Computational Screening of Layered Materials for Multivalent Ion Batteries

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ABSTRACT: Batteries based on multivalent ion (such as Al$^{3+}$, Ca$^{2+}$, and Mg$^{2+}$) intercalation materials have attracted extensive research interest due to their impressive capacity improvement and cost reduction compared with Li-ion batteries. However, the materials for state-of-the-art multivalent ion batteries still suffer from drawbacks such as sluggish ion mobility, poor rate performance, and low cycle stability, bringing challenges for the design and investigation of new materials. Layered cathode materials are widely applied in current commercial batteries due to their outstanding ionic conductivity and structural stability, which may also hold the key for the cathodes of multivalent batteries. Therefore, combining database screening and density functional theory computations, we evaluated the layered compounds in Materials Project database by theoretical capacity, thermodynamic stability, experimental availability, voltage, volume variation, electronic conductivity, and ionic migration barrier and achieved over 20 kinds of layered cathode materials for multivalent batteries. Through Mg ion substitution for Ca sites, we further achieved several kinds of cathode materials for Mg-ion batteries with ideal stability, voltage, and ion diffusion barriers. We hope the methodology and screened materials could promote the development of multivalent ion batteries.

INTRODUCTION

With the increasing threat of the energy crisis and environmental deterioration caused by the consumption of fossil fuels, the utilization of renewable and clean energy sources becomes a crucial challenge in the 21st century. The most promising renewable energy sources, such as wind, solar, hydroelectric, and geothermal energies, distribute unevenly in time and space, which give rise to the demands for energy storage devices with high energy density. However, the state-of-the-art energy storage devices are still far from the requirement for large-scale energy storage. Li-ion batteries (LIBs) have achieved extensive application in portable electronic devices and electric vehicles due to their outstanding ionic conductivity and structural stability, which may also hold the key for the cathodes of multivalent batteries. Therefore, combining database screening and density functional theory computations, we evaluated the layered compounds in Materials Project database by theoretical capacity, thermodynamic stability, experimental availability, voltage, volume variation, electronic conductivity, and ionic migration barrier and achieved over 20 kinds of layered cathode materials for multivalent batteries. Through Mg ion substitution for Ca sites, we further achieved several kinds of cathode materials for Mg-ion batteries with ideal stability, voltage, and ion diffusion barriers. We hope the methodology and screened materials could promote the development of multivalent ion batteries.

The multivalent ion battery, composed of an intercalation cathode and a multivalent metal (such as Mg, Al, Ca, and Zn) anode, has shown considerable potential for a higher energy density, better safety, and much lower cost.5 Especially, the Mg and Al anodes exhibit volumetric capacities of 3833 and 8046 mAh cm$^{-3}$, respectively, which are far beyond those of Li (2062 mAh cm$^{-3}$) and Na (1128 mAh cm$^{-3}$).5,8 The significantly improved volumetric capacity could be attributed to the multielectron redox reaction for every individual ion and the higher densities of Mg and Al. Besides, the ionic radii of Mg$^{2+}$ (0.86 Å) and Al$^{3+}$ (0.53 Å) are smaller than that of Li (0.9 Å), further increasing the energy density. Moreover, the dendrite formation in Mg-ion batteries (MIBs) is less serious than that in LIBs, and the metal anodes of Mg and Al are much more stable than Li and Na when exposed in air or even in humid atmosphere, greatly improving the safety and reliability.8 The abundance of the multivalent ions in the earth’s crust is also much higher than Li, which ensures acceptable cost in large-scale application. Consequently, Al-ion batteries (AlIBs) and Mg-ion batteries are regarded as a possible solution to the current problems of energy density and safety of batteries. Though the ion insertion in AlIB cathodes is complicated due to the participation of anions, the Al$^{3+}$ intercalation mechanism has also been explored,9,10 which exhibits advantage over Al$^{3+}$Cl$^{-}$ insertion without consuming the electrolyte during the electrochemical process. Besides Mg and Al, Ca-ion batteries (CIBs) also attract more and more research interest due to its ideal reduction potential (only 170 mV above Li) and faster reaction kinetics than Mg, which...
guarantee a higher energy density and better performance at high rates.\textsuperscript{11}

However, the superior energy density of a battery could not be realized by the anode alone, and the cathode is more crucial for the performance of current multivalent batteries. At present, the cathode materials for state-of-the-art multivalent batteries are still far from applications due to the drawbacks such as sluggish ion mobility, poor rate performance, and low cyclic stability. As successfully implemented in LIBs, layered intercalation materials exhibit the advantages of outstanding ionic conductivity and structural stability, which might hold the key for multivalent battery cathodes.\textsuperscript{3,8,12} Consequently, layered materials are always promising candidates for the multivalent battery cathode, and an impressive progress has been achieved both theoretically and experimentally. Compared with experiments, density functional theory (DFT) computations are able to skip the costly and time-consuming preparation procedure and directly provide the information about the electrochemical performance of materials, which show a remarkable credibility and efficiency. Notably, high-throughput computational material screening approaches are capable to utilize the tremendous data generated by previous experimental and computational studies, further improving the efficiency of materials investigation and design.\textsuperscript{2,4,13}−\textsuperscript{18} We have successfully employed the high-throughput computational screening method to design novel electrode materials for sodium-ion batteries and obtained a set of candidate materials.\textsuperscript{19} Herein, we further extend our screening method to design cathode materials for multivalent batteries. In this work, by combining DFT computations and database screening approaches, we evaluated more than 50,000 inorganic compounds in Materials Project (MP) database by theoretical capacity, thermodynamic stability, experimental availability, voltage, volume variation, electronic conductivity, and ionic migration barrier and proposed several cathode materials for multivalent batteries with a promising electrochemical performance.\textsuperscript{20,21} Moreover, some new cathode materials for Mg-ion batteries with satisfactory stability, voltage, and ion diffusion barriers were further achieved by ion substitution.

## RESULTS AND DISCUSSION

The database screening approach is introduced in the computational part. During the screening process, the compounds that could not satisfy our criteria were excluded stepwise. The remaining structure numbers at each screening step are summarized in Figure 1 and Table S1. For further comparison with single valent ions, we also screened Li-, Na-, and K-containing compounds and collected the statistics under the same criteria. Among all the criteria that we set, the characterization of layered structures always rules out over 76\% of the candidates because the three-dimensional connected materials are the majority in the database. As expected, a theoretical capacity of 120 mAh g\textsuperscript{-1} excluded more single valent metal-containing compounds (35–52\%) than the multivalent metal-containing compounds (6–14\%), indicating the higher capacity of multivalent batteries. For all the metal elements, around 50\% of the compounds could meet the criteria of band gap of <2.5 eV. Na- and K-containing compounds show an obviously lower proportion of alloys (lower than 12\%) compared with the rest (32–59\%), which may be attributed to the high reactivities of Na and K metals. Interestingly, the numbers of Li- and Mg-containing compounds (13,943 and 9818, respectively) are much larger than those of the rest (lower than 4900 for each metal element). But only lower than 12\% Mg- and Li-containing compounds could be found in Inorganic Crystal Structure Database (ICSD), while for the remaining metal elements, the proportion is greater than 38\%, which demonstrates a large number of theoretically predicted Mg-and Li-containing compounds in the MP database.

After screening the MP database with our criteria for band gap, theoretical capacity, stability, nonalloy, and layered structure, 33 Al-, 80 Ca-, and 25 Mg-containing compounds were obtained. The theoretical capacity and band gap distribution of these compounds are shown in Figure 2. The distribution suggests that the theoretical capacity of Al-containing compounds is the highest compared with the others, which could be attributed to the higher valence of Al\textsuperscript{3+}. Additionally, the band gaps of the obtained Al-containing compounds are generally lower than the rest, indicating their better electronic conductivity. Because Mg\textsuperscript{2+} and Ca\textsuperscript{2+} belong to the same main group and share the same charge numbers,
the Mg- and Ca-containing compounds show a similar distribution.

Then, we examined their structural and energy change upon the metal ion deintercalation. In many LIB cathode materials, the metal ions do not have to be completely extracted from the host, and the remaining metal ions could protect the structure from serious variation during the charge/discharge process, thus resulting in a better cyclability. In that light, we checked the lattice parameter change and average voltage by partially deintercalated structures, in which the metal ions were deintercalated until the capacity exceeds 120 mAh g\(^{-1}\). In order to evaluate the structural maintenance, we took the change lower than 15% as the criterion for each lattice parameter, including the lattice constant \(a\), \(b\), or \(c\), the angle \(\alpha\), \(\beta\), or \(\gamma\), and the cell volume. Besides, the average voltage could also be achieved by the energy difference between the pristine and deintercalated structure. The criteria for the voltages of Al (1.0–2.5 V), Ca (1.5–3.5 V), and Mg (1.5–3.5 V) ion deintercalation were set according to the reported common voltage ranges.\(^{12}\) After screened by all the criteria in Figure 4, the metal ion diffusion barrier of obtained candidates were further calculated by climbing image nudged elastic band (CI-NEB) method. Their key features as cathode materials are shown in Table 1, and their structures are plotted in Figure 3.

Two kinds of MAX phase materials, Al\(_{4}\)C\(_3\) and Ti\(_2\)AlN\(_3\), were obtained as cathode materials for AIBs. It has been reported that the monolayers of MAX phases, also termed as MXene, have great potential as anode materials for Li\(^+\), Na\(^+\), K\(^+\), Mg\(^+\), Ca\(^+\), and Al-ion batteries, but the application of the bulk phase MAX materials in cathode materials has hitherto rarely been studied.\(^{22,23}\) Compared with the MXene monolayer anodes, an Al atom in MAX binds with two M\(_2\)X\(_3\) layers rather than one. Therefore, the interaction is much stronger than that in MXene anodes, and the voltage of these bulk phase MAX materials is suitable for AIB cathode materials. Besides, the energy barriers (0.92 and 0.93 eV) are also acceptable for Al ion diffusion; thus, the thermodynamic and dynamic properties of these MAX phase materials suggest their potential as cathode materials for AIBs. Three kinds of Mg-containing candidate materials were achieved for MIBs. Among them, the application of Mg\(_2\)V\(_2\)O\(_5\) as cathode materials for MIBs has been extensively studied both theoretically and experimentally, demonstrating the credibility of our method.\(^{24–27}\) For the rest two materials, the high ionic diffusion barriers might lead to a poor electrochemical performance at high rates. Most of our screening results are Ca-containing compounds. Although they all possess considerable voltage and capacity, previous investigations on those materials focused on the preparation, magnetism, electronic properties, catalysis, etc.\(^{28–34}\) To the best of our knowledge, among those materials, only CaMn\(_2\)O\(_4\) has been evaluated as a CIB cathode material.\(^{35}\) According to our results, the Ca ion diffusion barriers in those materials are higher than 1 eV except for Ca\(_3\)(Ga\(_N\)\(_2\)). The large radii and multiple charges seriously hinder the Ca ion migration in these hosts, which limit the application to some extent. Note that the Al, Ca, and Mg ions in these materials could be substituted by each other through ion exchange or electrochemical processes.\(^{36–41}\) Because most of our obtained cathode materials are for CIBs, the hosts for Ca ions might also be applied to AIBs and MIBs. Especially, because Ca and Mg ions share the same valence and coordination number, the Mg substitution at Ca sites would cause a less structural variation. Besides, the smaller Mg ion could also reduce the energy barrier of ion diffusion and exhibit a better rate performance. Based on this consideration, we substituted Ca with Mg in all 16 kinds of obtained CIB cathode materials and investigated their structural change. According to the change in the space group and lattice parameters, we selected eight well-maintained structures upon substitution, and further validated their dynamical stability by ab initio molecular dynamics (AIMD).

Figure S3 shows that all the compounds keep their original structures after 10 ps at 600 K, suggesting their excellent stability and experimental feasibility. Then, we calculated the voltage and diffusion barriers (Table 2 and Figure S4). As

### Table 1. Candidate Compounds with Key Features as Cathode Materials\(^{a}\)

| element | formula | MP ID | band gap (eV) | \(E_{\text{null}}\) (eV) | capacity (mAh g\(^{-1}\)) | voltage (V) | \(V_{\text{change}}\) (%) | barrier (eV) |
|---------|---------|-------|--------------|----------------|-----------------|-------------|----------------|-------------|
| Al      | Al\(_4\)C\(_3\) | 569,458 | 0.00 | 0.01 | 301 | 2.1 | −4.6 | 0.92 |
|         | Ti\(_2\)AlN\(_3\) | 568,934 | 0.00 | 0.00 | 309 | 2.0 | 4.6 | 0.93 |
| Ca      | Ca\(_4\)(Ga\(_N\)\(_2\)) | 571,162 | 1.91 | 0.00 | 509 | 1.9 | −15.0 | 0.82 |
|         | Ca\(_4\)Mn\(_2\)O\(_4\) | 19,042 | 0.48 | 0.02 | 470 | 3.1 | 16.7 | 1.76 |
|         | Ca\(_4\)RuO\(_4\) | 3258 | 0.00 | 0.03 | 437 | 3.1 | −5.3 | 1.56 |
|         | Ca\(_4\)V\(_2\)O\(_4\) | 18,952 | 1.29 | 0.04 | 561 | 2.6 | −6.4 | 1.60 |
|         | Ca\(_4\)V\(_2\)O\(_5\) | 7466 | 0.00 | 0.01 | 249 | 3.4 | −13.6 | 4.14 |
|         | Mg\(_2\)V\(_2\)O\(_5\) | 19,003 | 2.30 | 0.03 | 260 | 2.1 | 2.2 | 1.06 |

\(^{a}\)\(E_{\text{null}}\) represents the energy above hull, and \(V_{\text{change}}\) is the volume change during multivalent metal ion deintercalation.
shown in Table 2, the Mg substitution at Ca leads to a slight volume decrease due to the smaller radius of Mg. Most of the obtained structures maintain the same space group of their precursors, while Mg₃Ru₂O₇ and MgV₃O₇ change to the similar space group. Generally, the Mg substitution would cause a voltage decrease of 0.4–0.9 V, but the values are still acceptable for MIBs cathode except Mg(PRu)₂. As expected, most of the substituted structures show lower ion diffusion barriers. Especially, the energy barriers of Mg₂RuO₄ (PBCA), Mg₃Ru₂O₇, and Mg₄Mn₂O₇ changed to 0.68, 0.71, and 0.58 eV, respectively, which are pretty ideal values compared with current bulk MIB cathode materials. Therefore, those compounds generated by substitution could serve as promising MIB cathode materials. Additionally, the substitution of Ca by other metal elements (such as Al and Zn) may also provide more excellent cathode materials.

**CONCLUSIONS**

By the combination of database screening and DFT computational investigation, we screened the MP database and achieved 21 kinds of novel cathode materials for Al-, Ca-, and Mg-ion batteries with proper theoretical capacity, thermodynamic stability, experimental feasibility, voltage,
volume variation, electronic conductivity, and ionic migration barrier. Then, we further substituted Ca in the obtained CIB cathode materials by Mg and successfully obtained seven kinds of MIB cathode materials with reduced ion diffusion barriers. Especially, the Mg ion diffusion barriers in Mg$_2$RuO$_4$ (PBCA), Mg$_3$Ru$_2$O$_7$, and Mg$_4$Mn$_2$O$_7$ are 0.68, 0.71, and 0.58 eV, respectively, which are satisfactory for current MIB cathode materials. We hope that our screening method could be extended to explore more electrode materials for multivalent batteries, and our achieved compounds could bring inspiration to the development of Al-, Ca-, and Mg-ion batteries.

## COMPUTATIONAL SECTION

The flow diagram of our screening process based on the MP database and our DFT computation is shown in Figure 4. We chose the compound inherently containing only one of Al, Ca, and Mg element; thus, their capability to serve as the host for multivalent ions is guaranteed. For the convenience of computational studies, the compounds containing lanthanide, actinide, and noble gas elements were excluded. Then, we evaluated their stability by two criteria; the compounds must have an energy above hull of <0.05 eV/atom and an ICSD ID. The energy above hull of a compound is the energy difference between itself and the most stable phase combination at this element ratio in the phase diagram; therefore, a lower energy above hull suggests a better thermodynamic stability. Besides, a compound with an ICSD ID means that it has been included in the ICSD and experimentally realized accordingly.\textsuperscript{42,43} Afterwards, we examined their key features as layered cathode materials and kept the compounds with band gaps of <2.5 eV and a theoretical capacity of >120 mAh g$^{-1}$. As usual, the theoretical capacity was calculated under the assumption that

| formula          | space group | original space group | MP ID    | $V_{\text{change}}$ (%) | $V_{\text{change}}$ (%) | voltage (V) | barrier (eV) |
|------------------|-------------|----------------------|----------|-------------------------|-------------------------|-------------|--------------|
| Mg$_2$RuO$_4$    | PBCA        | PBCA                 | 21,466   | -16.4                   | -6.8                    | 2.4         | 0.68         |
| Mg$_2$RuO$_4$    | BMAB        | BMAB                 | 4208     | -14.8                   | -2.3                    | 2.7         | 1.22         |
| Mg$_3$Ru$_2$O$_7$| CM21        | BM21B                | 3258     | -14.9                   | -5.1                    | 2.3         | 0.71         |
| Mg$_4$Mn$_2$O$_7$| CMCA        | CMCA                 | 18,952   | -18.7                   | 7.4                     | 1.7         | 0.58         |
| MgNb$_2$O$_4$    | BMAB        | BMAB                 | 29,792   | -9.6                    | -4.0                    | 2.0         | 2.98         |
| MgV$_2$O$_7$     | P21         | PCMN                 | 19,347   | -5.6                    | -5.6                    | 1.8         | 1.73         |
| MgV$_4$O$_9$     | P4/N        | P4/N                 | 18,866   | -5.3                    | -10.9                   | 1.7         | 3.23         |
| Mg(PRu)$_2$      | I4/MMM      | I4/MMM               | 5157     | -6.6                    | -3.7                    | 0.9         | 2.62         |

"The original space group and MP ID are those of their Ca-containing precursors. $V_{\text{change}}$ is defined as the volume change in the substitution of Ca by Mg, and $V_{\text{change}}$ is the volume change upon Mg deintercalation in the derived cathode materials."
all the cations were extracted from the host. The compounds composed by all metal elements (ally) usually induce alloying during the ion extraction/intercalation process; thus, we also excluded those composed of only metal elements (including Si) from the candidates because we focused on intercalation cathodes. Next, we selected the layered structures by a dimensional classification algorithm, which has been proved credible and efficient. After that, we obtained a set of Mg/Al/Ca-containing layered compounds with proper element composition, thermodynamic stability, theoretical capacity, and electronic conductivity.

DFT computations were performed with Vienna ab initio simulation package (VASP). We adopted the projector augmented wave (PAW) method to describe the ion–electron interactions and the Perdew–Burke–Ernzerhof (PBE) functional for the exchange–correlation energy. An energy cutoff of 520 eV was chosen for the plane-wave basis set. Because the strong electron correlation effects of some transitional metal element may induce large errors in the voltage calculation, we used DFT+U method with the U–J parameters in accordance with the MP database (Table S2). The DFT-D3 method with Becke–Jonson damping was applied to achieve a more accurate evaluation of the van der Waals interactions. The Monkhorst-Pack k-point mesh with a k-point separation lower than 0.03 Å was used to sample the first Brillouin zone. The average voltage \( V_{\text{ave}} \) was calculated by

\[
V_{\text{ave}} = \left( E_{\text{de}} - nE_{\text{m}} - E_0 \right)/(nzF)
\]

where \( E_{\text{de}} \) is the energy of the deintercalated structure, \( E_{\text{m}} \) is the energy of each metal atom in the metal bulk phase, \( E_0 \) is the energy of the structure before deintercalation, \( n \) is the extracted metal atom number, \( z \) is the valence of metal ions (+3 for Al and +2 for Mg/Ca), and \( F \) is the Faraday constant. The change in lattice parameters \( (x_{\text{change}}, x) \) could be the lattice constant \( a, b, \) or \( c \), the angle \( \alpha, \beta, \) or \( \gamma \), and the cell volume could be defined as

\[
x_{\text{change}} = \left( x_{\text{de}} - x_0 \right)/x_0
\]

where \( x_0 \) represents the lattice parameters of the deintercalated structure, and \( x_0 \) is the lattice parameters of the original structure. The metal ion diffusion pathways and energy profiles were calculated by the CI-NEB method. We adopted 10 ps AIMD at 600 K to evaluate the dynamical stability and chose a canonical (NVT) ensemble, Nose–Hoover thermostat, and a time step of 2 fs.

**ASSOCIATED CONTENT**

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00482.

Statistics of database screening process; the U value of DFT+U computation; the resulting structure after ab initio molecular dynamics; and the ion migration energy profile and pathway (PDF).

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