Lithium ion batteries (LiBs) are commonly used as sources of power in portable electronics because of their high gravimetric capacity and power density, owing to the lighter molecular weight of lithium. Commercially available LiBs typically use graphite as the anode, LiCoO₂ as the cathode, and LiPF₆ in alkyl carbonate solvents as the electrolyte. The choice of materials for different components of LiBs, such as electrodes, electrolyte, current collectors, and the interactions between them, determine the overall battery performance. Increased energy demands have intensified the efforts to improve commercially available LiBs, especially to power electric vehicles and for load leveling applications. Materials with higher capacities than that of graphite and LiCoO₂ have been studied as electrode materials to improve the energy density of LiBs.\(^4\)\(^,\)\(^5\)

Different classes of materials that have been synthesized and tested for their electrochemical performance as prospective anode materials can be broadly divided into three classes based on their reactivity with lithium: intercalation, alloying, and conversion materials. Apart from carbon-based compounds, oxides of titanium that store lithium by means of intercalation have been studied because of their stability, wide availability, low cost, and good reversible capacity at an operating potential of 1.5 V vs Li/Li\(^+\). But their theoretical capacity, which is lower than that of graphite (372 mAh g\(^{-1}\)), and poor electron conductivity have limited their application in high energy density LiBs. Alloying anode materials such as Si, Sn, SnO, SnO\(_2\), and Ge have higher theoretical capacities than graphite, but are limited by high volume expansion and high irreversible capacity losses after first cycle. Research has been carried out to overcome these issues by using multiphase composites, intermetallic composites, and by improving the purity of the alloys. A new generation of LiBs named Nexelion was manufactured by SONY in 2005 using a tin based amorphous material (Sn-Co-C composite) as the anode. This battery showed improved temperature performance, along with increased capacity and energy density, as compared to conventional LiBs but the long term cyclability was lower.\(^6\)\(^,\)\(^7\)

Conversion materials, such as transition metal oxides (MO\(_x\); where M is Mn, Fe, Co, Ni, or Cu), metal sulfides (MS\(_x\)), metal phosphides (MP\(_x\)) and metal nitrides (MN\(_x\)), have also been investigated as prospective anode materials for high energy density LiBs because of their high theoretical capacities and high capacity retention with subsequent charge-discharge cycles.\(^8\)\(^,\)\(^9\)\(^,\)\(^10\)\(^,\)\(^11\)\(^,\)\(^12\) However, commercialization of conversion-driven metal oxide anodes has been limited by their poor electrical conductivity and poor cycling performance.\(^13\)\(^,\)\(^14\)

In contrast to intercalation electrode materials, conversion and alloying materials have been found to exhibit lithium capacities that exceed the limits anticipated on the basis of reaction stoichiometry.\(^15\)\(^,\)\(^16\) In the case of RuO\(_2\), a growing body of experimental and theoretical evidence supports the idea that most of this “extra” or “superstoichiometric” capacity originates from the storage of lithium at the grain boundaries (or interfaces) of multiple solid phases that are formed within the electrode material. Recently, based on first principles density functional theory (DFT) calculations, we were able to show that the interfacial storage mechanism was also responsible for the observed extra capacity in SnO\(_2\), an alloying material, and that it was also operational in SnS\(_2\).

Simultaneous advances in DFT methods and high-performance computing platforms have made the first principles DFT approach a reasonable alternative for rapidly screening LiB electrode materials. Computation serves as a reliable and inexpensive tool,\(^22\)\(^,\)\(^23\) provided the methods and models can be validated against experiments. Validated computational approaches make it possible to understand several aspects of LiBs, such as structural stability of lithiated and delithiated phases, voltage calculations, charge distribution and kinetics of lithium diffusion process.\(^23\)\(^,\)\(^24\) In this work, first principles DFT computational protocols and analysis methods developed in previous work from our group\(^25\) are applied to study the lithiation of the transition metal oxides MnO\(_2\), CoO, NiO, and CuO, as well as the main group metal oxide SnO\(_2\). Experimentally, each of these materials have been shown to exhibit lithium capacities beyond theoretical stoichiometric limits. Structural analyses were carried out to understand the molecular mechanisms by which lithium is accommodated in these materials, providing insights that are difficult or impossible to obtain experimentally. To the best of our knowledge, this is the first computational study of these materials in the context of LiB anodes.

**Computational Methods**

Total energy calculations for lithiation of the metal oxides studied were carried out in the framework of DFT implemented through Vienna Ab Initio Simulation Package (VASP).\(^16\)\(^,\)\(^36\) The exchange-correlation energy was described using the Perdew, Burke and Ernzerhof (PBE) form of the generalized gradient approximation. The potential due to core electrons was accounted for by the projector augmented wave (PAW) method, which combines the features of pseudopotential approach and the linear augmented plane wave method.\(^35\)\(^,\)\(^36\) Kohn-Sham orbitals for valence electrons were expanded in terms of plane wave basis set with a cutoff energy of 520 eV.\(^16\)
Energy minimization calculations involved a series of electronic and ionic minimization steps to find the actual ground state for a given input structure. Electronic minimization was carried out using residual minimization-direct inversion in the iterative subspace (RMM-DIIS) method where the Hamiltonian matrix is diagonalized iteratively and self consistently.\textsuperscript{31} Forces acting on the atoms were calculated followed by the relaxation of atomic positions by the conjugate gradient method. A Monkhorst-Pack mesh ($7 \times 7 \times 7$) was used for sampling the k-points in the first Brillouin zone.\textsuperscript{37} The true ground state energies of systems involving the magnetic metals Ni, Co, and Mn, were calculated by performing spin-polarized calculations.

The equilibrium voltage for the lithiation of metal oxides was calculated using the Nernst equation:\textsuperscript{2}
\[ E = -\frac{\Delta G}{x F} \]  
where \( x \) represents the number of lithium atoms, and \( F \) is the Faraday’s constant. Following the approach of Mueller et al.,\textsuperscript{38} the change in Gibbs free energy, \( \Delta G \), is approximated by the change in electronic energy. The appropriateness of using the GGA approach for the transition metals with unpaired electrons in the d orbitals was confirmed by comparing voltages obtained from GGA with those from GGA+U calculations for a few cases, as discussed in the following section.

In the low capacity regime, the following equation was used to determine the free energy change:
\[ \Delta G \approx \Delta E = E_{(MO)_1 Li_x} - x E(\text{Li}) - E(MO)_n \]  
At a lithium content beyond the conversion limit, the energy of the pure metal oxide (MO)\textsubscript{n} was replaced with the energy of the conversion limit island structure Li\textsubscript{2x} (MO)\textsubscript{n}. This is similar to the approach taken by Courtney et al.\textsuperscript{39} to compute the voltage profile for lithium-tin alloys where multiple lithium-tin alloys with well-characterized crystal structures were used as “reactants” at various points along the curve. Specific capacities of metal oxides in terms of mAh g\textsuperscript{-1} were calculated as a function of the number of lithium atoms using the formula:
\[ \text{Capacity} = \frac{1000Fx}{3600M} \]  
where \( x \) is the number of atoms of lithium and \( M \) is the molar mass of working cells of MOs, the factor of 1000 converts Amperes to milliAmperes, and the factor of 3600 converts seconds to hours.

Stoichiometric limits of the maximum capacities attained by different anode materials depend on their reactivity with lithium. Transition metal oxides undergo “conversion” reactions by which lithium reacts with oxygen, resulting in the dispersion of pure metal, typically as nanometer-scale islands, in a lithium oxide matrix:
\[ \text{MO}_n + 2x\text{Li} + 2xe^- \leftrightarrow M + x\text{Li}_2\text{O} \]  
For the oxides studied here, \( x = 1 \) and, therefore, two lithium atoms are stored for the reduction of every metal atom, which means that the limiting lithium capacity, based on conversion reaction stoichiometry, is a Li:M ratio of 2:1. Experimental studies on transition metal oxide anode materials have reported capacities higher than this conversion limit. Metals such as Sn, Ge, Si, and Sb react with lithium by means of alloying to form Li-M alloys of different compositions:
\[ y\text{M} + x\text{Li} \leftrightarrow M_x L_y \]  
Certain simple metal oxides, such as SnO, SnO\textsubscript{2}, Sb\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, GeO\textsubscript{2}, ZnO, and spinel structured complex metal oxides such as ZnCo\textsubscript{2}O\textsubscript{4}, ZnFe\textsubscript{2}O\textsubscript{4}, Zn\textsubscript{2}Sn\textsubscript{3}O\textsubscript{6}, CdCO\textsubscript{3}, have reactivity with lithium that follows a two-step process. The metal oxides are reduced to respective metals followed by formation of Li-M alloys.\textsuperscript{31} For SnO, the alloying material studied here, the relevant reactions are:
\[ \text{SnO} + 2\text{Li} \rightarrow \text{Sn} + \text{Li}_2\text{O} \]  
\[ 5\text{Sn} + 22\text{Li} \rightarrow \text{Li}_{12.3}\text{Sn}_5 \]  
leading to a maximum capacity of 6.4 Li per mole of Sn.

The computational approach is as follows: the unit cells of each oxide is optimized with sufficiently high energy cut-offs and sufficiently fine k-point grids, as described earlier. A supercell is constructed from the optimized unit cell with the formula (MO)\textsubscript{12}. In one series of calculations, lithium atoms are added to the crystalline supercells at the most open positions within the lattice. As lithiation progresses, conversion reactions at finite temperatures lead to the formation of metal islands dispersed in a sea of Li\textsubscript{2}O. The ability of DFT structural optimizations, which are essentially 0 K processes, to spontaneously form islands is inhibited by energy barriers for major atom rearrangement. To circumvent this difficulty, the second series of calculations started with working cells of a metal island dispersed in a Li\textsubscript{2}O matrix with a 2:1 ratio of Li:M, specifically Li\textsubscript{12.3}M\textsubscript{1.7}O\textsubscript{12}. These are referred to as “island” structures, where every oxygen atom is bonded to two lithium atoms. Further lithiation of these island structures were performed to study the effects of lithiation beyond the conversion limit.

Identifying the most optimal distribution of Li within a metal oxide lattice is a well-recognized challenge. Studies on lithiation of silicon have employed Voronoi-Delaunay triangulation methods to identify lithium positions that may potentially yield the lowest energy structures, based on the largest spherical void within the structure.\textsuperscript{40} Chan et al.\textsuperscript{41} have noted that this approach does not always actually yield the lowest energy structure when the atom positions are optimized. We employ a simple algorithm discussed in our previous work\textsuperscript{28} where the distance of a random position from the nearest atom is used to identify such positions. Given the large number of random positions considered at each step (100,000 for each Li added), it seems reasonable to assume that our approach also successfully identifies the most open positions. However, alternate placements of atoms were also examined to confirm that the minimum energy structure for a given lithium content had indeed been identified. These alternate structures were generated in a couple of ways: (a) DFT molecular dynamics simulations were done at elevated temperatures for at least 10 ps, followed by minimum energy structural optimization; and (b) for a given ratio of Li:M, metal atoms were swapped among the optimized structures of the oxides studied (for instance, Cu atoms in CuO was swapped with Mn) and energy minimized. In the vast majority of cases, these attempts did not find lower energy structures compared to those found by the approach described in Ref. 20. At each capacity, the structure that yields the higher voltage (or lower energy) is more favorable thermodynamically, and is used to fit the variation of voltage with specific capacity to a superposition of hyperbolic tangent functions to generate the computed discharge curves:
\[ E = \sum_{j=0}^{3} A_j \left[ 1 - \tanh \left\{ \alpha_j (x - \beta_j) \right\} \right] \]  
where \( x \) is the number of lithium ions in the cell (see Eq. 3) and \( A_j, \alpha_j, \) and \( \beta_j \) are fitting parameters.

### Results and Discussion

#### First discharge curves

-Voltages obtained using different GGA functionals and the same functionals augmented with the Hubbard correction (GGA+U) were compared in our previous work on lithiation of RuO\textsubscript{2}\textsuperscript{20} and the relative voltage trends were found to be similar. In the present study, we compared PBE and PBE+U voltages for Li, MnO, Li, CoO, Li, CuO, and Li, NiO at a few values of \( x \), as shown in Table 1, where Eqs. 1 and 2 have been used to compute voltages. The U parameter for Mn, Co, Cu, and Ni were taken from the work of Jain et al.\textsuperscript{43} The conclusion from this comparison, consistent with that in the case of RuO\textsubscript{2},\textsuperscript{20} is that the +U correction has minimal impact on equilibrium voltages. Therefore, the results and associated discussion presented here are based on GGA results.

When comparing experimental and computational discharge curves, allowance must be made for the fact that experimental voltages are affected by the non-equilibrium kinetics of lithiation in real time whereas computations are related to equilibrium thermodynamics.\textsuperscript{39} For this reason, cell potentials computed from equilibrium free
Table I. Comparison of equilibrium voltages computed from PBE and PBE+U energies using Eq. 1 and the relationship in Eq. 2. The U parameters for the transition metals are taken from Ref. 43: $U_{\text{Mn}} = 3.9$, $U_{\text{Co}} = 3.4$, $U_{\text{Ni}} = 6.0$, $U_{\text{Cu}} = 4.0$.

|        | $E_{\text{GGA}}$ (V) | $E_{\text{GGA}+U}$ (V) | $E_{\text{GGA}}$ (V) | $E_{\text{GGA}+U}$ (V) | $E_{\text{GGA}}$ (V) | $E_{\text{GGA}+U}$ (V) | $E_{\text{GGA}}$ (V) | $E_{\text{GGA}+U}$ (V) |
|--------|----------------------|------------------------|----------------------|------------------------|----------------------|------------------------|----------------------|------------------------|
| Supercell | 1                   | 1.04                   | 1.05                 | 2.09                   | 2.05                 | 2.00                   | 2.00                 | 2.07                   | 2.05                 |
|         | 2                   | 0.61                   | 0.67                 | 1.38                   | 1.35                 | 1.31                   | 1.31                 | 1.61                   | 1.64                 |
| Island  | 2                   | 0.67                   | 0.78                 | 1.45                   | 1.57                 | 1.56                   | 1.56                 | 1.45                   | 1.43                 |
|         | 3                   | 0.51                   | 0.51                 | 1.05                   | 1.17                 | 1.22                   | 1.22                 | 1.23                   | 1.22                 |
|         | 4                   | 0.43                   | 0.44                 | 0.79                   | 0.92                 | 0.98                   | 0.98                 | 1.01                   | 1.01                 |

energies (see Eq. 1) are expected to be higher than those recorded in the laboratory under finite current conditions. The peak voltages obtained from methods that allow the system to fully equilibrate at a given capacity, such as galvanostatic intermittent titration technique (GITT),$^{44,45}$ are more appropriate for comparison with computed results. In Fig. 1, we compare three experimental recordings$^{43}$ of discharges from MnO powder samples (50 – 70 μm particle size) coated with carbon. The two GITT curves shown in Fig. 1 connect the peaks of the recorded curves shown in Figs. 4a and 4c of Ref. 40. It is immediately clear that the agreement between the computed and experimental data improves when longer relaxation times are allowed in the GITT experiments.

The variation of voltage with capacity for lithiation of the two types of working cells described earlier (“supercell” and “island”) are compared against experimental first discharge curves in Fig. 2 for MnO,$^{44}$ CoO,$^{46}$ in Fig. 3 for NiO,$^{47}$ CuO,$^{48}$ and in Fig. 4 for SnO.$^{49}$

![Figure 1](image1.png) Comparison of computed voltage profile with experimental GITT data.$^{44}$ The solid red line represents the best fit to Eq. 8.$^{20}$

![Figure 2](image2.png) Comparison of computed and experimental first discharge curves for MnO (left),$^{44}$ and CoO (right).$^{46}$ The solid red lines are the best fit to computed voltages. The solid blue lines are the experimental discharge curves digitized from the indicated references.

![Figure 3](image3.png) Comparison of computed and experimental first discharge curves for NiO (left),$^{47}$ and CuO (right).$^{48}$ The solid red lines are the best fit to computed voltages. The solid blue lines are the experimental discharge curves digitized from the indicated references.
Among the lithiated structures displayed for different ratios of Li:M, the structure corresponding to Li:M ratio of 2:1 represents the island structure. Taking into account the factors mentioned above, the trends in the computed voltage-capacity data are found to be qualitatively similar to that of experimental first discharge curves.

As already noted, transition metal oxides such as MnO, CoO, and NiO react with lithium by means of a conversion reaction where metal is reduced from a formal oxidation state of +2 to 0 accompanied by formation of Li₂O.¹⁵

\[
\text{MO} + 2\text{Li} \leftrightarrow \text{Li}_2\text{O} + \text{M}
\]  

[9]

Thus, the capacity predicted by conversion reactions in these oxides corresponds to a 2:1 ratio of Li to M. This translates to 755.6 mAh g⁻¹ for MnO, 715.4 mAh g⁻¹ for CoO, and 717.6 mAh g⁻¹ for NiO. The experimental maximum capacities, as evidenced from Figs. 2 and 3, are 1243.5 mAh g⁻¹ for MnO, 1163.2 mAh g⁻¹ for CoO and 1372.4 mAh g⁻¹ for NiO. Understanding the molecular mechanism responsible for the “extra” capacity in these materials is the main focus of this work.

In contrast to MnO, CoO, and NiO, the reactions of CuO with Li are more complex. There is considerable experimental evidence that the metal is reduced to an intermediate lower oxidation state before being reduced to metallic copper,⁵⁰–⁵² which may be formally represented as a two step process (however, evidence points to co-existence of all three oxidation states at intermediate capacities,⁵⁰ leading to elemental Cu at higher capacities):

\[
\text{CuO} + \text{Li} \rightarrow \text{Cu}_2\text{O} + 1/2\text{Li}_2\text{O} \tag{10}
\]

\[
\text{Cu}_2\text{O} + \text{Li} \rightarrow 2\text{Cu} + 1/2\text{Li}_2\text{O} \tag{11}
\]

The distinct plateaus observed in the experimental first discharge curve for CuO at ~2 V, extending to ~102 mAh g⁻¹ (0.3 mol Li per mol CuO) and ~1.4 V extending to ~400 mAh g⁻¹ (1 mol Li per mol CuO) can be attributed to the overlap of the two step reaction mechanism.⁴⁸ Débart et al.⁵⁰ have shown that these plateaus extend to higher capacities when the current rate is lowered (see Figs. 1 and 2 of Ref. 50) suggesting that the two reactions may occur sequentially in the thermodynamic limit of zero current. The computational results, which correspond to this limit, also show two plateaus extending to capacities corresponding, respectively, to 1 mol Li and 2 mol Li per mol of CuO, which is consistent with this interpretation.

In the computed first discharge curve for lithiation of crystalline CuO, shown in Fig. 3, the first plateau at 2.1 V fades at a specific capacity of 336.9 mAh g⁻¹, where the ratio of Li:Cu is 1:1. The second plateau at ~1.7 V fades at 673.9 mAh g⁻¹, where the ratio of Li:Cu is 2:1. Once again, the maximum experimental capacity exceeds the 2:1 stoichiometric limit (673.9 mAh g⁻¹), reaching 1247.1 mAh g⁻¹. In contrast to transition metals, the main group metal Sn reacts reversibly with Li to form alloys. Lithiation of SnO leads to the formation of Li₂Sn up to an Li:Sn ratio of 2:1, similar to the transition-metal oxides. This is followed by formation of various Li-Sn alloys, culminating in Li₂Sn₃, the stable alloy with the highest lithium content corresponding to an Li:Sn ratio of 4:1.⁵³,⁵⁴ The lithium capacity corresponding to the conversion limit of a 2:1 Li:Sn ratio in SnO is 398 mAh g⁻¹. The cumulative capacity at the 4:1 alloying limit (6.4:1 ratio of Li:Sn) is 1273 mAh g⁻¹. The experimentally recorded maximum capacity is 1372.5 mAh g⁻¹, which exceeds both of these limits. The excess capacity in this case has been attributed to the formation of Li₂O.⁴⁹

Computational studies allow the structural evolution of the electrode materials in response to increasing lithium content to be examined in detail, which provides useful information on the molecular mechanism of lithium storage. To this end, the following structural analyses of lithiated metal oxides are carried out: (a) quantity and distribution of “free” volume (see below), (b) number of nearest neighbors, (c) radius of gyration, and (d) lithium environment analysis. The rationale behind each of these diagnostic methods are explained below, along with the results obtained.

**Free volume analysis.**—We define “free volume” as the volume within the working cells that are available for additional lithium accommodation. In our experience,²⁰ the most energetically favorable locations for the incoming lithium are the “most open” spaces within the electrode material. Repeated trials with various structures have confirmed this hypothesis. In order to determine the magnitude and distribution of free volume beyond the conversion limit, energy optimized structures of lithiated metal islands in Li₂O matrix were subjected to this analysis. A detailed description of this method is provided in our previous work.²⁰ Briefly, the procedure consists of placing virtual spheres that are 1 Å in diameter in the working cell one at a time. For each sphere placement, up to 100,000 random positions were selected in the working cell, and if the virtual sphere at one of those locations did not overlap with an atom or a previously placed sphere, then that position was chosen for a sphere placement. The criterion for determining the overlap of the sphere with an atom is based on the sphere radius of 0.5 Å and the van der Waals radii of the respective atoms.⁵⁵ This process was repeated until no positions could be found for the placement of an additional sphere without overlaps. The number of virtual spheres accommodated by a working cell, \(N_{\text{spheres}}\), provides a measure of the amount of “free” volume available. The environment of the spheres was then characterized based on the number and types of atoms surrounding each sphere. If three or more neighbors were of type M, the environment was considered “bulk metal”, while if two or more neighbors of oxygen were present, it was labeled to be in the “oxide” phase. The remaining spheres were classified as being at the “interface”.

The results of free volume analysis are shown in Fig. 5. The availability of free volume in the “oxide” region remains roughly constant in all cases, indicating that once the Li₂O has been formed, it does not accommodate additional Li atoms. For the bulk metal, the free volume increases for MnO, CoO, and NiO with higher lithium content, but plateaus near \(x = 5\). In contrast, the free volume in bulk metal for CuO and SnO increases as a function of lithiation throughout the entire range studied. The free volume available in the interface region is found to be highest for MnO, while lowest for CuO and SnO, the metals with more electrons. In general, it appears that for transition metal oxides, the more electrons there are in the valence shell, the more free volume is created in the bulk metal phase, and less at the interface. The behavior of SnO is fundamentally different from the transition metals and will be discussed below.

**Number of nearest neighbors.**—An analysis was carried out to calculate the average number of nearest neighbors surrounding each atom in the working cell. The number of nearest neighbors was determined from the radial distribution function between different atoms. If the distance between two atoms was within the first peak of the radial distribution function, they were considered to be nearest neighbors.²⁰
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Figure 5. Comparison of free volume (as represented by $N_{\text{sphere}}$) available at the bulk metal (left), interface (middle), and oxide (right) regions of different metal oxides with increase in lithium content.

Figure 6. The number of nearest neighbors for M-M (left), and the number of lithium atoms surrounding M (right) as a function of lithiation.

This was carried out for the atom pairs: M-M, M-O, M-Li, and O-Li for the lithiated island structures as presented in Fig. 6.

The number of M-M nearest neighbors is nearly constant for transition metal oxides, with Mn-Mn having the highest value (~5 atoms), suggesting that the Mn island, once formed, remains tightly bound and unperturbed by additional lithiation. The variation in nearest neighbors of Mn-Li is also negligible. Thus the added lithium atoms do not occupy the space near Mn atoms, which is consistent with the free volume analysis for MnO, showing that it has the least free volume in bulk metal (Fig. 5). For NiO and CoO, the number of Ni-Ni and Co-Co nearest neighbors are slightly lower (~4 atoms) than that for Mn-Mn. Furthermore, Ni and Co show a modest increase in the number of lithium nearest neighbors with lithiation. This implies that lithium-metal bonding is prevalent in these materials, and that it disrupts metal-metal bonding to a modest degree. The behavior of CuO in Fig. 6 is rather different from the other transition metal oxides, and from SnO. Inspection of the lithiated CuO structures in Fig. 3 suggests that the copper metal forms linear or branched chains at higher lithium content. This observation is supported by Fig. 6a where we note that CuO has the smallest number (~2–3 atoms) of Cu-Cu nearest neighbors among the transition metal oxides, as would be expected in the case of linear or branched chains of Cu atoms. Compared to the other transition metals, Cu also has a higher number of Li neighbors (Fig. 6b), indicating that the Li are stored in regions close to the metal chains. The formation of chains is further confirmed by the higher “bulk metal” and lower interfacial free volume for CuO (Figs. 5a, 5b) which can be understood as an artifact of the classification algorithm. As explained above, a virtual sphere with three or more Cu nearest neighbors is classified as “bulk” metal while spheres that do not belong to “bulk” or “oxide” phases are assigned as belonging to the interfacial region.

In contrast to the transition metal oxides, SnO shows a steady decrease in the number of Sn-Sn neighbors as lithiation progresses beyond the conversion limit of 2:1, while the number of Sn-Li neighbors increase. These trends are consistent with the formation of Sn-Li alloys.

Radius of gyration.—The radius of gyration, $R_g$, of the metal species is a useful diagnostic to evaluate the structural compactness of metal islands. In keeping with the convention used in the analysis of polymers, we define

$$R_g = \frac{1}{N_M} \sum_{i=1}^{N_M} (r_i - r_{\text{com}})^2$$

where $N_M$ is the number of metal atoms of a given species in the working cell, and $r$ is the position of a particular metal atom with respect to the center of mass, $r_{\text{com}}$, of that metal species. The $R_g$ values calculated for this work as a function of lithiation are shown in Fig. 7.

Figure 7. Analysis of radius of gyration of metal islands as a function of lithium content.
The radius of gyration of transition metal islands does not show large variations as a function of lithiation. This indicates that their structures are not significantly impacted by variation in lithium content. On the other hand, the Sn metal becomes widely dispersed at high lithium content, which is to be expected, and consistent with large volume expansion, in the case of alloy formation. CuO is often to fall in between these extremes. However, visual inspection of lithiated Cu structures in Fig. 3, along with the nearest neighbor data shown in Fig. 6a, shows that rather than getting dispersed, the Cu atoms form connected chains at high lithium content. This contributes to the larger $R_g$ at low lithium content, but without the alloy formation that occurs in SnO. As a consequence, the larger free volume available in the region identified as ‘bulk metal’ for Cu, as shown in Fig. 5, can be attributed to the storage of Li along Cu atomic chains.

**Local environment analysis.**—We analyzed the lithium environment from the island structures, which was classified in a similar fashion as the free volume analysis described in section (a). If a lithium atom was near three metal atoms, it was classified as “bulk metal,” two or more oxygen atoms, “oxide,” and the remaining was considered to be “interface” using the criteria described in previous work. The number of lithium atoms in each type of environment was determined as a function of lithium content, and is given in Fig. 8.

The variation in number of lithium atoms in the oxide region remains fairly constant with increase in lithium content in all metal oxides considered. The number of lithium atoms in the bulk Mn region increases slightly at low lithiation levels, and remains constant at higher amounts. At the same time, the number of lithium atoms in the interfacial region steadily increases throughout the entire lithiation range, indicating that the added lithium atoms are at the interface. This is consistent with the observation in Fig. 5 that MnO has the highest availability of interfacial free volume among the transition metal oxides considered. NiO and CoO follow similar trends, although the lithium content in the bulk metal region is higher, and the number of Li atoms in the interfacial region is lower than that of MnO. CuO has the highest number of lithium atoms in the bulk metal region among the transition metal oxides. This can be understood in the light of the earlier discussion of the classification of free volume in CuO due to formation of chains and the storage of lithium atoms along the chains of Cu atoms. Note that the formation of Cu chains is further supported by the high radius of gyration of Cu atoms (Fig. 7) compared to the other transition metal oxides. These chains percolate through the electrode material and help maintain electrical contact during charge-discharge cycles. They may contribute to the high capacity retention recorded in experimental studies on pure CuO.32-34

In contrast to transition metal oxides, the radius of gyration of Sn begins with a higher value and further increases with the addition of Li atoms. A decrease in the number of Sn-Sn nearest neighbors, and increase in Sn-Li nearest neighbors are observed (Fig. 6). This implies that Sn atoms move apart on lithiation and the added lithium atoms occupy the region within the metal atoms resulting in the formation of Sn-Li alloys. Therefore, the availability of free volume for lithium storage in the bulk metal region is found to be highest of all the metal oxides considered. Consistent with this, the local environmental analysis confirms that lithium atoms are more likely to be present in the bulk metal region in SnO. The lithium content in the interfacial region remains negligible until the cumulative conversion and alloying limit of $x = 6.4$ is exceeded, corresponding to a capacity of 1273 mAh g$^{-1}$. At this point, as shown in Fig. 8b, the interfacial region between the alloy and the lithium oxide phases begins to accommodate the newly added lithium. This suggests that, even in alloying materials, interfacial storage could be responsible for at least some of the observed capacity beyond the stoichiometric limit of conversion and alloying. Experimentally, capacities as high as 1372.5 mAh g$^{-1}$ have been reported for SnO.45

**Conclusions**

The molecular mechanisms for storage of lithium were studied through first principles DFT computations for the transition metal oxide conversion anode materials MnO, CoO, NiO, CuO and the main group conversion/alloying material SnO. First discharge curves were obtained based on calculations for lithiation of supercell and island structures. The trends observed in the computed first discharge curves were found to be qualitatively similar to those reported by experiments, and showed the super-stoichiometric capacities of these materials. Structural analyses of lithiated structures revealed that the “extra” capacities can at least partially be attributed to the interfacial storage of lithium in both conversion and alloying metal oxides.

One of the main discoveries from structural analyses was the complex behavior of the interfaces between the various solid phases created within the electrode material during lithiation. In purely conversion materials, such as the transition metal oxides studied, the interfaces between the metal islands and lithium oxide are of interest. In the case of alloying materials such as SnO, the relevant interface is between the alloy and the lithium oxide. In each case, the interface was found to evolve with lithiation and give rise to “free volume” that accommodated additional lithium once the conversion/alloying limits were reached.

The closely packed Mn atoms facilitate large interfacial storage of lithium, while it is comparatively less in the case of Ni, and Co, since they are not as tightly bound. Cu atoms tend to form chains as opposed to formation of clusters, which reduces the interfacial free volume. Furthermore, these chains allow the metal atoms to percolate the material further, potentially allowing a pathway to maintain conductivity through more cycles than the other transition metal oxides. The formation of Li-Sn alloys results in high lithium storage capacities, although interfacial storage is negligible. Storage of lithium at the metal-Li$_2$O interface is found to influence the maximum lithium storage capacities; the amount of interfacial free volume found in different metal oxides depends on the nature of metal, and its reactivity with lithium. This study helps in assessment of suitability of metal oxides as potential LiB anodes by studying their interactions with lithium at the atomic level.

The “superstoichiometric” capacity in metal oxide anode materials has often been attributed to the formation of an SEI-like polymeric layer.56 While there is evidence that such layers may contribute to the overall capacity, detailed experiments on RuO$_2$ has clearly established the presence of elemental lithium within the electrode material at the
highest capacities.\textsuperscript{17} The computational discharge curves presented here and the associated structural analysis also point to the storage of lithium in the interfaces between the metal (or alloy, in the case of SnO) and oxide phases. These results, as well as analyses presented in previous work from our group,\textsuperscript{20,21} suggest that the electrode material itself contributes to the observed capacity beyond the conversion and alloying limits.

The computations presented here show that first principles computations can provide useful insights into the molecular mechanisms operational in a wide range of electrode materials, provided that one accounts for the differences between the non-equilibrium, finite time, conditions under which experimental results are recorded and the infinite time thermodynamic limit represented by the calculations. When computational and experimental discharge curves qualitatively agree, analysis of the computed structures also provides mechanistic insights which may be difficult to obtain through experiments alone.

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