Oxygen Character in the Density of States as an Indicator of the Stability of Li-ion Battery Cathode Materials

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Abstract

Oxygen gas evolution from lithium battery cathode materials during charging to high voltages is a known mechanism leading to cathode instability and ultimately Li-ion batteries fires. We present the simple thesis that the tendency toward oxygen destabilization in metal-oxide materials used as lithium ion battery cathodes can be correlated to the amount of oxygen-derived weight in the partial density of states (PDOS) near the Fermi level (E_F), which is easily calculable with Density Functional Theory (DFT). If the oxygen PDOS dominates the total DOS at E_F at any point during delithiation (charging), electrons are withdrawn from the O rather than the M states, and the O^{2-} ions are oxidized to peroxide (O_2^{2-}), and then often to O_2 gas. A demonstration of the utility of this perspective is given using DFT to calculate the PDOS for compounds with a broad range of structures, transition metals and degrees of lithiation: $LiFePO_4$, Li_2CuO_2 , $LiCoO_2$, $LiNiO_2$, and Li_2RuO_3 . The resulting computational spectra correlate well to the experimental stability in the modeled compounds. We conclude that the oxygen stability of cathode materials derives from their fundamental electronic structure as function of changing voltage (and lithiation).

1.0

Introduction

Lithium-ion batteries have been an enabling technology for mobile phones, computer tablets and laptops as their lightweight, compact formats reliably provide hours or even days of power to electronics, and

consumers can easily replenish their energy from standard power outlets on electric grids. The most common active materials used in rechargeable batteries for portable electronics are a lithium cobalt oxide (nominally LiCoO_2) cathode and a graphitic carbon anode, which are separated by a porous polymeric membrane and saturated in a carbonate-based electrolyte to yield a battery with a nominal voltage of 3.7 V vs Li^+/Li^0 . The more recent application of Li-ion batteries to electric and hybrid vehicles has raised the stakes for Li-ion battery technology, as the batteries have been integrated into high-voltage buses (300 V) in large formats. Such applications demand very high energy density, along with the capability for high power in a safe, low-cost battery. The demand for all of these qualities simultaneously has stimulated widespread research into alternative cathode materials

In metal-oxide cathode materials, a major safety and performance concern is O_2 evolution, which can occur when the metal oxide is severely delithiated from overcharging or overheating. Such overcharging can occur in a multi-cell pack when one cell is an outlier in manufacturing, such that one cell is overcharged but the nominal pack voltage appears normal [1] but can also occur due to underlying and intrinsic materials instabilities at various stages of lithiation. Experimentally, Oxygen loss from cathode materials (e.g., LiCoO_2 , LiNiO_2 and LiMnO_2) was first identified by ex-situ thermogravimetric analysis [2], and has also been shown during the chemical extraction of Li^+ from delithiated LiCoO_2 , meant to simulate the effect of overcharging [3]. O_2 release is not only exothermic, but liberated O_2 can react with the solvent, SEI, and possibly the aluminum-metal current collectors. The loss of O_2 with decreasing Li^+ content in Li_xCoO_2 during overcharge has been attributed to the oxidation of the oxygen anions in the lattice to O_2 rather than further oxidation of the cobalt cations [3]. A possible reaction for O_2 -gas loss from delithiated Li_xCoO_2 ($x < 0.5$) during thermal runaway is given in Eqns 1-3 [4].

An analogous process can take place in other metal-oxide cathode materials as a function of Li content, leading to capacity fade in the best case and catastrophic breakdown in the worst.

In this work, we look at the problem of oxidation of cathode anion sites from a quantum mechanical perspective, using a density functional theory (DFT) approach. We show that the shift from redox chemistry at the cation (metal) site to oxidation of the oxygen atoms as a function of state-of-charge can be predicted by examining the weight of the partial density of states PDOS at the Fermi energy. By correlating our calculations to experimental observations, we show that electronic instabilities driven by unstable oxygen can be predicted by noting when the oxygen PDOS becomes a majority. This provides an easy and relatively fast method of screening materials for a safe level of delithiation is therefore a useful tool in the design of new materials as Li ion battery cathodes.

1.1

Background

Oxidation of O^{2-} ions in a cathode compound can be understood from a quantum mechanical perspective by considering how electronic states are formed and occupied in the cathode material. During charging, electrons are withdrawn from the highest filled electronic state defined as the Fermi energy (E_F). In a typical transition metal oxide cathode, this state is the anti-bonding state formed by hybridization of a cationic $3d$ and an oxygen $2p$ state, as shown in Figure 1 using a $\text{Co}^{3+}/\text{Co}^{4+}$ redox couple as an example.

Figure 1: A schematic of the bonding/antibonding states of Co and O for two valencies of Co (Co^{3+} and Co^{4+}). The strength of the splitting and hybridization depends on the distance between states as $1/\Delta$. For Co^{3+} , the distance Δ_1 mixes relatively less oxygen into the anti-bonding states than the distance Δ_2 for Co^{4+} .

The admixture of oxygen into anti-bonding and cobalt into bonding states is determined by the strength of hybridization which is given analytically (to second order) as t^2/Δ , where Δ is the energy distance between the $3d$ and $2p$ states and t is the overlap of the orbitals. Both these quantities depend on the structure of the material and the oxidation and spin state of the cations [5]. Quite generally, though, it is clear that a lower energy $3d$ state produces stronger hybridization and admixture via a smaller Δ . Since the energy of a state depends on its electron occupancy, the valence of a $3d$ ion is inversely related to its energy. Thus, a higher oxidation state in the metal $3d$ cation corresponds to higher oxygen content in the anti-bonding state from which an electron will be withdrawn.

In a real material, the energy states as described above are broadened into energy bands, which can be calculated from first principles. Subsequently, the amount of oxygen and metal weight in the anti-bonding band at the Fermi energy can be calculated. In the case that the oxygen weight is comparable to the metal $3d$ weight, any electrons withdrawn from this band, for instance during charging, will come substantially from around the real space oxygen site instead of the transition metal site. In other words, the expected redox reaction is violated in favor of oxidizing the oxygen, giving rise to possible formation of peroxide (O_2^{2-}), and then O_2 gas:

The energy level of the oxygen bands, therefore, sets a limit on redox reactions. Goodenough showed that the voltage of a $3d$ material is related to the height of the $3d$ bands in the material and described the maximum voltage from a $3d$ redox couple as being “pinned” to the level of the O $2p$ bands [6]. From a different perspective, Huggins proposed that the operational potential of a battery is a suspect in its oxygen stability/safety, regardless of the materials chemical compositions and the crystal structures of the phases involved, by relating the Gibb’s free energy to the oxygen partial pressure and suggested that high voltages would inevitably lead to O_2 formation [7].

We take the perspective that the voltage constraint, oxygen instability and “pinning” phenomena can be understood and even predicted by an accurate determination of the amount of oxygen mixed into the states at E_F . Simply put, we state that if the amount of O is equal to or greater than the amount of transition metal character in the band from which electrons are withdrawn, the system will be unstable toward oxidation of O^{2-} and oxygen gas release. We further propose that relatively simple first principles density functional theory (DFT) calculations can provide this accurate determination via a calculation of the partial density of states (PDOS). We calculate the metal/oxygen admixture for a selection of cathode materials with a broad range of structures, compositions, and voltages to gauge the oxygen instability. When possible, we make correspondence to available experimental data. This methodology is simple, effective, and requires many fewer calculations than would an evaluation of oxygen stability via full chemical reactions and materials decomposition, even at the simplest level as given in Equations 1-3.

1.2

Materials

We choose five materials for our calculations, the structures of which are shown in Figure 2. First we examine two extreme cases: $LiFePO_4$, which is highly stable throughout the charge cycle, and Li_2CuO_2 which is highly unstable even at the beginning of the charge cycle. $LiFePO_4$ has the olivine structure both in the fully lithiated

and fully delithiated states [8]. Li_2CuO_2 begins as the planar $Immm$ structure, but transforms to the $C2/m$ structure (not shown) during cycling while simultaneously losing oxygen and experiencing severe capacity loss at each cycle [9]. Having used these two examples to bookend the limits of stability, we examine the practical battery material, LiCoO_2 and its structural counterpart: LiNiO_2 . Both are isostructural layered materials of the $R\bar{3}m$ space group [10],[11]. Li_xCoO_2 is a well-known and stable cathode material, as long as $x > 0.5$. However, as seen by Gupta and Manthiram [3], further delithiation can lead to oxygen instability in the following progressive oxidation reactions to peroxide in which the O is in a -1 oxidation state (Eq. 4) and then O_2 gas in which its oxidation state is effectively 0 (Eq. 5). Oxide coatings on LiCoO_2 have been shown to suppress O_2 evolution in Eq. 5 [12], a complex interaction with the electrolyte that is still under investigation.[13] LiNiO_2 and its modified counterpart, $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$, lose oxygen on their first charge cycle, causing a subsequent decrease in capacity [14, 15]. In thermal analysis, LiNiO_2 loses O_2 at a lower temperature than LiCoO_2 , indicating that it is less stable [2, 16].

Finally, we investigate Li_2RuO_3 which is interesting because of its high capacity and its excellent conductivity deriving from a semi-metallic nature [17, 18]. This compound, when doped with tin or manganese has recently been shown to derive additional capacity from formation of *reversible* peroxo- groups rather than O_2 during charging [19]. Li_2RuO_3 has a $C2/c$ structure, which is a variation on the $R\bar{3}m$ structures, but with some of the metal sites instead occupied by Li.

Figure 2: Crystal structures of (a) olivine, $Pnmb$ LiFePO_4 , (b) $Immm$ Li_2CuO_2 , (c) $R\bar{3}m$ LiCoO_2 and LiNiO_2 and (d) $C2/c$ Li_2RuO_3

2.0

Computational Methods

DFT has been widely advertised as a tool to study the electronic attributes and structural phases of battery materials [20, 21]. The methodology is based on establishing the ground state charge density, and thereby the density of states, magnetic configuration, wave functions, etc., of a system with many atoms by solving multiple single particle Schrodinger-like equations with an effective potential (mean field) representing the net effect of the many-electron system. It has been shown that DFT can accurately reproduce measured structural parameters and open circuit voltages in a wide variety of Li ion battery cathode materials [22].

Within DFT, there is a necessary approximation to a part of the energy potential, called the exchange-correlation potential. Mostly commonly used are the standard local density approximation and generalized gradient approximations (LDA and GGA) [23, 24]. These have been shown to be very accurate for systems without highly localized electrons. However, the majority of redox couples in Li^+ cathode materials come from localized $3d$ states for which the LDA/GGA approximations, while still providing accurate structural information, can fail badly at the electronic level. A very common remedy for the LDA/GGA shortcomings is the LDA+U theory, in which a Hubbard-like “U” term is added to the potential [25]. LDA+U theory can be effective in obtaining the correct electronic ground state and is computationally efficient, but requires a separate choice of “U” for each element within a material and each set of valence orbitals of that element. Furthermore, the choices for “U” are not universal; values vary across structural types and valencies. While the vast majority of orbitals require no “U” correction at all, an inaccurate choice for those that do can result in an incorrect sequence of redox couples in mixed cationic materials and/or erroneous voltage profiles. Most importantly for our purposes, it will not correctly reproduce the hybridization level in the anti-bonding level at the Fermi energy.

For this work, we choose a functional that treats all electronic states on the same footing rather than applying a correction to a selected subset. This eliminates the both necessity of choosing individual parameters for each element/orbital as well as of defining the orbitals themselves from density. In specific, we use the HSE06 functional [26] as implemented in the Vienna Ab-initio Simulation Program (VASP) [27]. While using this functional has the unfortunate effect of increasing the computational expense by an order of magnitude, it has been shown to correctly reproduce the position of d bands relative to oxygen bands [28] and to correctly establish voltages in metal oxide cathode materials [29].

We fully relax the lattice constants and ionic positions of all constituent atoms at each examined Li concentration until they reach their lowest energy state. We calculated systems with multiple Li orderings and found that different ordering produce small changes in energy and even smaller changes in the densities of states. We chose the lowest calculated energy configuration for each final presented set of data. All relaxations are performed with a 6x6x4 grid of k-points followed by a final self-consistent calculation with 12x12x8 k-points in the lowest energy cell. For simplicity the spin majority and spin minority states have been added together and plotted on the same axis.

3.0

Results: PDOS Calculations

3.1

Stable and unstable endpoints

We begin with a demonstration of two contrasting compounds: oxygen stable Li_xFePO_4 , and oxygen unstable Li_xCuO_2 . The PDOS for these compounds are presented in Figure 3. Each Li^+ ion withdrawn during charging shifts one electron's worth of states below E_F to empty electron states above E_F , as indicated by arrows in the Figure. For Li_xFePO_4 , the withdrawal of one electron per formula unit represents full charge. The electron state that moves across E_F in this system is dominated by the Fe contribution with a tiny admixture of oxygen. By subtracting the charge densities calculated before and after electron withdrawal, we can image the hole left behind in the material. In FePO_4 , the cloud of charge missing from the system is localized around a Fe site with

very small remnants near oxygen. This indicates a metal valence change and the typical redox chemistry associated with the charge/discharge process in stable cathodes, leaving the oxygen in its preferred 2-valency. In contrast, the states that cross E_F upon withdrawal of one electron in Li_xCuO_2 are dominated by oxygen, with only minority Cu content. As can be seen in the charge density plot, the missing charge is delocalized and has been pulled heavily from around oxygen atoms, leaving the compound susceptible to peroxide formation.

Figure 3: Partial density of states for M and O in $\text{Li}_x\text{FePO}_4/\text{Li}_2\text{CuO}_2$ at full discharge (top) and full/partial charge (bottom). Filled states are to the left of the Fermi energy (set to zero) and empty states to the right. A close-up of the hole states left behind after withdrawal of an electron are shown adjacent to each DOS plot. The removed charge is clearly centered around Fe for LiFePO_4 , but comes heavily from oxygen in Li_2CuO_2 .

There is yet one further Li^+ ion available to be withdrawn, once the Cu-based compound has reached LiCuO_2 . Were it to be removed, the associated electron would come from the states below E_F in the bottom panel. These are almost entirely composed of oxygen and removing charge would even further destabilize the oxygen toward peroxide formation and finally O_2 (g).

The results of the PDOS calculations in these materials can be correlated to their cycling properties. Li_xFePO_4 is well known to be stable and repeatedly cycleable across the entire range of x , with almost no loss of oxygen [30]. Li_xCuO_2 , on the other hand, exhibits immediate and dramatic capacity loss when cycled [31]. While a standard redox reaction would proceed reversibly according to Eq. 6, when O^{2-} is oxidized, the reaction is no longer fully reversible, peroxide is formed along with by-product phase CuO , and capacity is lost at each step, according to Eqs. 7,8.

The loss of O_2 gas has been inferred by the formation of CuO phases forming in conjunction with irreversible capacity loss during the cycling of Li_2CuO_2 [31].

3.2

Layered transition metal cathodes

Having shown that the PDOS correlates to oxygen stability/instability, at least in very clear-cut cases, we examine the more complex cases of LiCoO_2 and LiNiO_2 , two isostructural compounds which are neither fully stable nor fully unstable. These have been calculated before by Laubach, *et al.* [32]. By their calculations, the Co PDOS always was above the O PDOS at the Fermi level, although there was extensive hybridization between the Co 3d and O 2p states at $x < 0.5$ of O^{2-} anions. By comparison, LiNiO_2 showed the reverse, with the O PDOS always higher than the Ni PDOS, although the authors were not as confident with this computational result. The source of their hesitation was their use of DFT+U, which as mentioned previously, may skew the

energy order of the Ni and O states and which we avoid with our use of HSE06. Xiao *et al.* [33], also using DFT+U, calculated the PDOS of Li_2MO_2 with $M = \text{Ti, Mn, Co}$ which has the same structure as LiCoO_2 but with 1/3 of the transition metal species replaced by Li. This work emphasized the connection between the PDOS and oxygen stability, as we do here, and provides an additional example of the utility of the method.

Figure 4: PDOS of successive stages of delithiation of Li_xCoO_2 with all energies shifted so that E_F is at zero. Arrows point from filled states at one stage to emptied states at the next stage. The lower panel shows a predicted PDOS for a compound in which 1/6 further electrons are withdrawn, even after all the Li is gone.

Figure 4 shows Li_xCoO_2 for $x = 1$, $x = 0.33$, and $x = 0$ in the top three panels. At full lithiation (top panel), the states just below E_F have substantial oxygen character, but are majority Co. When 1/3 of the Li is removed, electrons pulled from these states are shifted above E_F (second panel), where it can be seen that their character is somewhat reorganized, but remains mainly Co-like. The new states located at E_F have an increased oxygen weight (compared to the discharged compound). When electrons are removed from these states to achieve the fully delithiated compound (third panel), a similar process occurs: the Co vs. O composition appears somewhat reorganized but Co character dominates, indicating that Li^+ and e^- withdrawal should be chemically stable for the full range of Li content. At about 3 eV above E_F , there are empty states with a substantial, though not

dominant, amount of oxygen character. This means that charge has been removed from around the oxygen site, but is not conclusive in terms of whether or not a peroxide instability is incipient. It is certainly clear that the electron states below E_F increase in oxygen content as Li is removed.

In the final panel of Figure 4, we use a computational technique to remove a further electron from the LiCoO_2 system, despite there being no Li left. Specifically, we reduce the number of electrons in the system and charge compensate by using a uniform negative background charge that integrates to the exact number by which the electrons were reduced.

In this case, it is clear that the removed electrons have dominant oxygen character, indicating oxidation of the O^{2-} ions. Although experimental removal of electrons in precisely this manner is impossible, our calculated spectrum demonstrates that the $\text{Co}^{3+}/\text{Co}^{4+}$ redox couple is unavailable in this compound and attempts to access it would likely result in peroxide formation. A possible physical realization of this circumstance is a Li_xCoO_2 compound with Co vacancies or with Co over-coordinated to O, such as might occur at surfaces in nanoscale materials, in systems with phase impurities such as Co_3O_4 , or in mixed cationic systems with Co^{3+} as a component. Indeed, the observed instability of LiCoO_2 increases if the LiCoO_2 particles are nanoscale [34].

Figure 5: The PDOS of Li_xNiO_2 at various Li content. The Fermi energy has been shifted to zero. Arrows point from filled states at one stage to emptied states at the next stage.

Figure 5 shows the PDOS of Li_xNiO_2 , which is isostructural to LiCoO_2 (at least at full lithiation) but has one additional electron in the system. Looking at the top panel of Figure 5, compared to the top panel of Figure 4, one can immediately see that the Ni-based compound has significantly more oxygen in the states just below E_F . In fact, the oxygen is dominant for LiNiO_2 at the top of the filled spectrum. When Li^+ ions and electrons are removed to form $\text{Li}_{0.33}\text{NiO}_2$, one can see that the Ni/O contributions are reorganized somewhat (as was seen in the Co compound), such that the emptied states above E_F are now Ni dominated, though just barely. There is heavy oxygen character in these states, indicating that O^{2-} is likely partially oxidized during charging.

Thomas, et al. [11], claimed that in Li_xNiO_2 , lithium could not be extracted for $x < 0.4$ (< 4.25 V vs Li^+/Li^0) because the lack of interaction of between the layers brought on by loss of mediating Li^+ ions would necessitate an unfavorable Ni valency combined with ionic migration to stave off structural reorganization. Our calculations show that slightly before this point, a structural or chemical reorganization will be brought about by oxidation of the O^{2-} ions. This can surely be *related* to the unfavorable Ni valency of Thomas *et al.*, but our perspective differs in that it is an undesirable oxygen valency, precipitated by the high Ni valency, which brings the d-bands very low in energy and drives the instability. The difference in the metal oxide stability and energetic barriers to high Li extraction between LiCoO_2 and LiNiO_2 are borne out by experimental results, which confirm that LiNiO_2 loses O_2 at a much lower temperatures than LiCoO_2 during thermal analysis measurements [16]. LiNiO_2 is also known to lose significant oxygen and thus capacity on its first charge cycle. The good correspondence between the practical measurements of O loss and the calculated oxygen admixture into the relevant electronic states provides strong evidence that the PDOS calculated with DFT (using an accurate functional) embodies the global changes in the M and O electronic states of the materials, and can be used as a predictive tool for oxygen stability.

3.3

Ruthenate cathodes

Finally, we present PDOS calculations to investigate the oxygen stability of Li_2RuO_3 , variations of which are now being suggested as high capacity materials through electron contributions from their

oxygen ions via O anion oxidation to peroxide (Eq 5). The top panel of Fig. 8 shows the fully discharged system with Ru-dominated states just below E_F . Upon removal of one Li^+ ion and one electron (middle panel), these states move above E_F and remain mainly Ru-like, indicating that this step accesses the $\text{Ru}^{4+}/\text{Ru}^{5+}$ redox couple and should be stable and fully reversible. The next states to be accessed at E_F have significantly heavier oxygen character, though Ru is still barely the majority. The final panel shows this next step, which is ostensibly accessing the $\text{Ru}^{5+}/\text{Ru}^{6+}$ redox couple. However, in the emptied states above E_F , Ru character and O character are approximately equal, indicating a propensity toward oxidation of the O^{2-} ions to O_2^{2-} and eventual formation of O_2 . The spectra is reminiscent of delithiated LiNiO_2 in which heavy oxygen character exists in the emptied states, but the transition metal bands are still perhaps slightly above the oxygen bands. Looking at the spectrum now below E_F in the bottom panel, it is clear that the states are mainly of oxygen-like character. In other words, an attempt to access the $\text{Ru}^{6+}/\text{Ru}^{7+}$ couple will surely result instead in a change to the oxygen valency. Recently published literature indicates that in systems where Ru is partially replaced by electrochemically inactive ions, such as Mn^{4+} or Sn^{4+} there is peroxide (O_2^{2-}) formation at high levels of delithiation [35]. This is in perfect agreement with our calculations since Mn^{4+} or Sn^{4+} would force the system to access the $\text{Ru}^{6+}/\text{Ru}^{7+}$ couple where oxygen states dominate. In Tarascon's work,^{[19],[35]} the peroxide formation is a reversible source of capacity via Eq. 4 and does not lead to an overall materials instability via irreversible O_2 loss (Eq 5). This seems to be a unusual state of affairs in cathode materials, as O_2 loss has previously only been prevented by coating lithium metal oxides with inert metal oxides [12, 13]. It is not clear why peroxide formation provides extra (and reversible) capacity rather than an instability in the case of the doped Li_2RuO_3 compounds, but this oxidation step does not progress to $\text{O}_2(\text{g})$ loss and overall battery instability as it does in others (LiCoO_2 , LiNiO_2 , etc.). Unfortunately, Li_2RuO_3 is not a heavily studied material, and there are no reports of Li_2RuO_3 oxygen stability, beyond the work of Sarkar, *et al.* which infers O_2 loss on the first charge cycle [36]. Our

Figure 6: The PDOS of Li_xRuO_3 at various Li content. The Fermi energy has been shifted to zero. Arrows point from filled states at one stage to emptied states at the next stage.

prediction method, therefore, is shown to accurately gauge the instability of the oxygen toward peroxide formation, but is not able to predict why the peroxide remains stable in the material.

There are other indications in the literature of other materials with anomalously high Li^+ capacity, which may be attributable to peroxide formation such as high surface area V_2O_5 [37]. Capacities on the order of 4 Li^+ per V cation are reported in V_2O_5 aerogels, suggesting an unlikely $\text{V}^{5+}/\text{V}^{1+}$ redox couple. It was postulated that vanadium vacancies in the high surface area structure could serve as additional sites for charge balance during Li^+ insertion, without a change in V valency [38]. However, in the delithiated material, since no further d electrons (beyond V^{5+}) are available, the likely result of such vacancies is partial oxidation of oxygen sites. Note that V_2O_5 aerogel are also highly unstable to cycling, consistent with O_2 loss through the reduction of O sites.

At the simple level of PDOS only, our calculations cannot determine the final state that the O^{2-} ions take during

excessive delithiation in materials such as Li_2RuO_3 or high surface area V_2O_5 , but can only predict when the first step toward O_2 (g) release, *i.e.* peroxide formation, is likely in the bulk material. Further experimental and computational studies to illuminate the underlying mechanisms that stabilize the oxidized oxygen states are highly desirable. The role of the surface in the peroxide formation is also another key area for research.

4.0

Discussion

Our DFT calculations for the PDOS of the M and O character of delithiated metal oxides match well to experimental observations of their propensity to lose, or evolve, O_2 upon delithiation or charging. The electrochemical and structural attributes of the five materials studied in this report are summarized in Table I.

Table 1: Attributes of the four Li-ion battery cathode materials compared in this article, presenting a range of potentials, stability/cyclability, and structures.

Discharged Cathode	Charged Cathode	Structure	Redox plateau vs Li^+/Li^0	Capacity mAh/g	Operational voltage range (V)	Voltage for O_2 evolution	REF
LiCoO_2	$\text{Li}_{0.5}\text{CoO}_2$	$R\bar{3}m$	3.8 V $\text{Co}^{3+}/\text{Co}^{4+}$	140	2.7–4.2 V	>4.6 V	[4],[10], [16]
LiNiO_2	$\text{Li}_{0.5}\text{NiO}_2$	$R\bar{3}m$	3.4 V $\text{Ni}^{3+}/\text{Ni}^{4+}$	140	2.5–3.9 V	4.2 V	[4],[11], [16]
Li_2RuO_3	LiRuO_3	$C2/c$	3.65 V $\text{Ru}^{4+}/\text{Ru}^{5+}$	160	3.0–4.0 V	unknown [19]	[18, 19, 35]
Li_2CuO_2	LiCuO_2	$Immm$ to $C2/m$	3.0 V $\text{Cu}^{2+}/\text{Cu}^{3+}$ 2.5 V $\text{Cu}^{2+}/\text{Cu}^{1+}$	180	1.5–3.7 V	> 2.0 V	[9, 31, 39]
LiFePO_4	$\text{Li}_{0.5}\text{FePO}_4$	$Pnmb$	3.4 V $\text{Fe}^{3+}/\text{Fe}^{4+}$	110	2.5–4.0 V	N/A	[8, 30]

The propensity of the materials to evolve oxygen during delithiation is shown in Figure 7. The area where the material is stable to cycling is in green, and its oxygen evolution region is in red, except for Li_2RuO_3 where the higher potentials are denoted in purple due to the uncertainty about whether the material loses O_2 or forms a peroxide ion during charging, which can be reversed to oxygen anions during discharge. Interestingly, from Fig. 7, there appears to be no clear correlation to the operational potential of the material and its stability. The propensity of the material to evolve oxygen appears to be determined by a range of interdependent factors, including the valency of the electrochemically active ion, the material's crystal structure, and the local oxygen coordination, with no *direct* correlation to its E^0 value, e.g. the ΔG value of its reaction for Li^+ insertion (for example, Eq. 6). For LiCoO_2 , LiNiO_2 and Li_2CuO_2 , in fact, the propensity for O_2 loss follows the reverse trend, and increases as the E^0 value decreases, contradicting the proposal that high voltage cathode materials *per se* are less safe [7]. In the case of the LiFePO_4 , the O states themselves are lowered via strong bonding with the P anions, such that the electronic states always maintain a heavy M character, which is the so-called polyanionic inductive effect [40]. In the 3d transition metal compounds with Co, Ni, and Cu, the 3d bands move down in energy as a function of increasing nuclear charge. LiCoO_2 has little oxygen character at E_F at each state of delithiation. Li_xNiO_2 starts to evolve O_2 at $x < 0.4$ when the Ni^{4+} cation bands hybridize so strongly with oxygen that electrons are removed from both sites. In Li_2CuO_2 , the very deep Cu d bands result in primarily O character at E_F even when fully lithiated. In Li_2RuO_3 , the O^{2-} ions do not become oxidized until the valency is higher than Ru^{5+} . This unusual stability owes to the fact that 4d states are more weakly bound to the nucleus than 3d states and therefore are located further from the oxygen states.

Figure 7: Schematic of voltage range for Li-ion battery cathodes vs variation in Li content (x). The nominal charge voltage of the material, or E^0 , is denoted with a black line. The voltage region in which the materials evolve O_2 is shown in red, with the exception of Li_2RuO_3 , which is thought to instead reversibly form stable peroxy species on its surface [35].

Therefore, each material has a unique set of circumstances that govern its electronic character, and how it is oxidized during charging. Whereas it would be attractive to have a “one size fits all” theory for O_2 evolution from lithium ion battery cathodes, it appears that each material must be studied individually, with consideration of its metal constituents, crystal structure, local coordination and orbital character. All of these factors can be taken into account simultaneously and accurately within DFT. Whether it eventually leads to actual O_2 evolution, oxygen instability at the electrolyte, or a reversible structural or chemical change, oxidation of O^{2-} can be fundamentally understood and predicted through a relatively simple calculation of the PDOS of the cathode material.

5.0

Conclusions

Using DFT with the HSE06 functional that applies a correction to the exchange potential for both transition metal and oxygen orbitals, we are able to correlate the propensity of material to evolve O_2 during

charging or delithiation to its oxygen character in PDOS calculations. O_2 loss appears to be strongly correlated to the underlying electronic structure of the material, and not its reaction potential toward Li^+ . When the presence of oxygen character in the states from which electrons are withdrawn during the charge cycle is greater than the metal character, the O anions in the material are destabilized. Oxidation of the oxygen anions causes instability and/or peroxide formation, and ultimately the propensity of a material to lose O_2 . Oxidation of the O^{2-} ions can also lead to capacity fade, structural phase transitions or even lead to thermal runaway when a reaction with the electrolyte occurs. While our calculations cannot predict the eventual electrochemical consequences of O^{2-} oxidation, they can serve as a predictor of possible instabilities. As researchers probe new materials, both experimentally and by computational discovery, these relatively straightforward PDOS measurements, if done accurately, are a useful tool for screening the electronic stability range as a function of state of charge.

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