

Design Principles for Aqueous Na-Ion Battery Cathodes

Xingyu Guo, Zhenbin Wang, Zhi Deng, Bo Wang, Xi Chen, and Shyue Ping Ong*

Cite This: https://dx.doi.org/10.1021/acs.chemmater.0c01582



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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.** Na_{0.44}MnO₂ (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 Na_{0.44}MnO₂ 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 Na_xMM'(XO₄)₃. $R\bar{3}c$ -Na₃V₂(PO₄)₃ is the most widely investigated NASI-CON-type cathode in conventional SIBs.¹³ Recently, $\bar{R}c$ -Na₃VTi(PO₄)₃¹⁴ and Na₃MnTi(PO₄)₃¹⁵ have also been investigated as electrodes in symmetric aqueous batteries



Figure 1. Crystal structures of representative ASIB cathodes. (a) $Na_{0,44}MnO_{27}$ (b) NASICON: $Na_3V_2(PO_4)_{37}$ (c) Fe-based phosphates: NaFePO₄, and (d) PBAs: cubic $Na_2FeCu(CN)_{6}$.

and exhibit significantly improved long-term cycling stability compared with $Na_3V_2(PO_4)_3$.¹⁶

 Received:
 April 14, 2020

 Revised:
 July 25, 2020

 Published:
 July 27, 2020



formula	working potential (V vs Na/Na ⁺)	electrolyte (pH)	current rate	capacity (mA h/g)	cycling voltage range (V vs Na/Na ⁺)	retention (%)/cycles	refs
Na _{0.44} MnO ₂	2.00-3.50	1 M NaClO ₄ in 1:2 EC/DMC	5C	128	2.0-4.0	77/1000	27
$Na_{0.44}MnO_2$	3.35-3.60	$1 \text{ M Na}_2 \text{SO}_4 (7)$	4C	45	3.35-3.60	100/1000	4
Na _{0.44} MnO ₂	2.91-3.41	$1 \text{ M Na}_2 \text{SO}_4 (7)$	2C	47	2.84-3.59	88/200	5
Na _{0.44} MnO ₂	2.46-2.76	1 M Na ₂ SO ₄ (13.5)	2C	32	2.31-2.91	100/400	6
$Na_3V_2(PO_4)_3$	3.4	1 M NaClO ₄ in 1:2 EC/DMC	10C	106	2.3-3.9	84.9/1000	13
$Na_3V_2(PO_4)_3$	3.4	$1 \text{ M Na}_2 \text{SO}_4 (7)$	8.5C	209 (F/g)	2.91-3.84	32/30	28
$Na_2VTi(PO_4)_3$	3.33	$1 \text{ M Na}_2 \text{SO}_4 (7)$	5C	51	2.91-3.51	92/500	14
Na ₂ VTi(PO ₄) ₃	2.16	$1 \text{ M Na}_2 \text{SO}_4 (7)$	5C	50	2.11-2.91	94/500	14
Na ₃ MnTi(PO ₄) ₃	2.12-4.01	1 M NaClO ₄ in 1:1 EC/PC + 5% FC	2C	119	1.5-4.0	92/500	29
$Na_3MnTi(PO_4)_3$	2.14-3.54	$1 \text{ M Na}_2 \text{SO}_4 (7)$	1C	56.5	2.14-3.54	98/100	15
$Na_2FeP_2O_7$	2.52-3.24	1 M NaClO ₄ in PC	C/20	90	2.0-4.5	100/80	30
$Na_2FeP_2O_7$	2.50-3.30	aqueous electrolyte	1C	65	2.75-3.65	86/300	18
NaFePO ₄	3.48	1 M NaClO ₄ in 98:2 PC/FEC	C/20	125	2.2-4.3	90/50	31
NaFePO ₄	2.55-3.2	$1 \text{ M Na}_2 \text{SO}_4 (7)$	1C	70	2.45-3.3	90/30	17
$Na_4Fe_3(PO_4)_2P_2O_7$	2.75-3.25	1 M NaClO ₄ in EC/PC	1C	99	1.8-4.3	90/50	19
$Na_4Fe_3(PO_4)_2P_2O_7$	2.50-3.25	1 M Na ₂ SO ₄ (6)	1C	84	2.5-3.4	74/50	19
$K_{0.6}Ni_{1.2}Fe(CN)_6$	3.30	$1 \text{ M NaNO}_{3}(2)$	8.3C	51		100/5000	21
$Na_{1.4}Cu_{1.3}Fe(CN)_6$	3.52	Na ₂ SO ₄	5C	57		93/500	22

Table 1. Electrochemical Properties of Representative Cathodes for ASIBs

- 3. Fe phosphates. Olivine-NaFePO₄, pyrophosphate-Na₂FeP₂O₇, and mixed anionic phosphate Na₄Fe₃(PO₄)₂P₂O₇ 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 $A_x P[R(CN)_6]_{1-y} \cdot nH_2O$ (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, $K_{0.6}Ni_{1.2}Fe(CN)_6 \cdot 3.6H_2O$ and $Na_{1.4}Cu_{1.3}Fe(CN)_6 \cdot 8H_2O$ 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 O_2 and H_2 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 H_2O/O_2 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.¹⁶ found that the capacity of carboncoated $Na_3V_2(PO_4)_3$ 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,²⁴ 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 cointercalation 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 projectoraugmented 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 U^{35} applied for 3d transition metals. The U parameters used were similar to those from the Materials Project.³ For Ti and V containing compounds, calculations were also performed using the screened hybrid Heyd–Scuseria–Ernzerhof (HSE) functional^{37,38} 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 atomsin 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 equation⁴¹

$$V = -\frac{E_{\text{DFT}}(\text{Na}_{n}X) - E_{\text{DFT}}(\text{Na}_{n-x}X) - xE_{\text{DFT}}(\text{Na})}{xe}$$
(1)

where $E_{\text{DFT}}(\cdot)$ denotes the DFT calculated total energy and *e* 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.⁴² All initial sodiated structures were obtained either from the Materials Project³⁶ or the ICSD database.⁴³ All partially desodiated structures were determined by enumerating all symmetrically distinct orderings in sufficiently large supercells using the adaptor to the enumlib library⁴⁴ in pymatgen.⁴⁰ 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.*,⁴⁵ 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 $pH = -log[H^+]$

$$[reactants] + H_2O = [products] + mH^+ + ne^-$$
(2)

the Nernst equation

$$nFE = \Delta G_{\rm r}$$

$$= \Delta G_{\rm r}^0 + 2.303 \times RT \times \log \frac{[\text{reactants}]}{[\text{products}]}$$

$$- 2.303 \times RT \times m \times \text{pH}$$
(3)

can be used to relate the external potential, E, to the change of the Gibbs free energy of the reaction, ΔG_r . ΔG_r^0 denotes the Gibbs freeenergy 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 ($\Delta G_{\rm pbx}$) with respect to the stable domains on Pourbaix diagram as a function of pH and potential (*E*).^{46,47} The focus of this work is on the potential range from -2 to 2 V *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, $\Delta G_{\rm pbx}$ 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.^{48,49} Here, the PBE functional without Hubbard U was adopted to avoid possible mixing of the diffusion barrier with a charge-transfer barrier.⁵⁰ 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 H_2 and O_2 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 ΔG_{pbx} and forming solid phases in decomposition products on the Pourbaix





Figure 2. Screening workflow for high-performance ASIB cathodes.

diagram tends to exhibit superior long-term cycling stability. Based on previous work by Singh *et al.*⁴⁷ on photoanodes, $\Delta G_{\rm pbx} < 0.5$ 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.^{50,51} 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_{hull}) .⁴² Stable phases have zero E_{hull} , and the higher its E_{hull} , the more unstable a phase is. A typical E_{hull} threshold of 30–50 meV/atom was used to identify synthesizable materials in previous high-throughput screening works.^{51,52} The potential for high ionic conductivity can be estimated by computing the Na-ion migration barriers (E_a) for percolating Na diffusion pathways using NEB calculations. In conventional SIB cathodes, the predicted E_a values in facile Na⁺ diffusion pathways are generally less than 500 meV.⁵³

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 electrodes 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.^{55,56}

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

Voltage and Aqueous Stability of Known ASIB Cathodes. Na_{0.44}MnO₂. Figure 3a shows the calculated



Figure 3. (a) Calculated voltage profile of Na_xMnO_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 $Na_{0.44}MnO_2$. Regions containing solid phases are shaded green.

voltage profile of Na_xMnO_2 , which exhibits nine plateaus within the voltage range of 2–3.3 V versus Na/Na⁺. The computed profile and voltages are in good agreement with experimental observations.⁵⁷ In the neutral electrolyte (pH = 7), the cathode can be cycled within the potential range of 2.31–3.53 V versus Na/Na⁺ (blue region) with a theoretical capacity of 100 mA h/g, whereas in a basic electrolyte (pH = 13.5) (orange region in Figure S2), the electrochemical window shifts to 1.91–3.14 V versus Na/Na⁺ with a smaller theoretical capacity of 80 mA h/g.

Figure 3b shows the computed Pourbaix diagram of $Na_{0.44}MnO_2$, which plots the stable species in the Na-Mn-O-H system with a Na/Mn ratio of 0.44:1 under various pH

values and potentials. In regions within the electrochemical window of aqueous electrolytes, Na forms Na⁺ ion in most regions. Mn is stable in an alkaline environment at high potential (*e.g.*, E > 0.17 V *vs* SHE at pH = 7) by forming manganese oxides, whereas Mn²⁺ ion forms in acidic conditions (pH < 4) or low potential regions. It may be observed that the solid phase Na_{0.44}MnO₂ does not appear in any region on the Pourbaix diagram, which suggests that it is thermodynamically metastable in an aqueous reservoir. It should be noted, however, that Na_{0.44}MnO₂ is a stable phase (*E*_{hull} = 0) on the nonaqueous Na–Mn–O phase diagram.

The aqueous stability of Na_xMnO₂ cathode during the cycling process was evaluated by computing $\Delta G_{\rm pbx}$ 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 NaMn₈O₁₆ form, and $\Delta G_{\rm pbx}$ of Na_xMnO₂ is less than 0.1 eV/cation. With Na⁺ intercalating into the host structure, solid Mn₂O₃ along with Na⁺ ions become more stable on the Pourbaix diagram, and $\Delta G_{\rm pbx}$ of Na_xMnO₂ slightly increases. As the potential decreases to below 3.25 V versus Na/Na⁺, $\Delta G_{\rm pbx}$ dramatically increases and reaches 1.0 eV/cation at 2.31 V versus Na/Na⁺. In these potential regions, Na_xMnO₂ fully decomposes into Na⁺ and Mn²⁺.

In contrast, Na_xMnO₂ is predicted to be more stable in a basic electrolyte (Figure 4b), with relatively smaller $\Delta G_{\rm pbx}$ (<0.5 eV/cation) within 2.0–3.14 V *versus* Na/Na⁺. Similarly, the small $\Delta G_{\rm pbx}$ 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}MnO₂ becomes stable within 2.81–2.87 V *versus* Na/Na⁺ in aqueous electrolytes with $\Delta G_{\rm pbx} = 0$ eV/cation. In addition, $\Delta G_{\rm pbx}$ starts to increase as solvated ion species become stable when the potential is lower than 2.81 V *versus* Na/Na⁺.

The change of ΔG_{obx} with potential can be related to the cycling stability of Na0,44MnO2 cathode observed in experiments.⁴⁻⁶ For example, in a neutral electrolyte (1 M Na_2SO_4 with pH = 7), the capacity of a Na_{0.44}MnO₂/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 vs Na/Na⁺).⁴ Pang et al.⁵ 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, $\Delta G_{\rm pbx}$ of Na_xMnO_2 at a potential larger than 3.35 V versus Na/Na^+ is lower than 0.1 eV/cation and solid-phase NaMn₈O₁₆ forms in decomposition products, whereas the measured slightly lower cycling stability within lower potential ranges can be anticipated because of larger $\Delta G_{\rm pbx,}$ and formation of all ion phases on the Pourbaix diagram when E < 3.25 V versus Na/ Na⁺. In a basic electrolyte (1 M Na₂SO₄ 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 ΔG_{nbx} (<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 ~0.0591 log C_{Na^+} eV/Na (Figure 4).



Figure 4. ΔG_{pbx} of Na_xMnO₂ as a function of potential (*E*) in (a) neutral (pH = 7) and (b) basic (pH = 13.5) aqueous electrolytes. The red dashed line indicates the limit of $\Delta G_{\text{pbx}} = 0.5$ eV/cation for materials to be stable in aqueous electrochemical environments.⁴⁷



Figure 5. Voltage profile of (a) $Na_xV_2(PO_4)_3$ (x = 1-3) and (b) $Na_xTiV(PO_4)_3$ (x = 1-3) cathodes. The electrochemical stability window at pH = 7 is shaded blue. The experimental voltage profile is from refs.^{13,14}

NASICON Electrodes. Figure 5a,b presents the calculated voltage profiles of $Na_xV_2(PO_4)_3$ and $Na_xTiV(PO_4)_3$, respectively. In all cases, the voltages are substantially underestimated relative to experimental values,^{13,14} similar to previous DFT results on the NASICON systems.⁵⁰ 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 $Na_3V_2(PO_4)_3$ and ΔG_{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, ΔG_{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 V³⁺/V⁴⁺. Thus, the observed capacity fading of Na₃V₂(PO₄)₃ cathode in 1 M Na₂SO₄ neutral electrolyte¹⁶ can be anticipated by the large ΔG_{pbx} and the decomposition into nonsolid phases when cycled within 2.7–3.6 V *versus* Na/Na⁺.

Compared with Na₃V₂(PO₄)₃, the introduction of Ti in Na₂TiV(PO₄)₃ leads to the formation of TiO₂ 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, $\Delta G_{\rm pbx}$ of Na₂TiV(PO₄)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 Na₂TiV(PO₄)₃ to NaTiV(PO₄)₃. Then, $\Delta G_{\rm pbx}$ reaches 0.5 eV/cation at 3.53 V *versus* Na/Na⁺. Unlike Na₃V₂(PO₄)₃ cathode, which exhibits severe capacity fading in ASIBs,^{16,28} Na₂TiV(PO₄)₃ shows excellent cycling performance in 1 M Na₂SO₄ aqueous electrolyte (pH = 7) with greater than 90% retention of its initial capacity after 500 cycles when cycled





(b) Calculated Pourbaix diagram of Na₂TiV(PO₄)₃

Figure 6. Calculated Pourbaix diagram of (a) $Na_3V_2(PO_4)_3$ and (b) $Na_2TiV(PO_4)_3$. Regions containing solid phases are shaded green.



Figure 7. ΔG_{pbx} of (a) Na_xV₂(PO₄)₃ and (b) Na_xTiV(PO₄)₃ as a function of potential (*E*) in a neutral aqueous electrolyte (pH = 7). The red dashed line indicates the limit of $\Delta G_{\text{pbx}} = 0.5 \text{ eV}/\text{cation}$ for materials to be stable in aqueous electrochemical environments.⁴⁷



Figure 8. Calculated voltage profiles of (a) olivine-Na_xFePO₄ (x = 0-1), (b) Na_xFeP₂O₇ (x = 1-2), and (c) Na_xFe₃(PO₄)₂P₂O₇ (x = 1-4) cathodes; the experimental voltage profiles are from refs.^{17,19} The electrochemical stability window at pH = 7 is shaded blue.

within 2.11–3.51 V versus Na/Na⁺.¹⁴ Both the lower $\Delta G_{\rm pbx}$ of Na_xTiV(PO₄)₃ as well as the formation of solid TiO₂ in the high-potential region may contribute to suppression of V dissolution. Similar results were also observed for Na₃MnTi-(PO₄)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 Na₂FeP₂O₇ and Na₄Fe₃(PO₄)₂(P₂O₇) 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-NaFePO₄ and Na₂FeP₂O₇ 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.

Figure 9a shows the Pourbaix diagram of the olivine-NaFePO₄ cathode. Within the electrochemical stability



Figure 9. Calculated Pourbaix diagram of NaFePO₄ regions containing solid phases are shaded green.

window of the aqueous electrolyte, Fe forms solid Fe₂O₃ in most regions (*e.g.*, E > -0.2 V vs SHE at pH = 7). In the low-potential region (near the H₂ gas evolution potential), Fe²⁺, Fe(OH)⁺, and solid Fe₃O₄ are stable in acidic, neutral, and alkaline electrolytes, respectively. P forms H_xPO_yⁿ⁻ 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



Figure 10. ΔG_{pbx} of (a) Na_xFePO₄, (b) Na_xFeP₂O₇, and (c) Na_xFe₃(PO₄)₂P₂O₇ as a function of potential in neutral aqueous solution [pH = 7 for (a,b) and pH = 6 for (c)]. The red dashed line indicates the limit of $\Delta G_{\text{pbx}} = 0.5$ eV/cation for materials to be stable in aqueous electrochemical environments.⁴⁷



Figure 11. Left: O_2/H_2 evolution potential *vs* pH in water. Right: Experimentally measured average voltage *vs* theoretical capacity of known SIB cathodes. The marker is colored by the calculated ΔG_{pbx} at $C_{Na^+} = 1$ M and pH = 7. Triangle markers indicate the solid phases in decomposition products with H₂O, whereas square markers indicate nonsolid phases in decomposition products. ΔG_{pbx} of cathodes with an average voltage larger than 3.53 V *vs* Na/Na⁺ were not computed because of the evolution of O₂ and are represented in gray round markers. Red dashed lines indicate the electrochemical window of neutral aqueous electrolytes. Blue and green dashed lines indicate the upper limit of O₂ evolution potential in the acidic aqueous electrolyte (pH = 0) and the lower limit of H₂ evolution potential in the basic aqueous electrolyte (pH = 14), respectively.

made in the Pourbaix diagrams of $Na_2FeP_2O_7$ and $Na_4Fe_3(PO_4)_2P_2O_7$ (Figure S4a,b, respectively).

All three cathodes exhibit low $\Delta G_{\rm pbx}$ ($\leq 0.32 \, {\rm eV}/{\rm cation}$) 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.^{17,18} For Na₄Fe₃(PO₄)₂P₂O₇, Fernández-Ropero *et al.*¹⁹ 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.⁵¹ The following compounds were selected: NASICON-Na₃Me₂(PO₄)₃ (Me = Fe, V);^{16,58} olivine-NaMePO₄ (Me = Fe);¹⁷ pyrophosphate Na₂MeP₂O₇ (Me = Mn, Fe, Co);^{18,59,60} mixed anion phosphates Na₄Me₃(PO₄)₂P₂O₇ (Me = Fe,

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formula	space group	$E_{\rm hull}~({\rm meV/atom})$	voltage range (V vs Na/Na ⁺)	$\Delta G_{ m pbx}^{ m max}$ (eV/cation)	pН	capacity (mA h/g)	barrier (meV)
$Na_3Fe_2(PO_4)_3$	Сс	2	2.5-3.53	0.5	7	90	383
Na_2FePO_4F	Pbcn	0	2.5-3.53	0.2	7	124	277
$Na_2Fe_3(PO_4)_3$	C2/c	21	2.12-3.35	0.5	10	110	419
Na ₃ FeCO ₃ PO ₄	$P2_1/m$	0	2.39-3.23	0.3	14	95.8	531
Na ₃ MnCO ₃ PO ₄	$P2_1/m$	0	2.39-3.23	0.3	12	96	446

Table 2. Calculated Electrochemical Properties of Promising Candidates for Cathodes in ASIBs^a

^{*a*}The voltage range refers to the range where the materials are stable in solution. $\Delta G_{\text{pbx}}^{\text{max}}$ and capacity refer to the maximum ΔG_{pbx} and accessible capacity in this voltage range, respectively. Barrier is the highest Na⁺ migration barrier in the facile pathways.

Mn, Co, Ni);^{19,61} alluaudite $Na_2Me_3(PO_4)_3$ (Me = Fe);⁶² α - and β -NaVOPO₄.^{63,64}

- 2. Carbonophosphates. The sidorenkite $Na_3MeCO_3 PO_4$ was first proposed by Hautier *et al.*⁶⁵ from highthroughput calculation as potential cathode materials for SIBs. Among the predicted structures, $Na_3MnCO_3PO_4$ and $Na_3FeCO_3PO_4$ have been successfully synthesized and investigated as cathodes in SIBs with high capacity.^{66,67}
- 3. Sulfates. A new alluadite $Na_2Me_2(SO_4)_3$ (Me = Fe) was reported as an SIB cathode with high redox potential (3.8 V vs Na/Na⁺) and Na ion conductivity.⁶⁸
- 4. **Oxyfluorides.** Oxyfluorides have the potential to enable cathodes with high working potential because of the highly electronegative fluoride anion. The oxyfluorides investigated in this work include Pbcn—Na₂MePO₄F (Me = Fe, Co),^{69,70} P2₁/*c*—Na₂MePO₄F (Me = Mn),⁷¹ $Pna2_1$ —NaVPO₄F,⁷² and Na₃(VO_x)₂(PO₄)₂F_{3-2x} (x = 0, 1).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⁺) to be used in ASIBs.

Among the cathodes with the average voltage within the electrochemical window of neutral aqueous electrolytes, the Vbased cathodes generally exhibit high reactivity with water (high $\Delta G_{pbx} \ge 0.5 \text{ eV/cation}$) 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.¹⁶ The Fe-based cathodes generally exhibit far better aqueous stability, though with somewhat lower average voltages. Na2FeP2O7, olivine-NaFePO₄, and Na₄Fe₃(PO₄)₂P₂O₇ have already been studied as cathodes in ASIBs. NASICON-Na₃Fe₂(PO₄)₃ has been investigated as an anode in ASIBs with the Fe^{2+}/Fe^{3+} redox potential at 2.5 V versus Na/Na⁺.⁷⁴ Our results show that it can be used as cathodes in ASIBs with the activated Fe^{3+}/Fe^{4+} redox pair at a potential of ~ 3.0 V versus Na/Na^{+.58} Na₂FePO₄F, which shows an average voltage at around 3.0 V versus Na/Na⁺ with a theoretical capacity of 124.2 mA h/g^{69} is a promising candidate for cathodes in ASIBs because of its high average working potential as well as high aqueous stability $(\Delta G_{\rm nbx} = 0.2 \text{ eV/cation at } 3.0 \text{ V } \nu \text{s Na/Na}^+)$. The average voltages of alluadite-Na $_2$ Fe $_3$ (PO $_4$) $_3$ and sidorenkite-Na $_3$ Fe- $(CO_3)(PO_4)$ are somewhat too low in neutral electrolytes, resulting in a significant compromise in energy density in ASIBs. Nevertheless, they are potentially interesting cathodes in basic electrolytes when paired with appropriate lowervoltage anodes. Fe-based cathodes tend to form solid phases within 2.5-3.53 V versus Na/Na⁺ in aqueous solution, and most compounds with Fe^{2+}/Fe^{3+} redox pairs are electrochemically active within this voltage range. Thus, looking for novel structures containing Fe^{2+}/Fe^{3+} redox pairs may achieve new cathodes in ASIBs.

In acidic aqueous electrolytes, several other cathodes— Na₃MnCO₃PO₄, Na₂MnPO₄F, NaVOPO₄, and Na₃(VO)₂(PO₄)₂F—are predicted to have an average voltage below the increased O₂ evolution potential. Na₂Fe₂(SO₄)₃ and the two V-containing cathodes—NaVOPO₄ and Na₃(VO)₂(PO₄)₂F—exhibit high reactivity with water (similar to the other V-containing cathodes) (see Figure S5(b)). Further, the observed charge potential of Na₂MnPO₄F cathode in the nonaqueous electrolyte is very high (~3.8 V vs NaNa⁺), and the Pourbaix diagram analysis predicts that Na₂MnPO₄F is highly unstable in acidic solutions, making it less promising for ASIB applications (see Figure S3). Hence, only Na₃MnCO₃PO₄, which has multiple voltage plateaus, has been selected for detailed analysis.

Detailed Studies of Promising Candidates. Table 2 summarizes the computed electrochemical properties of the five promising ASIB cathode candidates. A detailed discussion of each material is presented here.

NASICON-Na₃Fe₂(PO₄)₃ and Na₂FePO₄F. The calculated redox potential of the Fe³⁺/Fe⁴⁺ couple in NASICON-Na₃Fe₂(PO₄)₃ is 4.2–4.3 V versus Na/Na⁺. The experimental values were reported to be 3.0–3.6 V versus Na/Na⁺ with solid solution behavior,⁵⁸ making part of the Fe³⁺/Fe⁴⁺ capacity accessible in aqueous electrolyte (Figure S7a). The low ΔG_{pbx} and solid Fe₂O₃ formed at potential E > 2.5 V versus Na/Na⁺ mean that a stable capacity of ~90 mA h/g should be achievable in neutral aqueous electrolytes (Figure S7c). A facile one-dimensional diffusion mechanism with a barrier of 383 meV is observed from the CI-NEB calculations (Figure S8), suggesting the high rate capability for Na₃Fe₂(PO₄)₃ cathode in ASIBs.

Sharma *et al.*⁷⁵ have previously reported Na₂FePO₄F as a cathode in a 17 M NaClO₄ "water-in-salt" electrolyte, with a reversible capacity of 85 mA h/g and no significant capacity loss after 100 cycles. Although the highly concentrated aqueous electrolyte shows relatively high viscosity (5 mm² s⁻¹), high cost, and complex electrolyte/electrode interface phenomena,⁷⁶ our results suggest that Na₂FePO₄F may also exhibit excellent electrochemical performance in standard low-cost, high diffusivity aqueous electrolytes (Figures S9 and S10).

 $Na_3FeCO_3PO_4$ and Alluadite- $Na_2Fe_3(PO_4)_3$. The calculated voltage profile of $Na_3FeCO_3PO_4$ (Figure 11a) shows one plateau at 2.66 V versus Na/Na^+ , which is in line with previous experimental results⁶⁷ in nonaqueous electrolytes. $Na_3FeCO_3PO_4$ is predicted to be stable in basic solution with small ΔG_{pbx} (<0.3 eV/cation). Similarly, alluadite- $Na_2Fe_3(PO_4)_3$ exhibits three computed voltage plateaus at 3.24, 3.23, and 2.23 V versus Na/Na^+ (Figure S13a), whereas solid-solution behavior was observed with an average working potential of 2.75 V versus Na/Na^+ .⁶² Here, we propose that alluadite-Na₂Fe₃(PO₄)₃ can be cycled within the potential range of 2.12–3.35 V *versus* Na/Na⁺ in the basic electrolyte with pH of 10 (Figure S13c). 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.

 $Na_3MnCO_3PO_4$. Na_3MnCO_3PO_4 was reported to exhibit a large charge/discharge potential gap in the nonaqueous electrolyte.⁶⁶ 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_3MnCO_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, Na₂FePO₄F and Na₂Fe₃(PO₄)₃ 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, Na₃FeCO₃PO₄ and Na₃MnCO₃PO₄, 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 wellestablished 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, Na₃Fe₂(PO₄)₃, Na₂FePO₄F, Na₃MnCO₃PO₄, Na₃FeCO₃PO₄, and alluadite-Na₂Fe₃(PO₄)₃, 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

③ 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_xMnO₂ in the basic electrolyte; calculated voltage profiles, Pourbaix diagram, and $\Delta G_{\rm pbx}$ of Na₃MnTi(PO₄)₃ cathode; Pourbaix diagram of Na₂FeP₂O₇ and Na₄Fe₃P₄O₁₅ cathodes; calculated $\Delta G_{\rm pbx}$ as a function of pH of selected cathodes at their average voltage; aqueous stability analysis of Na₂MnPO₄F; 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 92093-0448, United States; ◎ orcid.org/0000-0001-5726-2587; Email: ongsp@eng.ucsd.edu

Authors

- Xingyu Guo Materials Science and Engineering Program, University of California San Diego, La Jolla, California 92093-0448, United States; © orcid.org/0000-0002-3456-5347
- Zhenbin Wang Department of NanoEngineering, University of California San Diego, La Jolla, California 92093-0448, United States; Occid.org/0000-0002-7016-9245
- **Zhi Deng** Department of NanoEngineering, University of California San Diego, La Jolla, California 92093-0448, 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.

ACKNOWLEDGMENTS

This work was supported by GEIRI North America under project no. SGRIDGKJ[2017]841. The authors also acknowledge computing resources provided by Triton Shared Computing Cluster (TSCC) at UC San Diego, the National Energy Research Scientific Computing Center (NERSC), and the Extreme Science and Engineering Discovery Environment (XSEDE) supported by the National Science Foundation under grant no. ACI-1053575.

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