Computational Framework for a Systematic Investigation of Anionic Redox Process in Li-rich Compounds

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Abstract

Anionic redox processes play a key role in determining the accessible capacity and cycle life of Li-rich cathode materials for batteries. We present a framework for investigating the anionic redox processes based on data readily available from standard DFT calculations. Our recipe includes a method of classifying different anionic species, counting the number of species present in the structure and a preconditioning scheme to promote anionic redox. The method is applied to a set of Li$_x$MnO$_3$ ($1 \leq x \leq 2$) structures to identify the evolution of anionic redox processes during cycling. Additionally, we investigate how different choices of exchange-correlation functionals affect the formation of anionic redox species. The preconditioning of the structures is shown to promote the formation of peroxo-like species. Furthermore, the choice of exchange-correlation functional has a large impact on the type of anionic redox species present, and thus care must be taken when considering localization in anionic species.

Introduction

Anionic redox processes are currently an intensely studied topic in battery research as it allows a significant increase in the accessible energy capacity in Li-rich cathodes in lithium-ion batteries. Li$_2$MnO$_3$ is one of the Li-rich cathode materials where the anionic redox is known to make a dominant contribution to its high theoretical capacity of around 460 mAh g$^{-1}$. Li$_2$MnO$_3$ has a layered rocksalt-type structure, and was initially thought to be chemically inert as Mn$^{4+}$ in octahedral oxygen coordination cannot be oxidized to Mn$^{5+}$. However, it was found through electrochemical measurements that cycling was indeed possible. Many possible explanations for the cyclability were suggested, and anionic redox is regarded as one of the main contributors. Li$_2$MnO$_3$ suffers from a fast capacity fading, particularly in the initial cycling step. Its fast capacity fading is also attributed to the anionic redox process which leads to an irreversible and potentially dangerous evolution of oxygen gas.

It is desirable to promote reversible anionic redox processes while suppressing the irre-
versible ones, thereby achieving the maximum energy capacity without suffering from a poor cyclability. Optimizing the reversibility requires an in-depth understanding of the anionic redox processes, such as the correlation between the local environment of the oxygen species to its redox activity. A detailed understanding of the correlation can ultimately guide the design process of the new battery electrode materials and set desired operating conditions (e.g., operating temperature and voltage range) for the longevity of the batteries.

Computational methods such as density functional theory (DFT) allow one to probe the local processes on the atomic level, which are difficult to achieve using experimental techniques. In particular, DFT simulations allow one to carry out “controlled experiments” where specific atomic arrangements are imposed, and the corresponding electronic structures in the vicinity of individual atoms are analyzed. In the context of electronic structures, anionic redox is the presence of electron holes on the oxygen species which leads to the change in its oxidation state.

Despite such detailed control, standard recipes and workflows for systematic investigations of anionic redox reactions in theoretical calculations are still lacking. Large scale studies involving many calculations are becoming more popular, and these standard recipes/workflows are needed to carry out such studies efficiently. In computational research for battery electrode materials, the most prominent examples are (1) screening of materials for materials discovery using automated workflows and (2) analysis of disordered materials using cluster expansion method.

Two key aspects need to be carefully considered when studying anionic redox using DFT: a systematic method for classifying the type of anionic species and the choice of exchange-correlation functional. Anionic redox can manifest in several types of species, as a single oxygen ion, $O^-$, as short-bond oxygen pairs or as delocalized states in the O-2p bands. Short-bond oxygen pairs can emerge as peroxide, superoxide and molecular oxygen, which we label collectively as peroxo-like species. The fully lithiated structure of Li$_2$MnO$_4$ is shown in Fig. (a), and a partially delithiated structure containing peroxo-like species is
shown in Fig. 1(b). We propose an algorithm for determining the types of anionic species present in the structures based on data readily accessible from standard DFT calculations.

Figure 1: Structure of rocksalt Li$_x$MnO$_3$. (a) Fully lithiated Li$_2$MnO$_3$. (b) Partially lithiated Li$_{1.22}$MnO$_3$ containing both superoxide and peroxide, highlighted by a dashed black circle. The bond with 1.32 Å is identified as superoxide, and the bond with 1.42 Å as a peroxide. The sum of local magnetic moments on the superoxide and peroxide were 0.83 $\mu_B$ and 0.11 $\mu_B$, respectively.

The choice of exchange-correlation functional plays an important role as the self-interaction error in DFT makes the localization of electron holes challenging. Recent anionic redox reaction studies$^{9,11,26}$ have employed the Heyd-Scuseria-Ernzerhof (HSE06)$^{27}$ hybrid functional to avoid introducing a bias between the cationic and anionic redox reactions. Although the HSE06 functional allows one to describe the localized states,$^9$ it is accompanied by a high computational cost, which makes it unsuitable for larger-scale studies. Furthermore, HSE is a highly tunable functional with a parameter $\alpha$, and it has been shown that tuning $\alpha$ leads to different results that do not consistently outperform the alternatives with lower computational costs.$^{28-30}$

A common approach when studying transition metal (TM) oxides is to use the generalized gradient approximation (GGA) functionals such as the Perdew-Burke-Ernzerhof (PBE)$^{31}$ functional and apply a Hubbard $U$ correction on the TM-$d$ orbitals. However, this approach is problematic for systems where both cationic and anionic localization may occur since the former will be favored over the latter. One could also apply the $+U$ correction on the O-$p$ orbitals which introduces an additional parameter to balance.$^{32}$ The strongly constrained and appropriately normed (SCAN)$^{33}$ functional from the meta-GGA family is a less expensive alternative compared to the hybrid functionals. It has recently been gaining
popularity as this non-empirical and parameter-free functional has been shown to provide an improved description of the band gaps and localized states compared to those of the GGA functionals.\textsuperscript{34–36} In this work, we compare the evolution of anionic redox processes during delithiation for the PBE+U approach to the SCAN functional as these are the two most viable candidates for large volumes of calculations.

Another crucial issue is that the structural optimization algorithm may be “trapped” in a local energy minimum configuration. The formation of short distance oxygen bonds is often accompanied by a transition barrier\textsuperscript{9}, preventing the classical relaxation schemes from locating such states. Here, we propose a preconditioning scheme based on the Ewald summation\textsuperscript{37} energies in order to promote the formation of localized anionic redox and to investigate the stability of peroxo-like species in the lattice.

Chen and co-workers\textsuperscript{38} applied a cluster expansion method to Li\textsubscript{2}MnO\textsubscript{3} in order to determine the most stable structure during cycling and to reproduce information such as charge/discharge voltage curves. Cluster expansion approaches may require a large number of DFT calculations, and they assumed the structure remained layered which reduces the considered configuration space. While Li\textsubscript{2}MnO\textsubscript{3} is known to be a layered structure at full lithiation, it is also known to undergo phase transitions\textsuperscript{7,10,39,40} and similar Li-rich structures are known to become disordered during delithiation.\textsuperscript{41} In this work, we lift the constraint where the material remains layered and consider the structures in the rocksalt lattice where the Mn and Li species share the cationic sublattice; the evolution of anionic redox processes is analyzed on cation-disordered structures, which lays the ground for future cluster expansion studies.

Results

A set of 101 structures, with varying degree of substitutional disorder and lithiation levels, are generated for this study. The unaltered initial configurations where all of the atoms are
placed at the ideal lattice sites are denoted as “pristine” structures. An Ewald preconditioning has been applied to all of the configurations to promote the electronic localization which has led to an additional 85 initial structures that are denoted as “Ewald” structures. Ewald structures are constructed by promoting the creation of peroxo-like species around those crystal sites where the Coulombic potential is the lowest. A detailed information on the generation of the initial structures and Ewald preconditioning can be found in the Methods section. Both pristine and Ewald structures are calculated while the atomic positions and the cell geometry are optimized.

Furthermore, three functionals were applied to the entire dataset: the SCAN functional; PBE with a Hubbard U correction on the Mn-$d$ orbitals, denoted as PBE+$U_{\text{Mn}}$; and PBE with +U on Mn-$d$ and O-$p$ orbitals, denoted as PBE+$U_{\text{Mn,O}}$. It is noted that HSE functional is not included in the comparison because of its high computational cost.

**Classification of Redox Activity**

An algorithm for determining the types of local anionic species present in the structures is developed, and the flow chart describing the algorithm is illustrated in Fig. 2. The presented algorithm avoids manual inspection of individual data points, making the analysis more robust and reproducible. The algorithm categorizes the localized anionic species into singular oxygen ($O^-$), peroxide ($O_2^{2-}$), superoxide ($O_2^-$) and molecular oxygen ($O_2$), which respectively have 1, 2, 3 and 4 localized holes. The oxygen species without any localized hole is labelled as “lattice oxygen.” The anionic species are categorized mainly based on the bond distance between two oxygen atoms, $d_{\text{OO}}$, and the local magnetic moment, $\mu$. The hole localization in the oxygen pair reduces the bond length due to the removal of electrons in anti-bonding orbitals, and the resulting spin-pairing can be observed via local magnetic moments of the oxygen pairs. The peroxide and superoxide shown in Fig. 1(b) are identified using the scheme from Fig. 2.

It is more difficult to identify a hole localized on a single oxygen ($O^-$) due to the lack
Figure 2: Flowchart of the algorithm for classifying the anionic species. Nearest oxygen neighbor and the local magnetic moment are denoted as NN and $\mu$, respectively. $\sum \mu_i$ is the sum of the local magnetic moments on the considered oxygen pair, and $d_{OO}$ is the distance between the nearest oxygen pairs. The change in Bader charge is denoted as $\Delta q_O$.

of significant structural distortions around it. Furthermore, the local magnetic moments are not reliable for determining $O^-$ species as contributions from delocalized holes are indistinguishable from that of localized holes. An alternative approach to locate $O^-$ is to look at the change in the charge density; we use the Bader charge of the oxygen species to determine whether or not the oxygen species have a localized hole. More specifically, we use the deviation of the Bader charge in the oxygen species from the average of every oxygen species in structures at the same lithiation level and denote it as $\Delta q_O$ ($\Delta q_O = q_O - \langle q_O \rangle$, where $\langle q_O \rangle$ is the average Bader charge of all oxygen species at a given lithiation level). The threshold of $\Delta q_O$ for distinguishing $O^-$ from the lattice oxygen is set to $-0.45$ e$^-$ based on observation (see supplementary information for more details). It is noted that the cutoff values in Fig. 2 are determined heuristically which can serve as a guide value for further studies beyond Li$_2$MnO$_3$.

Cationic redox activity is another crucial aspect to consider as it is the main contributor of the redox activity for most cathode materials. While magnetic moments have been used
previously to identify TM redox activity, identifying the oxidation state of Mn from the magnetic moment is challenging, especially when vacancies are introduced upon delithiation. Li vacancies distort the TM-O octahedra, and the crystal field splitting in an octahedral field is no longer applicable. We opted to use the change in Bader charge for distinguishing Mn species ($\Delta q_{Mn} = q_{Mn} - \langle q_{Mn} \rangle$, where $\langle q_{Mn} \rangle$ is the average Bader charge of all Mn species at a given lithiation level). A cutoff of 0.1 e$^-$ was chosen, i.e. $\Delta q_{Mn} > 0.1$ means that Mn$^{4+}$ has been reduced to Mn$^{3+}$. We have compared $\Delta q_{Mn}$ in Mn$_2$O$_3$ and MnO$_2$, which respectively have the nominal oxidation state +3 and +4. $\Delta q_{Mn}$ is computed to be 0.10 e$^-$, 0.05 e$^-$ and 0.11 e$^-$ for PBE+U$_{Mn}$, PBE+U$_{Mn,U}$ and SCAN, respectively, which suggests that 0.1 e$^-$ is a suitable choice.

The possibility of Mn to oxidize is not considered in this study. It may seem counter-intuitive to consider the reduction of Mn (Mn$^{4+}$ to Mn$^{3+}$) upon delithiation while not considering the oxidation. The oxidation would require Mn$^{4+}$ to oxidize to Mn$^{6+}$ because the Mn$^{5+}$ state is highly unlikely to occur. Cationic reduction, on the other hand, has been observed in other materials where anionic redox processes take place. One noted example is Li$_3$VS$_4$ where V$^{5+}$ reduces to V$^{4+}$ during delithiation concomitantly to anionic local reduction of S$^{2-}$ to (S$_2$)$^2-$.

Preconditioning and the Formation of Peroxo-like Species

The Ewald preconditioning scheme was applied to the entire set of 101 structures in order to promote the formation of peroxo-like species by manually overcoming the transition barriers. The relative energies of the structures relaxed from the Ewald-preconditioned structures with respect to the structures relaxed from the pristine structures are shown in Fig. 3. Here, the relaxed structures are classified into four categories based on the presence of the peroxo-like species: absence of peroxo-like species in both pristine and the Ewald-preconditioned structures (blue cross); presence of peroxo-like species in both cases (orange square); peroxo-like species present only in the pristine structures (green triangle); peroxo-like species present...
only in the Ewald-preconditioned structures (red circle). The relative energy, $\Delta E$, is defined as $\Delta E = E_{\text{Ewald}} - E_{\text{pristine}}$, where $E$ is the total DFT energy. A negative $\Delta E$ means that the energy of the structure relaxed from the Ewald structure is more stable, and vice versa. It should be noted that DFT has a systematic error which overestimates the stability of peroxo-like species\cite{44}. However, this systematic error does not affect the results of this study (see supplementary information for more details).

![Figure 3: Relative energies of the structures relaxed from the Ewald preconditioned and pristine structures for the three considered functionals. Labels indicate the presence of the peroxo-like species after the relaxation. The black dashed line represents $\Delta E = 0$. Structures are sorted by category and by energy.](image)

It can be seen in Fig. 3 that the Ewald preconditioning promotes the anionic redox activity. A significant portion of the dataset corresponds to the case where the peroxo-like species are present only in the Ewald-preconditioned structures (red circle) — 75%, 27% and 51% for PBE+$U_{\text{Mn}}$, PBE+$U_{\text{Mn,O}}$ and SCAN functionals, respectively. On the other hand, there are only two instances where the opposite is true (green triangle). These observations support our original motivation where the energy barrier may prevent the classical relaxation scheme from locating the localized holes.

Interestingly, a majority of the red circles are above $\Delta E = 0$, indicating that the anionic redox does not always stabilize the system. In other words, the presence of anionic redox does not necessarily result in more stable configurations. The Ewald preconditioning causes formation of the peroxo-like species even when it is not energetically favorable. However, preconditioning has a benefit of breaking the initial symmetries present in the pristine structures. Two red circles with large negative $\Delta E$ values in all of the three functionals are good
examples showcasing the benefit of breaking the initial symmetry that the pristine structures were not able to escape.

While preconditioning promotes the formation of peroxo-like species, it does not guarantee the formation. Surprisingly, there are also rare cases where the peroxo-like species are found only in the pristine structures (two green triangles). In addition, a substantial portion of the structures in Fig. 3 show no formation of peroxo-like species (blue crosses) for all three functionals considered. Furthermore, many of the structures in Fig. 3(a) and (c) have $\Delta E = 0$, indicating that the pristine and Ewald-preconditioned structures converged to nearly identical final structures. Converging to nearly identical structures is more pronounced for the SCAN functional when no peroxo-like species are observed. Most of the blue crosses for PBE+U$_{Mn,O}$ functional in Fig. 3(b), on the other hand, lie below $\Delta E = 0$, which further highlights the importance of escaping local minima even in the absence of anionic redox activity.

Preconditioning promotes the formation of peroxo-like species, which aligns with the initial expectations. However, peroxo-like species are often energetically less favorable, and preconditioning does not necessarily result in the more stable configurations. It is difficult to escape the local energy minimum configurations for both the pristine and Ewald-preconditioned structures. Therefore, one should be cautious in drawing conclusions on the formation of anionic redox species based on either one method; it is important to start the calculations with more than one initial structure and select the most stable configuration for the analysis.

**Evolution of Anionic Redox**

The evolution of oxygen gas during cycling of Li$_2$MnO$_3$ has been attributed to the formation of peroxo-like species and $O^-$, which eventually form peroxo-like species. The evolution of the localized anionic redox species at varying lithiation levels are investigated by counting the average number of holes in each anionic redox species at each lithiation level as shown
Assuming no cationic reduction occurs during delithiation, every available hole would be supplied from the removal of Li; the number of holes would thus match the number of Li removed. However, the total amount of holes in the system is slightly higher than the number of removed Li in some cases, owing to the reduction of Mn$^{4+}$ to Mn$^{3+}$ releasing additional holes. As the amount of electrons in the system must be conserved, holes which have not been localized in O are considered delocalized in the O-2$p$ bands for the purposes of this study.

![Graph](image)

Figure 4: Average number of anionic redox species at varying levels of lithiation. Lines belong to the secondary $y$-axis, and denote the average delocalized and total amount of holes in the cell per formula unit, as well as the amount of holes provided by removal of Li.

A clear trend where the number of localized holes (thus the number of anionic redox species) increases as Li$_2$MnO$_3$ is further delithiated, can be seen in Fig. 4. The observed trend aligns well with an increased number of Li vacancies leading to an increase in the number of holes, which in turn increases the probability in which the holes get localized to form the anionic redox species. As the formation of these species are the main driving force
for the formation of oxygen gas, evolution of oxygen gas is expected to be more profound at higher delithiation levels. Previous calculations on Li$_2$MnO$_3$ have shown that a substantial delithiation was required for the formation of peroxides under the restriction where the structures remain layered. However, we observed the possibility of peroxide formation at very early stages of delithiation when layering restriction is lifted.

The +U correction counteracts the self-interaction errors in DFT and promotes the localization onto specific atomic orbitals. It can be seen from Fig. 4(b) that applying +U on the O-$p$ orbitals results in a higher likelihood of forming O$^-$ species rather than peroxo-like species compared to the other two functionals; PBE+$U_{Mn,O}$ stabilizes the O$^-$ localization more than the peroxo-like localization by a factor of two. The prevalence of the O$^-$ formation can also be seen in Fig. 3(b), where the number of structures without peroxo-like species (blue crosses) is larger compared to the other functionals. Furthermore, PBE+$U_{Mn,O}$ promotes the largest amount of reduction in the Mn, moving additional holes from the Mn ions onto the oxygen species.

Discussion

A framework for investigating the anionic redox processes using DFT calculations has been developed. The presented method is capable of estimating the amount of localized anionic redox and the trends in the evolution of anionic redox during cycling, all based on data readily available from standard DFT calculations. Our method serves as a recipe for other computational studies for understanding and designing of stable Li-rich materials. The recipe allows one to classify, and subsequently quantify, the types of anionic redox species in a given set of structures, which in turn allows for further investigations for stabilizing and controlling the anionic redox processes in the material design.

A preconditioning scheme was applied to the initial set of pristine structures in order to promote the formation of peroxo-like species. The preconditioning resulted in an increased
number of peroxo-like species, but their presence was not always energetically favorable. The dependence on the initial structure highlights the fact that the structure optimizer used in DFT calculations finds a local energy minimum structure, and care must be given in analyzing the presence of the anionic redox species.

The choice exchange-correlation functional was shown to have a significant impact on the amount of anionic redox during the delithiation process. While each functional resulted in different tendencies in how anionic redox presents itself, it is difficult to judge the performance of the functionals without experimental references of this kind. The SCAN and PBE+U$_{\text{Mn}}$ functionals both find comparable amounts of peroxide species; however, they disagree on the amount of superoxide. Conversely, the PBE+U$_{\text{Mn,O}}$ functional prefers the formation of O$^-$ over peroxo-like species.

We found that the formation of localized anionic species begins early in the delithiation phases. As this was not observed in previous DFT studies, the assumption of perfect layering was restricting the peroxo formation, as well as the structural initialization. Furthermore, the structure needs to be considered in a disordered form for any cluster expansion model or large-scale screening studies on these types of material in order to describe the structural transformations during delithiation. A careful consideration of the functional choice was also seen to be crucial, as this has a large influence on the general trends in the structure database.

**Methods**

**Preparation of Preconditioned Structures using Ewald Summation**

In order to assist the structure optimization algorithm in the formation of peroxo-like species, we manually compress an oxygen pair. However, due to the size of the configurational space, it is not feasible to initialize the system with every possible oxygen pair compression. Instead, we developed a scheme based on the Ewald summation technique in order to locate
the most probable locations for the peroxo-like species formation.

We assume the two most probable peroxo-like species to form are peroxides and superoxides. A peroxide species requires the localization of 2 holes (h$^+$), and a superoxide requires 3 h$^+$. Each Li vacancy in the cell provides a single h$^+$. Under the constraint of charge neutrality, there are only a certain number of ways to place any number of peroxides and superoxides in the cell, depending on the number of vacancies. The oxygen pairs with the lowest Ewald summation energies are then selected as the most likely candidates for peroxo-like species formation. The Ewald summation was calculated using the pymatgen code, and the Ewald preconditioning scheme is summarized as follows:

1. Count number of h$^+$ and determine all possible permutations of superoxide and peroxide species which fulfill the charge neutrality.

2. Initialize nominal oxidation states +1 for Li, +4 for Mn and −2 for O.

3. Distribute remaining charge from the Li vacancies evenly across all atoms in the cell such that the total oxidation state is 0.

4. Calculate site energies from the Ewald summation.

5. Locate oxygen pairs with the lowest average site energy.

6. Place 1 peroxo-like species, prioritizing the placement of superoxides first.

   - Peroxide: Set bond length to 1.53 Å and oxidation state of each oxygen in the pair to −1.

   - Superoxide: Set bond-length to 1.30 Å and oxidation state of each oxygen in the pair to −0.5.

7. Distribute remaining negative charge over all other atoms such that the total oxidation state is 0.

8. Repeat step 4 until all possible peroxo-like species have been placed.
9. Repeat step 1 for all possible permutations in new structures.

**Preparation of Structures**

The structures were prepared in the Atomic Simulation Environment (ASE)\textsuperscript{18}. Disordered Li-rich Li$_2$MnO$_3$ has a rocksalt lattice with Li and Mn sharing the cationic sites and O occupying the anionic sites. In order to properly sample different configurations, supercells of varying sizes were used, with the largest being $3 \times 3 \times 3$. Additionally, Li vacancies are introduced into the cell which further increases the configurational space. However, as Li$_x$MnO$_3$ is known to release oxygen during cycling, we limit our study to $1 \leq x \leq 2$ to capture the behavior of the initial cycle. As it is practically not feasible to sample every configuration, an initial population of 35 structures were generated randomly, and 66 subsequent structures were generated using simulated annealing technique to find the minimum energy configurations from a cluster expansion fit using the CLEASE\textsuperscript{49} software package. A total of 101 disordered configurations were generated at varying degrees of lithiation. Application of the Ewald preconditioning scheme resulted in an additional 85 structures.

**Computational Details**

The calculations were performed in the Vienna \textit{ab initio} Simulation Package (VASP) DFT code\textsuperscript{50,51} with a plane wave basis set, using a 650 eV cutoff for the valence electrons. The core electrons were treated in the projector augmented wave (PAW)\textsuperscript{52} formalism. The $k$-space was sampled using a $\Gamma$-centered Monkhort-Pack grid\textsuperscript{53} with a $k$-point density of 3.5 points per Å$^{-1}$. The atomic positions and cell were relaxed until the force per atom is converged to 0.05 eV Å$^{-1}$ or less using the conjugate gradient algorithm as implemented in VASP, and the total energy is converged to within $10^{-5}$ eV.

We employed 3 different functionals: the meta-GGA functional, SCAN\textsuperscript{33}, the GGA+U approach\textsuperscript{54} with the PBE\textsuperscript{31} functional, with the correction of $U = 3.9$ eV placed on the Mn-$d$
orbitals, as recommended by the materials project\textsuperscript{19}, and finally, a PBE+U calculation with $U = 3.9 \text{ eV}$ on the Mn-$d$ orbitals and $U = 6 \text{ eV}$ on the O-$p$ orbitals, which fits the band gap of Li$_2$O$_2$.\textsuperscript{32} The Hubbard-$U$ corrections have been normalized, using a custom modification of the VASP code.\textsuperscript{55}

**Data availability**

All the initial structures and the corresponding resulting relaxed structures presented in this work are available on DTU Data with the identifier “doi:10.11583/DTU.10264988”.

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**Supplementary Information**

**Estimating the Total Redox Activity**

The change in Bader charge on the individual species, $\Delta q$, is shown in Fig. 5. The Li species have a constant state of charge as seen in Fig. 5(a), which confirms that they are not redox active in this system. A positive $\Delta q_{\text{Mn}}$ in Fig. 5(b) corresponds to the extraction of a hole (electron addition), and $\Delta q_{\text{Mn}} = 0.1$ is interpreted as reduction from Mn$^{4+}$ to Mn$^{3+}$, based on the difference in Bader charge in MnO$_2$ and Mn$_2$O$_3$, which is observed to coincide with the onset of a plateau. Conversely, a negative $\Delta q_{\text{O}}$ in Fig. 5(c) corresponds to the addition of an electron hole. The onset of the plateau is used to determine the cutoff value for identifying
Figure 5: Change in Bader charge, $\Delta q$, on each individual species in the considered set of structures. Charge is referenced to the average charge on the same species at the same degree of lithiation. Oxygen which have already been assigned to a peroxo-like species have been excluded. Red line in (b) and (c) correspond to the selected cutoff values for identification of Mn$^{3+}$ and localized O$^-$, respectively.

the localized O$^-$, and it was at $\Delta q_O = -0.45$, which is interpreted as the formation of a O$^-$ species.

Including Systematic Error Corrections for Peroxo-like Species

Figure 6: Stability of the Ewald versus the pristine structures, correcting for systematic errors in the peroxo-like species.

In Fig. 6 the presence of peroxo-like species has been adjusted by adding an energy correction of 0.2 eV, $-0.2$ eV and 0 eV per peroxo-like species for PBE+$U_{\text{Mn}}$, PBE+$U_{\text{Mn,O}}$ and SCAN, respectively. This is due to DFT systematically overestimating the stability of the short-distance oxygen species. These corrections, however, only show very minor adjustments to the original un-corrected figure, and thus does not affect the overall conclusions.
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