ABSTRACT: Here, we develop design rules for aqueous sodium-ion battery cathodes through a comprehensive density functional theory study of the working potential and aqueous stability of known cathode materials. These design rules were applied in a high-throughput screening of Na-ion battery cathode materials for application in aqueous electrolytes. Five promising cathode materials, NASICON-Na₃Fe₂(PO₄)₃, Na₂FePO₄F, Na₃FeCO₃PO₄, alluadite-Na₂Fe₃(PO₄)₃, and Na₃MnCO₃PO₄, were identified as hitherto-unexplored aqueous sodium-ion battery cathodes, with high voltage, good capacity, high stability in aqueous environments, and facile Na-ion migration. These findings pave the way for practical cathode development for large-scale energy-storage systems based on aqueous Na-ion battery chemistry.

INTRODUCTION

Aqueous sodium-ion batteries (ASIBs) have recently gathered intensive interest for large-scale energy-storage systems.¹,² Compared to nonaqueous batteries, the use of a nonflammable, inexpensive, and environmentally-safe aqueous electrolyte in ASIBs not only offers high reliability but also lowers the cost of manufacture and maintenance. The rapid ionic diffusion in the aqueous electrolyte, which is generally 2 to 3 orders of magnitude higher than that in a nonaqueous electrolyte, also enables high rate capability in ASIBs.³

Much research effort has been directed toward the design of ASIB cathodes with both higher energy densities and long-term cycling stabilities.¹,² Figure 1 and Table 1 summarize the main cathodes that have been studied for ASIB applications. They can be broadly categorized into four families:

1. Mn oxides. Na₀.₄₄MnO₂ (space group: Pbam) is among the most well-studied cathodes in ASIBs. Its electrochemical performance varies in different voltage ranges and electrolytes.⁴⁻⁶ Whereas most Mn oxides exhibit capacitive behavior in aqueous electrolytes,⁷⁻¹¹ Na₀.₄₄MnO₂ exhibits consecutive biphasic reactions with Na⁺ intercalation.⁴ The interconnected diffusion channels and the abundant vacancies in the structure facilitate Na⁺ diffusion in the charge/discharge processes.³

2. NAtrium Super Ionic CONductor (NASICON). The NASICON compounds have been extensively studied as sodium-ion battery (SIB) cathodes because of their open framework, which enables facile Na⁺ diffusion.¹² The general formula of NASICON is NaₓMM’(XO₄)₃. R₃C-Na₃V₂(PO₄)₃ is the most widely investigated NASICON-type cathode in conventional SIBs.¹³ Recently, R₃C-Na₃VTi(PO₄)₃ and Na₃MnTi(PO₄)₃ have also been investigated as electrodes in symmetric aqueous batteries and exhibit significantly improved long-term cycling stability compared with Na₃V₂(PO₄)₃.¹⁶
Table 1. Electrochemical Properties of Representative Cathodes for ASIBs

<table>
<thead>
<tr>
<th>formula</th>
<th>working potential (V vs Na/Na⁺)</th>
<th>electrolyte (pH)</th>
<th>current rate (mA h/g)</th>
<th>cycling voltage range (V vs Na/Na⁺)</th>
<th>retention (%)/cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₆₄₋₈₄MnO₂</td>
<td>2.00–3.50</td>
<td>1 M NaClO₄ in 1:2 EC/DMC</td>
<td>5C 128</td>
<td>2.0–4.0</td>
<td>77/1000 27</td>
</tr>
<tr>
<td>Na₆₄₋₈₄MnO₂</td>
<td>3.35–3.60</td>
<td>1 M Na₂SO₄ (7)</td>
<td>4C 45</td>
<td>3.35–3.60</td>
<td>100/1000 4</td>
</tr>
<tr>
<td>Na₆₄₋₈₄MnO₂</td>
<td>2.91–3.41</td>
<td>1 M Na₂SO₄ (7)</td>
<td>2C 47</td>
<td>2.84–3.59</td>
<td>88/200 5</td>
</tr>
<tr>
<td>Na₆₄₋₈₄MnO₂</td>
<td>2.46–2.76</td>
<td>1 M Na₂SO₄ (13.5)</td>
<td>2C 32</td>
<td>2.31–2.91</td>
<td>100/400 6</td>
</tr>
<tr>
<td>NaV₂(P₂O₇)₃</td>
<td>3.4</td>
<td>1 M NaClO₄ in 1:2 EC/DMC</td>
<td>10C 106</td>
<td>2.3–3.9</td>
<td>84.9/1000 13</td>
</tr>
<tr>
<td>NaV₂(P₂O₇)₃</td>
<td>3.4</td>
<td>1 M NaClO₄ (7)</td>
<td>8.5C 209 (F/g)</td>
<td>2.91–3.84</td>
<td>32/30 28</td>
</tr>
<tr>
<td>Na₀.₆Ni₁.₂Fe(CN)₆</td>
<td>3.3</td>
<td>1 M Na₂SO₄ (7)</td>
<td>5C 51</td>
<td>2.91–3.51</td>
<td>92/500 14</td>
</tr>
<tr>
<td>Na₀.₆Ni₁.₂Fe(CN)₆</td>
<td>2.16</td>
<td>1 M Na₂SO₄ (7)</td>
<td>5C 50</td>
<td>2.11–2.91</td>
<td>94/500 14</td>
</tr>
<tr>
<td>Na₀.₆MnTi(P₃O₇)₆</td>
<td>2.12–4.01</td>
<td>1 M NaClO₄ in 1:3 EC/PC + 5% PC</td>
<td>2C 119</td>
<td>1.5–4.0</td>
<td>92/500 29</td>
</tr>
<tr>
<td>Na₀.₆MnTi(P₃O₇)₆</td>
<td>2.14–3.54</td>
<td>1 M Na₂SO₄ (7)</td>
<td>1C 56.5</td>
<td>2.14–3.54</td>
<td>98/100 15</td>
</tr>
<tr>
<td>NaFePO₄</td>
<td>2.52–3.24</td>
<td>1 M NaClO₄ in PC</td>
<td>C/20 90</td>
<td>2.0–4.5</td>
<td>100/80 30</td>
</tr>
<tr>
<td>NaFePO₄</td>
<td>2.50–3.30</td>
<td>aqueous electrolyte</td>
<td>1C 65</td>
<td>2.75–3.65</td>
<td>86/300 18</td>
</tr>
<tr>
<td>NaFePO₄</td>
<td>3.48</td>
<td>1 M NaClO₄ in 98:2 PC/FEC</td>
<td>C/20 125</td>
<td>2.2–4.3</td>
<td>90/50 31</td>
</tr>
<tr>
<td>NaFePO₄</td>
<td>2.55–3.2</td>
<td>1 M Na₂SO₄ (7)</td>
<td>1C 70</td>
<td>2.45–3.3</td>
<td>90/30 17</td>
</tr>
<tr>
<td>NaFe(P₃O₇)₃²P₂O₇</td>
<td>2.75–3.25</td>
<td>1 M NaClO₄ in EC/PC</td>
<td>1C 99</td>
<td>1.8–4.3</td>
<td>90/50 19</td>
</tr>
<tr>
<td>NaFe(P₃O₇)₃²P₂O₇</td>
<td>2.50–3.25</td>
<td>1 M Na₂SO₄ (6)</td>
<td>1C 84</td>
<td>2.5–3.4</td>
<td>74/50 19</td>
</tr>
<tr>
<td>K₀.₄Ni₁.₂Fe(CN)₆</td>
<td>3.30</td>
<td>1 M NaNO₃ (2)</td>
<td>8.3C 51</td>
<td>100/5000</td>
<td>20/1000 21</td>
</tr>
<tr>
<td>Na₄₋₄Cu₃Fe(CN)₆</td>
<td>3.52</td>
<td>Na₂SO₄</td>
<td>5C 57</td>
<td>93/500</td>
<td>22/1000 22</td>
</tr>
</tbody>
</table>

3. Fe phosphates. Olivine-NaFePO₄, pyrophosphate-Na₄Fe₂(P₂O₇)₃, and mixed anionic phosphate Na₆₄₋₈₄Fe(CN)₆·Na₂PO₄ have been investigated as cathodes in ASIBs, given the fact that the average redox potential of Fe²⁺/Fe³⁺ in phosphate compounds is usually located within the electrochemical stability window of the aqueous electrolyte.¹⁷–¹⁹

4. Prussian blue analogues (PBAs). PBAs, with a general chemical formula of A[P[R(CN)₆]₁₋₆nH₂O (A = alkali or alkaline ion, P and R = transition metals), have been demonstrated as excellent cathode materials for ASIBs because their open three-dimensional framework enables fast ionic diffusion and superior cycling stability.²⁰ In particular, K₀.₄Ni₁.₂Fe(CN)₆·3.6H₂O and Na₄₋₄Cu₃Fe(CN)₆·8H₂O show great performance in aqueous electrolyte during electrochemical cycling of Na⁺ ions.²¹,²²

Unlike cathodes in conventional SIBs, which usually operate at a potential larger than 3.5 V versus Na/Na⁺, cathodes in ASIBs must have working potentials within the evolution potential of O₂ and H₂ gas, that is, 2.31–3.53 V versus Na/Na⁺ in a neutral electrolyte. Also, dissolution of electrodes and side reactions with the aqueous electrolyte, such as electrode materials reacting with H₂O/O₂ and proton intercalation into electrode materials, can adversely affect the long-term cycling stability of ASIBs. Possible strategies to mitigate these side reactions include coating the electrode, eliminating oxygen, and adjusting the pH of the electrolyte.²³ However, the intrinsic instability of electrode materials in aqueous environment still leads to significant performance reduction of ASIBs. For example, Zhang et al.²⁴ found that the capacity of carbon-coated NaV₂(P₂O₇)₃ fades steadily from 94.5 mA h/g to about 10 mA h/g within only 30 cycles in 1 M Na₂SO₄ electrolyte when being charged/discharged at a rate of 10 C because of cathode dissolution. Whereas first principles methods have been applied extensively to the study of battery materials, there have been relatively few computational studies of ASIB cathode materials, and most are focused on the PBA family.²⁵,²⁶

In this work, we derive design rules by benchmarking first principles predictions of the working potential and aqueous stability on representative ASIB cathode materials. The scope includes all cathodes tabulated in Table 1, with the exception of the PBAs as these have been studied extensively previously, and possible water intercalation in these systems complicates their analysis.²⁶ We then apply these design rules to the high-throughput screening of known SIB cathode materials for application in aqueous electrolytes, identifying several hitherto-unexplored candidates for further exploration.

**METHODS**

**Density Functional Theory Calculations.** All spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation package within the projector-augmented wave method.³²,³³ The exchange–correlation functional used for structural relaxation and energy calculations was the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation functional³⁴ with Hubbard U³⁵ applied for 3d transition metals. The U parameters used were similar to those from the Materials Project.³⁶ For Ti and V containing compounds, calculations were also performed using the screened hybrid Heyd–Scuseria–Ernzerhof (HSE) functional³⁷,³⁸ and the strongly constrained and appropriately normed (SCAN) functional.³⁹ The energy cutoff of plane wave was 520 eV, and the k-point density was at least 1000/(number of atoms in the cell). All calculations were performed in a ferromagnetic configuration, initialized with low spin for Co and high spin for all other transition metals. All crystal structure manipulations, input/output file generation, and data analysis were performed using the Python Materials Genomics (pymatgen) package.⁴⁰

**Voltage Profile.** The average intercalation potential of Na into a host X versus Na/Na⁺ was calculated by the equation:

$$V = -\frac{E_{DFT}(NaX_{\infty}) - E_{DFT}(Na_{\infty}X) - \epsilon xE_{DFT}(Na)}{xe}$$

where $E_{DFT}(\cdot)$ denotes the DFT calculated total energy and $\epsilon$ is the electron charge. In this work, the average voltage was calculated based on a one-electron-per-transition-metal redox reaction for all materials.
The voltage profiles were constructed by using all stable phases from the pseudobinary phase diagram of the sodiated and desodiated compounds (Figure S1), obtained using the convex hull construction. All initial sodiated structures were obtained either from the Materials Project or the ICSD database. All partially desodiated structures were determined by enumerating all symmetrically distinct orderings in sufficiently large supercells using the adaptor to the enumlib library in pymatgen. For each composition, at least 20 lowest electrostatic energy (computed via the Ewald summation method) configurations were selected for the convex hull construction.

Pourbaix Diagram. Pourbaix diagrams were computed using the formalism developed by Persson et al., which combines ab initio calculated solid phases with experimental aqueous reference states. In a chemical system M, the Pourbaix stable domains are determined based on the knowledge of all possible equilibrium redox reactions in the M–O–H chemical space. For the following reaction in an aqueous medium at a given pH = −log[H+]

\[
[\text{reactants}] + H_2O = [\text{products}] + nH^+ + ne^-
\]  

(2)

can be used to relate the external potential, \(E\), to the change of the Gibbs free energy of the reaction, \(\Delta G_r\). \(\Delta G_r^0\) denotes the Gibbs free-energy change of the reaction under standard state, \(F\) is the Faraday constant, \(R\) is the gas constant, and \(T\) is the temperature. Thus, the most stable species in the aqueous environment can be determined by minimizing \((\Delta G_r + nFE)\) across all possible reactions for a given pH and \(E\).

The metastability of a cathode was evaluated by computing its Gibbs free-energy difference (\(\Delta G_{\text{px}}\)) with respect to the stable domains on Pourbaix diagram as a function of pH and potential (\(E\)). The focus of this work is on the potential range from 0 to 14 versus the standard hydrogen electrode (SHE) and the pH range from 0 to 14. Unless otherwise stated, the concentration of Na+ ion is set at 1 M, and the concentrations of all other ions are set at 10\(^{-6}\) M, which are typical operating conditions for ASIBs. It should be noted that a number of non-H/O atoms are conserved in the phase transformations between cathodes and stable species in an aqueous environment. Hence, \(\Delta G_{\text{px}}\) is normalized by the total number of non-H/O atoms with units of eV/cation.

Diffusion Barriers. The sodium vacancy migration barriers were calculated using the climbing image nudged elastic band (CI-NEB) method. Here, the PBE functional without Hubbard U was adopted to avoid possible mixing of the diffusion barrier with a charge-transfer barrier. The force convergence criterion was 0.05 eV/Å.

**RESULTS**

**Screening Workflow.** Our proposed screening workflow for ASIB cathodes is given in Figure 2. For operation in aqueous environments, a cathode must satisfy the following criteria:

1. Suitable working potential within the H2 and O2 evolution potential range (e.g., 2.31–3.53 V vs Na/Na\(^+\) in the neutral solution). For practical energy densities, the average working potential in the literature is typically higher than 3 V versus Na/Na\(^+\) in the neutral electrolyte (Table 1).
2. High aqueous stability. Within the potential range of interest, a cathode with low \(\Delta G_{\text{px}}\) and forming solid phases in decomposition products on the Pourbaix diagram tends to exhibit superior long-term cycling stability. Based on previous work by Singh et al., on photoanodes, \(\Delta G_{\text{px}} < 0.5\) eV/cation (ideally 0 eV/cation) indicates low reactivity in aqueous environments.

In addition to the above criteria, any cathode (for ASIBs or otherwise) must also be synthesizable and have relatively high Na\(^+\) diffusivity for high rate capability. The synthesizability of a material is computationally estimated by its energy above the linear combination of stable phases in the DFT-calculated 0 K phase diagram (\(E_{\text{hull}}\)). Stable phases have zero \(E_{\text{hull}}\), and the higher its \(E_{\text{hull}}\) the more unstable a phase is. A typical \(E_{\text{hull}}\) threshold of 30–50 meV/atom was used to identify synthesizable materials in previous high-throughput screening works. The potential for high ionic conductivity can be estimated by computing the Na-ion migration barriers (\(E_n\)) for percolating Na diffusion pathways using NEB calculations. In conventional SIB cathodes, the predicted \(E_n\) values in facile Na\(^+\) diffusion pathways are generally less than 500 meV.

It should be noted that the criteria were established based purely on thermodynamic considerations; kinetic factors can contribute to stabilization of the materials in aqueous environments. For example, the electrochemical stability window of the aqueous electrolyte is usually slightly larger...
than 1.23 V because of overpotentials.54 Kinetic barriers (to ion diffusion for instance) may also retard cathode dissolution. Although these kinetic factors are difficult to directly compute, they can be accounted for by relaxation of the thermodynamic thresholds for screening purposes. Also, we only explore the aqueous stability of bulk cathodes in this work, whereas surface/interface effects and particle size may have an influence on the electrochemical properties of cathodes in ASIBs. For example, nanostructured electrocatalysts may exhibit better performance in terms of facile ion/electron transport, reduced changes of the electrodes, and increased utilization of active materials during charge/discharge processes, but increased surface/interface area may also result in destabilization of the electrode in aqueous solutions.

We will first benchmark the DFT-computed working potentials and $\Delta G_{pbx}$ for the seven well-known ASIB cathodes listed in Table 1 (excluding the PBAs).

**Voltage and Aqueous Stability of Known ASIB Cathodes.** $\text{Na}_{0.44}\text{MnO}_2$. Figure 3a shows the calculated voltage profile of $\text{Na}_x\text{MnO}_2$ ($x = 0.22–0.66$). The electrochemical stability windows at pH = 7 are shaded blue. The experimental voltage profile is from ref 57. (b) Calculated Pourbaix diagram of $\text{Na}_{0.44}\text{MnO}_2$. Regions containing solid phases are shaded green.

![Figure 3.](https://dx.doi.org/10.1021/acs.chemmater.0c01582)

Figure 3. (a) Calculated voltage profile of $\text{Na}_x\text{MnO}_2$ ($x = 0.22–0.66$). The electrochemical stability windows at pH = 7 are shaded blue. The experimental voltage profile is from ref 57. (b) Calculated Pourbaix diagram of $\text{Na}_{0.44}\text{MnO}_2$. Regions containing solid phases are shaded green.

The aqueous stability of $\text{Na}_x\text{MnO}_2$ cathode during the cycling process was evaluated by computing $\Delta G_{pbx}$ as a function of potential in different electrolytes (pH and Na concentration). In a neutral electrolyte (Figure 4a), when being charged at a high potential of 3.30–3.50 V versus Na/Na⁺, Na⁺ ions and solid NaMn$_{0.66}$O$_{16}$ form, and $\Delta G_{pbx}$ of Na$_{0.44}$MnO$_2$ is less than 0.1 eV/cation. With Na⁺ intercalating into the host structure, solid MnO$_3$ along with Na⁺ ions become more stable on the Pourbaix diagram, and $\Delta G_{pbx}$ of Na$_{0.44}$MnO$_2$ slightly increases. As the potential decreases to below 3.25 V versus Na/Na⁺, $\Delta G_{pbx}$ dramatically increases and reaches 1.0 eV/cation at 2.31 V versus Na/Na⁺. In these potential regions, Na$_{0.44}$MnO$_2$ fully decomposes into Na⁺ and Mn$^{2+}$.

In contrast, Na$_{x}$MnO$_2$ is predicted to be more stable in a basic electrolyte (Figure 4b), with relatively smaller $\Delta G_{pbx}$ (<0.5 eV/cation) within 2.0–3.14 V versus Na/Na⁺. Similarly, the small $\Delta G_{pbx}$ is coupled with the formation of all solid phases on the Pourbaix diagram within the potential range of 2.81–3.14 V versus Na/Na⁺. Na$_{0.42}$MnO$_2$ becomes stable within 2.81–2.87 V versus Na/Na⁺ in aqueous electrolytes with $\Delta G_{pbx} = 0$ eV/cation. In addition, $\Delta G_{pbx}$ starts to increase as solvated ion species become stable when the potential is lower than 2.81 V versus Na/Na⁺.

The change of $\Delta G_{pbx}$ with potential can be related to the cycling stability of Na$_{0.44}$MnO$_2$ cathode observed in experiments.55–56 For example, in a neutral electrolyte (1 M Na$_2$SO$_4$ with pH = 7), the capacity of a Na$_{0.44}$MnO$_2$/activated carbon cell shows no sign of decay after 1000 cycles when cycled within 3.35–3.60 V versus Na/Na⁺, whereas significant capacity fading was observed at lower potentials (<3.35 V versus Na/Na⁺). Pang et al.55 also observed 88% retention of the initial cycling after 200 cycles within the potential range of 2.91–3.41 V versus Na/Na⁺. In our calculations, $\Delta G_{pbx}$ of Na$_{0.44}$MnO$_2$ at a potential larger than 3.35 V versus Na/Na⁺ is lower than 0.1 eV/cation and solid-phase NaMn$_{0.66}$O$_{16}$ forms in decomposition products, whereas the measured slightly lower cycling stability within lower potential ranges can be anticipated because of larger $\Delta G_{pbx}$ and formation of all ion phases on the Pourbaix diagram when $E < 3.25$ V versus Na/Na⁺. In a basic electrolyte (1 M Na$_2$SO$_4$ with pH = 13.5), a stable capacity of 32 mA h/g was achieved with no significant capacity reduction after 400 cycles at 2C rate when cycled within 2.31–2.91 V versus Na/Na⁺.6 The stable cycling stability in basic electrolytes is in line with the low computed $\Delta G_{pbx}$ (<0.2 eV/cation) and formation of solid phases in decomposition products in this voltage range.

We also find that in regions where Na⁺ ions are stable, increasing the concentration of Na⁺ ions slightly decreases the dissolution tendency of electrodes by $\sim 0.0591 \log C_{Na^+}$ eV/Na (Figure 4).
NASICON Electrodes. Figure 5a,b presents the calculated voltage profiles of Na$_x$V$_2$(PO$_4$)$_3$ and Na$_x$TiV(PO$_4$)$_3$, respectively. In all cases, the voltages are substantially underestimated relative to experimental values, similar to previous DFT results on the NASICON systems. Although the use of HSE and SCAN functionals does substantially increase the voltage of the lower redox couples, they remain far below the experimental value. We therefore adopted the experimental redox potentials as the electrochemical window of interest in the following aqueous stability analysis.

Figures 6a and 7a show the calculated Pourbaix diagram of Na$_3$V$_2$(PO$_4$)$_3$ and $\Delta G_{pbx}$ at pH = 7, respectively. From Figure 6a, V forms solid vanadium oxides in low-voltage regimes (e.g., $<0 \, V$ vs SHE at pH = 7). With an increase in the external potential, V in higher oxidation states becomes more stable as VO$_n^-$ ions. At pH = 7, $\Delta G_{pbx}$ increases with the increase of potential and reaches 0.65 eV/cation at 3.37 V versus Na/Na$^+$ (Figure 7a), which is equal to the experimental redox potential of V$^{3+}$/V$^{4+}$. Thus, the observed capacity fading of Na$_3$V$_2$(PO$_4$)$_3$ cathode in 1 M Na$_2$SO$_4$ neutral electrolyte can be anticipated by the large $\Delta G_{pbx}$ and the decomposition into nonsolid phases when cycled within 2.7–3.6 V versus Na/Na$^+$. Compared with Na$_3$V$_2$(PO$_4$)$_3$, the introduction of Ti in Na$_2$TiV(PO$_4$)$_3$ leads to the formation of TiO$_2$ solid phases within the voltage range of 2.0–3.8 V versus Na/Na$^+$ on the Pourbaix diagram (Figure 6b). In a neutral electrolyte, $\Delta G_{pbx}$ of Na$_2$TiV(PO$_4$)$_3$ increases from 0.17 to 0.42 eV/cation as the potential is increased from 2.16 to 3.33 V versus Na/Na$^+$. With the continued increase of potential, a biphasic reaction occurs from Na$_2$TiV(PO$_4$)$_3$ to NaTiV(PO$_4$)$_3$. Then, $\Delta G_{pbx}$ reaches 0.5 eV/cation at 3.53 V versus Na/Na$^+$. Unlike Na$_3$V$_2$(PO$_4$)$_3$, Na$_2$TiV(PO$_4$)$_3$ shows excellent cycling performance in 1 M Na$_2$SO$_4$ aqueous electrolyte (pH = 7) with greater than 90% retention of its initial capacity after 500 cycles when cycled between 2.7 and 3.6 V versus Na/Na$^+$. Regions containing solid phases are shaded green.

Figure 5. Voltage profile of (a) Na$_x$V$_2$(PO$_4$)$_3$ ($x = 1–3$) and (b) Na$_x$TiV(PO$_4$)$_3$ ($x = 1–3$) cathodes. The electrochemical stability window at pH = 7 is shaded blue. The experimental voltage profile is from refs. 13,14.

Figure 6. Calculated Pourbaix diagram of (a) Na$_3$V$_2$(PO$_4$)$_3$ and (b) Na$_2$TiV(PO$_4$)$_3$. Regions containing solid phases are shaded green.
both the lower ΔG_{pbx} of Na_xTiV(PO_4)_3 as well as the formation of solid TiO_2 in the high-potential region may contribute to suppression of V dissolution. Similar results were also observed for Na_3MnTi-(PO_4)_3 electrodes (Figure S3), which exhibit stable electrochemical performance experimentally.15

Fe-Based Phosphates. Figure 8a—c presents the calculated voltage profile of three Fe-based cathode materials. Here, we consider the voltage profile operating on the Fe^{2+}/Fe^{3+} couple only; even though additional Na can potentially be removed from Na_2FeP_2O_7 and Na_4Fe_3(PO_4)_2(P_2O_7) to access the Fe^{3+}/Fe^{4+} couple, the voltages are far too high for ASIBs. All three cathodes exhibit voltages within the electrochemical stability window of the aqueous electrolyte (pH = 7) related to the Fe^{2+}/Fe^{3+} redox couple and thus are able to deliver large capacities in ASIBs. Olivine-NaFePO_4 and Na_2FeP_2O_7 have theoretical capacities of 154.2 mA h/g and 97.2 mA h/g, respectively, in the aqueous electrolyte, which are in good agreement with the experimentally achieved capacities. Na_4Fe_3(PO_4)_2P_2O_7 has a theoretical capacity of 129.0 mA h/g, but its final voltage plateau lies close to the oxygen evolution potential and therefore may not be accessible experimentally.16

Figure 9a shows the Pourbaix diagram of the olivine-NaFePO_4 cathode. Within the electrochemical stability window of the aqueous electrolyte, Fe forms solid Fe_2O_3 in most regions (e.g., E > −0.2 V vs SHE at pH = 7). In the low-potential region (near the H_2 gas evolution potential), Fe^{2+}, Fe(OH)^+, and solid Fe_2O_3 are stable in acidic, neutral, and alkaline electrolytes, respectively. P forms H_3PO_4^- ions within the water-splitting window in the aqueous environment and does not affect the formation of Fe- and Na-based stable species on the Pourbaix diagram. Similar observations can be
made in the Pourbaix diagrams of Na₂FeP₂O₇ and Na₄Fe₃(PO₄)₂P₂O₇ (Figure S4a,b, respectively).

All three cathodes exhibit low $\Delta G_{\text{pbx}}$ ($\leq 0.32$ eV/cation) in the range of their working potential, and a solid phase of Fe₂O₃ forms in high potential regions (>2.67 V vs Na/Na⁺) in a neutral electrolyte (Figure 10a−c). Both olivine-NaFePO₄ and Na₂FeP₂O₇ cathodes exhibit stable cycling behaviors in experiments. For Na₄Fe₃(PO₄)₂P₂O₇, Fernández-Ropero et al. detected a small component of dissolved Fe (0.1%) along with a thin layer of solid Fe₃O₄ after immersing the sample in 1 M Na₂SO₄ solutions (pH = 6) for 72 h. Furthermore, the oxidation of electrodes in aqueous solution was confirmed by powder X-ray diffraction and inductively coupled plasma analysis after the stability tests, and the authors ascribed the modest cycling stability to the oxidation and dissolution of electrode materials.

**Screening for New ASIB Cathodes.** The screening workflow in Figure 2 was applied to well-known cathodes in the following chemistries:

1. **Phosphates.** Phosphate-based electrodes are known for their stable open frameworks and high working potential because of the strong covalent bonding and inductive effect of the phosphate anion. The following compounds were selected: NASICON-Na₃Me₂(PO₄)₃ (Me = Fe, V), olivine-NaMePO₄ (Me = Fe), pyrophosphate Na₄Me₃P₂O₇ (Me = Mn, Fe, Co), and mixed anion phosphates Na₂Me₃(PO₄)₂P₂O₇ (Me = Fe,
Mn, Co, Ni)\textsuperscript{3,61} alluadite Na\textsubscript{2}Me\textsubscript{3}(PO\textsubscript{4})\textsubscript{3} (Me = Fe)\textsuperscript{62} α- and β-NaVOPO\textsubscript{4}\textsuperscript{63,64}.

2. Carbonophosphates. The sidorenkite Na\textsubscript{3}MeCO\textsubscript{3}PO\textsubscript{4}, was first proposed by Hauriet et al.\textsuperscript{65} from high-throughput calculation as potential cathode materials for SIBs. Among the predicted structures, Na\textsubscript{3}MnCO\textsubscript{3}PO\textsubscript{4} and Na\textsubscript{3}FeCO\textsubscript{3}PO\textsubscript{4} have been successfully synthesized and investigated as cathodes in SIBs with high capacity.\textsuperscript{66,67}

3. Sulfates. A new alluadite Na\textsubscript{2}Me\textsubscript{3}(SO\textsubscript{4})\textsubscript{3} (Me = Fe) was reported as an SIB cathode with high redox potential (3.8 V vs Na/Na\textsuperscript{+}) and Na ion conductivity.\textsuperscript{68}

4. Oxysulfates. Oxysulfates have the potential to enable cathodes with high working potential because of the highly electronegative fluoride anion. The oxysulfates investigated in this work include Pbcn—Na\textsubscript{2}MePO\textsubscript{3}F (Me = Fe, Co)\textsuperscript{69,70} P\textsubscript{2}1/c—Na\textsubscript{2}MePO\textsubscript{3}F (Me = Mn)\textsuperscript{71} P\textsubscript{n}a\textsubscript{2}—NaVPO\textsubscript{4}F\textsuperscript{72} and Na\textsubscript{3}(VO\textsubscript{2})\textsubscript{2}(PO\textsubscript{4})\textsubscript{2}F\textsubscript{3–2x} (x = 0, 1).\textsuperscript{73}

Figure 11 summarizes the aqueous electrochemical properties of all compounds investigated. It may be observed that the average redox potential of Co- and Ni-based phosphates are too high (>3.94 V vs Na/Na\textsuperscript{+}) to be used in SIBs.

Among the cathodes with the average voltage within the electrochemical window of neutral aqueous electrolytes, the V-based cathodes generally exhibit high reactivity with water (high ΔG\textsubscript{ph} ≥ 0.5 eV/cation) and lack of solid decomposition products in aqueous solution, which suggest that they are intrinsically unstable in aqueous environments. This observation is in line with experimental observations.\textsuperscript{16} The Fe-based cathodes generally exhibit far better aqueous stability, though with somewhat lower average voltages. Na\textsubscript{2}FePO\textsubscript{4}O\textsubscript{4}, olivine-NaFePO\textsubscript{4}, and Na\textsubscript{2}Fe(PO\textsubscript{4})\textsubscript{2}O\textsubscript{4} have already been studied as cathodes in SIBs. NASICON-Na\textsubscript{2}Fe\textsubscript{3}(PO\textsubscript{4})\textsubscript{3} has been investigated as an anode in SIBs with the Fe\textsuperscript{3+/4+} redox potential at 2.5 V versus Na/Na\textsuperscript{+}.\textsuperscript{74} Our results show that it can be used as cathodes in SIBs with the activated Fe\textsuperscript{3+/4+} redox pair at a potential of ~3.0 V versus Na/Na\textsuperscript{+}.\textsuperscript{58} Na\textsubscript{2}FePO\textsubscript{4}F, which shows an average voltage at around 3.0 V versus Na/Na\textsuperscript{+} with a theoretical capacity of 124.2 mA h/g,\textsuperscript{63} is a promising candidate for cathodes in SIBs because of its high average working potential as well as high aqueous stability (ΔG\textsubscript{ph} = 0.2 eV/cation at 3.0 V vs Na/Na\textsuperscript{+}). The average voltages of alluadite-Na\textsubscript{2}Fe\textsubscript{3}(PO\textsubscript{4})\textsubscript{3} and sidorenkite-Na\textsubscript{2}Fe(PO\textsubscript{4})\textsubscript{3} (PO\textsubscript{4})\textsubscript{3} are somewhat too low in neutral electrolytes, resulting in a significant compromise in energy density in SIBs. Nevertheless, they are potentially interesting cathodes in basic electrolytes when paired with appropriate low-voltage anodes. Fe-based cathodes tend to form solid phases within 2.5–3.53 V versus Na/Na\textsuperscript{+} in aqueous solution, and most compounds with Fe\textsuperscript{3+/4+} redox pairs are electrochemically active within this voltage range. The calculated maximum voltage of alluadite-Na\textsubscript{2}Fe\textsubscript{3}(PO\textsubscript{4})\textsubscript{3} and sidorenkite-Na\textsubscript{2}Fe(PO\textsubscript{4})\textsubscript{3} (PO\textsubscript{4})\textsubscript{3} is 3.0 V versus Na/Na\textsuperscript{+}, which is in line with previous experimental results\textsuperscript{75} in nonaqueous electrolytes. Na\textsubscript{2}FePO\textsubscript{4}F is predicted to be stable in basic solution with small ΔG\textsubscript{ph} (<0.3 eV/cation). Similarly, alluadite-Na\textsubscript{2}Fe\textsubscript{3}(PO\textsubscript{4})\textsubscript{3} exhibits three computed voltage plateaus at 2.34, 3.23, and 2.23 V versus Na/Na\textsuperscript{+} (Figure S13a), whereas solid-solution behavior was observed with an average working potential of 2.75 V versus Na/Na\textsuperscript{+}.\textsuperscript{62} Here, we propose that...
alluadite-Na$_2$Fe$_3$(PO$_4$)$_3$ can be cycled within the potential range of 2.12–3.35 V versus Na/Na$^+$. Both cathode candidates exhibit reasonable diffusion barriers of 400–500 meV (Figures S12 and S14). An anode with a low working potential should be coupled with these cathodes in basic solution to achieve a high energy density in ASIBs.

$Na_xMnCO_3PO_4$, $Na_3MnCO_3PO_4$ was reported to exhibit a large charge/discharge potential gap in the nonaqueous electrolyte. Our calculations (Figure S15a) indicate that $Na_3MnCO_3PO_4$ has three voltage plateaus at 4.08, 3.80, and 3.04 V versus Na/Na$^+$. Whereas $Na_2MmCO_3PO_4$ is predicted to be unstable in acidic aqueous solution within a high potential regime (Figure S15c), the aqueous stability analysis (Figure S15d) predicts that it is stable within the potential range of 2.39–3.23 V versus Na/Na$^+$ in a basic electrolyte ($pH = 12$) with facile Na$^+$ conductivity (Figure S16).

All five cathodes are predicted to exhibit high aqueous stability across wide voltage ranges and thus may have large accessible capacities in aqueous electrolytes. In particular, $Na_2FePO_4F$ and $Na_2Fe_3(PO_4)_4$ cathodes are predicted to have theoretical capacities of 124 and 110 mA h g$^{-1}$ in aqueous solution, respectively, which outperform most of the known ASIB cathodes in the literature (see Table 1). Also, the excellent electrochemical properties of the two promising sidorenkites, $Na_2FeCO_3PO_4$ and $Na_3MnCO_3PO_4$, show that the easily synthesizable, low cost carbonophosphate family is a potential new class of ASIB cathodes.

**CONCLUSIONS**

To conclude, we have performed a comprehensive investigation of the working potential and aqueous stability of well-established ASIB cathodes using DFT calculations. A set of rigorous design rules and a screening workflow to identify potentially promising ASIB cathodes were developed. By applying this screening workflow to a large database of known SIB cathode materials, five promising cathode materials, $Na_2Fe_3(PO_4)_4$, $Na_2FePO_4F$, $Na_3MnCO_3PO_4$, $Na_2FeCO_3PO_4$, and alluadite-$Na_2Fe_3(PO_4)_4$, were identified that exhibit high voltage, good capacity, high stability in aqueous environments, and facile Na-ion migration. These findings pave the way for practical cathode development for large-scale energy-storage systems based on aqueous Na-ion chemistry.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c01582.

Calculated binary phase diagrams of all compounds; calculated voltage profile of Na$_x$MnO$_2$ in the basic electrolyte; calculated voltage profiles, Pourbaix diagram, and $\Delta G_{pka}$ of $Na_xMnTi_2(PO_4)_3$ cathode; Pourbaix diagram of $Na_2FeP_2O_7$ and $Na_4Fe_3P_4O_15$ cathodes; calculated $\Delta G_{pka}$ as a function of pH of selected cathodes at their average voltage; aqueous stability analysis of $Na_3MnPO_{4}F$; and detailed calculations of the selected promising candidates as cathodes in ASIBs (PDF)

**AUTHOR INFORMATION**

Corresponding Author
Shyue Ping Ong — Department of NanoEngineering, University of California San Diego, La Jolla, California 92039-0448, United States; orcid.org/0000-0001-7526-2587; Email: ongsp@eng.ucsd.edu

Authors
Xingyu Guo — Materials Science and Engineering Program, University of California San Diego, La Jolla, California 92039-0448, United States; orcid.org/0000-0002-3456-5347
Zhenbin Wang — Department of NanoEngineering, University of California San Diego, La Jolla, California 92039-0448, United States; orcid.org/0000-0002-7016-9245
Zhi Deng — Department of NanoEngineering, University of California San Diego, La Jolla, California 92039-0448, United States
Bo Wang — GEIRI North America, San Jose, California 95134, United States
Xi Chen — GEIRI North America, San Jose, California 95134, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.chemmater.0c01582

Notes
The authors declare no competing financial interest.

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