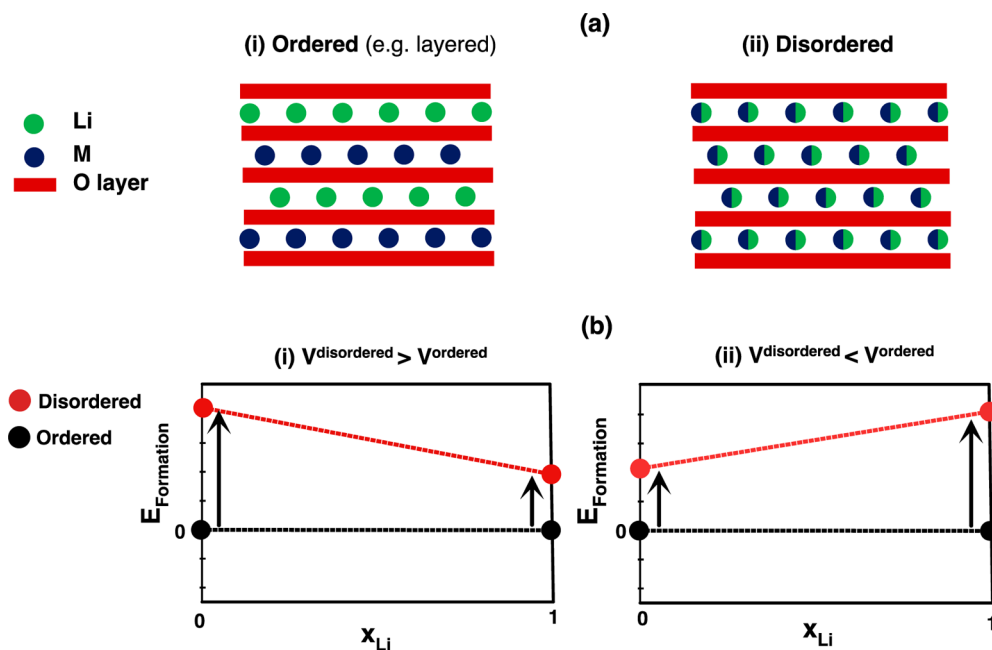


Figure 1. (a) Cation arrangement in ordered (left; the layered structure is shown as an example) and disordered (right) structures. The layers displayed in the figure are the (111) planes of the FCC cation sublattice. (b) The voltage of the disordered structure is larger than the voltage of the ordered structure if the disordering energy is larger in the delithiated limit than in the lithiated limit ($E_{\text{MO}_2}^{\text{dis}} - E_{\text{MO}_2}^{\text{ord}} > (E_{\text{LiMO}_2}^{\text{dis}} - E_{\text{LiMO}_2}^{\text{ord}})$) (i). Conversely, the voltage of the disordered structure is smaller than the voltage of the ordered structure if the disordering energy is smaller in the delithiated limit than in the lithiated limit ($E_{\text{MO}_2}^{\text{dis}} - E_{\text{MO}_2}^{\text{ord}} < (E_{\text{LiMO}_2}^{\text{dis}} - E_{\text{LiMO}_2}^{\text{ord}})$) (ii).

of the voltage profile. The average voltage controls the total energy deliverable from the electrochemical reaction, while the slope of the voltage profile determines the fraction of capacity accessible in a certain voltage window. In this paper, we use first-principles methods to understand and quantify the effect of cation disorder on the average Li-insertion voltage of transition-metal oxides.

In order to isolate the effect of cation disorder from other parameters such as the Li/TM ratio (in other words, the Li-excess or Li-deficiency level), we consider the average voltage of stoichiometric transition metal oxides. The effect of cation disorder on transition metals undergoing a $3^+/4^+$ redox reaction is investigated through a systematic study of first-row LiMO_2 compounds ($M = \text{Ti, V, Cr, Mn, Fe, Co, Ni}$). Among these compounds, LiTiO_2 and LiFeO_2 disorder at the solid-state synthesis temperature,¹⁹ while LiVO_2 ¹¹ and LiCrO_2 ^{9,10} can disorder upon cycling at room temperature. Co and Ni, although not found to disorder in the stoichiometric LiMO_2 form (with the exception of high-energy ball-milling²⁰), disorder as part of mixed transition metal compounds ($\text{LiM}_{0.5}\text{Ti}_{0.5}\text{O}_2$ compounds, where $M = \text{Mn, Fe, Co, Ni}$)^{21–24} and can also form disordered surface layers upon cycling in a mixed-transition metal environment such as NCA²⁵ and Li-excess NMC.^{15,16}

In summary, this study aims at providing a quantitative examination of the effect of cation disorder on the $3^+/4^+$ redox couple of stoichiometric lithium transition metal oxides and thereby also providing insights on the effect of cation disorder on the building blocks of more complex bulk or surface cation-disordered systems.

METHODOLOGY

Ordered and disordered states of a lithium transition-metal oxide are schematically illustrated in Figure 1a and are based on the rocksalt

framework, consisting of interpenetrating cation (Li and M) and anion (O) FCC sublattices. In the cation sublattice, Li and transition metals are octahedrally coordinated by oxygen (LiO_6 and MO_6 octahedra). In an ordered state, Li and M atoms occupy distinct periodic sublattices of the FCC rocksalt cation framework (Figure 1a–i). Examples of experimentally observed ordered LiMO_2 structures include the layered, $\text{Li}_2\text{M}_2\text{O}_4$ spinel (the LT- LiCoO_2 structure obtained by overlithiating LiM_2O_4 spinel compounds), γ - LiFeO_2 , and orthorhombic structures.¹⁹ In the fully disordered state, Li and TM atoms randomly occupy sites of the FCC rocksalt cation framework (Figure 1a–ii). Note that cation-disordered structures need not be fully random but can in fact exhibit short-range order.²¹ In this paper, we only consider the limit of fully disordered lithium transition metal oxides, which allows for an estimation of the maximal voltage difference from the ideal ordered phase.

The average open-circuit voltage resulting from the intercalation of one formula unit of Li in a stoichiometric MO_2 compound, with respect to metallic Li, is given by eq 1.²⁶ This relation is general and is valid for both ordered and disordered structures.

$$e\overline{\Delta V} = -(\underline{G}_{\text{LiMO}_2} - \underline{G}_{\text{MO}_2} - \underline{G}_{\text{Li-metal}}) \quad (1)$$

In eq 1, $\overline{\Delta V}$ is the average (open-circuit) voltage and $\underline{G}_{\text{LiMO}_2}$, $\underline{G}_{\text{MO}_2}$, $\underline{G}_{\text{Li-metal}}$ are the free energy of the lithiated transition metal oxide, delithiated transition metal oxide, and metallic lithium compounds, expressed in electronvolts per formula unit. The difference between the disordered and ordered average voltage is obtained by expressing eq 1 for ordered and disordered structures and taking the difference between the two expressions. The result is given in eq 2:

$$e(\overline{\Delta V}_{\text{dis}} - \overline{\Delta V}_{\text{ord}}) = (\underline{G}_{\text{MO}_2}^{\text{dis}} - \underline{G}_{\text{MO}_2}^{\text{ord}}) - (\underline{G}_{\text{LiMO}_2}^{\text{dis}} - \underline{G}_{\text{LiMO}_2}^{\text{ord}}) \quad (2)$$

Equation 2 can be simplified further by neglecting the configurational entropy of ordered structures and by noting that the configurational entropy of a fully random structure is the same in the lithiated and delithiated limits ($S = -k \sum_i x_i \ln(x_i)$). As a result, the difference in average voltage between the disordered and ordered structure depends only on the relative energy of the two structures:

$$e(\overline{\Delta V}_{\text{dis}} - \overline{\Delta V}_{\text{ord}}) = \Delta E_{\text{MO}_2}^{\text{dis}} - \Delta E_{\text{LiMO}_2}^{\text{dis}}$$

$$\text{with } \Delta E_{\text{Li}_x\text{MO}_2}^{\text{dis}} = E_{\text{Li}_x\text{MO}_2}^{\text{dis}} - E_{\text{Li}_x\text{MO}_2}^{\text{ord}} \quad (3)$$

Note that, in eq 3, we define the “disordering energy,” $\Delta E_{\text{Li}_x\text{MO}_2}^{\text{dis}}$, as the energy difference between the fully disordered structure and the ordered structure at a given Li concentration.

The voltage change upon disorder is controlled by the relative disordering energy in the lithiated and delithiated limits (Figure 1b). If the disordering energy is larger in the delithiated limit than in the lithiated limit ($\Delta E_{\text{MO}_2}^{\text{dis}} > \Delta E_{\text{LiMO}_2}^{\text{dis}}$), the voltage of the disordered structure is higher than the voltage of the ordered structure (Figure 1b–i). Conversely, if the disordering energy is smaller in the delithiated limit than in the lithiated limit ($\Delta E_{\text{MO}_2}^{\text{dis}} < \Delta E_{\text{LiMO}_2}^{\text{dis}}$), the voltage of the disordered structure is smaller than the voltage of the ordered structure (Figure 1b–ii).

In this paper, we compare the voltage of fully disordered LiMO_2 with the voltage of the LiMO_2 ordered ground-state structure for first-row LiMO_2 compounds ($M = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$). The lithiated ground-state structure is calculated to be the layered structure for $\text{Li}(\text{Co}, \text{Ni}, \text{V}, \text{Cr})\text{O}_2$, the $\gamma\text{-LiFeO}_2$ structure for $\text{Li}(\text{Fe}, \text{Ti})\text{O}_2$, and the orthorhombic structure for LiMnO_2 . These ground-state structures are all validated by experimental results,¹⁹ with the exception of LiTiO_2 , which cannot be synthesized in its ground-state structure as it disorders at normal solid-state synthesis temperatures.¹⁹ Note that, in the case of LiTiO_2 , the $\gamma\text{-LiFeO}_2$ structure is equivalent to the lithiated anatase structure.

The energies of ordered ground-state structures are calculated within the Hubbard-U corrected Generalized Gradient Approximation (GGA+U) to Density Functional Theory (DFT), using the PBE exchange-correlation functional.^{27,28} The U parameters are extracted from the work of Jain et al.²⁹ The energy of the cation-disordered structure is calculated using the cluster expansion technique,^{30–34} which parametrizes the energy of any cation arrangement using a finite number of effective cluster interactions (ECI's). The accuracy of the cluster expansion fits is such that disordered voltages are determined to within ± 50 mV. Cluster expansions are fitted using the compressive sensing paradigm,³³ and the energies of disordered structures are calculated using the Cluster Assisted Statistical Mechanics (CASM) software.³⁴ Cluster expansion predictions are found to be consistent with direct energy evaluations of a pseudo-disordered state using Special Quasi-Random Structures (SQS).^{35,36} Further details are given in the Supporting Information.

RESULTS

Figure 2a shows the disordering energy in the lithiated and delithiated limits for first-row LiMO_2 compounds ($M = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$). In the Discussion section of this paper, we explain how experimental observations and electronic structure trends explain the position of most disordering energies calculated in Figure 2a.

These disordering energies can be used to calculate the voltage difference between disordered and ordered structures via eq 3. The results are illustrated in Figure 2b. Cation disorder increases the voltage of transition metals that have a higher disordering energy in the delithiated limit (Ti, Mn, Fe, Co, Ni), while it decreases the voltage of transition metals that have a higher disordering energy in the lithiated limit (V, Cr). The difference between the disordered voltage and the ordered ground-state voltage varies between extremal values of ~ -0.3 V (for LiCrO_2) and ~ 0.6 V (for LiTiO_2 and LiNiO_2).

Figure 2c shows the absolute average voltage values of the disordered and lithiated ground-state structures (see also Table S1 of the Supporting Information). Both sets of voltages follow the general trend that transition metals with higher atomic number display larger voltages, due to the lower energy of the

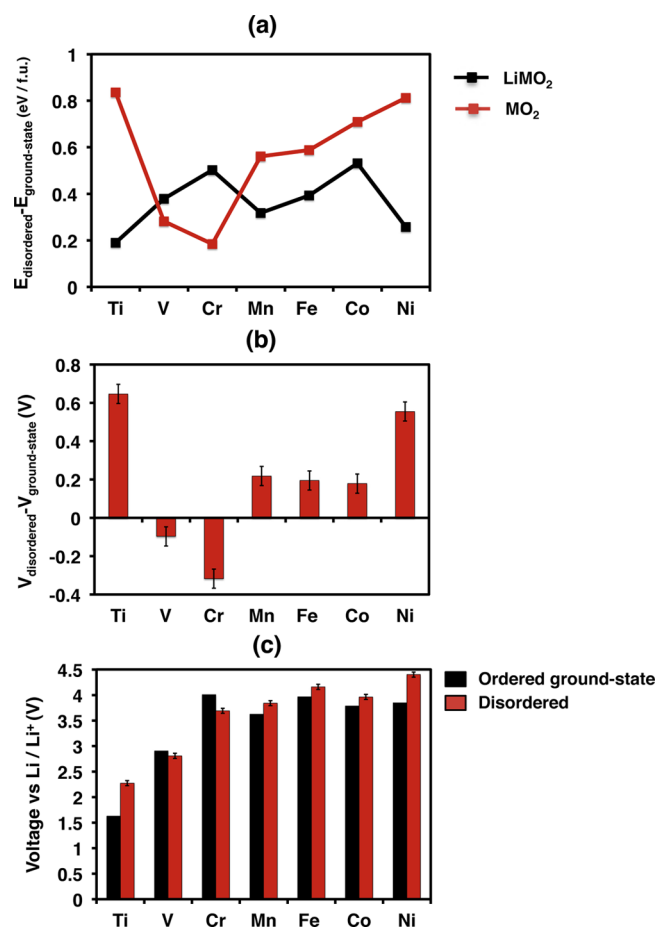


Figure 2. (a) Disorder energy (with respect to the LiMO_2 ground-state structure) for different transition metals, in the LiMO_2 and MO_2 limits. (b) Voltage difference between disordered LiMO_2 and the LiMO_2 ordered ground state. (c) Absolute average voltage for fully disordered and ground-state LiMO_2 structures.

3d transition metal band as the atomic number of the transition metal increases.²⁶ The LiMO_2 transition-metal oxide compound with the highest disordered average voltage is predicted to be LiNiO_2 at ~ 4.4 V (compared to ~ 3.9 V for the layered structure).

Direct comparison of the predicted disordered voltages with experimental results is difficult, as disordered LiMO_2 compounds cannot be electrochemically cycled given their poor Li diffusivities (Li excess is required to enable macroscopic diffusivity in cation-disordered rocksalts^{6,7}). The only disordered material that has been partially cycled in the LiMO_2 family is disordered LiTiO_2 , which is formed *in operando* upon lithium insertion in rutile TiO_2 .^{12,13} Particle nanosizing allows for small diffusion lengths (as low as 10 nm^{12,13}), which partially compensates for the poor diffusivity of Li in stoichiometric disordered LiTiO_2 . After a first discharge, during which disordered LiTiO_2 is formed, the voltage profile changes and the average voltage upon cycling of 200 mAh/g ($\text{LiTiO}_2 \leftrightarrow \text{Li}_{0.4}\text{TiO}_2$) is found to be on the order of 1.8 V.^{12,13} This value is lower than the 2.25 V value calculated in the present study (Figure 2c and Table S1 of the Supporting Information). However, only 60% of the theoretical capacity can be accessed upon charge, indicating that the average voltage for full Li extraction is likely higher than the experimentally reported value. Furthermore, significant hysteresis is still present in the

experimental charge–discharge profile curves even at low rates, rendering the extraction of the average open circuit voltage difficult. We further note that our 2.25 V prediction is consistent with the experimentally observed 2.2–2.3 V plateau associated with $\text{Ti}^{3+/4+}$ redox in disordered $\text{Li}_{1+z/3}\text{Ni}_{1/2-z/2}\text{Ti}_{1/2+z/6}\text{O}_2$ ³⁷ and $\text{Li}_{1.2}\text{Ni}_{0.33}\text{Ti}_{0.33}\text{Mo}_{0.14}\text{O}_2$.³

Our prediction of a high disordered $\text{Ni}^{3+/4+}$ voltage (~ 4.4 V) is consistent with the observed inaccessibility of the $\text{Ni}^{3+/4+}$ redox in the disordered Li-excess $\text{Li}_{1.2}\text{Ni}_{0.33}\text{Ti}_{0.33}\text{Mo}_{0.14}\text{O}_2$ compound.³ While this disordered material shows very high reversible capacity, XANES analyses demonstrate that the transition metal redox activity is in fact limited to the $\text{Ni}^{2+/3+}$ redox couple, with the remainder of capacity attributed to reversible redox capacity from the $\text{O}^{2-/-1-}$ redox couple.³ The redox level of this $\text{O}^{2-/-1-}$ couple would therefore be accessible before the disordered $\text{Ni}^{3+/4+}$ couple, which is calculated in this work to be at ~ 4.4 V.

To further corroborate the high voltage of the $\text{Ni}^{3+/4+}$ redox in the disordered form, we performed a cluster expansion fit of fully disordered $\text{LiTi}_{0.5}\text{Ni}_{0.5}\text{O}_2$, which is the material from which Li-excess $\text{Li}_{1.2}\text{Ni}_{0.33}\text{Ti}_{0.33}\text{Mo}_{0.14}\text{O}_2$ is derived. This compound can indeed be written as a solid solution between $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Li}_{1.6}\text{Mo}_{0.4}\text{O}_2$ ($\text{Li}_{1.2}\text{Ni}_{0.33}\text{Ti}_{0.33}\text{Mo}_{0.14}\text{O}_2 = 2/3(\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2) + 1/3(\text{Li}_{1.6}\text{Mo}_{0.4}\text{O}_2)$). A ternary cluster expansion fit was performed, achieving an accuracy of ± 50 meV (cf Supporting Information).

Using this method, the average voltage for $\text{Ni}^{2+/4+}$ oxidation in fully disordered $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ (where Li, Ni, and Ti randomly populate the cation sublattice) was calculated to be 4.2 ± 0.05 V. We find that this prediction is consistent with the 3.6–4.8 V voltage range obtained during charge profiles of disordered $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ between $x_{\text{Li}} = 0.05$ and $x_{\text{Li}} = 0.7$.²² We note, however, that experimental voltages display significant hysteresis and are only available between $x_{\text{Li}} = 0.05$ and $x_{\text{Li}} = 0.7$, thus rendering extraction of the (open circuit) average voltage difficult. On the basis of our theoretical predictions, the $\text{Ni}^{3+/4+}$ redox in $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ is therefore higher than 4.2 V (which constitutes an average over the two-step $\text{Ni}^{2+/3+}$ and $\text{Ni}^{3+/4+}$ redox processes), in general agreement with the 4.4 V $\text{Ni}^{3+/4+}$ average voltage predicted for fully disordered LiNiO_2 . We therefore speculate that the high voltage of disordered $\text{Ni}^{3+/4+}$ is a common feature in cation-disordered rocksalts.

DISCUSSION

Experimental observations and electronic structure trends explain the position of most disordering energies calculated in Figure 2a, as detailed in the following paragraphs.

We find that while most LiMO_2 compounds increase their average voltage upon disordering, when $M = \text{Cr}$ or V the average voltage decreases with disorder (by 0.3 and 0.1 V, respectively). Furthermore, in the MO_2 limit, the disordering energies of VO_2 and CrO_2 are found to be significantly lower than the disordering energy of other transition metals (~ 200 – 280 meV/f.u. compared to ~ 600 meV/f.u. and above for other transition metals), thus making these transition metal compounds more likely to disorder upon delithiation. This is in agreement with experimental observations, as layered LiVO_2 ¹¹ and LiCrO_2 ^{9,10} are known to disorder *in operando* upon charge. Although 200 meV/f.u. is still too large to drive a transition to a fully random structure at room temperature (the entropy term $TS = -kT \ln(2)$ being only ~ 35 meV/f.u. for a fully random MO_2 system at room temperature), it is possible that these compounds only partially disorder upon cycling at

room temperature, or that cation disorder occurs at intermediate Li compositions (the concavity of the disordered free energy curve being more pronounced than that of the ordered free energy curve due to the larger voltage slope).

On the LiMO_2 side, the disordering energy of lithiated LiTiO_2 is calculated to be the smallest among all first row transition metals. Consistent with this result, LiTiO_2 experimentally disorders at solid-state synthesis temperatures.¹⁹

The trend in the disordering energy of LiMO_2 (Figure 2a) is generally upward as the electron count on the TM increases, with only Mn and Ni modifying the upward trend. It is notable that both Mn and Ni are Jahn–Teller active in the +3 state.³⁸ Cation disorder creates local distortions in MO_6 octahedra, by virtue of the large variety of local environments around transition metal atoms. Because Mn^{3+} and Ni^{3+} are Jahn–Teller active, they can accommodate a certain degree of MO_6 distortion along the Jahn–Teller distortion mode.³⁸ This additional degree of freedom contributes to lowering the disordering energy of these compounds and therefore breaks the general upward trend.

Electronic structure arguments can also be used to justify points of high disordering energy in Figure 2a. Transition metal ions with a low spin d^6 configuration (Co^{3+} , Ni^{4+}) or high spin d^3 electronic configuration (Cr^{3+} , Mn^{4+}) have filled or half-filled (respectively empty) t_{2g} (respectively e_g) bands and consequently favor highly symmetrical octahedral MO_6 environments. While the disordered rocksalt structure (space group $Fm\bar{3}m$) has perfect octahedral symmetry (i.e., point group O_h) on a macroscopic scale, the local symmetry of each cation site depends on the stochastic occupation of the neighboring sites and is therefore generally lower than in ordered arrangements. The disordering energy for d^6 and d^3 compounds is therefore expected to be high, as cation disorder leads to distortions of the MO_6 octahedra. In agreement with this statement, LiCrO_2 (Cr^{3+}) and LiCoO_2 (Co^{3+}) are found to have the highest disordering energies among lithiated LiMO_2 compounds, and NiO_2 (Ni^{4+}) is found to have the highest disordering energy among delithiated MO_2 compounds. MnO_2 (Mn^{4+}), while not a maximum value in the MO_2 curve, sits at a much higher disordering energy than neighboring CrO_2 , which can be attributed to the electronic structure of Mn^{4+} as described above.

The disordering energy of LiFeO_2 , however, is not consistent with experimental observations. LiFeO_2 is known to disorder at solid state synthesis temperatures.¹⁹ The data in Figure 2a however suggest that the disordering energy of LiFeO_2 is higher than the disordering energy of lithiated transition metals such as LiVO_2 , LiMnO_2 , and LiNiO_2 , which do not disorder at solid-state synthesis temperatures. It is possible that experimentally synthesized LiFeO_2 has in fact a certain level of off-stoichiometry, as partial reduction of Fe^{3+} to Fe^{2+} , mediated by oxygen loss, is likely at synthesis temperatures.³⁹ It is also possible that PBE+U overestimates the disordering energy of LiFeO_2 . In the latter case, the predicted voltage change for LiFeO_2 upon disorder would be underestimated. This potential underestimation, however, does not change the conclusions presented in this paper, among which is that the voltage of LiFeO_2 increases upon disorder.

This study has shown that, depending on the transition metal species, cation disorder can lead to an increase or a decrease of the average (open-circuit) voltage (Figure 2b). We note that this conclusion is in disagreement with a previous result presented in the literature.¹⁸ Using a simplified model for the

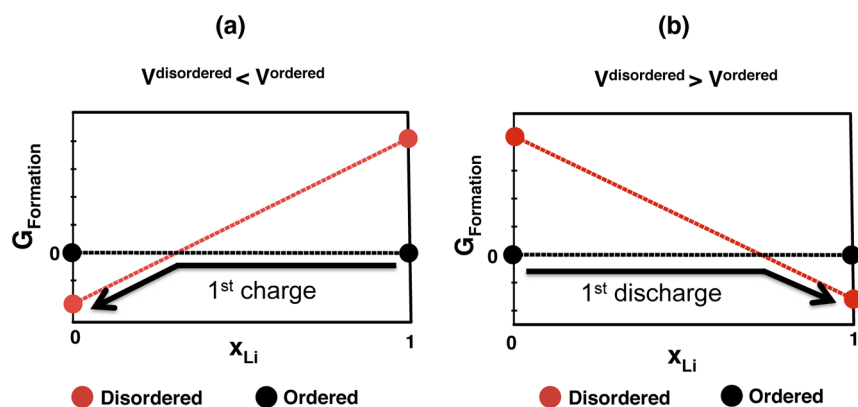


Figure 3. Free energy landscape and ensuing voltage relations for compounds that disorder *in operando* during (a) delithiation ($\overline{\Delta V}^{\text{dis}} < \overline{\Delta V}^{\text{ord}}$) and (b) lithiation ($\overline{\Delta V}^{\text{dis}} > \overline{\Delta V}^{\text{ord}}$).

average voltage based on chemically intuitive quantities, it was argued that the voltage of disordered LiMO_2 compounds is necessarily higher than the voltage of their ordered counterparts. This statement, however, can be shown to be in contradiction with the existence of compounds that disorder *in operando* during delithiation, such as LiVO_2 ⁸ and LiCrO_2 .^{9,10} Such materials are ordered in their lithiated forms, thus guaranteeing that the disordering energy is high enough to prevent cation disorder upon synthesis (Figure 3a). At a certain level of delithiation, the disordered state becomes thermodynamically favorable over the ordered state, leading to *in operando* cation disorder upon first charge. During subsequent cycles, the materials cycle in the disordered form. By virtue of the relative free energies of the ordered and disordered states in the lithiated and delithiated limits (Figure 3 a), the condition $(E_{\text{MO}_2}^{\text{dis}} - E_{\text{MO}_2}^{\text{ord}}) < (E_{\text{LiMO}_2}^{\text{dis}} - E_{\text{LiMO}_2}^{\text{ord}})$ is necessarily verified (the left-hand term is negative, while the right-hand term is positive). Consequently, the voltage of the disordered state is necessarily lower than the voltage of the ordered state. This analysis further rationalizes the voltage drop observed following first charge in the Li-excess $\text{Li}_{1.211}\text{Mo}_{0.467}\text{Cr}_{0.3}\text{O}_2$ compound,⁶ which also disorders *in operando* upon delithiation.

Conversely, compounds that disorder *in operando* during lithiation must have a higher voltage in their disordered form than in their ordered form (Figure 3b). Using the reasoning presented in the previous paragraph, the relative ordered and disordered free energies in the lithiated and delithiated limits ensure that $(E_{\text{MO}_2}^{\text{dis}} - E_{\text{MO}_2}^{\text{ord}}) > (E_{\text{LiMO}_2}^{\text{dis}} - E_{\text{LiMO}_2}^{\text{ord}})$. Consequently, the voltage of the disordered state is necessarily higher than the voltage of the ordered state. This analysis explains the increase in average voltage that is observed after the first discharge of $\text{Li}_{1+y}\text{VO}_3$ ⁸ and rutile TiO_2 .^{12,13}

This analysis provides general rules for the voltage evolution of materials that disorder *in operando*. In systems that allow it, *in operando* cation disorder can therefore be used as leverage to increase or decrease the average voltage. Certain Cr-containing compounds, for example, are known to disorder upon delithiation (LiCrO_2 ,^{9,10} $\text{Li}_{1.211}\text{Mo}_{0.467}\text{Cr}_{0.3}\text{O}_2$ ⁶). The reduction in the average voltage that ensues can be leveraged to access more capacity at moderate voltages before competing mechanisms, such as oxygen oxidation^{40,41} or oxygen loss,⁴² occur at higher voltages. In line with this statement, the disordered $\text{Li}_{1.211}\text{Mo}_{0.467}\text{Cr}_{0.3}\text{O}_2$ compound was experimentally shown to access the $\text{Cr}^{3+/4+}$ redox at the end of charge with minimal competing redox from oxygen loss.⁴³ In $\text{Li}_{1+y}\text{VO}_3$, *in*

operando cation disorder during lithiation is also leveraged to increase the low voltage in the initial ordered compound, thus enabling higher energy density in this compound. Note that the previous analysis does not apply to compounds that experience a change of chemical composition in conjunction with cation disorder (surface cation disorder mediated by oxygen loss is one such instance).^{3,15–17,25}

General conclusions about the relative average voltages of the ordered and disordered phases cannot be drawn, however, for materials that disorder upon synthesis. In this family of compounds (LiFeO_2 ,¹⁹ LiTiO_2 ,¹⁹ $\text{LiM}_{0.5}\text{Ti}_{0.5}\text{O}_2$ (M = Mn, Fe, Co, Ni),^{21–23} $\text{Li}_{1+x}\text{Nb}_y\text{M}_z\text{O}_2$ [M = Mn, Fe, Co, Ni],^{1,2} $\text{Li}_{1.2}\text{Ni}_{0.33}\text{Ti}_{0.33}\text{Mo}_{0.14}\text{O}_2$,³ $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Fe}_{1-3x}\text{O}_2$,⁴ $\text{Li}_{4/3}\text{Ni}_{1/3}\text{Mo}_{1/3}\text{O}_2$),⁵ the free energy difference between the disordered state and the ordered ground-state in the lithiated limit is small enough to ensure that cation disorder can occur at synthesis temperatures (the energy increase upon disorder being compensated by the $-TS$ term at high temperature). There is no *a priori* relationship, however, between the relative disordering energy in the lithiated and delithiated limits for these compounds. The disordering energy can be higher in the delithiated limit, which leads to a higher disordered voltage (such as is the case for LiTiO_2 and LiFeO_2 calculated in this study). It is also possible that compounds in this family be even easier to disorder in the delithiated limit, in which case the voltage of the disordered phase would be lower than that of the lithiated ordered ground state.

Our analysis also suggests that the disordered voltage of the $\text{Ni}^{3+/4+}$ redox is high. This conclusion, demonstrated both for disordered LiNiO_2 and disordered $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$, has important implications, as Ni is an important high-voltage transition metal for Li-ion battery cathodes. While the large voltage of the disordered $\text{Ni}^{3+}/\text{Ni}^{4+}$ couple leads to a beneficial increase in energy density, it can also lead to the appearance of competitive redox processes. Such processes include oxygen oxidation^{40,41} and oxygen evolution.⁴² The ~ 4.4 V range calculated for the $\text{Ni}^{3+/4+}$ redox suggests that the disordered $\text{Ni}^{3+/4+}$ redox can be hard to access in practice, consistent with the large oxygen activity observed at ~ 4.2 V in disordered Li-excess $\text{Li}_{1.2}\text{Ni}_{0.33}\text{Ti}_{0.33}\text{Mo}_{0.14}\text{O}_2$ and $\text{Li}_{4/3}\text{Ni}_{1/3}\text{Mo}_{1/3}\text{O}_2$.^{3,5} If oxygen oxidation is to be avoided, transition metals with lower disordered voltages such as Cr, Mn, Co, and Fe may be preferable over Ni. On the other hand, if oxygen oxidation were to be reversibly achieved without degradation of overall performance, synthesizing disordered materials with a high $+3/+4$ redox voltage may be a valid design strategy. However,

limiting the voltage alone may not be the only avenue to preventing oxygen evolution, as no oxygen loss has been observed in $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ even at potentials as high as 4.8 V,⁴⁴ and the conditions for oxygen loss have not yet been clearly understood. We further note that, in addition to the cation arrangement, the interaction with other cation species present is another factor that might affect the voltage. This effect is exemplified by cation-disordered $\text{Li}_{4/3}\text{Ni}_{1/3}\text{Mo}_{1/3}\text{O}_2$ ⁵ which exhibits a significantly lower average intercalation voltage over the accessible $\text{Ni}^{2+/4+}$ range (<4.1 V) than layered $\text{Li}_4\text{NiTeO}_6$ (>4.2 V),⁴⁵ possibly owing to the difference in the electronegativity of Mo and Te.

Finally, we note that, in addition to thermal disordering and *in operando* cation disorder, cation disorder can also be introduced in lithium transition metal oxides by mechanochemical synthesis routes. Obrovac et al. reported the mechanochemical preparation and electrochemical performance of cation-disordered LiMO_2 for $M = \text{Ti, Mn, Fe, Co, and Ni}$.²⁰ However, in stoichiometric composition, disordered LiMO_2 was generally found to exhibit only limited electrochemical activity, so that the data do not allow for the accurate extraction of the average open-circuit voltage.

CONCLUSIONS

Using first-principles calculations, this work demonstrates that, depending on the transition metal species, cation disorder can result in an increase or a reduction of the average Li intercalation voltage of lithium transition-metal oxides. Transition metals that have a higher disordering energy in the MO_2 limit display larger average voltages than their ordered ground states, while transition metals that have a higher disordering energy in the LiMO_2 limit display a lower voltage than their ordered ground state. Cation disorder can significantly alter the average voltage of lithium transition metal oxides (ΔV between -0.3 and 0.6 V) and can therefore lead to significant changes in their voltage operating windows. In particular, the disordered $\text{Ni}^{3+/4+}$ redox was found to be high (~ 4.4 V in LiNiO_2), suggesting that it is likely to be preceded by oxygen activity in disordered compounds.

Last, we showed that compounds that disorder *in operando* during delithiation have a lower voltage in their disordered form, while compounds that disorder *in operando* during lithiation have a higher voltage in their disordered form. Our work therefore establishes the first bases toward rational design of high-capacity Li-excess disordered transition-metal oxides based upon voltage considerations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.chemmater.6b00205](https://doi.org/10.1021/acs.chemmater.6b00205).

Cluster expansion methodology and values of the disordered voltages (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: gceder@berkeley.edu.

Author Contributions

^{||}These authors contributed equally to the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Yabuuchi, N.; Takeuchi, M.; Nakayama, M.; Shiiba, H.; Ogawa, M.; Nakayama, K.; Ohta, T.; Endo, D.; Ozaki, T.; Inamasu, T.; Sato, K.; Komaba, S. High-Capacity Electrode Materials for Rechargeable Lithium Batteries: Li_3NbO_4 -Based System with Cation-Disordered Rocksalt Structure. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (25), 7650–7655.
- (2) Wang, R.; Li, X.; Liu, L.; Lee, J.; Seo, D.-H.; Bo, S.-H.; Urban, A.; Ceder, G. A Disordered Rock-Salt Li-Excess Cathode Material with High Capacity and Substantial Oxygen Redox Activity: $\text{Li}_{1.25}\text{Nb}_{0.25}\text{Mn}_{0.5}\text{O}_2$. *Electrochem. Commun.* **2015**, *60*, 70–73.
- (3) Lee, J.; Seo, D.-H.; Balasubramanian, M.; Twu, N.; Li, X.; Ceder, G. A New Class of High Capacity Cation-Disordered Oxides for Rechargeable Lithium Batteries: Li–Ni–Ti–Mo Oxides. *Energy Environ. Sci.* **2015**, *8*, 3255–3265.
- (4) Glazier, S. L.; Li, J.; Zhou, J.; Bond, T.; Dahn, J. R. Characterization of Disordered $\text{Li}(1+x)\text{Ti}_2\text{Fe}(1-3x)\text{O}_2$ as Positive Electrode Materials in Li-Ion Batteries Using Percolation Theory. *Chem. Mater.* **2015**, *27*, 7751–7756.
- (5) Yabuuchi, N.; Tahara, Y.; Komaba, S.; Kitada, S.; Kajiyama, Y. Synthesis and Electrochemical Properties of Li_xMoO_5 –NiO Binary System as Positive Electrode Materials for Rechargeable Lithium Batteries. *Chem. Mater.* **2016**, *28*, 416–419.
- (6) Lee, J.; Urban, A.; Li, X.; Su, D.; Hautier, G.; Ceder, G. Unlocking the Potential of Cation-Disordered Oxides for Rechargeable Lithium Batteries. *Science* **2014**, *343*, 519–522.
- (7) Urban, A.; Lee, J.; Ceder, G. The Configurational Space of Rocksalt-Type Oxides for High-Capacity Lithium Battery Electrodes. *Adv. Energy Mater.* **2014**, *4*, 1400478.
- (8) Pralong, V.; Gopal, V.; Caignaert, V.; Duffort, V.; Raveau, B. Lithium-Rich Rock-Salt-Type Vanadate as Energy Storage Cathode: Li_2-xVO_3 . *Chem. Mater.* **2012**, *24* (1), 12–14.
- (9) Lyu, Y.; Ben, L.; Sun, Y.; Tang, D.; Xu, K.; Gu, L.; Xiao, R.; Li, H.; Chen, L.; Huang, X. Atomic Insight Into Electrochemical Inactivity of Lithium Chromate (LiCrO_2): Irreversible Migration of Chromium Into Lithium Layers in Surface Regions. *J. Power Sources* **2015**, *273*, 1218–1225.
- (10) Bo, S.; Li, X.; Toumar, A. J.; Ceder, G. Layered-to-Rocksalt Transformation in Desodiated Na_xCrO_2 ($x = 0.4$). *Chem. Mater.* **2016**, *28* (5), 1419–1429.
- (11) Ozawa, K.; Nakao, Y.; Wang, L.; Cheng, Z.; Fujii, H.; Hase, M.; Eguchi, M. Structural Modifications Caused by Electrochemical Lithium Extraction for Two Types of Layered LiVO_2 (R3m). *J. Power Sources* **2007**, *174* (2), 469–472.
- (12) Baudrin, E.; Cassaignon, S.; Koelsch, M.; Jolivet, J.; Dupont, L.; Tarascon, J. Structural Evolution During the Reaction of Li with Nano-Sized Rutile Type TiO_2 at Room Temperature. *Electrochem. Commun.* **2007**, *9* (2), 337–342.
- (13) Wang, D.; Choi, D.; Yang, Z.; Viswanathan, V. V.; Nie, Z.; Wang, C.; Song, Y.; Zhang, J.-G.; Liu, J. Synthesis and Li-Ion Insertion Properties of Highly Crystalline Mesoporous Rutile TiO_2 . *Chem. Mater.* **2008**, *20* (10), 3435–3442.

- (14) Hwang, S.; Chang, W.; Kim, S. M.; Su, D.; Kim, D. H.; Lee, J. Y.; Chung, K. Y.; Stach, E. A. Investigation of Changes in the Surface Structure of $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ Cathode Materials Induced by the Initial Charge. *Chem. Mater.* **2014**, *26* (2), 1084–1092.
- (15) Zheng, J.; Xu, P.; Gu, M.; Xiao, J.; Browning, N. D.; Yan, P.; Wang, C.; Zhang, J.-G. Structural and Chemical Evolution of Li- and Mn-Rich Layered Cathode Material. *Chem. Mater.* **2015**, *27* (4), 1381–1390.
- (16) Yan, P.; Nie, A.; Zheng, J.; Zhou, Y.; Lu, D.; Zhang, X.; Xu, R.; Belharouak, I.; Zu, X.; Xiao, J.; Amine, K.; Liu, J.; Gao, F.; Shahbazian-Yassar, R.; Zhang, J.-G.; Wang, C.-M. Evolution of Lattice Structure and Chemical Composition of the Surface Reconstruction Layer in $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ Cathode Material for Lithium Ion Batteries. *Nano Lett.* **2015**, *15* (1), 514–522.
- (17) Boulineau, A.; Simonin, L.; Colin, J.-F.; Canévet, E.; Daniel, L.; Patoux, S. Evolutions of $\text{Li}_{1.2}\text{Mn}_{0.61}\text{Ni}_{0.18}\text{Mg}_{0.01}\text{O}_2$ During the Initial Charge/Discharge Cycle Studied by Advanced Electron Microscopy. *Chem. Mater.* **2012**, *24* (18), 3558–3566.
- (18) Saubanere, M.; Ben Yahia, M.; Lebegue, S.; Doublet, M. L. An Intuitive and Efficient Method for Cell Voltage Prediction of Lithium and Sodium-Ion Batteries. *Nat. Commun.* **2014**, *5*, 5559.
- (19) Hewston, T. A.; Chamberland, B. L. A Survey of First-Row Ternary Oxides LiMO_2 ($M = \text{Sc-Cu}$). *J. Phys. Chem. Solids* **1987**, *48*, 97–108.
- (20) Obrovac, M. N.; Mao, O.; Dahn, J. R. Structure and Electrochemistry of LiMO_2 ($M = \text{Ti, Mn, Fe, Co, Ni}$) Prepared by Mechanochemical Synthesis. *Solid State Ionics* **1998**, *112*, 9–19.
- (21) Chang, S. H.; Kang, S.-G.; Song, S.-W.; Yoon, J.-B.; Choy, J.-H. Crystal Structure and Spectroscopic Properties of $\text{Li}_x\text{Ni}_{1-y}\text{Ti}_y\text{O}_2$ and Their Electrochemical Behavior. *Solid State Ionics* **1998**, *86–88*, 171–175.
- (22) Küzma, M.; Dominko, R.; Meden, A.; Makovec, D.; Bele, M.; Jamnik, J.; Gaberšček, M. Electrochemical Activity of $\text{Li}_2\text{FeTiO}_4$ and $\text{Li}_2\text{MnTiO}_4$ as Potential Active Materials for Li Ion Batteries: a Comparison with $\text{Li}_2\text{NiTiO}_4$. *J. Power Sources* **2009**, *189* (1), 81–88.
- (23) Yang, M.; Zhao, X.; Bian, Y.; Ma, L.; Ding, Y.; Shen, X. Cation Disordered Rock Salt Phase $\text{Li}_2\text{CoTiO}_4$ as a Potential Cathode Material for Li-Ion Batteries. *J. Mater. Chem.* **2012**, *22* (13), 6200–6205.
- (24) Kang, K.; Carlier, D.; Reed, J.; Arroyo, E. M.; Ceder, G.; Croguennec, L.; Delmas, C. Synthesis and Electrochemical Properties of Layered $\text{Li}_{0.9}\text{Ni}_{0.45}\text{Ti}_{0.55}\text{O}_2$. *Chem. Mater.* **2003**, *15* (23), 4503–4507.
- (25) Hwang, S.; Chang, W.; Kim, S. M.; Su, D.; Kim, D. H.; Lee, J. Y.; Chung, K. Y.; Stach, E. A. Investigation of Changes in the Surface Structure of $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ Cathode Materials Induced by the Initial Charge. *Chem. Mater.* **2014**, *26* (2), 1084–1092.
- (26) Aydinol, M. K.; Kohan, A. F.; Ceder, G. Ab Initio Calculation of the Intercalation Voltage of Lithium-Transition-Metal Oxide Electrodes for Rechargeable Batteries. *J. Power Sources* **1997**, *68*, 664–668.
- (27) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (28) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple - Errata. *Phys. Rev. Lett.* **1997**, *78*, 1396.
- (29) Jain, A.; Hautier, G.; Moore, C. J.; Ping Ong, S.; Fischer, C. C.; Mueller, T.; Persson, K. A.; Ceder, G. A High-Throughput Infrastructure for Density Functional Theory Calculations. *Comput. Mater. Sci.* **2011**, *50* (8), 2295–2310.
- (30) Sanchez, J. M.; Ducastelle, F.; Gratias, D. Generalized Cluster Description of Multicomponent Systems. *Phys. A* **1984**, *128*, 334–350.
- (31) De Fontaine, D. Cluster Approach to Order-Disorder Transformations in Alloys. *Solid State Phys.* **1994**, *47*, 33–176.
- (32) Wolverton, C.; De Fontaine, D. Cluster Expansions of Alloy Energetics in Ternary Intermetallics. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *49*, 8627–8642.
- (33) Nelson, L. J.; Hart, G. L. W.; Zhou, F.; Ozoliņš, V. Compressive Sensing as a Paradigm for Building Physics Models. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *87*, 035125.
- (34) Van der Ven, A.; Thomas, J. C.; Xu, Q.; Bhattacharya, J. Linking the Electronic Structure of Solids to Their Thermodynamic and Kinetic Properties. *Mathematics and Computers in Simulation* **2010**, *80* (7), 1393–1410.
- (35) Zunger, A.; Wei, S.-H.; Ferreira, L. G.; Bernard, J. E. Special Quasirandom Structures. *Phys. Rev. Lett.* **1990**, *65* (3), 353.
- (36) Shin, D.; van de Walle, A.; Wang, Y.; Liu, Z.-K. First-Principles Study of Ternary Fcc Solution Phases From Special Quasirandom Structures. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *76* (14), 144204.
- (37) Zhang, L.; Noguchi, H.; Li, D.; Muta, T.; Wang, X.; Yoshio, M.; Taniguchi, I. Synthesis and Electrochemistry of Cubic Rocksalt Li-Ni-Ti-O Compounds in the Phase Diagram of $\text{LiNiO}_2\text{-LiTiO}_2\text{-Li}[\text{Li}_{1/3}\text{Ti}_{2/3}]\text{O}_2$. *J. Power Sources* **2008**, *185* (1), 534–541.
- (38) Marianetti, C. A.; Morgan, D.; Ceder, G. First-Principles Investigation of the Cooperative Jahn-Teller Effect for Octahedrally Coordinated Transition-Metal Ions. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2001**, *63* (22), 224304.
- (39) Gaskell, D. R. *Introduction to the Thermodynamics of Materials*, 5th ed.; Taylor and Francis Group, 2008.
- (40) Koga, H.; Croguennec, L.; Ménétrier, M.; Mannesiez, P.; Weill, F.; Delmas, C. Different Oxygen Redox Participation for Bulk and Surface: a Possible Global Explanation for the Cycling Mechanism of $\text{Li}_{1.20}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{O}_2$. *J. Power Sources* **2013**, *236*, 250–258.
- (41) Sathiyar, M.; Rousse, G.; Ramesha, K.; Laisa, C. P.; Vezin, H.; Sougrati, M. T.; Doublet, M. L.; Foix, D.; Gonbeau, D.; Walker, W.; Prakash, A. S.; Ben Hassine, M.; Dupont, L.; Tarascon, J. L. Reversible Anionic Redox Chemistry in High-Capacity Layered-Oxide Electrodes. *Nat. Mater.* **2013**, *12*, 827.
- (42) Thackeray, M. M.; Kang, S.-H.; Johnson, C. S.; Vaughey, J. T.; Benedek, R.; Hackney, S. A. Li_2MnO_3 -Stabilized LiMO_2 ($M = \text{Mn, Ni, Co}$) Electrodes for Lithium-Ion Batteries. *J. Mater. Chem.* **2007**, *17* (30), 3053–3272.
- (43) Lee, J. Cation-Disordered Oxides for Rechargeable Lithium Battery Cathodes. Doctoral Thesis, Massachusetts Institute of Technology, 2015, pp 1–128.
- (44) Makimura, Y.; Ohzuku, T. Lithium Insertion Material of $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ for Advanced Lithium-Ion Batteries. *J. Power Sources* **2003**, *119–121*, 156–160.
- (45) Sathiyar, M.; Ramesha, K.; Rousse, G.; Foix, D.; Gonbeau, D.; Guruprakash, K.; Prakash, A. S.; Doublet, M. L.; Tarascon, J. M. $\text{Li}_4\text{NiTeO}_6$ as a Positive Electrode for Li-Ion Batteries. *Chem. Commun.* **2013**, *49* (97), 11376–11378.