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Electronic structure and properties of lithium-rich complex oxides

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Abstract

Lithium-rich complex transition-metal oxides Li_2MoO_3 , Li_2RuO_3 , Li_3RuO_4 , Li_3NbO_4 , Li_5FeO_4 , Li_5MnO_4 and their derivatives are of interest for high-capacity battery electrodes. Here, we report a first-principles density-functional theory study of the atomic and electronic structure of these materials using the Heyd-Scuseria-Ernzerhof (HSE) screened hybrid functional which treats all orbitals in the materials on equal footing. Dimerization of the transition-metal ions is found to occur in layered Li_2MoO_3 , in both fully lithiated and partially delithiated compounds. The Ru–Ru dimerization does not occur in fully lithiated Li_2RuO_3 , in contrast to what is commonly believed; Ru–Ru dimers are, however, found to occur in the presence of neutral lithium vacancies caused by lithium loss during synthesis and/or lithium removal during use. We also analyze the electronic structure of the complex oxides and discuss the delithiation mechanism in these battery electrode materials.

Keywords

complex oxides; battery materials; delithiation mechanism; metal—metal dimerization; electronic structure; first-principles calculations

1 Introduction

Lithium-rich complex transition-metal oxides have been of great interest for lithium-ion battery electrodes due to their high theoretical capacity. These materials include layered oxides Li_2MoO_3 ,^{1,2} Li_2RuO_3 ,^{3,4} and Li_3RuO_4 ,⁵ and antiurite Li_5FeO_4 ⁶ as well as their derivatives.^{7–11} It has been reported that some of these battery materials exhibit both cationic and anionic redox behavior.^{6,12} An understanding of the delithiation mechanism would necessarily require a detailed knowledge of the materials' electronic structure.¹³ On another fundamental aspect, metal–metal bond disproportionation has been reported to occur on the transition-metal sublattice in Li_2MoO_3 and Li_2RuO_3 ,^{1,2,14} the two layered oxides with a honeycomb transition-metal network. The phenomenon is, however, not well understood. Previous reports on the phenomenon have been conflicting and indicated that

the occurrence of the Ru–Ru dimerization may be dependent on the synthesis procedure.^{15,16}

Computational studies of the above mentioned materials have been carried out by different research groups,^{4,5,15,17–20} often using first-principles calculations based on density-functional theory (DFT) within the local-density (LDA) or generalized gradient (GGA) approximation^{21,22} and/or the DFT+*U* extension²³ where *U* is the on-site Coulomb correction. There are, however, limitations with these methods when applied to complex transition-metal oxides. It is well known that the self-interaction error (SIE) inherent to LDA and GGA leads to the overdelocalization of electrons; as a result, the methods fail in localized electron systems. The DFT+*U* method can help mitigate the SIE problem; however, it requires a priori knowledge of the *U* parameter for each orbital in each element. As discussed in Ref. 24, the usual DFT+*U* calculations with *U* applied only on the transition-metal *d* orbitals leave the oxygen *p* states uncorrected; as a result, the calculations may not be able to reproduce the correct physics and chemistry, especially in cases where there is strong mixing between the transition-metal *d* and oxygen *p* states and/or when the oxygen *p* states can play an important role.

We herein report a first-principles study of the Li-rich complex oxides using a hybrid DFT/Hartree-Fock method²⁵ that mitigates the SIE. In hybrid functional calculations, all electronic states in the materials are treated on equal footing. This helps avoid a possible misalignment of the transition-metal *d* versus oxygen *p* states in the energy spectrum. It has been demonstrated that the electronic structure of complex transition-metal oxides is better described by hybrid functionals than by the other DFT methods,^{26,27} especially of those with a subtle interplay among charge, spin, and lattice degrees of freedom.¹³ The focus of this work is on the electronic structure, particularly the nature of the electronic states near the band edges, in the different materials, and its implications on the delithiation mechanism during the initial stages of lithium extraction. The dimerization of the transition-metal ions in layered oxides Li₂MoO₃ and Li₂RuO₃ is also discussed.

2 Methods

Our calculations are based on DFT, using the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE),²⁸ the projector augmented wave (PAW) method,²⁹ and a plane-wave basis set, as implemented in the Vienna *Ab Initio* Simulation Package (VASP).³⁰ The Hartree-Fock mixing parameter (α) and the screening length are set to their standard values, 0.25 and 10 Å, respectively, unless otherwise noted. The plane-wave basis-set cutoff is set to 500 eV and spin polarization is included.

Calculations for bulk Li₂MO₃ (two formula units per unit cell), Li₃MO₄ (two formula units per unit cell), or Li₃FeO₄ (eight formula units per unit cell) are carried out using a Γ -centered 8×8×7, 7×7×6, or 4×4×4 *k*-point mesh. The experimental atomic structures of Li₃RuO₄, Li₃NbO₄,⁵ and Li₃FeO₄³¹ are used as the initial structures in the calculations; for the other compounds, the initial atomic structures are taken from those in the Materials Project³² database. Mixed-metal compounds are created through partial substitution of transition metals in the host compounds. Larger, up to 4×4×1 (192-atom), supercells are also

used in the study of bond disproportionation on the transition-metal sublattice and delithiation mechanism. In all calculations, structural optimizations are performed with the HSE functional and the force threshold is chosen to be 0.01 eV/Å.

DFT+ U calculations³³ based on the the GGA version of Perdew, Burke, and Ernzerhof (PBE),³⁴ hereafter referred to as PBE+ U , are also carried out for comparison. The effective U value, i.e., $U - J$, varies from 0 to 2 eV.

3 Results and Discussion

3.1 Transition metals on the honeycomb network: To dimerize or not to dimerize?

Figure 1 shows the atomic structure of select Li-rich complex oxides. The lattice parameters of all the single phases considered in this work are summarized in Table 1. The structure of Li_2MO_3 ($M = \text{Mo}, \text{Ru}$) and Li_3RuO_4 has alternate Li and M/Li layers. In Li_2MO_3 , the transition metal forms a honeycomb network in the M/Li layer [Fig. 1(a)]; in Li_3RuO_4 , Ru forms zigzag chains. In these oxides, as well as in Li_3NbO_4 , the transition metal is octahedrally coordinated with oxygen. The transition metal in Li_5MO_4 ($M = \text{Fe}, \text{Mn}$) is, on the other hand, tetrahedrally coordinated [Fig. 1(c)]. We find that in these complex oxides, except Li_2MoO_3 (see more below), the antiferromagnetic (AF) and ferromagnetic (FM) spin configurations are almost degenerate in energy.

In layered Li_2MoO_3 , bond disproportionation occurs on the transition-metal network with all Mo ions dimerized. An AF configuration of Li_2MoO_3 with alternate up and down spins is lower in energy than the FM one by 74 meV per formula unit (f.u.). In this AF configuration, the Mo–Mo dimers have a calculated bond length of 2.45 Å, significantly shorter than the lengths (3.09 Å and 3.17 Å) of the other Mo–Mo bonds. The Mo ions has a calculated local magnetic moment of $0.79\mu_B$, significantly smaller than that expected of Mo^{4+} with two unpaired d electrons. They can thus be regarded as *effectively* Mo^{5+} . In the FM configuration, the bond length within the Mo–Mo dimer is 2.47 Å, compared to that of 3.15 Å of the other Mo–Mo bonds; half of the Mo ions has a local magnetic moment of $0.45\mu_B$ and the other half has that of $1.17\mu_B$. Note that the undimerized FM configuration of Li_2MoO_3 is higher in energy than the dimerized AF one by 262 meV/f.u.; in the former, the Mo–Mo bond lengths are 2.86 Å and 3.11 Å, and the Mo ions has a magnetic moment of $1.68\mu_B$. Clearly, the Mo–Mo dimerization leads to reduced local magnetic moments. This is because some Mo $4d$ electrons participate in the formation of Mo–Mo covalent bonds, which leads to a reduction in the number of electrons contributing to effective localized moments, an effect believed to also occur in other materials with transition-metal dimers.³⁵ The bond lengths obtained in our calculations for the low-energy and dimerized configuration of Li_2MoO_3 are in excellent agreement with the short and long Mo–Mo bonds of 2.524 Å and 3.255 Å observed in experiments.¹

Interestingly, Ru–Ru dimerization is not observed in fully lithiated Li_2RuO_3 , except in PBE + U calculations with $U = 1.5$ eV or in HSE calculations with very small mixing parameter values (e.g., $\alpha < 0.10$); see Fig. 2. The results reported in Fig. 2 are obtained in calculations using the large, $4 \times 4 \times 1$ (192-atom), supercells to release possible constraints on the crystal symmetry. Note that in the PBE+ U calculations, the U term is applied only on the Ru $4d$

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orbitals and the O $2p$ states remain uncorrected. In materials such as Li_2RuO_3 where there is strong mixing between the transition-metal (Ru) d and oxygen p states (see Sec. 3.2), the PBE+ U calculations would have limited predictive power. Our results show that, for a reasonable choice of the computational method (here, HSE with $\alpha \sim 0.10$ – 0.25), the non-dimerization configuration of fully lithiated Li_2RuO_3 is lower in energy than the dimerization one. In undimerized Li_2RuO_3 , the Ru–Ru bond lengths are calculated to be 2.93 Å, 2.94 Å, and 2.99 Å, and the Ru ions have a local magnetic moment of about $1.6\mu_B$ (obtained in the HSE calculations with $\alpha = 0.25$). For comparison, the calculated bond lengths are ~ 2.5 Å and 3.1 Å and the magnetic moment is $\sim 0.8\mu_B$ in the high-energy, dimerized Li_2RuO_3 .

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The fact that the Ru–Ru dimerization configuration of fully lithiated Li_2RuO_3 is energetically less favorable in our HSE calculations with $\alpha \sim 0.10$ – 0.25 is consistent with the absence of Ru–Ru dimers in the vast majority of Li_2RuO_3 single-crystals.¹⁵ Our HSE results are also in contrast to those obtained in LDA/GGA, often reported in the literature, in which Ru–Ru dimers are found even in pristine Li_2RuO_3 . The discrepancy can be ascribed to the well-known tendency of LDA/GGA to overdelocalize electrons and hence to favor metal–metal dimerization.

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Note that we do, however, observe Ru–Ru dimerization in Li_2RuO_3 in the presence of neutral lithium vacancies. In calculations using supercell sizes ranging from unit cells (2 f.u.) to $4\times 4\times 1$ supercells (32 f.u.), a Ru–Ru dimer is found to form in the vicinity of the void formed by the removal of a lithium. In a $4\times 4\times 1$ supercell, for example, which corresponds to $\sim 3\%$ lithium vacancy, the Ru–Ru dimer has a bond length of 2.75 Å, compared to 2.92–3.00 Å of the other Ru–Ru bonds. This value is in excellent agreement with the short Ru–Ru bond of 2.73 Å in some Li_2RuO_3 single-crystals reported by Wang et al.¹⁵ Note that Miura et al.³⁶ reported a slightly smaller value (2.568 Å) for the short Ru–Ru bond in polycrystalline Li_2RuO_3 . All these values are larger than the bond length (~ 2.50 Å) of the Ru–Ru dimer in the dimerization (and high-energy) configuration of Li_2RuO_3 .

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Given the fact that the dimerization configuration is higher in energy in fully lithiated Li_2RuO_3 , the experimental observation of the Ru–Ru dimerization in some (nominally) fully lithiated Li_2RuO_3 samples reported in the literature could be due to the presence of lithium vacancies caused by lithium loss during the preparation of the material at high temperatures. Indeed, Jimenez-Segura *et al.*¹⁶ reported that the dimer formation is sensitive to the preparation procedure and the amount of the RuO_2 impurity phase is increased after the repeated grinding and heating steps which indicates lithium loss. It is also possible that both the undimerized and dimerized structures can coexist in a Li_2RuO_3 sample.

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In both Li_2MoO_3 and Li_2RuO_3 , we speculate that the dimerization on the transition-metal network may contribute to the amorphization or the high level of disorder observed in the (delithiated) materials during electrochemical cycling.^{1,3,7} Further computational and experimental studies are, however, needed to understand the effects of metal–metal dimerization on the structural stability of the materials during extended cycling as well as on the electrochemical performance in general.

3.2 Electronic structure vis-à-vis delithiation mechanism

In lithium-ion batteries, Li^+ ions and electrons are extracted from the cathode material during charge. This results in the formation of negatively charged lithium vacancies and electron holes in the material.¹³ As discussed in detail in Ref. 13, since the electron holes are introduced at the valence-band maximum (VBM), the electronic structure of the material at the VBM determines the nature of the holes and hence the nature of the oxidation reaction. In the following, we will therefore focus on the electronic structure near the band edges.

Figures 3(a) and 3(b) show the electronic density of states (DOS) of Li_2MoO_3 in the AF and FM spin configurations. The band gap is calculated to be 1.58 eV (AF) or 1.12 eV (FM) within the HSE functional ($\alpha = 0.25$); the gaps are direct in both cases. The electronic structure near the band-gap region are predominantly composed of the Mo 4*d* states. In the AF spin configuration, for example, one Mo atom in Li_2MoO_3 contributes 62% to the electronic states at the VBM, whereas each O atom contributes only about 2%–8%. Given the feature of the electronic structure of Li_2MoO_3 , oxidation is expected to occur on the transition metal in the material upon delithiation. Indeed, our explicit calculations show that, upon removal of a lithium, one of the Mo ions (effectively Mo^{5+} ions due to Mo–Mo dimerization; see Sec. 3.1) is oxidized to one with a local magnetic moment of $\sim 0\mu_{\text{B}}$, which can be identified as effectively Mo^{6+} . Our results are thus consistent with the oxidation to Mo^{6+} observed in experiments.²

Partially Mn-substituted $\text{Li}_2\text{Mo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ is created by replacing one of the two Mo atoms in the unit cell with Mn. In this mixed-metal compound, Mn is found to be stable as high-spin Mn^{3+} (3*d*⁴) and Mo as Mo^{5+} (4*d*¹). The change in the charge states of the transition metal ions due to the Mn–Mo interaction is consistent with that previously observed in Mo-doped Li_2MnO_3 .³⁷ The electronic structure reported in Fig. 3(c) indicates that the highest valence band is predominantly the Mo 4*d* states whereas the lower valence band is predominantly the Mn 3*d* states. We find that, upon lithium removal, Mo^{5+} is oxidized to Mo^{6+} before Mn^{3+} is oxidized to Mn^{4+} , consistent with the arrangement of the Mo^{5+} 4*d* and Mn^{3+} 3*d* bands in the energy spectrum. Note that this arrangement and hence the order in which the redox couples are activated may be dependent on the doping level or, more specifically, the feature of the valence-band top of a specific chemical composition and its atomic arrangement.

Figures 3(d) show the DOS of Li_2RuO_3 . In this ruthenate, Ru is stable as low-spin Ru^{4+} (4*d*⁴). The calculated band gap is 1.27 eV (indirect) within HSE ($\alpha = 0.25$), which appears to be consistent with the “semiconducting” behavior reported by Kobayashi *et al.*³⁸ The electronic structure near the band gap region is predominantly the Ru $t_{2g}^4 e_g^0$ states (Note that in an octahedral lattice environment, the five transition-metal *d*-states are split into a lower triplet t_{2g} and an upper doublet e_g). Each Ru atom in the cell contributes 40% to the electronic states at the VBM whereas there is only up to 4% from each O atom. Upon removal of a lithium, two Ru ions in the vicinity of the void left by the removed Li^+ ion move closer to each other and form a Ru–Ru dimer with the Ru–Ru bond length of 2.75 Å; see Fig. 4. The two Ru ions in the dimer have a calculated magnetic moment of $1.84\mu_{\text{B}}$, compared to about $1.6\mu_{\text{B}}$ of the other Ru (i.e., Ru^{4+}) ions. The value is smaller than that

expected of Ru^{5+} with three unpaired electrons. This, again, shows that dimerization leads to reduced local magnetic moments; see Sec. 3.1 for the case of Li_2MoO_3 .

Figures 3(e) and 3(f) show the electronic structure of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ and $\text{Li}_2\text{Ru}_{0.5}\text{Ti}_{0.5}\text{O}_3$. In the partially Mn-substituted compound, Mn is stable as Mn^{4+} ($3d^3$). The Mn $3d$ states are high up in the conduction band, whereas the top of the valence band is predominantly the Ru $4d$ states. The Mn ion is thus electrochemically inactive in $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$, similar to that in Li_2MnO_3 .²⁴ In the partially Ti-substituted compound, Ti is stable as Ti^{4+} ($3d^0$) and the Ti $3d$ states are also high up in the conduction band. The electronic structure of $\text{Li}_2\text{Ru}_{0.5}\text{Sn}_{0.5}\text{O}_3$ (not shown in the figure) is very similar to that of $\text{Li}_2\text{Ru}_{0.5}\text{Sn}_{0.5}\text{O}_3$. As far as the delithiation mechanism is concerned, these partially Mn-, Ti-, and Sn-substituted compounds are similar to the parent compound Li_2RuO_3 in which Ru is the electrochemically active center, at least in the early stages of delithiation.

Figure 5(a) shows the electronic structure of Li_3RuO_4 . In this compound, Ru is stable as Ru^{5+} ($4d^3$) with a calculated magnetic moment of $2.08 \mu_B$. The calculated band gap is 2.11 eV, an indirect gap. The electronic structure near the band-gap region is predominantly composed of the $\text{Ru } t_{2g}^4 e_g^0$ states. Each Ru atom in the primitive contributes about 23% to the states at the VBM, where each O atom only contributes about 5–8%. We find that, upon delithiation, oxidation occurs mainly on the Ru ion with Ru^{5+} oxidized to what can be identified as Ru^{6+} ($4d^2$) with a calculated magnetic moment of $\sim 1.4 \mu_B$, which is consistent with the fact that the highest occupied states in the electronic structure of Li_3RuO_4 are predominantly composed of the Ru $4d$ states.

The electronic structure of Li_3NbO_4 , on the other hand, is characterized by having predominantly the O $2p$ states at the valence-band top and the Nb $4d$ states at the conduction-band bottom; see Fig. 5(b). The calculated band gap is 5.39 eV (direct). Upon delithiation, oxidation occurs on oxygen, turning O^{2-} in Li_3NbO_4 into O^- (i.e., a localized hole on oxygen). The delithiation mechanism in this Li-rich oxide thus involves anionic redox.

Figures 5(c) and 5(d) shows the electronic structure of the partially Nb- and Mo-substituted compounds. In $\text{Li}_3\text{Ru}_{0.5}\text{Nb}_{0.5}\text{O}_4$, Nb is stable as Nb^{5+} ($4d^0$). The electronic structure near the band gap region is predominantly Ru $4d$ states; the Nb $4d$ states are high up in the conduction band. Upon delithiation, oxidation will therefore occur on Ru whereas Nb is electrochemically inactive. In $\text{Li}_3\text{Ru}_{0.5}\text{Mo}_{0.5}\text{O}_4$, Ru and Mo are stable as Ru^{4+} ($4d^4$) and Mo^{6+} ($4d^0$), respectively. There is thus charge transfer between the two transition-metal ions. The Mo $4d$ states are in the conduction band, whereas the top of the valence band is predominantly composed of the Ru $4d$ states. Upon lithium removal, Ru^{4+} is oxidized to Ru^{5+} during the early stages of delithiation.

Figures 6(a) and 6(b) show the electronic structure of Li_5FeO_4 and Li_5MnO_4 . In these compounds, the transition metal is tetrahedrally coordinated with oxygen with the five transition-metal d -states split into a lower doublet e and an upper triplet t_2 . Iron in Li_5FeO_4 is stable as high-spin Fe^{3+} ($3d^5$) with a calculated magnetic moment of $4.04 \mu_B$. The calculated band gap is 4.41 eV (direct). The electronic structure near the band gap region is

composed of the Fe $e^2t_2^3$ and O $2p$ states. A detailed analysis shows that each Fe atom contributes 3.3% to the electronic states at the VBM, whereas each O atom contributes about 2.1–2.5%. In Li_5MnO_4 , Mn is stable as Mn^{3+} ($3d^4$) with a calculated magnetic moment of $3.62\mu_B$. The electronic structure near the band gap region is composed of the Mn $e^2t_2^2$ and O $2p$ states and the calculated band gap is 2.25 eV (direct). Each Mn atom contributes 5.3% to the electronic states at the VBM, whereas each O atom contributes 1.1–2.1%. In both compounds, the first stage of delithiation (i.e., the removal of the first lithium from the unit cell) is associated with the oxidation of Fe^{3+} (Mn^{3+}) to Fe^{4+} (Mn^{4+}). Later stages are expected to involve oxidation of both the transition metal and oxygen. It has been reported that both cationic and anionic redox occur in Li_5FeO_4 .⁶

4 Conclusions

We have carried out a hybrid density-functional study of the atomic and electronic structure of select lithium-rich complex oxide battery electrode materials. Dimerization of the Mo ions is observed in layered Li_2MoO_3 , even in the fully lithiated compound. In layered Li_2RuO_3 , Ru–Ru dimerization occurs only upon lithium removal or when the material is Li-deficient, in contrast to what is commonly believed that the dimerization occurs in the fully lithiated compound. There is a reduction in the local magnetic moments associated with the dimerization. In light of the calculated electronic structure, we have discussed the delithiation mechanism during the initial stages of lithium extraction in Li_2MoO_3 , Li_2RuO_3 , Li_3RuO_4 , Li_3NbO_4 , Li_5FeO_4 , Li_5MnO_4 and their derivatives. Our work forms a basis for further theoretical and experimental analysis and ultimately for understanding the properties of the lithium-rich complex oxides.

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Figure 1:
Atomic structure of select Li-rich complex oxides: (a) Li_2RuO_3 (monoclinic, $C2/m$), (b) Li_3RuO_4 (monoclinic, $P2/a$), and (c) Li_5FeO_4 (orthorhombic, $Pbca$). Large (gray) spheres are Li , medium (blue) are Ru or Fe , and small (red) are O .

Figure 2: Total-energy difference between the dimerization and non-dimerization configurations of fully lithiated Li_2RuO_3 , obtained in PBE+ U and HSE calculations with different U and α values. Negative values mean the non-dimerization configuration is lower in energy than the dimerization one. The dashed lines are just to guide the eyes.

Figure 3:

Total and projected electronic density of states of (a) antiferromagnetic and (b) ferromagnetic Li_2MoO_3 , (c) $\text{Li}_2\text{Mo}_{0.5}\text{Mn}_{0.5}\text{O}_3$, (d) Li_2RuO_3 , (e) $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$, and (f) $\text{Li}_2\text{Ru}_{0.5}\text{Ti}_{0.5}\text{O}_3$ with the majority (minority) spin channel plotted separately on the positive (negative) y -axis. The zero of energy is set to the highest occupied states.

Figure 4:

The removal of a lithium from the Li_2RuO_3 supercell results in a negatively charged lithium vacancy (i.e., a void formed by the removal of a Li^+ ion, in the Li layer behind the dimer; not shown in the figure), a Ru-Ru dimer, and an electron hole localized on the dimer. The iso-value for the charge-density isosurface (yellow) is set to $0.05 \text{ e}/\text{\AA}^3$. Large (gray) spheres are Li, medium (blue) are Ru, and small (red) are O; for clarity, not all the atoms in the supercell are shown.

Figure 5:

Total and projected electronic density of states of (a) Li_3RuO_4 , (b) Li_3NbO_4 , (c) $\text{Li}_3\text{Ru}_{0.5}\text{Nb}_{0.5}\text{O}_4$, and (d) $\text{Li}_3\text{Ru}_{0.5}\text{Mo}_{0.5}\text{O}_4$ with the majority (minority) spin channel plotted on the positive (negative) y -axis. The zero of energy is set to the highest occupied states.

Figure 6:

Total and projected electronic density of states (DOS) of (a) Li_5FeO_4 and (b) Li_5MnO_4 with the majority (minority) spin channel plotted on the positive (negative) y -axis. The zero of energy is set to the highest occupied states.

Table 1:

Lattice parameters and band gaps (E_g) of Li-rich complex oxides, obtained in HSE calculations

			Calculated	Experimental	E_g
Li ₂ MoO ₃	<i>P1</i>	AF	$a = 4.972 \text{ \AA}, b = 4.960 \text{ \AA}, c = 5.224 \text{ \AA}, \alpha = 98.24^\circ, \beta = 108.58^\circ, \gamma = 62.80^\circ$		1.58 eV
		FM	$a = 4.998 \text{ \AA}, b = 4.994 \text{ \AA}, c = 5.227 \text{ \AA}, \alpha = 98.18^\circ, \beta = 108.63^\circ, \gamma = 62.33^\circ$		1.12 eV
Li ₂ RuO ₃	<i>C2/m</i>	FM	$a = 5.105 \text{ \AA}, b = 8.901 \text{ \AA}, c = 5.095 \text{ \AA}, \beta = 109.12^\circ$	$a = 5.021 \text{ \AA}, b = 8.755 \text{ \AA}, c = 5.119 \text{ \AA}, \beta = 108.95^\circ$ (Ref. 15)	1.27 eV
Li ₃ RuO ₄	<i>P2/a</i>	FM	$a = 5.077 \text{ \AA}, b = 5.857 \text{ \AA}, c = 5.121 \text{ \AA}, \beta = 110.29^\circ$	$a = 5.085 \text{ \AA}, b = 5.872 \text{ \AA}, c = 5.125 \text{ \AA}, \beta = 110.21^\circ$ (Ref. 5)	2.11 eV
Li ₃ NbO ₄	<i>$\bar{4}3m$</i>	FM	$a = b = c = 8.435 \text{ \AA}$	$a = b = c = 8.442 \text{ \AA}$ (Ref. 5)	5.39 eV
Li ₅ FeO ₄	<i>Pbca</i>	FM	$a = 9.173 \text{ \AA}, b = 9.153 \text{ \AA}, c = 9.114 \text{ \AA}$	$a = 9.218 \text{ \AA}, b = 9.213 \text{ \AA}, c = 9.159 \text{ \AA}$ (Ref. 31)	4.41 eV
Li ₅ MnO ₄	<i>Pbca</i>	FM	$a = 8.686 \text{ \AA}, b = 9.348 \text{ \AA}, c = 9.322 \text{ \AA}$		2.25 eV