Computational Screening of Oxide Perovskites as Insertion-Type Cathode Material

Johannes Döhn and Axel Groß*

The electrification of the transportation sector exacerbates all issues concerning the use of critical materials in state-of-the-art batteries and, therefore, urges the development of new technologies based on potentially greener and more abundant materials. One research trend is the substitution of Li as shuttle ion with other elements such as Na, K, Mg, Ca, Zn, Al, that is, the so-called post-Li technology. Although significant progress has been achieved in this field recently, these novel battery chemistries are mostly not matured yet. In the present work, the development of new battery materials by screening the materials’ class of oxide perovskites as high-energy insertion-type cathode material is addressed. Based on density functional theory calculations, the specific energy, the energy density, the volume change, and the energy above hull are derived for 280 compounds and appropriate screening criteria are employed. In a second step, the diffusion barriers are determined for the most suitable materials. Eventually, MgNbO₃, ZnVO₃, and AlMoO₃ are suggested as candidate materials for post-Li batteries for further investigation with MgNbO₃ appearing particularly promising.

1. Introduction

The electrification of transportation devices is widely regarded as crucial for the transition towards renewable energy systems[1–3] but, while electric vehicles (EV) based on hydrogen fuel cells continuously suffer from high fuel costs due to unfavorable round trip efficiencies,[4,5] the price for Li-ion batteries, scaled by their energy capacity, has been reduced by about 97% since market introduction in 1991, accompanied by significant performance gains.[6] Accordingly, the growth of the battery market for light-duty EVs exceeds all expectations[7–9] and batteries are at least considered as viable options for heavy-duty EVs[10] and short-to-medium distance shipping.[11] The consequence of this ongoing trend is the steeply rising demand for the materials used, escalating all the environmental, geopolitical, and social challenges in their acquisition.[12–14] A circulatory material flow could offer a remedy in the described scenario, but issues concerning sustainable manufacturing[15] and recycling[12,16] of currently used battery materials are not fully resolved yet. Therefore, it does not come as a surprise that the use of more abundant and potentially greener materials has been suggested by several authors.[17–19]

In order to suffice user demands on range and flexibility of mobile applications, one particular requirement on the energy storage is high energy density and/or high specific energy.[20] Concerning batteries, although substantial improvements on the engineering level have been made recently, on the materials’ side, there are so far no post-Li alternatives reaching up to the performance of state-of-the-art technologies based on lithium-ion shuttles.[8,9] One research trend, therefore, aims at rendering Li-ion technology more sustainable. This can obviously be done by replacing critical materials with less critical ones, as is reflected in the trend toward Co- and Ni-free LFP cathodes[21] or in the substitution of natural graphite by the synthetic equivalent.[22] Also performance enhancement of current technology may decrease the materials exploitation, for example, by increasing the cycle life of the battery or by elevating the energy that can be stored in a certain amount of material. A completely different but recently strongly pronounced idea is the substitution of Li as the shuttle ion. Due to chemical similarity, the most obvious candidate is the earth-abundant element Na. Unfortunately, although material classes from Li-ion battery technology can also be used for Na-ion batteries, they do not reach the same performance.[23–25] This problem is even more pronounced for other considered shuttle ions such as K, Mg, Ca, Zn, and Al. As a result, a complete research field focusing on the development of corresponding materials has evolved during the last years.[26] Many reviews highlight the progress in the field,[27–31] but the ultimate chemistries are yet to be found and the corresponding materials have to be developed.

One in many regards particularly interesting class of materials are oxide perovskites, which are named after the Russian politician and leisure time mineralogist L. A. Perovski, who allegedly enabled the discovery of the prototype crystal CaTiO₃ with its typical corner-sharing oxygen octahedra.[32] The first application of this class of materials was BaTiO₃, which has served as dielectric...
medium in capacitors since the 50s of the last century.[31]
Research then became aware of the tunability of these materials’
properties by substituting the cations on the A- and B-position in
ABO₃, which together with the oftentimes straightforward
synthesizability led to a range of applications. Examples can
be found in catalysis and electrocatalysis[34] but oxide perovskites
are also used as ionic conductors in solid oxide fuel cells[39] or as
supercapacitors.[36]

Despite their popularity, oxide perovskites have hardly been
studied for their use in post-Li systems. LiₓLa₁₋ₓTiO₃ has been
discussed as potential solid electrolyte material for Li-ion batter-
ies but intercalation of Na and Mg was not feasible.[37,38] On the
cathode side, CaMO₃ (M = Cr, Co, Fe, Mn, Ni, Mo) has been
studied with first-principles methods but no electrochemical
activity could be observed for the suggested material CaMnO₃
in a subsequent experiment.[39] On the other hand, Ca intercala-
tion into CaMnO₃ has been reported, although the process was
accompanied by partial degradation of the material.[40] To the
best of our knowledge, a more comprehensive investigation of
oxide perovskites with respect to battery materials particularly
for post-Li technology is still lacking.

In order to fill this gap, we employed density functional theory
(DFT) which is well suited to describe battery components on the
atomic level[41] to systematically investigate the materials’ class
of oxide perovskites as potential high-energy cathode materials for
the intercalation of the abovementioned shuttle ions. In total, we
performed DFT calculations on 280 different compounds and we
evaluated different properties such as theoretical specific energy,
theoretical energy density, theoretical volume change, and chemi-
ical stability. For those candidate materials with promising
properties, we additionally evaluated the diffusion barrier of
the corresponding ion. Eventually, we were able to narrow down
the initial material space to the three compounds MgNbO₃,
ZnVO₃, and AlMnO₃ which we suggest for further investigation.
MgNbO₃ seems to be the most promising candidate material
among these three.

### 2. Calculational Details

Oxide perovskites have the general stoichiometry ABO₃ where
the B-site cation is octahedrally coordinated with oxygen and the
A-site cation resides in the interstitial voids of these corner-
sharing octahedra. The ideal cubic structure only contains
five atoms per unit cell, but many real compounds are subject
to distortions of this highly symmetric phase, leading to a wide
range of geometries with lower symmetry, still fulfilling the
above given structural definition. These distortions can be clas-
sified in three categories: 1) tilting of the octahedra as famously
described by A. M. Glazer[42,43]; 2) Jahn–Teller distortions of the
octahedra; and 3) ferroelectrical displacement of the B-site cat-
ions within the octahedra.[44] It has been shown in a DFT analysis
that the energy is lowered significantly (several 100 meV atom⁻¹)
by structural distortions so the highly symmetric cubic phase is
not realized in many compounds.[45] On the other hand, combi-
ing only the distortions of type (1) and (3) gives rise to 61 sym-
metrically nonequivalent geometries,[46] a number which is far
too large for the screening of several hundred compounds.
Therefore, we decided to follow the rather pragmatic approach
of Emery and Wolverton[46] and only evaluate the most common
perovskite geometries, that is, the cubic phase (Pm₃m), the
rhombohedral phase (R3c), the tetrahedral phase (P4mm), and
the orthorhombic phase (Pnma) for every input stoichiometry.

In this computational screening study, we consider the shuttle
ions Li, Na, K, Mg, Ca, Zn, and Al. Thus the results of our mate-
rials screening are relevant both for Li-ion and for post-Li battery
technologies. To study insertion-type cathode materials, the
A-site has to be occupied by one of these shuttle ions Li, Na,
K, Mg, Ca, Zn, Al, while the BO₃ octahedra serve as host struc-
ture for the topotactic intercalation reaction. The B-side can
at least in principle be occupied by any other metal of the periodic
table,[47] but for our screening we chose a rather practical
approach and excluded all elements: 1) which are not stable
(Tc, Pm, the elements beyond Bi); 2) which are too toxic for
any real live technology (Be, As, Cd, Te, Hg, Ti, Pb); 3) which
are too rare for any large-scale application (Ru, Rh, Pd, Re,
Os, Ir, Pt, Au); and 4) which we excluded for stoichiometries
with untypical oxidation states, we excluded alkali and alkaline
earth metals due to their inertia to take up and release elec-
trons. This gives us in total 7⋅40 = 280 different stoichiome-
tries ABO₃ as input for the screening.

Furthermore, we focus on high-energy materials, which
enable the complete deinsertion of the A-site cations.
Therefore, we modeled the cathode material in the low state
of charge, that is, ABO₃ and in the high state of charge, that
is, BO₃, as depicted in Figure 1. Each structure was modeled
in the four abovementioned geometries, and the lowest energy
structure was used for the investigation of the battery properties.
Topotacticity of the intercalation reaction is thus introduced by
restricting both the low state of charge and the high state of
charge to a perovskite geometry although exactly the same
symmetry is not necessarily demanded.

The ground-state energy of every input structure was calcu-
lated using DFT employing the exchange–correlation functional
suggested by Perdew, Burke, and Ernzerhof.[48] Oxide materials
are known to exhibit self-interaction errors.[49–51] Hence we
added an on-site interaction term \( U \) (PBE + \( U \)) in the functional
form suggested by Dudarev et al.[52] with values of \( U_{CO} = 3.32 \),
\( U_{Ni} = 2.7 \), …

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**Figure 1.** Battery cathode materials based on the perovskite structure
considered in this study. The fully intercalated material ABO₃ represents
the low state of charge while the fully deintercalated material BO₃
represents the high state of charge of the cathode material in the battery.
All structures were restricted to the perovskite geometry.

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$U_{Fe} = 5.3$, $U_{Mn} = 3.9$, $U_{Mg} = 4.38$, $U_{Ni} = 6.2$, $U_V = 3.25$, and $U_{O} = 6.2$ eV. Note that this is on par with the functional as applied by the Materials Project database$^{[33]}$ rendering the calculations comparable. The ionic cores were treated with the projector augmented wave method$^{[34]}$ as implemented in the Vienna Ab Initio Simulation Package$^{[35-37]}$. Electronic wave functions were expanded up to energies of 600 eV and it was made sure that total energies converged within a few meV atom$^{-1}$ with respect to the number of $k$-points in the first Brillouin zone. All structures were optimized until the entries of the stress tensor and all forces were below 0.01 eV Å$^{-1}$ without constraining any internal degree of freedom. The spin state of many perovskites is still subject to ongoing debate$^{[58]}$ and the difference in ferromagnetic and nonmagnetic states may easily result in energetic errors of more than 1 eV atom$^{-1}$. Furthermore, it is well known$^{[59]}$ and also confirmed by our experience that sometimes the correct nonmagnetic ground state is not found when the calculation is initialized ferromagnetically. Therefore, we explicitly searched for high-spin and low-spin states for all possibly magnetic elements$^{[59]}$ while all other elements were initialized with low magnetic moment. No attempt was made to find antiferromagnetic states as this approximation typically results only in low energetic errors compared to ferromagnetic states$^{[60]}$ and the exact magnetic ordering is of no particular interest for the present study.

Theoretical specific energy $\rho_{grav}$ and theoretical energy density $\rho_{vol}$, both evaluated with respect to metal anode, have been approximated by

$$\rho_{grav} = \frac{E_{ABO_3} - E_{BO_3} - E_A}{M_{ABO_3}} \quad \text{and} \quad \rho_{vol} = \frac{E_{ABO_3} - E_{BO_3} - E_A}{V_{ABO_3}} \quad (1)$$

where $E_{ABO_3}$ and $E_{BO_3}$ are the DFT energies of the cathode materials in the corresponding state of charge and $E_A$ is the DFT energy of the metallic species A. $M_{ABO_3}$ and $V_{ABO_3}$ are the mass and the volume of the perovskite materials per formula unit. Zero-point energies and entropic contributions were neglected for all energetic considerations. The theoretical volume change was obtained by

$$\frac{\Delta V}{V} = \frac{V_{ABO_3} - V_{BO_3}}{V_{ABO_3}} \quad (2)$$

Chemical stability and synthesizability were addressed by comparing a compound’s energy to all possible configurations with the same stoichiometry (allotropes and potential decomposition products) that are available in the Materials Project database$^{[33]}$. The difference to the configuration with the lowest energy, commonly termed the energy above hull $E_{hull}$, was then evaluated. To be specific, $E_{hull}$ is the difference to the energetically most favorable phases which are built of exactly the same elements. Therefore, it represents a metric for thermodynamic stability, which can be seen as an indicator for synthesizability.$^{[61]}$ Still, we would like to stress that a compelling prediction of a materials’ synthesizability is clearly not possible. Here, only a few remarks on the calculation procedure shall be given. As described above, we used the same functional form as the Materials Project database, rendering the calculations in principle comparable. Nevertheless, deviating input parameters with respect to the basis set and the particular choice of the pseudopotentials can lead to differences in the resulting total energies. In order to minimize these deviations, not total energies but formation energies were compared. Two other problems arise due to this necessary procedure: 1) It is well-recognized that the O$_2$ molecule is overbound in the generalized gradient approximation calculations, leading to erroneous results for the formation energies of oxide species, and 2) some compounds were calculated with the PBE + U functional, whereas, for the metallic element phases, the original functional was used, again resulting in poor estimations for the formation energies. In order to account for these errors, we adapted the empirical corrections described by Wang et al.$^{[62]}$ Note also that we allowed negative values of $E_{hull}$ which means that the considered compound is lower in energy than the convex hull spanned by the compounds of the database.

Nudged elastic band (NEB) calculations$^{[63]}$ were employed to evaluate the diffusion barrier $E_{diff}$ of certain species. The A$_2$BO$_3$ supercells were created with $x = 0.0555/0.625$ in the high vacancy limit and $x = 0.9445/0.9375$ in the low vacancy limit, where the first number corresponds to cubic and tetragonal cells and the second one to rhombohedral and orthorhombic ones. We investigated all symmetrically non-equivalent diffusion paths, that is, one for cubic and rhombohedral cells, two for tetragonal, and three for orthorhombic ones. The calculations were performed with five images, only in some cases with convergence issues, the number was reduced to four or three. Optimized NEB algorithms$^{[64]}$ were used to optimize the ion positions until the forces on every ion were lower than 0.05 eV Å$^{-1}$. The climbing image method was used to ensure that the transition state was found.$^{[65]}$ Ab initio molecular dynamics simulations are another computational tool to study dynamical processes in batteries,$^{[66]}$ also in materials such as perovskites,$^{[67]}$ but their high numerical demand prohibits their use in computational screening studies.

### 3. Results

We will now describe our approach to screen the oxide perovskite materials. As described earlier, the full or empty electrode materials ABO$_3$ and BO$_3$, respectively, were considered in four different symmetries each. The one lowest in energy was then used for all further investigations. It has already been mentioned that in a previous study, distorted perovskites deviated by several 100 meV atom$^{-1}$ from the cubic structure.$^{[45]}$ Our investigation reveals that the difference may even be in the order of one eV atom$^{-1}$, as is deduced from the comparison of the total energies of the different polymorphs of VO$_3$ and AlVO$_3$ in Figure 2. While for some of the analyzed compounds as for instance VO$_3$ the energy difference between the polymorphs is only a few meV atom$^{-1}$ and the lowest-energy geometry only slightly deviates from the cubic structure, the octahedra in other compounds as for instance AlVO$_3$ are considerably tilted and distorted, leading to significant deviations in energy. This confirms once more that the cubic structure is an invalid approximation in many cases and taking into account the less symmetric phases is clearly necessary. In general, of all 280 ABO$_3$/BO$_3$ stoichiometries 206/161 attained the lowest energy in the orthorhombic...
phase, 52/77 in the rhombohedral phase, 17/42 in the tetrahedral phase, and 5/0 in the highly symmetric cubic phase.

The battery properties which are directly accessible from the calculations are depicted in Figure 3. In the energy-related plots, the rows for Mg, Ca, and Al nicely mirror the advantage of multivalent batteries, that is, high energy density with respect to both, weight and volume. Zn is an exception as it has the least negative standard electrode potential of the analyzed shuttle ions. In order to filter potential high-performance materials, we compared the obtained values to state-of-the-art electrode materials investigated on an equal level of theory. Commonly used cathode materials as LiCoO$_2$ (LCO), LiMn$_2$O$_4$ (LMO), and LiFePO$_4$ (LFP) have for instance been investigated within the PBE + U framework by Chevrier et al.\cite{68} and the derived properties shown in Table 1 serve as reference for the screening in the present work. Although on the material’s level, LCO outperforms LMO and LFP by far, the latter two materials suffice the performance criteria of EV batteries,\cite{9} which means they can be considered high-energy cathode materials. Thus, we set our screening criteria accordingly. In absolute numbers: we demand a high-performance cathode to possess $\rho_{\text{grav}} > 500 \text{ Wh kg}^{-1}$ and $\rho_{\text{vol}} > 2000 \text{ Wh dm}^{-3}$.

Figure 2. Total energy per atom for the different distortions of VO$_3$ and AlVO$_3$ as example. The lowest energy structures are depicted for both cases. The structure of VO$_3$ is almost cubic and the different modeled distortions hardly differ in energy, whereas in AlVO$_3$ the octahedra are severely tilted and distorted and the orthorhombic phase is more than 1 eV atom$^{-1}$ lower in energy than the ideal cubic phase.

Figure 3. Derived battery properties for 280 ABO$_3$ compounds. Green indicates preferable values for the given property whereas red means the opposite. This is why the color code goes from red (low values) to green (high values) in the case of the theoretical specific energy and the theoretical energy density, but from green (low values) to red (high values) in the case of the theoretical volume change and the energy above hull.
The volume change of the electrode upon intercalation is another relevant quantity, as too high values may lead to stress and strain and eventually pulverization of the material. Visual inspection of Figure 3 shows that in contrary to the energy-related properties, which are strongly dependent on the A-site cation, the volume change rather seems to be related to the element on the B-site, although this trend is not as clear. In general, many of the investigated materials, in particular most of the lanthanide-containing compounds, show a change in volume of over 20\%abs which is the maximum of the color code in Figure 3. Again, we compared these values to the ones derived from Chevrier et al.\cite{68} and set our screening criterion for volume change a bit more loosely to $\Delta V < 10\%_{\text{abs}}$.

The use of $E_{\text{null}}$ to estimate synthesizability is common practice as has been thoroughly discussed in a recent review.\cite{61} In that regard, $E_{\text{null}} = 0$ indicates that a certain material is positioned on the convex hull and, therefore, claimed to be thermodynamically stable. Nevertheless, due to imperfections of DFT, the negligence of kinetic effects, and unknown complications in the synthesis procedure, positive values for $E_{\text{null}}$ may still correspond to synthesizable materials, and synthesis of materials with $E_{\text{null}} = 0$ may fail.\cite{61} Furthermore, one has to keep in mind that although at the time of writing this manuscript the Materials Project database contains over 150 000 crystal structures evaluated with DFT, there may be stable compounds missing in the database, so the convex hull which is spanned by the comprised materials and which our computation of $E_{\text{null}}$ relies on may be incomplete.

Here, we aim at a criterion to discard all unsynthesizable materials, but the choice of the appropriate threshold value for $E_{\text{null}}$ is a challenging task. Studies similar to the present one use values in the range of 50-100 meV atom$^{-1}$\cite{51,69} but also smaller thresholds can be found in literature.\cite{47} On the other hand, the authors of the correction scheme we employed\cite{62} report a root mean square error of 92 meV atom$^{-1}$ in the prediction of formations energies for a dataset of 222 compounds, which means that outliers may have errors far beyond 100 meV atom$^{-1}$. Therefore, we decided to set the screening criterion to $E_{\text{null}} < 200$ meV. While this value potentially allows many unstable materials to pass the stability screening, it insures that the likelihood of discarding a stable material with potentially promising battery properties is very small.

This approach is further justified by the comparison of our stability predictions to a recent study on the prediction of stable perovskites by a machine learning approach.\cite{50} In this study, the authors designed the stability descriptor $\tau$ based on oxidation states and ionic radii, where $\tau < 4.18$ indicates perovskite structure with an accuracy of 92\% for oxides. We have evaluated $\tau$ for the perovskites of our own dataset where values for the ionic radii were available in the extended list of Ouyang.\cite{71} Figure 4 shows that the descriptor-based method predicts stable perovskites up to roughly $E_{\text{null}} = 200$ meV atom$^{-1}$, implying that lower threshold values for the screening would possibly lead to the rejection of stable compounds. As a result of the high threshold value, only few compounds ABO$_3$ are filtered out due to the stability criterion (see Figure 3). On the contrary, the deintercalated cathode host BO$_3$ is predicted to be unstable for many B-cations (Al, Si, Sc, Ti, Mn, Co, Ga, Zr, Sn, Sb, Hf, Bi, Ho, Er, Tm, Lu), rendering all corresponding materials as unsuitable for high-energy battery electrodes.

Among the 280 compounds, there are 30 which passed the presented screening process. Further, 17 were discarded since either for ABO$_3$ or BO$_3$ the perovskite structure collapsed during the DFT geometry optimization, leaving only 13 compounds for which we determined the energetic barrier for the solid-state diffusion of the A-cation. Commonly, 650 meV are assumed as maximum diffusion barrier, still allowing sufficient charge/ discharge rates in nanostructured materials.\cite{27,72} As shown in Figure 5, none of the perovskite structures in the low vacancy limit and hardly any in the high vacancy limit fulfill this criterion, in contrast to, for example, spinel materials.\cite{13,74} This observation is in line with previous studies on oxide perovskites.\cite{99,75} Notwithstanding, the screening reveals MgNbO$_3$, ZnVO$_3$, and AlMoO$_3$ as interesting materials, exhibiting sufficient mobility in the deintercalated state. Interestingly enough, the charge carriers for all these three materials are multivalent ions whose migration is usually hindered by high diffusion barriers.\cite{96,77} However, here these materials exhibit diffusion properties that are superior to those with monovalent ions among the considered favorable candidates.

Table 1. Battery properties of state-of-the-art cathode materials. The battery properties for LCO, LMO, and LFP were derived based on the DFT calculations of Chevrier et al.\cite{68} as described in the Calculation details. The threshold criteria have been derived in order to screen the material properties of Figure 3.

<table>
<thead>
<tr>
<th>Property</th>
<th>LCO</th>
<th>LMO</th>
<th>LFP</th>
<th>Screening criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_{\text{grav}}$ [Wh kg$^{-1}$]</td>
<td>1054</td>
<td>599</td>
<td>589</td>
<td>&gt;500</td>
</tr>
<tr>
<td>$\rho_{\text{zav}}$ [Wh dm$^{-3}$]</td>
<td>5214</td>
<td>2434</td>
<td>2056</td>
<td>&gt;2000</td>
</tr>
<tr>
<td>$\Delta V$ [%$_{\text{abs}}$]</td>
<td>3.47</td>
<td>4.25</td>
<td>4.45</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

![Figure 4](https://onlinelibrary.wiley.com/doi/10.1002/aesr.202300204)
Additionally, it is interesting that the value of $E_{\text{diff}}$ strongly differs depending on the exact path taken in the structure. In the case of AlMoO$_3$, for instance, the barrier varies by more than 2 eV within the three paths in the low vacancy limit and by more than 1 eV within the high vacancy limit. A comprehensive study taking all possible diffusion paths into account is thus necessary in the search for a channel for ionic diffusion. A further observation is the discrepancy of the barriers in the low vacancy limit and the high vacancy limit in many cases which amounts to roughly 2 eV as in the example of CaTaO$_3$. Since any volume effect on $E_{\text{diff}}$ can be excluded due to the imposition of the strongly limiting screening criterion, the discussed discrepancy indicates that the interaction of the shuffle ions on the A-site within the BO$_3$ host structure may significantly affect their ionic mobility.

An overview of the properties of the candidate materials is given in Table 2. While MgNbO$_3$ attains the lowest energy in the rhombohedral symmetry (R$3c$), ZnVO$_3$ and AlMoO$_3$ are energetically more favorable in the orthorhombic structure (Pnma). For the materials in the high state of charge, the tetragonal structure (P4mm) is attained in all three cases. The specific energy of all three materials is roughly in the range of LMO and LFP or slightly above (compare to Table 1). At the same time, with respect to the energy density, the candidate materials outperform LMO and LFP by far. For instance, the energy density of MgNbO$_3$ is 50% higher than that of LFP. The energetic performance of LCO, on the other hand, could not even be approached. The values for $V_{\text{hull}}$ indicate that NbO$_3$ and MoO$_3$ are probably stable materials whereas VO$_3$ is right under the threshold criterion and therefore not very likely to be stable. The corresponding intercalated compounds MgNbO$_3$, ZnVO$_3$, and AlMoO$_3$ are located in the intermediate range, that is, they are potentially, but not very likely, stable.

As discussed above, the diffusion barriers for MgNbO$_3$, ZnVO$_3$, and AlMoO$_3$ in the low vacancy limit are very high, whereas they show promising values in the deintercalated state. A closer look on the diffusion path for MgNbO$_3$ in Figure 6 reveals another interesting fact: The diffusion path in the intercalated material goes downhill. This indicates indeed that the initial and final configurations are not the energetically most favorable ones for the given stoichiometry, but the intermediate images seem to be more stable. We performed DFT geometry optimizations of the distinct images to confirm the outcome of the NEB calculations. The final structures of every image are visualized in the Supporting Information. They reveal that the perovskite-typical corner-sharing oxygen octahedra is retained in every image and the structure does not collapse. Hence, the intermediate images attaining lower energy are still perovskites. This may indicate that the true barrier for solid-state diffusion in the low vacancy limit is lower than the value given in Table 2. The barriers for ZnVO$_3$ and AlMoO$_3$ are very high, so electrochemical activity in these compounds is rather unlikely. The diffusion paths for all compounds in Figure 5 are provided in the Supporting Information. Note that also LiCrO$_3$, MgMoO$_3$, and AlVO$_3$ show downhill diffusion paths.

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Diffusion barriers of MgNbO$_3$. In the high vacancy limit, MgNbO$_3$ exhibits low diffusion barriers. In the low vacancy limit, the diffusion path goes downhill, indicating that the initial and the final structure are energetically unfavorable for the given stoichiometry. A more detailed discussion can be found in the text.
4. Conclusion

In the present work, 280 different oxide perovskites have been investigated as potential high-energy insertion-type cathode materials for batteries. Based on DFT calculations, the specific energy, the energy density, the volume change, and the energy above hull were derived for all compounds. Appropriate screening criteria on these properties were applied to filter out all unsuitable materials. Additionally, it was ensured that the perovskite structure was retained during DFT geometry optimization. For the 13 materials that passed the screening process, the diffusion barriers for the migration of the shuttle ions were derived. Again, a screening criterion ensuring sufficient ionic mobility was employed. None of the investigated compounds exhibited low diffusion barriers in the low vacancy limit and the compounds MgNbO₃, ZnVO₃, and AlMoO₃ only did in the high vacancy limit. After all, we were able to narrow down the initial 280 compounds to the three compounds MgNbO₃, ZnVO₃, and AlMoO₃ to be used in post-Li battery technologies with multivalent ions, which we suggest for further investigation. Of these materials, MgNbO₃ seems to be particularly promising, as there is reason to believe that the real diffusion barrier for MgNbO₃ in the low vacancy limit is considerably lower than suggested by our calculations.

To the best of our knowledge MgNbO₃ has never been synthesised, but similar niobate perovskites have been discussed in literature. For instance, ceramic materials within the solid-solution KₓNa₃₋ₓNbO₃ (0 < x < 1) have been studied due to their promising piezoelectric properties and LiNbO₃ is known for its ferroelectricity and its optical properties. Even more interesting, high ionic Li mobility was achieved in the defective perovskite material LiₓLa(1−x)/3NbO₃ but the research has not been extended to other shuttle ions.

We would still like to note that even if some material should be synthesizable according to our $E_{\text{hull}}$ criterion, it is not guaranteed that synthesis routes to prepare this particular material are available. Ideally such a screening study should be done jointly with materials synthesis experts. However, we view our screening study also as a motivation for our experimental colleagues to address the preparation of materials that have not been produced yet. In the present study the verifiably existing niobate compounds LiNbO₃, NaNbO₃, and KNbO₃ have been discarded due to high volume change in the case of Li and high diffusion barriers in the case of Na and K. However, our calculations suggest that especially the Mg-intercalated NbO₃ framework could be an interesting research direction in the development of high-energy cathode materials for Mg-based batteries.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

All electronic structure calculations used in this work are made available under the Creative Commons Attribution license (CC BY 4.0) on the NOMAD repository (https://nomad-lab.eu) within the dataset "Computational_Screening_of_Oxide_Perovskites_as_Insertion_Type_Cathode_Material", https://dx.doi.org/10.17172/NOMAD/2023.10.24-2.

Keywords

battery cathode materials, computational screening, density functional theory, energy storage, oxide perovskites

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