Stabilization of Lithium Transition Metal Silicates in the Olivine Structure

Xiaoqi Sun, Rajesh Tripathi, Guerman Popov, Mahalingam Balasubramanian, and Linda F. Nazar

ABSTRACT: While olivine LiFePO₄ shows amongst the best electrochemical properties of Li-ion positive electrodes with respect to rate behavior owing to facile Li⁺ migration pathways in the framework, replacing the [PO₄]³⁻ polyanion with a silicate [SiO₄]⁴⁻ moiety in olivine is desirable. This could allow additional alkali content and hence electron transfer, and increase the capacity. Herein we explore the possibility of a strategy toward new cathode materials and demonstrate the first stabilization of a lithium transition metal silicate (as a pure silicate) in the olivine structure type. Using Li₃InSiO₄ and Li₂ScSiO₄ as the parent materials, transition metal (Mn, Fe, Co) substitutions on the In/Sc site were investigated by computational modeling via atomic scale simulation. Transition metal substitution was found to be only favorable for Co, a finding confirmed by the successful solid state synthesis of olivine Li₁₁₀Co₈₋₉SiO₄. Stabilization of the structure was achieved by entropy provided by cation disorder.

INTRODUCTION

Lithium ion batteries are widely utilized as energy storage devices due to their high energy density, low cost, and small carbon footprint. However, further increase in energy density and safety of these batteries is needed in order to meet future electrochemical energy storage goals. In this regard, the discovery and synthesis of new positive electrode materials have led to significant achievements in the last few decades. Ever since Goodenough and co-workers proposed the use of LiFePO₄ as a positive electrode material, polyanion-based compounds have gained much attention. Olivine LiFePO₄ has been the most successful among these. Owing to facile Li⁺ conduction along one-dimensional (1D) pathways arising from ordering of the Li⁺ and Fe²⁺ on the two different octahedral sites in the lattice, and formation of a Li solid solution on partial states of charge/discharge at a moderate overpotential, LiFePO₄ exhibits some of the highest charge-discharge rates achieved in a Li-ion battery. Nonetheless, the specific energy of this material is rather modest. The electrochemical de-/intercalation of Li takes place at 3.45 V (vs Li), and the maximum specific capacity is only 170 mAh g⁻¹. Compounds based on PO₄³⁻ as well as other polyanion groups such as BO₃³⁻, SiO₄⁻², SO₄²⁻, and SO₄Fe³⁻ have been synthesized and examined for their Li-ion intercalation properties. Although lithium iron borates and fluorosilicates reversibly de-/intercalate lithium in either case does the specific energy improve much over the phosphates, Silicates, on the other hand, are a good alternative owing to the higher charge on the SiO₄⁴⁻ polyanion, which requires additional alkali capacity to balance the charge. Thus, in addition to silicon’s abundance and non-toxic properties, the SiO₄⁴⁻ anion has a high charge to weight ratio which leads to higher specific energy storage capacity (at least theoretically). In the first and most widely studied silicate based positive electrode material, Li₃MnSiO₄, two lithium ions are available for extraction, based on the Fe²⁺/Fe³⁺ and Fe³⁺/Fe⁴⁺ redox couples. However, the latter couple is at too high a voltage to be accessible, and thus only one lithium ion undergoes de-/intercalation. In addition, Li₂FeSiO₄ undergoes an irreversible phase transformation on the first cycle, leading to a decrease of the discharge voltage from 3.1 to 2.8 V, and hence a drop in the energy density. In order to use lithium transition metal silicates as potential high capacity electrodes for long-term applications, these materials must be synthesized in more robust framework types.

Once such framework is olivine, which is also adopted by many natural silicate minerals with a general formula of MₓMₘₓSiO₄ (Mᵣ, Mᵢ: cations). It comprises hexagonal close packed oxygen anions with the two MI and MII cations being octahedrally coordinated in sites 1 and 2, and Si⁴⁺ occupying 1/8 of the tetrahedral sites (Figure 1). Examples include materials where both Mᵣ and Mᵢ cations are in their +2 state, such as MgFeSiO₄ (where Mg and Fe are fully disordered over site 1 and site 2) and Mn₃SiO₄. However, in cases where the cations either have +1 or +3 charges such as in Li⁺Sc³⁺SiO₄ and Li⁺In⁺³SiO₄ their charge difference results in perfect cation ordering over the two octahedral M1 and M2 sites. This
makes these materials good potential Li-ion cathodes if a transition metal can be substituted for Sc or In. The voltage for Li extraction from LiMnSiO₄ (M = Mn, Fe, Co, Ni) is predicted to be around 5 V, which approaches the upper voltage limit of solid solution between LiFePO₄ and Fe₂SiO₄. Whereas substitution materials and combined neutron and synchrotron re-

Figure 1. Crystal structure of olivine. The M₆O₆ and M₈O₆ octahedra are shown in green and purple, respectively, while the SiO₄ tetrahedra are shown in blue.

three-body term was used for the SiO₄⁻ unit to account for the angle dependent nature of O–Si–O bonds, as previously used for other sulfate and phosphate units. The well-known shell model was employed to account for the polarizability effects of charged defects on the electronic charge clouds. The In–O interatomic potential was taken from the study of Fisher et al. on Ba₂In₂O₅ and the Sc–O interaction was adopted and refined from a publication of Minervini et al. on Sc doping in Cs₂O. Other atomic potentials such as O–O and Li–O were taken from another work of Fisher et al., while Si–O potentials adopted from the work of Sierka et al. were found to be the best for reproducing the olivine structural parameters of LiInSiO₄ and LiScSiO₄. The three body potential model used for the SiO₄⁻ unit was the same as that used for PO₄⁻ by Islam et al. Many different values for three body terms of SiO₄⁻ have been reported in the literature, and the value used in the current work was very close to that used by Sanders et al. for SiO₄. Interatomic potential values to study the doping energy of M⁺ ions (M–O potential) were taken from the work of Woodely et al. and Brathwaite et al. As argued previously, these interatomic potential methods are assessed primarily by their ability to reproduce observed crystal properties. Indeed, they are found to work well, even for compounds where there is undoubtedly a degree of covalency such as aluminophosphates.

The lattice relaxation about defects (such as Li vacancies) and migrating ions was calculated by an implementation of the Mott-Littleton scheme incorporated in the GULP code. This method partitions a crystal lattice into two regions, where ions in the inner region immediately surrounding the defect (on the order of ~700 ions) are relaxed explicitly. Relaxations of such a large number of ions are important for charge defects that introduce long-range electrostatic perturbations and are not easily treated by electronic structure methods. The outer region extends to infinity, with the outer lattice relaxations treated by quasi-continuum methods.

**Synthesis and Characterization.** Cobalt substituted LiInSiO₄ samples were synthesized by solid state reaction of Li₂CO₃ (Sigma-Aldrich, 99.4%), cobalt(III) acetylacetonate (Co(C₅H₇O₂)₃, Sigma-Aldrich, 99.99%), indium acetate (In(C₆H₁₂O₁₅)₃, Alfa, 99.99%), and SiO₂ (Alfa, 99.8%). Precursors were ball milled at 250 rpm for 10 h, heated at a 5 °C/min rate of 900 °C and annealed for 12 h, followed by 10 °C/min rate cooling to 700 °C and a temperature hold for 24 h. All steps were carried out under pure O₂. Iron/manganese, and the nonsubstituted LiInSiO₄ samples were obtained by a similar procedure (using Fe₂O₃ and Mn₂O₃ as the iron and manganese precursors, respectively), with heat treatment performed at 900 °C for 12 h under air, followed by cooling the material to room temperature at a rate of approximately 10 °C/min, as dictated by the natural cooling of the furnace.

For cobalt substituted samples, time-of-flight neutron diffraction experiments were performed at 100 K on the POWGEN powder diffractometer at the Oak Ridge National Laboratory, Tennessee, USA, and powder X-ray diffraction was performed at 100 K on beamline 11-BM at the Advanced Photon Source (APS) at the Argonne National Laboratory, Illinois, USA, with an average wavelength of 0.4137 Å. Diffraction data processing was carried out using GSAS and EXPGUL. Cobalt K-edge X-ray absorption near edge spectroscopy measurements were carried out at the sector 20-BM at the APS using a Si(111) crystal monochromator. Simultaneous cobalt metallic foil was run with the samples for energy calibration. The energy scale was calibrated by defining the first derivative maxima of Co foil as 7709 eV. The spectra were normalized to unity absorption well above the edge after a linear background subtraction with Demeter software. For other samples, powder X-ray diffraction was carried out with a PANalytical Empyrean diffractometer operating with Cu Kα radiation.

**EXPERIMENTAL SECTION**

**Atomistic Scale Simulation Methods.** This study used well established modeling techniques, which are detailed elsewhere, and hence only a general description will be given here. Interactions between ions in the olivine structures consist of a long-range Coulombic term and a short-range component representing electron–electron repulsion and van der Waals interactions. The short-range interactions were modeled using the two-body Buckingham potential (Supporting Information, Table S1). An additional interatomic potential was employed to account for the polarizability effects of charged defects on the electronic charge clouds. The In–O interatomic potential was taken from the study of Fisher et al. on Ba₂In₂O₅ and the Sc–O interaction was adopted and refined from a publication of Minervini et al. on Sc doping in Cs₂O. Other atomic potentials such as O–O and Li–O were taken from another work of Fisher et al., while Si–O potentials adopted from the work of Sierka et al. were found to be the best for reproducing the olivine structural parameters of LiInSiO₄ and LiScSiO₄. The three body potential model used for the SiO₄⁻ unit was the same as that used for PO₄⁻ by Islam et al. Many different values for three body terms of SiO₄⁻ have been reported in the literature, and the value used in the current work was very close to that used by Sanders et al. for SiO₄. Interatomic potential values to study the doping energy of M⁺ ions (M–O potential) were taken from the work of Woodely et al. and Brathwaite et al. As argued previously, these interatomic potential methods are assessed primarily by their ability to reproduce observed crystal properties. Indeed, they are found to work well, even for compounds where there is undoubtedly a degree of covalency such as aluminophosphates.

The lattice relaxation about defects (such as Li vacancies) and migrating ions was calculated by an implementation of the Mott-Littleton scheme incorporated in the GULP code. This method partitions a crystal lattice into two regions, where ions in the inner region immediately surrounding the defect (on the order of ~700 ions) are relaxed explicitly. Relaxations of such a large number of ions are important for charge defects that introduce long-range electrostatic perturbations and are not easily treated by electronic structure methods. The outer region extends to infinity, with the outer lattice relaxations treated by quasi-continuum methods.

**Results and Discussion.** Atomistic Scale Simulation of Transition Substitution into Olivine Silicate. Atomistic scale simulation methods have been successfully used to calculate relative substitution energies of different dopants in a given structure for olivine LiFePO₄ and many other technologically important compounds. In
the present work, we used this method to reproduce the crystal structures of olivine LiInSiO4 and LiScSiO4 based on the interatomic potential parameters that have been previously reported (Table S1). Table 1 compares the values obtained by these calculations to those reported experimentally using diffraction based methods,39 showing a maximum difference for any lattice parameter of 0.9%. Similar differences are also found for calculated and experimentally obtained In–O, Sc–O, and Si–O bond lengths (Table S2). Such small deviation between calculated and experimental results confirms the validity of the interatomic potentials that were used in further calculations in this work. The following two formulations—similar to the scheme used by Islam et al. previously for calculating substitution energies in LiMPO4,39—were used to calculate the energy required for doping Mn3+, Fe3+, and Co3+ into LiInSiO4 and LiScSiO4 (equations in Kröger Vink notation):

(1) Dopant occupies M2 site in the olivine structure:
   (a) M3+ (M = Mn, Fe, Co) in LiInSiO4
   \[ 2\text{In}_{\text{In}}^x + \text{M}_3 \text{O}_3 \rightarrow 2\text{M}_{\text{In}}^x + \text{In}_2\text{O}_3 \]  
   (1a)
   (b) M3+ (M = Mn, Fe, Co) in LiScSiO4
   \[ 2\text{Sc}_{\text{Sc}}^x + \text{M}_3 \text{O}_3 \rightarrow 2\text{M}_{\text{Sc}}^x + \text{Sc}_2\text{O}_3 \]  
   (1b)

(2) Dopant occupies M1 site in the olivine structure (formation of an antisite defect):
   (a) M3+ (M = Mn, Fe, Co) in LiInSiO4
   \[ 2\text{In}_{\text{In}}^x + 2\text{Li}_{\text{In}}^{\text{x+}} + \text{M}_3 \text{O}_3 \rightarrow 2\text{M}_{\text{In}}^{x+} + 2\text{Li}_{\text{In}}^{\text{+}} + \text{In}_2\text{O}_3 \]  
   (2a)
   (b) M3+ (M = Mn, Fe, Co) in LiScSiO4
   \[ 2\text{Sc}_{\text{Sc}}^{x+} + 2\text{Li}_{\text{Sc}}^{x+} + \text{M}_3 \text{O}_3 \rightarrow 2\text{M}_{\text{Sc}}^{x+} + 2\text{Li}_{\text{Sc}}^{x+} + \text{Sc}_2\text{O}_3 \]  
   (2b)

Equations 1a and 2a (or 1b and 2b) represent two extreme cases of the dopant ion completely occupying either site M1 or site M2 in the olivine structure. The energy of formation of the defect represented by eq 1a can be calculated as follows:

\[ E_{1a} = E_{\text{In}_{\text{In}}^x} + 2E_{\text{M}_{\text{In}}^x} - E_{\text{M}_3 \text{O}_3} \]  

and that represented by eq 2a:

\[ E_{2a} = E_{\text{In}_{\text{In}}^x} + 2E_{\text{M}_{\text{In}}^{x+}} + 2E_{\text{Li}_{\text{In}}^{\text{+}}} - E_{\text{M}_3 \text{O}_3} \]  

where \( E_{\text{M}_3 \text{O}_3} \) and \( E_{\text{In}_{\text{In}}^x} \) represent respective lattice energies and \( E_{\text{defect}} \) represents energy of formation of the isolated defect. Antisite defects are created together and tend to associate. This tendency was taken into account by introducing these two defects in the structure simultaneously. This strategy of calculating the energy of formation of associated defects was previously utilized for olivine LiMPO4 compounds.

The difference in energy of formation of defects represented by eqs 1a and 2a denotes the tendency of the substituted ion to be disordered over the two cationic sites in the olivine structure. Less difference in the energy will lead to equal distribution of cations over the two sites and therefore higher cationic disorder. This energy can be calculated as

\[ E_{\text{order}} = E_{2a} - E_{1a} = E_{\text{M}_{\text{In}}^{x+}} + E_{\text{Li}_{\text{In}}^{\text{+}}} - E_{\text{M}_3 \text{O}_3} \]  

Table 2 presents values of \( E_{\text{order}} \) for Mn3+, Fe3+, and Co3+ substitution in olivine LiInSiO4 and LiScSiO4. Positive values of the \( E_{\text{order}} \) indicate all substituents prefer site M2 over site M1, although \( E_{\text{order}} \) decreases from Mn3+ to Fe3+ to Co3+. This trend is apparent for both parent compounds. Because the value for Co3+ substitution in LiInSiO4 is lowest, it suggests that Co3+ could be significantly disordered in LiIn1−xCoxSiO4, whereas Mn3+ to Fe3+ may not. Although values calculated here apply only when a low degree of substitutions are used (assumption of noninteracting defects), these trends in \( E_{\text{order}} \) are expected to hold true even for high degrees of substitution.

**Experimental Investigation into Cation Substitution.**

Cation substitution behavior was examined experimentally by solid state synthesis, where a 1:1 molar ratio of the MI (Mn/Fe/Co) and MII (In/Sc) precursors was heated at 900 °C. Unfortunately, the XRD pattern of LiScSiO4 exhibited no evidence of any transition metal incorporation (data not shown), whereas substitution was successful in LiInSiO4 based on the shift in the d-spacings. Figure 2 compares the XRD patterns of the products obtained. The pattern for non-substituted LiInSiO4 is shown in the bottom trace of Figure 2 for comparison. Although some In2O3 impurity is present, the olivine structure is clearly the main phase. Comparison of the XRD patterns of the pristine and substituted materials shows that upon the addition of Mn in the precursors (InMn-11) little change is observed in the olivine phase of the product, and a significant amount of Mn2O3 is present, indicating substitution was not successful. The reflections of the In–Fe sample (InFe-11), on the other hand, are shifted to the right of LiInSiO4, indicating a decrease in the unit cell parameter that could arise from the partial substitution of In3+ by the smaller Fe3+ ion.
Nevertheless, the presence of Fe$_2$O$_3$ impurity peaks implies a rather low substitution level is achieved. In both samples, SiO$_2$ and other impurity peaks—presumably from Li/Si containing phases—are also present in the XRD patterns, further demonstrating the low level of cation substitution that is achieved. In contrast, the Co/In mixtures showed a more obvious shift of the olivine-based reflections in the XRD diffraction patterns (Figure 2): clear evidence for cation substitution. Along with the material prepared at a 1:1 ratio, (labeled as InCo-11), two other materials with different In/Co ratios were also synthesized, namely, at lower cobalt 3:1 (InCo-31) and higher cobalt 1:3 (InCo-13) concentrations. By comparison to LiInSiO$_4$, these three patterns show a shift to higher two-theta values (i.e., smaller cell parameters) with increasing Co concentration (Figure 3a, inset). Although minor impurities are observed in each case—arising mainly, from Li$_2$CoSiO$_4$, which starts to evolve beyond the 1:1 composition—overall the results demonstrate a higher level of substitution is obtained by increasing the Co content.

To obtain information about the cobalt oxidation state in the InCo samples is close to +2. The cation arrangement in the Co substituted olivine phase arising mainly, from Li$_2$CoSiO$_4$ whereas the Co$^{3+}$ in the standards were carried out, using CoO and Li$_2$CoSiO$_4$ as standards for Co$^{3+}$; Co$_3$O$_4$ for mixed Co$^{2+}$/Co$^{3+}$; and LiCoO$_2$ for Co$^{3+}$. In the near edge structure (XANES) measurements, surprisingly, the main cobalt edges of all three samples are close to those of Co$_3$O$_4$ and Li$_2$CoSiO$_4$, whereas the Co$^{3+}$ in the standards (Co$_3$O$_4$ and LiCoO$_2$) is clearly at higher energy (Figure 3b). This suggests that Co$^{2+}$ is mainly present in the final products, despite our use of a Co$^{3+}$ precursor under an oxidizing atmosphere (O$_2$) in the reaction. Reduction could be due to the presence of the acetylacetonate and acetate anions in the precursors, which provide a slightly reducing atmosphere. The size of the Co$^{2+}$ cation is comparable to Li$^+$ and In$^3+$, and hence it has good solubility in the olivine structure. The Li$_2$CoSiO$_4$ impurity evident in the XRD patterns of the 1:1 and 1:3 compositions affects their EXAFS spectra as well. A comparison of the data of the three InCo samples with the Li$_2$CoSiO$_4$ standard shows a distinct shift of the InCo-13 sample toward the standard (Figure S1) and suggests the highest amount of Li$_2$CoSiO$_4$ present in this material, in agreement with XRD (Figure 3a). The similarity between the EXAFS data for the InCo-11 and InCo-31 materials suggests they have the same average Co environment, meaning that their Li$_2$CoSiO$_4$ content is not too different (again, as suggested by XRD).

The cation arrangement in the Co substituted olivine phase was further examined by combined Rietveld refinement of SXRD and neutron diffraction (ND) data (Table 3), which.

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**Figure 2.** Comparison of the XRD patterns of transition metal substituted and nonsubstituted materials (laboratory diffractometer data, Cu Kα radiation, for In only, InMn-11 and InFe-11 materials; and synchrotron data (λ = 0.413738 Å), for the InCo-11 material) with 2θ adjusted to the wavelength of Cu Kα radiation. The impurity peaks are marked and labeled in the figure.

**Figure 3.** (a) XRD Comparison of cobalt substituted (synchrotron, λ = 0.413738 Å) and nonsubstituted (laboratory diffractometer, Cu Kα radiation, 2θ adjusted to synchrotron wavelength) samples, showing a right shift of olivine peaks with an increase of cobalt concentration as well as minor impurities. (b) The Co K edges XANES of cobalt substituted samples and the reference standards, demonstrating the Co oxidation state in the InCo samples is close to +2.

**Table 3. Crystallographic Data for Microcrystalline InCo-11: Li$_{0.8}$In$_{0.8}$Co$_{0.4}$SiO$_4$**

<table>
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<th>source</th>
<th>synchrotron</th>
<th>neutron time-of-flight (TOF)</th>
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<td>chemical formula</td>
<td>Phase 1 (83% wt %) = Li$<em>{0.8}$In$</em>{0.8}$Co$_{0.4}$SiO$_4$</td>
<td>Impurity phase 2 (17 wt %) = Li$_2$CoSiO$_4$, Pbnm, (S.G. 32, ICSD #: 8238)</td>
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<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>formula weight</td>
<td>Phase 1 = 213.06 g mol$^{-1}$</td>
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</tr>
<tr>
<td></td>
<td></td>
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</tr>
<tr>
<td>temperature</td>
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</tr>
<tr>
<td>wavelength</td>
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<td>1.333 Å</td>
</tr>
<tr>
<td>crystal system</td>
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<tr>
<td>space group (No.)</td>
<td>Phase 1 = Pbnm (62)</td>
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</tr>
<tr>
<td>a, b, c, α, β, γ</td>
<td>Phase 1: a = 4.8252(2) Å, b = 10.4681(3) Å, c = 6.02472(2) Å, α = β = γ = 90°</td>
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</tr>
<tr>
<td>V</td>
<td>Phase 1 = 304.316(1) Å$^3$</td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>Phase 1, Z = 4</td>
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<tr>
<td>d-spacing range</td>
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<td>0.490–9.475 Å</td>
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<td>R$_p$ (%)</td>
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<td>R$_{wp}$ (%)</td>
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<td>definition of R factors</td>
<td>$R_p = \sum_i</td>
<td>y_i(\text{obs}) - y_i(\text{calc})</td>
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provides information on site occupancies in solid lattices. We studied the InCo-11 sample because of its relatively large XRD peak shift and small impurity fraction. The stoichiometry of the olivine phase was determined to be Li$_0.8$In$_0.8$Co$_0.4$SiO$_4$ (from charge balance and assuming fully occupied sites, see equations and details in Supporting Information), indicating a similar amount of lithium and indium were substituted by cobalt. The distribution of the three cations was initially assigned to be equal over the two sites (Figure 1), and this was followed by a relaxation of their occupancies until the refinement converged. The simultaneous refinement of two sets of diffraction data (synchrotron X-ray and neutron, which allows us to probe the scattering of all atoms irrespective of their mass) together with the additional constraint of the overall composition (i.e., sum of the cation site occupancies on M1 + M2 = 2.0) converged to a highly stable refinement. This showed that the degree of Li$^+$-ion mixing over the two sites was negligible, so Li$^+$ was placed on site 1 with a fixed occupancy of 0.8 (see Supporting Information for details). Subsequent refinement (i.e., fractional coordinates, thermal parameters for all sites, and occupancies) showed that the In$^{3+}$ cation primarily occupies site 2, with only 2% disordered onto site 1. Co$^{2+}$, on the other hand, occupies both sites 1 and 2 (Figure 4 and Table S3). Thus, the olivine phase resembles the parent structure (cation ordered-LiInSiO$_4$) but cobalt disorders over the two sites. We also started the refinement with slightly different compositions and the outcome was the same—lithium and indium occupy cation sites M1 and M2, respectively, while Co distributes over the two sites. This is in complete agreement with the simulation result that shows a tendency toward Co disorder in the olivine lattice.

The experimental results clearly show that high Co substitution can be achieved in LiInSiO$_4$-olivine. Combined with the results of atomistic scale simulations, it appears that the ability of cobalt to disorder over two cationic sites contributes an additional entropic stability to the compound. The reduction of Co$^{3+}$ to Co$^{2+}$ allows a better match of cation sizes, promoting a high substitution level. At the same time, the fact that Co$_2$SiO$_4$ itself crystallizes in an olivine structure (fayalite) favors a solid solution with LiInSiO$_4$ in the final product and results in additional structural stability. On the other hand, cation disorder blocks the most facile 1D channel Li-ion migration pathway, forcing diffusion to take place along more hindered pathways. Because of this fact we were not able to observe significant electrochemical activity of the substituted materials. Nevertheless, reducing the cation diffusion length by using nanosized particles would potentially allow reversible Li-ion intercalation, as observed in triplite-LiFeSO$_4$F which also exhibits cation disorder, but shows good electrochemical behavior with nanocrystallites.

**CONCLUSIONS**

Atomistic scale simulations on transition metal (Mn, Fe, and Co) substitution into olivine-type LiScSiO$_4$ and LiInSiO$_4$ show that among the metals, cobalt has the highest tendency to adopt disorder in the structure. Cations are predicted to be disordered over site M1 and M2 in the olivine lattice. In fact, experimentally, only significant cobalt substitution is achieved in the LiInSiO$_4$ framework, accompanied by the reduction of Co$^{3+}$ to Co$^{2+}$. This suggests that the additional configurational entropy arising from cation disorder in the structure plays a major role in lowering the free energy of the substituted olivine material, Li$_x$In$_{1-x}$Co$_{2-x}$SiO$_4$, where Co$^{2+}$ substitutes for both Li$^+$ and In$^{3+}$. When unfavorable site mixing (owing to size or other effects) dominates, substitution is precluded. Our work demonstrates that substitution is promoted by increasing the entropic parameter as well as matching the ion sizes in the substituted structure, both of which help to lower the overall free energy.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b01453.

Short range potential parameters for LiInSiO$_4$ and LiScSiO$_4$, comparison between calculated and experimental bond lengths, combined neutron and X-ray refinement results, comparison of Co K edge EXAFS data, calculation of olivine composition to guide refinement (PDF)

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The authors declare no competing financial interest.
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