1. INTRODUCTION

Manganese-based oxides have long been studied as cathode materials for lithium batteries,\textsuperscript{2,3} with advantages of low cost and nontoxicity over cobalt-based compounds such as LiCoO\textsubscript{2}. Recently, Li-rich oxide compounds of Li\textsubscript{x}Mn\textsubscript{1-x}O\textsubscript{2}, alternatively written as Li\textsuperscript{1-x}M\textsubscript{1/3}O\textsubscript{2} (M = Ni, Mn, Co), with layered rock-salt structures have attracted considerable interest because they can deliver high reversible capacities in excess of 250 mAh/g\textsuperscript{4} due to the oxygen redox mechanism of Li\textsuperscript{+} ions exchanging with protons that are electrochemically inactive because Mn\textsuperscript{4+} ions are not expected to be oxidized further. However, it is now well established that Li can be electrochemically extracted and reinserted.\textsuperscript{11−17}

A common feature of Li-rich layered oxide cathodes is an irreversible high voltage plateau at around 4.5 V vs Li/Li\textsuperscript{+} during the first charge, even after the cation redox limit has been reached. This large extra capacity cannot be accounted for by transition metal oxidation. To explain the electrochemical activity beyond the transition metal redox limit in a Li-rich manganese oxide, Dahn et al.\textsuperscript{8} proposed oxygen loss from the crystal lattice as the charge compensation mechanism. Oxygen gas evolution during the first charge.\textsuperscript{9,10,12} However, direct extraction of oxygen ions from the bulk is unlikely due to prohibitively high oxide ion migration barrier energies (>1.5 eV).\textsuperscript{20,21} An alternative mechanism of Li ions exchanging with protons that are introduced by electrolyte decomposition has been proposed.\textsuperscript{11} Nevertheless, a recent solid-state nuclear magnetic resonance (NMR) study confirmed reversible Li extraction and insertion into the structure without proton exchange.\textsuperscript{16}

More recently, there has been significant debate regarding the oxygen redox chemistry of layered Li-rich oxides.\textsuperscript{7,13−14} Tarascon et al.\textsuperscript{39,43,44} attributed the extra storage capacity in 4d and 5d transition metal oxides (e.g., Li\textsubscript{x}Ru\textsubscript{1−x}Sn\textsubscript{3}O\textsubscript{10}) to the oxidation of O\textsuperscript{2−} to peroxide-like species (O\textsubscript{2})\textsuperscript{2−} and indicated the importance of metal-anion covalency in the oxygen redox process.\textsuperscript{45}

Li\textsubscript{2}MnO\textsubscript{3} is the end member of the Li-rich layered oxides\textsuperscript{11−13} which exhibits the characteristic first-charge plateau at 4.5 V. This material was originally considered to be electrochemically inactive because Mn\textsuperscript{4+} ions are not expected to be oxidized further. However, it is now well established that Li can be electrochemically extracted and reinserted.\textsuperscript{11−17} A first-charge capacity as large as 452 mAh/g has been reported, corresponding to 98% of lithium extraction from its structure.\textsuperscript{18} Both the electrochemical behavior and structure characterization of cycled Li\textsubscript{2}MnO\textsubscript{3} indicate the transformation from a layered to a spinel structure,\textsuperscript{7,11−15} a process involving Mn cation migration.

As with all Li-rich layered oxides, the origin of the electrochemical activity of Li\textsubscript{2}MnO\textsubscript{3} at 4.5 V is not fully understood. Oxygen gas evolution has been observed accompanying lithium extraction from Li\textsubscript{2}MnO\textsubscript{3} during the first charge.\textsuperscript{9,10,12} However, direct extraction of oxygen ions from the bulk is unlikely due to prohibitively high oxide ion migration barrier energies (>1.5 eV).\textsuperscript{20,21} An alternative mechanism of Li ions exchanging with protons that are introduced by electrolyte decomposition has been proposed.\textsuperscript{11} Nevertheless, a recent solid-state nuclear magnetic resonance (NMR) study confirmed reversible Li extraction and insertion into the structure without proton exchange.\textsuperscript{16}

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Bruce and co-workers\textsuperscript{7} investigated Li_{12}\left[\text{Ni}_{13}\text{Co}_{13}\text{Mn}_{0.54}\right]\text{O}_2 and confirmed that oxygen is lost from the lattice at 4.5 V; they also report that Li removal is charge compensated by localized holes on the oxygen atoms coordinated by Mn\textsuperscript{4+} and Li\textsuperscript{+}. Ceder and co-workers\textsuperscript{45} have examined layered and cation-disordered Li-excess oxides and proposed how specific local Li-excess environments lead to labile oxygen electrons that participate in the practical capacity; they also stress that covalency does not lead to a higher capacity than would be expected from the transition metal alone. Goodenough and co-workers\textsuperscript{46} indicate that on oxidation, holes are introduced into the O 2p bands of a layered manganese [IV] oxide; they also show that these oxygen holes are not cycled reversibly and might become trapped in peroxide ions.

It is apparent that the precise mechanism of Li-ion extraction from Li-rich Li_{2}MnO_{3} is not clearly established, especially in relation to the experimentally observed evolution of O\textsubscript{2} and structural transformation. In this work, delithiation reaction enthalpies and kinetic processes in Li_{2}MnO_{3} are studied using hybrid-density functional theory techniques. We show that Li extraction is accompanied by oxygen oxidation but that the oxygen hole (O\textsuperscript{2−}) species are not stable, leading to oxygen dimerization (with O–O ~ 1.3 Å) and eventually O\textsubscript{2} formation. The results suggest that reversible oxygen redox without major structural change is only possible if the O\textsuperscript{2−} hole can be stabilized and oxygen dimerization suppressed.

2. METHODS
All calculations were performed within the framework of density functional theory (DFT) using the Vienna ab initio simulation package (VASP).\textsuperscript{47} In order to obtain accurate chemical reaction energies, electron exchange and correlation were described using the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional.\textsuperscript{48} The HSE06 functional has been shown to reproduce formation enthalpies of metal oxides and yields Li intercalation potentials consistent with experimental values.\textsuperscript{49,50} The HSE06 functional also yields a O\textsubscript{2} dimer binding energy of ~5.16 eV, in excellent agreement with the experimental value, and gives a good description of electronic properties such as band gaps and oxygen hole states,\textsuperscript{51–53} which are essential for describing the oxygen redox chemistry in this study. Future work could also include explicit dispersion terms for interlayer interactions.\textsuperscript{54}

Valence electrons were described using a planewave basis set with a cutoff energy of 450 eV. The interactions between valence and core electrons were treated using the projector augmented-wave (PAW) method.\textsuperscript{55} The k-space was sampled with a k-point mesh with spacings smaller than 0.05 Å\textsuperscript{−1}. Spin-polarization effects were included, and ferromagnetic coupling between magnetic manganese cations was assumed.

Surface lithium extraction was modeled using a 9-layer Li_{2}MnO_{3} monolonic (011) surface slab model, which is equivalent to the rock-salt (001) surface. Each layer was composed of stoichiometric Li_{2}MnO_{3}, making this a type I nonpolar surface,\textsuperscript{56} and has been calculated to be the most stable surface of layered metal oxides.\textsuperscript{57} The real space charge density associated with the localized hole states was also calculated (i.e., an Li atom from a layer well below the bulk was also calculated, i.e., an Li atom from a layer well below the simulated surface, referred to as Li-bulk). The voltage required for the lithium extraction was calculated using the standard approach.\textsuperscript{58,59}

The changes in the electronic structure upon extraction of a single Li atom from different crystal sites are illustrated in Figure 1. The density of states plots show that lithium extraction produces localized hole states within the bandgap of Li_{2}MnO_{3}. This is in contrast to the metallic behavior after Li removal reported in previous DFT studies.\textsuperscript{52,53} Assuming a topotactic solid-solution type of Li extraction reaction without ion migration in Li_{2}MnO_{3}, oxygen is predicted to be the main oxidized species from previous static DFT calculations.\textsuperscript{52–53} However, the first charge plateau clearly indicates a two-phase type of Li extraction reaction.

The real space charge density associated with the localized hole state created by lithium extraction in each case is also illustrated in Figure 1, from which the oxidized chemical species can be identified. The extraction of a single Li atom from the bulk requires 5.24 V and is accompanied by hole localization on an oxygen adjacent to the vacated Li site, indicating oxygen oxidation O\textsuperscript{2−} → O\textsuperscript{2−} + e\textsuperscript{−} with the formation of an oxygen hole, O\textsuperscript{2−}. Extraction of Li-surf-A is also accompanied by oxygen oxidation but requires a lower potential of 4.56 V.

The difference in oxidation potential between surface and bulk oxides can be attributed to their different electrostatic environments. It is known that the reaction O\textsuperscript{2−} + e\textsuperscript{−} → O\textsuperscript{2−} in the gaseous phase is endothermic and that the existence of O\textsuperscript{2−} anions in the solid state is due to a stabilizing electrostatic potential created by positively charged cations. Consequently,
The oxidation potential of O$_2^-$ in the solid state varies and depends strongly on its site electrostatic environment.\textsuperscript{65,66} To understand the difference in behavior between the surface and the bulk, the electrostatic potential at different oxygen sites were calculated; the results are shown in Figure 2. Owing to a reduced cation coordination number, the electrostatic potential at some surface oxygen sites is higher, i.e., the potential well for an electron is shallower than that in the bulk by more than 1 V. In other words, O$_2^-$ is less stable at the surface and consequently requires less energy to be oxidized to O$^-$.

The extraction of the Li-surf-B atom produces a slightly lower potential of 4.43 V. This is accompanied by hole localization on a 5-fold coordinate Mn atom at the surface, in which the tetravalent Mn$^{4+}$ ion has been oxidized to the pentavalent ion, Mn$^{5+}$. Such an oxidation state is unusual, although it should be noted that Mn$^{5+}$ species have been discussed in relation to other manganese oxide battery materials such as Li$_2$MnO$_4$, Li$_2$Mn(BO$_3$)$_3$, and Li$_4$Mn$_2$O$_5$.\textsuperscript{67–69} This result is supported by the reduction of its magnetic moment from 2.95 to 2.22 $\mu_B$, corresponding to a change in electronic configuration from $d^3$ (Mn$^{4+}$) to $d^2$ (Mn$^{5+}$). The MnO$_5$ unit also adopts a trigonal bipyramidal geometry with very short Mn–O bonds, as shown in Figure S3. It should be stressed that oxidation to Mn$^{5+}$ is only accessible for 5-coordinate Mn at the surface. Thus, it can only account for a small fraction of the total capacity and is not the main redox process upon Li extraction.

3.2. Overall Delithiation Reaction. The long plateau observed during the first charge of Li$_2$MnO$_3$ indicates that delithiation proceeds by a two-phase reaction.\textsuperscript{11–13} Here, we examine the redox chemistry of the overall Li extraction reaction. First, the reaction to form MnO$_3$ without oxygen loss or phase transformation is considered:

$$\text{Li}_2\text{MnO}_3 \rightarrow 2\text{Li}^+ + 2e^- + \text{MnO}_3$$

In this reaction, we find that the calculated magnetic moment on Mn cations in the product MnO$_3$ has the same value, 2.9 $\mu_B$ (Mn$^{4+}$, $d^3$), as in Li$_2$MnO$_3$, whereas the magnetic moment on two-thirds of the oxygen ions increases from zero in Li$_2$MnO$_3$ to 0.8 $\mu_B$ in MnO$_3$. This result indicates the localization of holes on oxygen with the formation of O$^-$ hole species on anion sites closest to the vacated Li sites.

As shown in Figure 3, these localized hole states have a predominately oxygen 2$p$ character, with the lobes of the $p$ orbitals pointing toward the the vacant Li site Li site in the transition metal layer. Hence, Mn ions remain in their...
tetravalent (d³) state, and lithium extraction is accompanied by oxidation of O²⁻ to O⁻. MnO₃ can therefore be formally written as (Mn⁴⁺)(O²⁻)(O⁻)₂.

If delithiation ends with MnO₃ as the final product, then Li extraction from Li₂MnO₃ should be reversible since MnO₃ retains the original layered structure. However, this is not consistent with the experimentally observed structural transformation and oxygen evolution. Moreover, the calculated voltage for this topotactic reaction is 5.07 V, noticeably higher than the experimental lithium extraction potential of 4.5 V.

The simulated delithiation behavior of Li₂MnO₃ is distinctly different from that of Li₂RuO₃ and Li₂IrO₃ that contain 4d and 5d transition metal ions. In Li₂RuO₃ and Li₂IrO₃, some O—O distances are shortened spontaneously from 2.8 Å to around 2.4 Å upon Li extraction. Although this has been attributed to the formation of O²⁻ dimer species, its exact nature and direct O—O bonding at such a large separation needs further investigation. In contrast, such shortening of the O—O separation does not develop spontaneously in Li₂MnO₃ upon Li extraction from our calculations. It will be demonstrated below that the O—O bond formation in delithiated Li₂MnO₃ is predominantly a kinetic process that requires overcoming an energy barrier.

Next, the lithium extraction reaction accompanied by oxygen loss was considered:

\[ \text{Li}_2\text{MnO}_3 \rightarrow 2\text{Li}^+ + 2\text{e}^- + \text{MnO}_2 + \text{O}_2 \]  (2)

Here, MnO₂ is assumed to have the λ-MnO₂ spinel structure since this has the same cubic close-packed oxygen sublattice as Li₃MnO₃. In addition, structure characterization and electrochemical measurements suggest transformation from layered Li₃MnO₃ to a spinel-like structure upon cycling.¹¹,¹³

The calculated voltage for reaction 2 is 3.79 V, significantly lower than reaction 1 without oxygen loss. Therefore, reaction 2 is thermodynamically more favorable and consistent with the experimentally observed structural transformation and oxygen evolution.¹¹⁻¹⁴ Since O₂ is the reaction product, direct O—O bonding or oxygen dimer formation must be involved during the reaction. Reaction 2 can be viewed as reaction 1 followed by the decomposition of MnO₃ according to

\[ \text{MnO}_3 \rightarrow \text{MnO}_2 + \frac{1}{2}\text{O}_2 \]  (3)

which can also be written as

\[ (\text{Mn}^{4+})(\text{O}^2^-)(\text{O}^-)_2 \rightarrow (\text{Mn}^{4+})(\text{O}^2^-)_2 + \frac{1}{2}\text{O}_2 \]  (4)

This reaction is found to have a favorable enthalpy of −2.66 eV, a result that again implies that MnO₃ is not the final product of the delithiation process but instead decomposes to MnO₂ and O₂.

We note that the calculated equilibrium voltage for reaction 2 is slightly lower than experimental values. This difference is most likely due to the neglect of an overpotential associated with sluggish chemical reactions with poor kinetics. In any case, our results are consistent with recent studies, which indicate that oxygen redox is often observed in compounds that contain high proportions of Mn⁴⁺ and Li⁺ cations and that there is a balance between O²⁻ redox and oxygen loss.

3.3. Oxygen Dimer Formation and Manganese Migration. Li extraction from Li₃MnO₃ has been demonstrated above to be accompanied by the oxidation of O²⁻ to O⁻, leading to the reaction intermediate MnO₃ or (Mn⁴⁺)(O²⁻)(O⁻)₂. The O⁻ hole species is known to be unstable in the solid state. Direct detection of O⁻ species in metal oxides by EPR has only been reported at liquid-helium temperatures after irradiation. Recent theoretical studies have shown the instability of oxygen holes, O⁻, against the formation of the...
perroxide anion, O$_2^{2-}$, in metal oxides, that is, the reaction O$^-$ + O$^-$ → O$_2^{2-}$, has a negative formation enthalpy. Here, we show that the same oxygen dimer formation also occurs in MnO$_x$, which initially contains O$^-$ hole species. The formation of an oxygen dimer can then trigger migration of Mn atoms from the transition metal layer to the emptied Li layer.

Two reaction pathways were considered, involving initial O−O configurations along the c axis and in the ab plane, as shown in Figure 4. The reaction enthalpies and activation energies for each reaction step are illustrated in Figure 5. The simulations included full relaxation of all ions in the structure.

![Figure 5](https://example.com/figure5)

Figure 5. Energy profiles of the reaction pathways A and B shown in Figure 4. The dashed lines indicate energy barriers for the kinetic steps from configurations i to iv. As a reference point, the initial energy is set to 0 eV.

In reaction pathway A, two adjacent O$^-$ hole species in MnO$_3$, are separated by 2.5 Å across the transition metal layer in the initial configuration. They undergo dimerization and form a nonmagnetic oxygen dimer with an O−O bond length of 1.49 Å, corresponding to a perroxide anion O$_2^{2-}$. Further support for direct O−O bonding is given by the appearance of bonding and antibonding states in the DOS plots [Figure S4], which are consistent with the molecular orbital diagram of an O$_2$ molecule.

The reaction enthalpy for this oxygen dimerization process is favorable (−0.37 eV), suggesting that the oxygen dimerization is a thermodynamically driven process. The energy gain is a consequence of direct O−O bonding. Regarding kinetic barriers, the activation energy for the O−O bond formation is calculated to be 0.6 eV. This indicates that despite being lower in energy, the oxygen dimer in delithiated Li$_x$MnO$_3$ would not form spontaneously upon structure optimization in static DFT calculations at 0 K, this is because temperature effects are not included and may have been overlooked in previous DFT studies.

The formation of the oxygen dimer O$_2^{2-}$ is followed by the migration of an Mn ion as shown in Figure 4a. The Mn ion initially located on the octahedral site moves to the tetrahedral site above its initial position. Other studies including high resolution electron microscopy work have reported local cation migration from the transition metal layer into the Li layer of Li$_x$MnO$_3$ and related Li-rich oxides.

The O−O bond length of the oxygen dimer further shortens to 1.30 Å, indicating oxidation from a perroxide O$_2^{2-}$ to superoxide O$_2^{-}$ species. This is also reflected in the difference in electronic states between O$_2^{2-}$ and O$_2^{-}$ as shown in Figure S4. Oxidation from perroxide to superoxide requires one extra hole, which is obtained from the reduction of an O$^-$ species back to O$^{2-}$ elsewhere in the crystal.

The final step in reaction pathway A (from configuration iii to iv in Figure 4a) is the migration of the Mn ion on the tetrahedral site to an octahedral site that was originally occupied by Li before delithiation. The oxygen dimer remains a superoxide O$_2^{-}$ species, and the reaction enthalpy for this step is negative (−0.91 eV). Hence, the overall energy gain for reaction pathway A is 1.32 eV, again suggesting a thermodynamically driven process.

It should be stressed that without oxygen dimer formation, Mn ion migration would not have occurred because the total energy becomes higher (destabilizing the structure) along the same migration path. In other words, Mn ion migration is triggered by oxygen dimer formation.

Figure 4b shows reaction pathway B, which involves the dimerization of two O$^-$ species in MnO$_3$ that are initially separated by 2.75 Å within the ab plane. On the basis of the O−O bond length of 1.30 Å and the electronic structure, the oxygen dimer in configuration ii is identified as a superoxide O$_2^{-}$ species. Similar to reaction pathway A, the oxygen dimer formation is followed by the migration of an Mn cation from the transition metal layer to a tetrahedral site above its initial site. As the Mn migrates away from the superoxide species, it is further oxidized to a neutral oxygen dimer O$_2$ with an O−O bond length of 1.21 Å, consistent with the experimental O$_2$ bond length. In the final step, the tetrahedral Mn then migrates to an octahedral site in the vacant Li layer. All reaction steps in reaction pathway B are exothermic, and the overall energy gain is 2.64 eV.

Comparing the dimerization process in reaction pathways A and B, it appears that the oxygen dimer becomes more oxidized when coordinated by a smaller number of Mn cations. As the neutral O$_2$ molecule is a more stable species than perroxide O$_2^{2-}$ and superoxide O$_2^{-}$, owing to its less occupied antibonding σ* orbital, the neutral O$_2$ molecule should be the final oxidation product. This is consistent with our calculated reaction enthalpies, showing that a configuration with a more oxidized oxygen dimer species is more thermodynamically stable.

The calculated activation energies for oxygen dimer formation and Mn migration are not prohibitively high. Furthermore, these activation energies would decrease at the surface where the coordination number is lower or after subsequent oxygen dimers have formed. If this were not the case, oxygen evolution and structural transformation resulting from Mn migration would not be observed experimentally. Nonetheless, these kinetic steps with energy barriers help to rationalize the slow rate capability during the first charge, as well as the strong temperature dependence of the first charge capacity.

Progression of cooperative oxygen dimer formation and Mn migration will eventually lead to the final delithiation products MnO$_2$ and O$_2$. The remaining question is whether the presence of other 3d transition metal cations, such as Ni and Co or cation disordering can stabilize the oxygen holes and give rise to reversible oxygen redox behavior. This issue as well as complex calculations on the effect of the electrolyte at electrode surfaces are topics for future investigation.

4. CONCLUSIONS

Li$_x$MnO$_3$ is the end member of the Li-rich layered system $\alpha$Li$_x$MnO$_3$·(1−$\alpha$)LiMO$_2$, and its redox chemistry on Li extraction has been investigated using DFT simulations. High
level hybrid functionals were used in this work as they reproduce accurately the electronic structure of oxygen hole states. The following key points emerge: (a) Li extraction from Li$_2$MnO$_3$ is charge compensated by oxidation of the oxide anion, so that the overall delithiation reaction involves the evolution of O$_2$ (or lattice oxygen loss) as given by eq 2. (b) Localized holes on oxygen (O$^-$) are formed as the first step of oxidizing O$^{-2}$, but the hole species are not thermodynamically stable against dimerization to peroxide O$_2$$^{2-}$ or superoxide O$_2^-$.

The kinetic barrier for oxygen dimerization is relatively low, suggesting that oxygen holes (O$^-$) would not survive the time scale of a typical electrochemical reaction at room temperature. Once the oxygen dimer is formed, molecular O$_2$ is eventually released as a product of delithiation. (c) Oxygen dimerization facilitates Mn migration to the octahedral site in the vacant Li layer which leads to a spinel-like structure. (d) Overall, our results suggest that in order to utilize the oxide ion as a reversible redox center in topotactic electrochemical reactions, it is necessary to stabilize the O$^-$ hole species and prevent oxygen dimerization that can trigger transition metal cation migration and structural transformation. Future work should include improved characterization studies of oxygen hole and peroxide/superoxide species and of gaseous O$_2$ evolution.

Given the importance of high capacity oxide electrodes, the results presented here provide a greater understanding of lithium extraction and oxygen redox reactions that will help guide the optimization of new Li-rich materials for rechargeable lithium batteries.

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**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmate...6b02870.

Density of states for Li$_2$MnO$_3$; different Li sites on the topmost surface layer of Li$_2$MnO$_3$; local geometry around the surface Mn$^{2+}$ species; and local density of states for different dimer species (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(3) Manthiram, A.; Chemeweleski, K.; Lee, E.-S. A perspective on the high-voltage LiMn$_{0.5}$Ni$_{0.5}$O$_2$ spinel cathode for lithium-ion batteries. Energy Environ. Sci. 2014, 7, 1339–1350.
(5) Kim, J.; Johnson, C. S.; Vaughtey, J. T.; Thackeray, M. M.; Hackney, S. A.; Yoon, W.; Grey, C. P. Electrochemical and Structural Properties of xLi$_2$M$_{0.5}$Mn$_{0.5}$O$_2$ (1−x)LiMnO$_2$ Electrodes for Lithium Batteries (M $\neq$ Ti, Mn, Zr; 0 $\leq$ x $\leq$ 0.3). Chem. Mater. 2004, 16, 1996–2006.


