Spinel compounds as multivalent battery cathodes: a systematic evaluation based on \textit{ab initio} calculations\textsuperscript{†}

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Batteries that shuttle multivalent ions such as Mg\({^{2+}\text{ and Ca}^{2+}\text{ ions are promising candidates for achieving higher energy density than available with current Li-ion technology. Finding electrode materials that reversibly store and release these multivalent cations is considered a major challenge for enabling such multivalent battery technology. In this paper, we use recent advances in high-throughput first-principles calculations to systematically evaluate the performance of compounds with the spinel structure as multivalent intercalation cathode materials, spanning a matrix of five different intercalating ions and seven transition metal redox active cations.

We estimate the insertion voltage, capacity, thermodynamic stability of charged and discharged states, as well as the intercalating ion mobility and use these properties to evaluate promising directions. Our calculations indicate that the Mn\(_2\)O\(_4\) spinel phase based on Mg and Ca are feasible cathode materials. In general, we find that multivalent cathodes exhibit lower voltages compared to Li cathodes; the voltages of Ca spinels are \(~0.2\text{ V}\) higher than those of Mg compounds (versus their corresponding metals), and the voltages of Mg compounds are \(~1.4\text{ V}\) higher than Zn compounds; consequently, Ca and Mg spinels exhibit the highest energy densities amongst all the multivalent cation species. The activation barrier for the Al\(^{3+}\) ion migration in the Mn\(_2\)O\(_4\) spinel is very high (\(~1400\text{ meV}\) for Al\(^{3+}\) in the dilute limit); thus, the use of an Al based Mn spinel intercalation cathode is unlikely. Amongst the choice of transition metals, Mn-based spinel structures rank highest when balancing all the considered properties.

Broader context

The high price and limited volumetric capacity of the lithium ion battery (LIB) challenges its application in electric vehicles and portable electronics. Multivalent batteries, such as those utilizing Mg\(^{2+}\) or Ca\(^{2+}\) as the working ions, are promising candidates for beyond LIB technology due to the increase in volumetric capacity and reduced cost. In the present work, we use first-principles calculations to systematically evaluate the theoretical performance of the spinel structure host with the general formula AB\(_2\)O\(_4\) across a matrix of chemical compositions spanning A = \{Al, Y, Mg, Ca, Zn\} and B = \{Ti, V, Cr, Mn, Fe, Co, Ni\} for multivalent battery applications. The evaluation incorporates screening on voltage, capacity, thermodynamic structural and thermal stability as well as ion mobility and discusses the results in the context of available host structure sites, preference of the intercalating cation, and the oxidation state of the redox-active cation. Overall, the Mn\(_2\)O\(_4\) spinel phases paired with Mg\(^{2+}\) or Ca\(^{2+}\) emerge as the most promising multivalent cathode materials. As the first comprehensive screening of multivalent intercalation compounds across size, valence, and redox-states of the involved cations, our work is intended to provide guidance for future theoretical as well as experimental multivalent cathode development and design.

Introduction

To support the rapidly growing energy storage demands of future technologies such as electric vehicles, improved battery technologies are needed. Lithium (Li) ion batteries with good energy density, rechargeability and cycle life\textsuperscript{3} have been used to advance portable consumer electronics and recently, electric vehicles. However, further advancement of Li ion technology faces limits on the energy density of electrode materials,\textsuperscript{2,3} safety, and high cost. A multivalent battery technology, where an intercalation cathode host is paired with a metal anode, has the potential to store energy at significantly lower cost and volume.\textsuperscript{4,5} For example, Mg metal has much higher volumetric capacity (3833 mA h cm\(^{-3}\)) than graphite (\(~800\text{ mA h cm}^{-3}\))\textsuperscript{6} or even lithium metal (2046 mA h cm\(^{-3}\)). Furthermore, as many known intercalation hosts are limited by the available cation
insertion sites rather than by redox capability, one can expect improvements using multivalent intercalation on the cathode side. For instance, Mg$^{2+}$ carries two charges per ion while maintaining an ionic radius as small as that of a Li$^+$ ion, hence the charge storage capability is doubled at the same cation volumetric concentration. In addition, the natural abundance of multivalent elements, such as Mg and Ca, is significantly higher than that of Li (the atomic abundance of Mg is $\sim 10^4$ times larger than Li in the earth crust), which may decrease the cost of materials and guarantee supply even for multi-fold increases in the size of the energy storage market.

To date, there have been limited examples demonstrating the feasibility of rechargeable multivalent batteries, and among them, the focus has been on Mg technology. In the seminal work of Aurbach et al., it was demonstrated that Mg$^{2+}$ can intercalate into the Chevrel phase Mo$_6$S$_8$ at a potential of $\sim 1.0–1.3$ V and a maximum charge capacity of 135 mA h g$^{-1}$ for several hundreds of cycles.$^{6,8}$ Other materials have shown initial promise for multi-valent intercalation, such as layered V$_2$O$_5$ where Mg$^{2+}$ is inserted into the V$_2$O$_5$ inner layer spacing.$^{10,11}$ Ca$^{2+}$ has also been shown to intercalate into V$_2$O$_5$, supplying a voltage of $\sim 3.0$ V and an initial capacity of $\sim 450$ mA h g$^{-1}$. Other materials claimed to accommodate Mg$^{2+}$ insertion include MoO$_3$,$^{12–15}$ TiS$_2$ in both the cubic phase and layered phases,$^{16}$ NbS$_3$,$^{17}$ graphitic fluoride,$^{18}$ and CoSiO$_4$. However, due to limited Mg mobility in the host and possibly concurrent water and/or proton insertion, the cycling stability of these materials has so far been insufficient, resulting in rapid decomposition of the host material.$^{20,21}$

From the limited experimental studies performed to date, the feasibility of a battery technology based on multivalent intercalation is not yet clear. As the cathode will be a critical component of such a technology, it is important to assess the feasibility of multivalent insertion cathodes. In this work, we present a systematic computational study of multivalent intercalation within a fixed spinel-based host structure, using a set of seven redox-active cations and spanning size and valence differences between a set of intercalating $\{\text{Ca, Zn, Mg, Al and Y}\}$ cations to establish design trends and guidelines for future experimental work.

The spinel (prototype MgAl$_2$O$_4$, space group $Fd3m$) structure provides an excellent candidate for this study, encompassing a family of materials with the general formula AB$_2$O$_4$. The A and B ions are tetrahedrally and octahedrally coordinated by oxygen, respectively (Fig. 1). The B octahedrons form a network with percolating empty sites interconnecting in three directions. Spinel LiMn$_2$O$_4$ was first prepared by Thackeray et al.$^{22}$ and exhibits excellent performance as a cathode for Li intercalation with a voltage of 3–4 V versus Li metal.$^{23}$ The properties of the spinel structure are tunable, for example it has been observed that partially replacing Mn with Ni increases the voltage to 4.7 V,$^{24,25}$ and mixing Mn with Co and/or Cr increases the voltage even higher to $\sim 5$ V.$^{25,27}$

Experiment shows that spinel LiMn$_2$O$_4$ can be electrochemically converted to MgMn$_2$O$_4$ in aqueous Mg(NO$_3$)$_2$ electrolyte, and exhibits Mg$^{2+}$ reversible intercalation/deintercalation.$^{28}$ Spinel ZnMn$_2$O$_4$ has also demonstrated Zn$^{2+}$ insertion/deinsertion, providing a capacity of 210 mA h g$^{-1}$ for 50 cycles.$^{29}$ Recently, it was shown that Mg$^{2+}$ can intercalate/deintercalate into spinel-type Mn$_2$O$_4$ with a retained capacity of 155.6 mA h g$^{-1}$ after 300 cycles in 1 mol dm$^{-3}$ MgCl$_2$ aqueous electrolyte,$^{30}$ suggesting that further development could lead to a viable cathode with good energy density. Against this background it is intriguing to broadly consider a multivalent spinel cathode with possible intercalating cations $A = \{\text{Mg, Ca, Zn, Al, Y}\}$ that could theoretically produce a higher capacity than its Li counterpart due to the greater charge carried by each ion. Hence, in this paper, our aim is to evaluate the cathode performance of spinel phases for multivalent intercalation; we computationally evaluate the feasibility of a matrix of spinel compounds with different redox ion species and intercalating cation species. The redox ion was selected from the set $\{\text{Ti, V, Cr, Mn, Fe, Co, Ni}\}$, and the intercalating cation was selected from the set $\{\text{Mg, Ca, Zn, Al, Y}\}$. By substituting the cations in the A and B sites, respectively, we created 35 charged/discharged topotactic pairs and performed first-principles density functional theory (DFT) calculations for each of these pairs. We evaluate cathode performance through such quantities as the capacity, average voltage, energy density, and intercalating cation mobility. We also evaluate the thermodynamic structural and thermal stability. The detailed methodology can be found in previous literature.$^{31}$

**Methods**

We use the Vienna *ab initio* software package (VASP)$^{32}$ to perform the density functional theory calculations, with the projector augmented-wave method$^{33}$ to describe the ion–electron interactions and the generalized gradient approximation (GGA)$^{34}$ within the Perdew–Burke–Ernzerhof (PBE) framework$^{35}$ as the exchange–correlation functional. The calculation parameters are the same as those adopted by the Materials Project$^{36}$ and as implemented in the pymatgen software.
package, which have been previously tested to be appropriate to study Li-intercalation cathode materials. In the calculations, the \( U-J \) parameters to correct for non-cancellation of the self-interaction error in the d orbitals of the redox active species are set to \( U_C = 3.25 \) eV, \( U_{\text{Mn}} = 3.7 \) eV, \( U_{\text{Mn}} = 3.9 \) eV, \( U_E = 5.3 \) eV, \( U_{\text{Co}} = 3.32 \) eV, and \( U_{\text{Ni}} = 6.45 \) eV. The primitive spinel unit cell as illustrated in Fig. 1 is used for voltage and stability calculations. Brillouin zone sampling is performed on a \( 5 \times 5 \times 5 \) grid in \( k \)-space. Throughout this work, the cell shape, volume and atomic positions are relaxed, unless otherwise stated. All magnetic ions are initialized ferromagnetically.

All calculations in this paper assume that the transition metal host framework \('\text{B}_2\text{O}_4'\) remains structurally invariant during the operation of the battery (i.e., during intercalation and de-intercalation of ‘A’ cations). Additionally, we assume that the host can be synthesized with little/no disorder and remains that way during the operation of the cell. We acknowledge that spinels are well known to show varying degrees of cation disorder that may impact important material properties relevant for battery operation such as the activation energies and voltages reported herein. However, in the interest of providing a preliminary view of what is possible in multivalent systems, we have simplified our calculations and analysis.

The voltages of the compounds can be obtained from the difference in the total energy between the charged and discharged phases following Aydinol et al. The average voltage can be calculated as \( V = \Delta E/n_z \), where \( \Delta E = (E_{\text{charge}} + E_{\text{discharge}}) \) denotes the total energy change in the reaction, \( E_{\text{charge}} \) and \( E_{\text{discharge}} \) are the energy of the charged and discharged compounds respectively; \( E_{\text{M}} \) is the energy of multivalent intercalating species in metal form; \( n_z \) is the number of intercalating atoms participating in the reaction; and \( z \) represents the oxidation state of the intercalant. We adopt the units of eV and e for \( \Delta E \) and \( n_z \), respectively, so that no normalization factor (i.e., Faraday’s constant) needs to be introduced into the equation. We estimate the thermodynamic stability of the phases by the energy above the convex hull of stable phases, which is the energy released by decomposing the compound to the most stable combination of compounds at the same overall composition. The energy above the hull is always a non-negative number with the unit of eV per atom. The detailed procedure for the computation of the energy above the hull can be found in previous literature. As explained later in this paper, the thermal stability was determined by evaluating the critical chemical potential at which \( \text{O}_2 \) gas becomes favorable according to the methodology presented in Ong et al. Since the entropy of a reaction is dominated by the gas entropy and the entropy of the solid phase at room temperature, for the any reactions containing molecular \( \text{O}_2 \), we use the corrected \( \text{O}_2 \) chemical potential to include the well-known \( \text{O}_2 \) DFT calculation error as well as the \( \Delta \text{AV} \) contribution to the oxygen enthalpy by comparing with the experimental thermodynamic data for \( \text{O}_2 \) at 0.1 MPa at 298 K throughout the paper. For the thermal stability calculation, the temperature effect has been taken into account by adjusting the entropy term \( -T \Delta S \) of the \( \text{O}_2 \) chemical potential at given temperature. A more detailed description can be found in the ESI.

The calculations were automatically executed and analyzed using the FireWorks software package. In this work, hundreds of DFT calculations are performed across 70 compounds to generate the thermodynamic stability and thermal stability data.

Activation barriers were calculated with the nudged elastic band (NEB) method using the GGA-PBE functional. A \( U \) term was not included in these calculations as NEB is difficult to converge with GGA+U due to pronounced metastability of electronic states along the ion migration path. Furthermore, while GGA+U clearly improves the accuracy of redox reactions, there is no conclusive evidence that GGA+U performs better in predicting cation migration. The minimum energy paths (MEP) in the NEB procedure were initialized by linear interpolation of 8 images between the two fully relaxed end-point geometries, and each image is converged to \( <1 \times 10^{-3} \) eV per super cell. The MEPs were obtained in both the high vacancy limit and dilute vacancy limit, i.e. one mobile species per unit cell or one vacancy per unit cell. To ensure that fictitious interactions between the diffusing species are removed, a \( 2 \times 2 \times 2 \) supercell of the primitive cell was used, for which the inter-image distance is never less than 8 Å.

**Results and discussion**

The average intercalation voltage was calculated from the reaction energy \( \text{B}_2\text{O}_4 + A \rightarrow \text{AB}_2\text{O}_4 \) for the matrix of intercalating \( A = \{\text{Mg, Ca, Zn, Y, Al}\} \) ions and redox active transition \( B = \{\text{Ti, V, Mn, Fe, Co, Ni}\} \) metal cations. Fig. 2 shows the resulting voltage vs. the gravimetric capacity, where the color and shape of a data point indicate the intercalating ion, and the redox-active transition metal is given next to each data point. Voltages are referenced to the bulk metal of the intercalating ion, e.g., Mg metal for MgMn2O4 and Zn metal for ZnMn2O4.

As expected from the electrochemical series, and evidenced in Fig. 2, multivalent compounds have lower voltages than Li
cathodes. The Li spinel usually exhibits a voltage between 4 and 5 V,\textsuperscript{23,26,51} whereas we find that for multivalent spinel cathodes, the voltage is always less than 4 V versus the corresponding metal. Most Mg and Ca intercalation voltages vary between 2 and 4 V, which is lower than the values for Li (e.g., calculated voltage of LiMn\textsubscript{2}O\textsubscript{4} is \(\sim 0.7\) V higher than CaMn\textsubscript{2}O\textsubscript{4}).\textsuperscript{23,54} However, considering the additional charge carried by multivalent cations, a multivalent spinel cathode can still exhibit a significantly higher energy density than the corresponding Li version. For example, the gravimetric capacity of LiMn\textsubscript{2}O\textsubscript{4} is 143 mAh g\textsuperscript{–1},\textsuperscript{22,26} whereas the gravimetric capacity of MgMn\textsubscript{2}O\textsubscript{4} is almost double \(\sim 270\) mAh g\textsuperscript{–1}, which more than makes up for the slightly lower voltage. Hence, of the considered intercalating ions, Al, Y, Ca and Mg are all viable candidates from the perspective of energy density. However, the voltage of the Zn spinel compounds ranges between 1.3 V and 2.5 V, which even in the best case scenario amounts to approximately 600 W h kg\textsuperscript{–1}, about equal to the specific energy of LiFePO\textsubscript{4}.\textsuperscript{36,41}

The voltage for each multivalent intercalant is plotted as a function of the active redox metal in Fig. 3(a): the bi-valent ions Ca, Mg, and Zn follow a common trend as the redox couple is varied, different from the voltage trend of the tri-valent intercalants Al and Y. The difference originates largely from the different valence state of the transition metal in the discharged state. Insertion of the bi-valent cations induces a change in redox state from 4+ to 3+, whereas the tri-valent cation corresponds to a redox change from 4+ to 2.5+ for insertion into AB\textsubscript{2}O\textsubscript{4}.

In general, the Ca spinel has the highest voltage, followed by the Mg spinel compounds, Y compounds, Al compounds, and Zn compounds, in that order. For all the redox active cations \{B = Ti, V, Cr, Mn and Ni\} the voltage of the Mg compounds is lower than that of the Ca compounds by \(\sim 0.2\) V, and the voltages of Mg compounds are \(\sim 0.4\) V higher than Zn compounds. The three bi-valent intercalants show the same trend of voltage versus redox active metal: Ti\textsubscript{2}O\textsubscript{4} always has the lowest voltage among the transition metals considered. V\textsubscript{2}O\textsubscript{4} is the second lowest one but \(\sim 1.2\) V higher than Ti\textsubscript{2}O\textsubscript{4}. Mn\textsubscript{2}O\textsubscript{4} is \(\sim 0.3\) V higher than V\textsubscript{2}O\textsubscript{4}. Co\textsubscript{2}O\textsubscript{4} is \(\sim 0.6\) V higher than Mn\textsubscript{2}O\textsubscript{4}, and Ni\textsubscript{2}O\textsubscript{4} is slightly higher than Co\textsubscript{2}O\textsubscript{4} by \(\sim 0.1\) V. The Cr\textsubscript{2}O\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{4} spinels have the highest voltage, respectively \(\sim 0.6\) V and \(\sim 0.9\) V higher than Mn\textsubscript{2}O\textsubscript{4}. Bhattacharya et al.\textsuperscript{54} found a similar trend for the Li insertion voltage in spinels.\textsuperscript{54} We find that Li insertion\textsuperscript{55} occurs on average at about \(\sim 0.7\) V higher voltage than Ca insertion and \(\sim 0.9\) V higher than Mg insertion. Comparing this with the aqueous electrochemical series (\(E_{\text{Cu}}^0 = -3.04, E_{\text{Cu}_2O}^0 = -2.86, E_{\text{Mg}}^0 = -2.37, E_{\text{Zn}}^0 = -0.76\)) we find that the voltages are ordered according to the electrochemical series of the intercalating metal ion. However, while the voltage shift between Li and Mg is close to what is expected, the voltage reduction in moving from Li to Ca in the solid state is considerably larger than expected from the electrochemical series. This is likely due to the fact that the intercalant enters a tetrahedral site in the spinel, which for Ca is not nearly as favorable as for Mg and Li, and thus reduces the Ca intercalation voltage from what one would expect from the electrochemical series. Experimentally, Li has indeed been found to exhibit a higher voltage than Mg. In the Chevrel phase Mo\textsubscript{6}S\textsubscript{8}, the voltage difference between Li and Mg insertion is \(\sim 1.0–1.2\) V.\textsuperscript{57,58} For V\textsubscript{2}O\textsubscript{5}, the Li voltage is usually \(\sim 0.2\) V higher than that of Mg.\textsuperscript{57–59}

Because the data in Fig. 3(a) for trivalent cations averages the voltage over both the 3+/2.5+ and 4+/3+ redox couples, the intermediate 3+ states of the transition metals were calculated for the trivalent intercalants to investigate the impact of different redox states. Fig. 3(b) and (c) show the calculated voltage of the different redox pairs for the Al and Y spinel compounds, respectively. As expected, the 3+/2.5+ redox pairs exhibit a lower voltage compared to the 4+/3+ reactions, in good agreement with existing literature.\textsuperscript{2} In particular, when restricting focus to the 4+/3+ redox reaction, the Al and Y spinel compounds follow largely the same trend as Ca, Mg and Zn as shown in Fig. 3(a).

The capacity of cathode materials is important as it strongly influences the overall energy density of a cell. Fig. 4(a) shows the volumetric capacity of each AB\textsubscript{2}O\textsubscript{4} spinel as a function of the redox-active species and intercalating cation. The volumetric capacity of all the cathodes is higher than that of a Li spinel.
cathode at the same cation concentration due to the extra charge carried by each of the multivalent intercalants. Not surprisingly, Al$^{3+}$ leads to the highest capacity density, while Ca$^{2+}$ has the lowest. For a fixed valence of the intercalant, the volumetric capacity follows the ionic size of the intercalating cation. Hence, the volumetric capacities of Al$^{3+}$ compounds are higher than Y$^{3+}$ compounds by approximately 300 A h L$^{-1}$. For bi-valent cations, the capacities of Mg and Zn compounds are almost the same, consistent with the similar ionic size of Mg$^{2+}$ or Zn$^{2+}$.

Fig. 4(b) presents the volume expansion associated with the intercalation of each multivalent ion as a function of the redox-active cation, assuming intercalation to composition AB$_2$O$_4$.

The calculated (a) volumetric multivalent capacity and (b) volume change of the spinel structure as a function of the redox-active cation, assuming intercalation to composition AB$_2$O$_4$.

For Mg, Zn and Al insertion, the magnitude of the volume change normalized by the capacity is very similar to the volume changes observed for Li insertion compounds, and hence is not likely to lead to any practical design problems. For Ca and Y the volume change is larger – up to 30% increase in some cases.

The thermodynamic stabilities of the charged and discharged state are important considerations for possible cathode materials, as they may influence the cycle life as well as the synthesizability of the compounds. Thermodynamic stability can be measured by the driving force for a compound to separate into its most stable combination of compounds. From first principles, this is determined by comparing the energy of the compound with the convex energy hull of all ground states in the relevant phase diagram (see the ESI† for a detailed explanation). Fig. 5(a) and (b) provide this energy above the hull of each compound. The ground state hulls were determined from all the calculated compounds in the Materials Project database. A smaller energy above the hull implies that the material has a greater chance of being stable, e.g. at synthesis and upon cycling.

The Mg and Zn spinel phases (except ZnTi$_2$O$_4$) are all quite stable, exhibiting an energy above hull less than 0.011 eV per
atom. Such a small value of the decomposition energy falls well within the accuracy of our calculations\(^5\) or within relative changes between competing phases due to finite temperature effects. The Ca spinel structures are more thermodynamically unstable compared to the equivalent Mg and Zn compounds. This is consistent with Ca\(^{2+}\) normally preferring coordination

\[2\] conclude that MgMn\(_2\)O\(_4\), CaMn\(_2\)O\(_4\) and ZnMn\(_2\)O\(_4\) provide the

ered by the interaction with other cations. In terms of phase

\[3\] indicates that Fe\(_2\)O\(_4\) and Ni\(_2\)O\(_4\) are highly oxidizing, and are

tion temperatures should only be used to rank compounds

\[4\] temperature slightly above 100

\[5\] The calculated thermodynamic O\(_2\) evolution diagram of

charged host spinel compounds as a function of temperature. The vertical axis denotes how much O\(_2\) is predicted to be released from the compound per formula unit of B\(_2\)O\(_4\) as the material decomposes.

Fig. 6 The calculated thermodynamic O\(_2\) evolution diagram of charged host spinel compounds as a function of temperature. The vertical axis denotes how much O\(_2\) is predicted to be released from the compound per formula unit of B\(_2\)O\(_4\) as the material decomposes.
Li-rich limit (from \( \sim 600 \text{ meV} \) for Li migration in Ti\(_2\)O\(_4\) to \( \sim 300 \text{ meV} \) for vacancy migration in LiTi\(_2\)O\(_4\)),\(^{45}\) From kinetic Monte Carlo simulations, the room temperature self-diffusivity of Li was shown to span \( \sim 10^{-10} \) to \( 10^{-5} \text{ cm}^2 \text{ s}^{-1} \) between Li\(_{1-x}\)Ti\(_2\)O\(_4\) and LiTi\(_2\)O\(_4\), in good agreement with the excellent experimental rate-capability typically observed in Li spinel cathodes. Except in Mn\(_2\)O\(_4\), we could not converge the NEB for Al\(^{3+}\) due to the very large forces along the transition path, which is usually symptomatic of a very high barrier. The divalent barriers vary significantly with the chemical nature of the intercalant: Zn\(^{2+}\) (\( \sim 800-1000 \text{ meV} \)), Mg\(^{2+}\) (\( \sim 600-800 \text{ meV} \)), and Ca\(^{2+}\) (\( \sim 200-500 \text{ meV} \)). Although Ca\(^{2+}\) migration appears to be facile in our calculations, only in Mn\(_2\)O\(_4\) does Ca\(^{2+}\) prefer to occupy the tetrahedral site as opposed to the octahedral site (which can be observed in Fig. 7 as the energy along the migration path becomes negative when Ca is near the octahedral site in the Ni, Cr, and Co spinel). For this case, the migration barrier should be measured as the energy increase from the octahedral site to the maximum along the path (see Fig. 7). We find that for all fully intercalated phases, the tetrahedral sites are more stable than the octahedral sites, which indicates a cross-over in site preference with concentration for some of the intercalating cations.

**Discussion**

Technical extrapolations of projected multivalent chemistries to the cell level have shown that multivalent intercalation is one of the few technologies that can outperform Li-ion batteries in terms of energy density. In this paper we have used first principles calculations, well established in Li-cathode research,\(^{1,3,4,41,63,66}\) to evaluate the properties of multivalent-ion intercalation in spinel structures with different chemistries. We evaluated average insertion voltage, stability in the charged and discharged state, volume change upon intercalation, oxidation strength of the charged cathode, and the mobility of the multi-

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**Fig. 7** Computed minimum energy paths for migration of different intercalants between the tetrahedral sites in the spinel B\(_2\)O\(_4\) (B = Mn, Co, Ni, Cr) at the high vacancy limit (solid line) and dilute vacancy limit (dotted line), i.e. one mobile specie per supercell (2 \( \times \) 2 \( \times \) 1 of primitive cell).

**Fig. 8** Qualitative summary of multivalent spinel compounds based on multiple performance metrics, such as voltage, specific energy, thermodynamic stability of charged and discharged phases, thermal stability and intercalant mobility. The favorable (unfavorable) properties are represented with light (dark) color.
valent cations. Such first principles screening is important for this new field as multi-valent ion electrochemistry is not well established and, due to incompatibility between electrolytes and electrode materials, it can be difficult to obtain unambiguous experimental results on the performance of a specific cathode material.\textsuperscript{46,67,68} We found that the insertion voltage of Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Zn\textsuperscript{2+}, Al\textsuperscript{3+} and Y\textsuperscript{3+} against their respective metal anodes in general follows the electrochemical series but with quantitative variations due to the nature of the site preference of the intercalating ion. For example, Ca insertion voltages in spinels are lower than expected, as Ca in general prefers higher coordination than tetrahedral (commonly the most favorable site in the spinel structures). The Fe\textsubscript{2}O\textsubscript{4} and Ni\textsubscript{2}O\textsubscript{4} spinels are unlikely to function across the full capacity range due to the highly oxidizing and unstable nature of their fully charged states. As expected, Ti\textsubscript{2}O\textsubscript{4} spinels have low insertion voltage for most intercalants, and in addition, are fairly unstable. The V\textsubscript{2}O\textsubscript{4} and Cr\textsubscript{2}O\textsubscript{4} spinels are also fairly unstable in the charged state, and the V spinel exhibits a low insertion voltage for all intercalants besides Mg and Ca. From the perspective of stability, the most promising spinel chemistry is Mn\textsubscript{2}O\textsubscript{4} as it is stable in the charged state and fairly stable in the discharged state for several intercalating ions. Intercalant mobilities are generally low due to the high activation energies when transitioning between the tetrahedral and octahedral site, though they are clearly not only controlled by charge. For example, among the divalent ions Zn mobility is inferior to Mg, and Ca may have fairly good mobility in the spinel. Al\textsuperscript{3+} intercalation into the spinel structure can likely be excluded from consideration even though it has the peculiar feature that volume changes upon insertion are very small. The activation barrier for motion is very high for Al\textsuperscript{3+} in Mn\textsubscript{2}O\textsubscript{4} and its discharged spinels are all highly unstable. Somewhat surprisingly, and in contrast to experimental claims,\textsuperscript{69} we find that mobility of Zn in the spinel structure is very low, which in addition to its low insertion voltage, should exclude this system from further consideration for high energy density cathodes. The large intercalating ions such as Y\textsuperscript{3+} and Ca\textsuperscript{2+} are interesting, though the Y-spinel becomes unstable in the discharged limit. Both of these ions have reasonable insertion voltages and Ca\textsuperscript{2+} has better than expected migration barriers, due to its relative instability in the tetrahedral site. While this effect lowers the voltage from what would be expected by considering the electrochemical scale, it also seems to lower the migration barrier for motion. This may be similar to the more general principle that high energy defects in materials often have higher mobility.

Considering all computed properties, Mn\textsubscript{2}O\textsubscript{4} spinels are particularly interesting due to their stability (Fig. 8). Among the divalent cations, both Mg\textsuperscript{2+} and Ca\textsuperscript{2+} may potentially be mobile in the spinel structure, warranting further experimental and computational investigation (particularly at small particle sizes). Mixed spinel structures may provide a further promising avenue, as the Ni\textsuperscript{4+}/3+ and Co\textsuperscript{4+}/3+ show higher voltage than the Mn\textsuperscript{4+}/3+ redox couple and compounds such as LiNiMnO\textsubscript{4} are known to combine higher operating voltage with a relatively stable charged state.\textsuperscript{70,71} Improving the diffusivity should be a focus for all multivalent cathode materials.

Finally, a concern with spinels, as with all intercalation materials, is the occurrence of cation disorder. In the extreme case, normal spinels can convert to inverse spinels with part of the transition metals on the tetrahedral site. While in more common layered materials, lowering of the intercalant mobility by cation disorder is well understood through the contraction of the interlayer slab space by disorder,\textsuperscript{68} we are not aware of an equivalent study for spinels. Given the 3D and more rigid nature of the framework and the 3D diffusion network, one would expect spinels to be more tolerant to cation disorder. Nonetheless, we have performed a preliminary investigation into the driving force inverse spinel formation by adopting the same methodology as in Bhattacharya \textit{et al.}\textsuperscript{64} Based on small supercell calculations, we find that the normal spinel is always energetically favorable for Ca, Mg, Zn compounds (See Fig. S2 in the ESI†). Further information can be obtained from the study of Burdett \textit{et al.} who elucidated that cation disorder is strongly correlated to the relative size of the A and B ions.\textsuperscript{76} Hence, Li and Zn prefer to form normal spinels, and we do not expect cation disorder. Ca is large and has the possibility to occupy octahedral sites that forms inverse spinel. Similarly, Mg may show cation site disorder for Ni, Fe, Co when synthesized at high temperature. However, in the case that well ordered spinels cannot be formed at high temperature synthesis conditions, it may be still be possible to create the normal ordered spinel phase by chemical or electrochemical delithiation of the lithium spinels\textsuperscript{78,79} and inserting multivalent cations.

In summary, we have performed systematic calculations to screen for and discover improved multivalent cathode materials using the spinel structure as a general host. On the basis of all property calculations, the spinel Mn\textsubscript{2}O\textsubscript{4} is found to be a superior candidate with Ca\textsuperscript{2+} and possibly Mg\textsuperscript{2+} as mobile cations. It is our hope that our work provides a general guide and standard for future theoretical as well as experimental multivalent cathode development and design.

Acknowledgements

This work was intellectually led and fully supported by of the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the U. S. Department of Energy, Office of Science, Basic Energy Sciences. Work at the Lawrence Berkeley National Laboratory was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, under Contract no. DEAC02-05CH11231. We also thank the National Energy Research Scientific Computing Center (NERSC) for providing computing resources. The Materials Project (BES DOE Grant no. EDCBEE) is acknowledged for infrastructure and algorithmic support.

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