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Ab initio investigation of the stability of electrolyte/electrode interfaces in all-solid-state Na batteries
**Ab initio** investigation of the stability of electrolyte/electrode interfaces in all-solid-state Na batteries†

Valentina Lacivita,*a Yan Wang,*b Shou-Hang Bo,c and Gerbrand Ceder*ad

All-solid-state batteries show great potential for achieving high energy density with less safety problems; however, (electro)chemical issues at the solid electrolyte/electrode interface may severely limit their performance. In this work, the electrochemical stability and chemical reactivity of a wide range of potential Na solid-state electrolyte chemistries were investigated using density functional theory calculations. In general, lower voltage limits are predicted for both the reduction and oxidation of Na compounds compared with those of their Li counterparts. The lower reduction limits for the Na compounds indicate their enhanced cathodic stability as well as the possibility of stable sodium metal cycling against a number of oxides and borohydrides. With increasing Na content (or chemical potential), improved cathodic stability but also reduced anodic stability are observed. An increase in the oxidation voltage is shown for Na polyanion systems, including borohydrides, NaSICON-type oxides, and fluorophosphates, whereas the chalcogenides predictably display narrow electrochemical windows and high chemical reactivity. Our findings indicate some promising candidates for solid-state conductors and/or protective coating materials to enable the operation of high-energy-density all-solid-state Na batteries.

1 Introduction

The increasing demand for rechargeable batteries that deliver high energy density without safety hazards is driving the development of all-solid-state batteries (SSBs), in which liquid electrolytes are replaced by solid alkali conductors. Research in this field has led to the discovery of numerous solid electrolytes with room-temperature (RT) ionic conductivities of up to 10–20 mS cm⁻¹, which are comparable or even superior to those of common liquid electrolytes. These promising solid electrolytes include NaSICON-type oxides, garnets, and thiophosphates, such as Li₄GeP₂S₁₂ (ref. 5) and Li₃P₂S₁₁ (ref. 6) for lithium batteries, and NaₓPS₄ (ref. 7) and NaₓPSe₄ (ref. 8) for sodium batteries.

However, the high resistivity at the electrolyte/electrode interface severely limits the power and rate capabilities of SSBs. This high internal resistivity is attributed to chemical and/or electrochemical compatibility issues at the interface as well as mechanical issues (e.g., poor interfacial contact and volume changes). Examples of electrode/solid electrolyte combinations undergoing interfacial reactions include LiCoO₂/Li₂S–P₂S₅ (ref. 9) and LiCoO₂/Li₃La₃Zr₂O₁₂ (ref. 10) and their interfaces have been characterized using transmission electron microscopy. First-principles density functional theory (DFT) calculations have proven to be a valuable tool for the systematic investigation of the (electro)chemical compatibility at electrode/electrolyte interfaces.† DFT-computed 0 K phase diagrams can be used to derive the phase equilibria at the interface and to estimate the driving force for interface reactions and electrolyte decomposition when an external potential is applied.

Richards et al.12 and Zhu et al.13,14 have applied this computational approach to a number of electrolyte/electrode (and coating/cathode) interfaces relevant for all-solid-state lithium batteries. Contrary to the common belief that solid-state electrolytes have high intrinsic stability, they demonstrated that many electrolyte/electrode combinations display quite limited chemical and electrochemical compatibility. In most cases, an interface layer with multiple decomposition phases was predicted to form at the electrode/electrolyte contact. This interlayer, however, can be beneficial for the system stability if it is both ion-conducting and passivating. In this case, the interlayer acts as an electronic insulator, bridging...
the difference in the chemical potentials $\mu$ of all the atomic species between the electrolyte and electrodes.

Beyond a purely thermodynamic model, kinetic barriers for decomposition and chemical reactions may intervene to widen the effective voltage stability window of the electrolyte and possibly change the constitution of the interphase layer at the electrolyte/cathode interface. An estimate of the upper kinetic voltage limit for the electrolyte decomposition can be obtained by calculating the voltage corresponding to the topotactic extraction of an atom of the mobile species, as proposed by Tian et al.$^{14}$ These authors used a combination of DFT calculations and experiments to investigate the electrochemical stability of Na$_x$PX$_2$ (X = S, Se) solid electrolytes and their compatibility with various layered transition metal (TM) oxide cathodes for sodium-ion batteries. They verified that the anodic voltage limit measured for the electrolytes always lies between the computed thermodynamic upper bound and the potential for topotactic desodiation. Moreover, they reported evidence for electrolyte/cathode reactions for which the formation of intermediate products is kinetically favored over stable thermodynamic phases. One example is the Na$_3$PS$_2$–NaCrO$_2$ interface, for which they observed the formation of Na$_2$PS$_3$O at temperatures below 500 °C instead of the predicted products Na$_2$PO$_4$ and NaCrS$_2$. More recently, Tang et al.$^{15}$ applied finite-temperature ab initio molecular dynamics simulations to assess kinetic effects on the interface reactivity. They observed that contrary to thermodynamic models predicting the formation of stable [PO$_4$]$^{3-}$ groups via anion-exchange reactions, the formation of [SO$_4$]$^{2-}$-containing compounds and Na$_x$P is kinetically favored. In the same study, the authors also calculated the electrochemical stability and chemical reactivity of some well-known Na solid-state electrolytes with different cathode, anode, and buffer materials.

In this work, we aim to extend previous computational surveys on solid-state Na conductors$^{14,15}$ to provide a systematic and comprehensive overview of promising electrolyte/electrode and coating/electrode combinations for Na SSBs. We apply the computational approaches described in ref. 11–14 to estimate the electrochemical stability window of numerous solid-state electrolyte candidates, the kinetic voltage limits for Na extraction, and the chemical reactivity with different cathode materials. We investigate an extensive selection of materials, including known Na-ion conductors and possible decomposition or reaction products as well as possible coating layers. In addition, a comparison with relevant Li compounds is performed. In line with previous assessments,$^{14,15}$ we confirm general trends such as the greater electrochemical stability of oxides than that of sulfides/selenides and the existence of a large thermodynamic driving force for anion-exchange reactions between thiophosphates and layered TM oxide cathodes. Moreover, we show that sodium electrolytes generally exhibit improved cathodic (low-voltage) stability compared with their lithium analogues, thus giving prospects for the stable cycling of Na metal anodes. We find that the differences between sodium and lithium compounds in anodic (high-voltage) limits are not simply deducible from the electrochemical scale, but also relate to structural factors, such as the cation–anion radius ratio. Both the thermodynamic and kinetic upper voltage limits of compounds are favorably extended by covalent stabilization in polyanions such as phosphates and boranes, which emerge as materials that can tolerate charging potentials as high as 4–5 V.

## 2 Methods

In the current work, we adopt the methodology described in ref. 12, 16, and 17. We consider three different indicators of the stability of the solid-state electrolyte: (1) the pure thermodynamic voltage stability versus the metal anode (M), (2) the upper kinetic voltage limit for the extraction of one alkaline atom from the solid-state electrolyte, and (3) the chemical reactivity at the electrolyte/cathode interface.

### 2.1 Voltage window and interface chemical stability

Phase diagrams were constructed using the Python Materials Genomics (pymatgen) library$^{28}$ and a dataset of energies from DFT relaxation of compounds initialized using structural information obtained from the Inorganic Crystal Structure Database (ICSD)$^{19}$ or structures generated by a data-mined chemical substitution algorithm$^{29}$ (see Table S1 of the ESI † for more details). DFT calculations were performed using the generalized gradient approximation (GGA) to the exchange-correlation functional in the Perdew–Burke–Ernzerhof formulation,$^{21}$ as implemented in the Vienna Ab initio Simulation Package (VASP),$^{22}$ within the projector-augmented wave formalism.$^{23}$ The energy cutoff was set to 520 eV, and a k-point grid with a density of at least 500/(number of atoms) was used for all the computations. For compounds containing TM elements with localized d electrons, the GGA + U variation$^{24}$ of the density functional was adopted. Consistency across GGA and GGA + U calculations is maintained by the application of the mixing scheme as described in ref. 25. Moreover, GGA errors of reaction energies involving gas/liquid phase molecules were corrected using Wang et al.’s method.$^{26}$ Following Richards et al.$^{14}$ the formation energies were calculated from the nearest phases (i.e., the phases that define the low energy facet containing the target composition in the phase diagram) for which the experimental energies are available in the Kubaschewski$^{27}$ or NIST-JANAF$^{28}$ thermochemical tables. For example, the formation energy of NaZr$_2$(PO$_4$)$_3$, a compound not listed in the thermochemical tables, is calculated as the DFT energy of the reaction 2ZrO$_2$ + P$_2$O$_5$ + NaPO$_3$ $\rightarrow$ NaZr$_2$(PO$_4$)$_3$, to which are added the experimental formation energies of ZrO$_2$, P$_2$O$_5$ and NaPO$_3$. Such an approach allows benefitting from the higher accuracy of DFT reaction energies that are calculated between compounds whose elements are in the same oxidation states.$^{29}$ If no experimental data are available for some nearest phases, the corresponding elemental precursors are used for reference.

#### 2.1.1 Thermodynamic stability window of the solid-state electrolyte

The voltage stability window of a compound is calculated from its grand potential phase diagram. The window is defined as the range of M chemical potentials ($\mu_M$) over which each electrolyte is predicted to be stable, that is, when its grand potential
lies on the lowest surface of the optimized convex energy hull for the chemical system. Here, \( E(c) \) and \( n_M(c) \) represent the DFT energy and concentration of the alkali metal, respectively, at the relevant composition \( c \). The highest (lowest) chemical potential at which the electrolyte is stable is the cathodic (anodic) limit of the electrolyte.\(^{12}\)

### 2.1.2 Kinetic upper voltage limit of the solid-state electrolyte. In addition to the thermodynamic stability window defined in Section 2.1.1, the maximum kinetic voltage limit for a solid-state conductor can be defined as the potential at which one alkali ion \( M^+ \) and one electron \( e^- \) are extracted, \( i.e.,\)

\[
\Delta V = -(E_{\text{def}} - E_0 - \mu_M).
\]

where \( E_0 \) and \( E_{\text{def}} \) are the DFT bulk energies after structural relaxation of the pristine and defected compound, respectively.\(^{14}\) As both the extractions of \( M^+ \) and \( e^- \) are fast processes, it is unlikely that this voltage limit can be exceeded without rapid breakdown of the solid electrolyte. \( E_{\text{def}} \) is calculated at the supercell size convergence to ensure negligible interactions between defect images.

### 2.1.3 Chemical reactivity of the solid-state electrolyte with the cathode. The stability of the electrolyte/cathode interface is determined from the phase diagram of their combined chemistry, by considering the reaction (if any) between the electrode and electrolyte with the highest calculated driving force,\(^{12}\) namely

\[
\Delta E(c_a, c_b) = \min_{x \in [0, 1]} \{ E_{\text{pd}}(x c_a + (1 - x) c_b) - x E_{\text{pd}}(c_a) \}
\]

In the above equation \( x \) is the mixing fraction of the electrode and electrolyte compositions, \( c_a \) and \( c_b \), respectively; \( E_{\text{pd}}(c) \) and \( E_{\text{pd}}(c) \) are the respective convex hull minimum energies; and \( E_{\text{pd}}(x c_a + (1 - x) c_b) \) is the convex hull function returning the lowest energy equilibrium of the phases at the given composition.

### 2.2 Materials selection

Solid-state electrolyte (or coating) candidates were selected based on their Na content and electrochemical performance, as reported in the literature. We focused particularly on known solid-state Na-ion conductors with high ionic conductivity or with the potential for high ionic conductivity.

#### 2.2.1 Aluminates. Na-\(\alpha\)-alumina, \((1 + x)\)Na\(_2\)O-\(11\)Al\(_2\)O\(_3\), has been known as a solid-state Na-ion conductor for 50 years\(^{39}\) and was critical in the development of Na-S and (ZEBRA) batteries,\(^{33-34}\) which operate above 300 °C. In addition to the hexagonal \((P6_3/mmc)\) \(\beta\) form (NaAl\(_4\)O\(_{17}\)),\(^{35}\) a rhombohedral (\(R3\)m\(\beta\)) \(\beta\) form (Na\(_{1.67}\)Al\(_{1.67}\)O\(_{17}\)), has also been characterized.\(^{36}\) The latter exhibits a higher conductivity \((\sigma \approx 2 \text{ mS cm}^{-1} \text{ at RT})\) and has been proven to be stable against Na.\(^{37}\)

For comparison, we also considered the stability of NaAl\(_2\)O\(_3\) and of the Na-rich aluminates Na\(_3\)Al\(_2\)O\(_6\), Na\(_2\)Al\(_2\)O\(_6\), Na\(_{1.33}\)Al\(_2\)O\(_11\), and Na\(_{1.25}\)Al\(_2\)O\(_16\).\(^{38}\) NaAl\(_2\)O\(_3\) is a side product in \(\beta\)-alumina mixtures and has been used as a cathode coating material on LiCoO\(_2\).\(^{39}\) To our knowledge, no data on the ionic conductivity and stability window of the Na-rich aluminates have been reported yet.

#### 2.2.2 NaSICONs. The Na Super Ion CONductor (NaSICON) class of materials, Na\(_{1-x}\)Zr\(_2\)Si\(_2\)P\(_1-x\)O\(_{12}\) \((0 \leq x \leq 3)\), was first introduced in 1976\(^{40-41}\) as the outcome of a search for structures with fast alkali-ion transport. Because of their compositional diversity, these materials are very attractive in battery applications not only as solid electrolytes but also as electrodes.\(^{42}\) Their conductivity can reach levels of \(10^{-2} \text{ S cm}^{-1} \text{ at RT}^{33}\) however, NaSICONs suffer from large interfacial impedance and Na dendrite propagation, though promising solutions have recently been proposed.\(^{44}\) Degradation of NaSICON ceramics by molten Na has been observed for P-containing compositions in static corrosion tests, whereas the pure silicates appear to be kinetically stabilized.\(^{45}\)

#### 2.2.3 Antiperovskites and other oxides. Na\(_2\)OBr and Na\(_4\)O\(_2\) have cubic \((Pm\overline{3}m)\) and tetragonal \((Im\overline{3}m)\) antiperovskite structures, respectively. Recently, Zhu \textit{et al.}\(^{46}\) analyzed their Na-ion transport mechanisms and reported low ionic conductivities \((\sigma \approx 10^{-8} \text{ S cm}^{-1} \text{ at RT})\) activation energy \(E_a = 0.6-0.7 \text{ eV}\). Nonetheless, chemical modifications leave substantial room for improvement, \textit{e.g.}, by aliovalent substitution the conductivity of Na\(_2\)O\(_{0.05}\)Br\(_{6.4}\)\(_{0.4}\) reaches 0.19 mS cm\(^{-1}\) at 200 °C.\(^{47}\)

Other oxides such as Na\(_2\)SO\(_4\), Na\(_3\)PO\(_4\), and Na\(_3\)SiO\(_4\), are generally characterized by low ionic conductivity. However, they can be used as coating materials or end-members of better performing electrolyte solid-solutions such as Na\(_2\)SO\(_4\)/Na\(_3\)PO\(_4\)/Na\(_3\)SiO\(_4\),\(^{48,49}\) Na\(_3\)PO\(_4\)/Na\(_3\)SiO\(_4\),\(^{50,51}\) Na\(_3\)AlF\(_6\)/Na\(_2\)SO\(_4\), and Na\(_3\)PO\(_4\)/Na\(_3\)SiO\(_4\).

#### 2.2.4 Sulﬁdes and selenides. Na\(_2\)PS\(_4\) has been known as a Na-ion conductor for more than 25 years\(^{52}\) and has garnered renewed research interest since Hayashi \textit{et al.}\(^{7}\) reported a glass-ceramic phase containing cubic Na\(_2\)PS\(_4\) with \(\sigma = 2 \times 10^{-4} \text{ S cm}^{-1}\). Similar RT ionic conductivity has been reported for the isostructural selenide compound Na\(_2\)PSe\(_4\).\(^{8}\) One major issue with the use of Na\(_2\)PS\(_4\) and Na\(_2\)PSe\(_4\) as solid electrolytes is their instability against Na metal, as they decompose into Na\(_2\)S/Na\(_2\)Se + NaP forming a resistive interphase that grows in time.\(^{14,37}\) Glass–ceramic electrolytes exhibit even higher Na\(^+\) conductivities \((7.4 \times 10^{-4} \text{ S cm}^{-1} \text{ at RT})\), and cyclic voltammetry suggests they have remarkable electrochemical stability.\(^{33}\) Tetragonal Na\(_2\)SbS\(_4\) has also been described as a highly conductive phase \((\sigma > 1.1 \text{ mS cm}^{-1} \text{ at RT})\) stable in dry-air.\(^{34}\) Finally, the computation-assisted discovery of tetragonal Na\(_{10}\)^{2+}\(^{43}\)Sn\(_2P_2S_6\) with a RT ionic conductivity of 0.4 mS cm\(^{-1}\) \((E_a = 0.365 \text{ eV})\) and improved processability with respect to \(\beta\)-alumina and NaSICON compounds was recently reported.\(^{65}\)

#### 2.2.5 Borohydrides. Superionic conduction in alkali metal borohydrides is commonly associated with the thermally activated orientational disorder of the \(\text{[B}_4\text{H}_4]^+\) anions. Impedance measurements\(^{46}\) indicate exceptionally high Na\(^+\) conductivity in Na\(_3\)B\(_2\)H\(_4\) \((\text{on the order of } 0.1 \text{ S cm}^{-1})\) above its order-to-disorder (monoclinic-to-cubic) phase transition at approximately 529 K. Similar electrochemical behavior was also
observed for LiBH₄, where raising the temperature to approximately 390 K induces an orthorhombic-to-hexagonal phase change signaled by a dramatic increase in σ to 10⁻³ S cm⁻¹. Despite its high conductivity and good compatibility with Li metal, LiBH₄ is easily oxidized by metal oxide cathodes and thus requires coating to avoid large interfacial resistance and consequent capacity loss. The sodiated analogue, NaBH₄, also undergoes an order-to-disorder phase transition (from tetragonal to cubic) at temperatures above 190 K. The much lower transition temperature of NaBH₄ compared to Na₃B₁₂H₁₂ supports the observation by Lu and Ciucci that the rotation barrier for [B₄H₄]⁻ anions correlates positively with the anion size so that RT superionic conduction could be pursued by anion mixing.

2.2.6 Halo-aluminates. NaAlCl₄ is generally used as a catholyte (i.e., a molten salt secondary electrolyte) along with β-alumina in ZEBRA batteries. Similarly, molten eutectic mixtures of Na haloaluminate salts, NaAlX₄–ΔX₄ (with 0 < Δ < 4 and X/X⁺ = Cl, Br, I), have been used as electrolytes in the cathode composite to enable operation of molten Na metal halide batteries at substantially lower temperatures compared with the traditional ZEBRA system. The aluminum fluorides Na₃AlF₆ (cryolite) and Na₃AlF₁₄ (chaloid) exhibit fast Na-ion diffusion at high temperatures as revealed by nuclear magnetic resonance measurements.

2.2.7 Binaries. In addition to the materials listed above we will also discuss simple alkali binaries. By comparing Na and Li binaries with identical structures we can show how a good match of structure type with ion size enhances the anodic stability of a solid.

3 Results
3.1 Comparison of the electrochemical stability window of Na and Li binaries

Fig. 1 compares the stability windows of simple Na binary compounds with those of their Li analogues. Although these compounds may not be considered solid-electrolyte candidates by themselves due to their generally poor ionic conductivity (except for Li₃PO₄), it is instructive to compare their electrochemical stability as a basis to understand the behavior of more complex compounds. These binaries are generally used as synthesis precursors, e.g., MₓS or MₓSe in chalcogenide-based glassy electrolytes, or as additives (especially the halides) to improve the electrochemical performance of more complex electrolyte materials. In all of these binary materials, the anion is fully reduced; therefore, further reaction with the metal anode cannot occur and they are all stable down to 0 V against M/M⁺.

The RT crystal structures of the Na and Li binaries are isomorphous (see Table 1), which ensures that the differences in the thermodynamic voltage stability windows are exclusively due to differences in the chemistry. Indeed, all the hydrides, halides, and chalcogenides have a face-centered cubic structure (Fm3m) with M⁺ cations located in octahedral or tetrahedral sites depending on whether they are 1 : 1 (rock-salt) or 2 : 1 (anti-fluorite) binaries, respectively. The phosphides, instead, have both a hexagonal structure.

For simple binaries, such as MF, MCl, MBr, and MI, the anodic decomposition is into the elements and this creates a direct relationship between the formation enthalpy of the compound, ΔHf, and the anodic voltage limit: ΔHf ≈ −V. As Table 1 shows, the anodic stability of Na binaries is generally lower than that of Li binaries. This trend might be expected from the fact that the standard reduction potential for the reaction Na⁺(aq) + e⁻ → Na(s) is 0.33 V above that of Li, although reference to half-cell reduction potentials, which are dependent on the solvent and solute concentration, is not rigorously applicable. The exceptions to this trend are pairings with large anions such as Cl−, Br−, and I−, where the reduced size mismatch with Na⁺ plays a stabilizing role compared to the equivalent Li binaries. Such stabilization of the Na compounds with large anions, as compared to their Li equivalents, is confirmed by the experimental formation enthalpies in Table 1. We attribute this stabilization to the better match of the Na⁺ radius with those of the large halogen anions. In simple high-symmetry crystal structures, such as the rock-salt structure of these compounds, the lattice constant is the only geometric aspect that influences the formation enthalpy.
parameter that can be adjusted. When very small ions such as Li⁺ are paired with large anions, such as Br⁻ and I⁻, the difference in ionic radii creates a mismatch between anion–anion and cation–anion distances, which is, Fig. S1† shows the differences between the anodic voltages of Li and Na halides (ΔV) as a function of the anion radius.

Fig. 1 also shows that the nature of the oxidation products depends on the valence electron configuration of the anions. The oxidation of hydrides and halides yields their elementary references directly, whereas anions with higher valence (e.g., O²⁻, S²⁻, and P³⁻) usually transform into phases where the anion has an intermediate oxidation state. For example, both alkali oxides MO transform into peroxides MO₂ upon oxidation. However, although Li₂O₂ is known to be a fairly reactive species,⁷³,⁷⁴ Na₂O₂ is a stable bulk phase in an oxygen atmosphere,⁷⁵ which may contribute to the reduction of the anodic limit of Na₂O with respect to that of Li₂O. Similarly to Na₂O, the Na chalcogenides oxidize to intermediate phases with partially oxidized anions that are stable at RT, i.e., Na₂S₄ (ref. 76) and Na₂Se₂.⁷⁷ The Li chalcogenides lack these intermediate stable phases, which explains the direct oxidation of both Li₂S and Li₂Se to their elementary references at higher anodic voltages.

### 3.2 Electrochemical stability windows of Na solid-state electrolytes

#### 3.2.1 Thermodynamic voltage limits

Using the selection criteria outlined in section 2.2, we calculated the electrochemical stability window of Na solid-state electrolyte candidates as shown in Fig. 2 along with some reference compounds. A complete list of the predicted oxidation and reduction reactions is provided in the supplementary Table S1† For some of the selected compounds, namely Na₁₀SnP₂S₁₂, the NaSiCONs NaₓZrₓ(SiO₄)₃PO₄ and NaₓZrₓ(SiO₄)₃, and the aluminates NaₓAlₓOₓ and NaₓAlₓOₓ, the grand potential energy Φ(c,μ₉) (eqn (1)) was never observed on the lowest surface of the phase diagram hull, indicating that they are metastable or high-temperature phases. Therefore, in these cases, the thermodynamic voltage stability window was evaluated by shifting the phase diagram hull by +25 meV/atom (the average thermal energy at RT). Note that such a shift is solely intended to make these compounds thermodynamic ground-states but does not modify the voltage limits in any meaningful way.

The sulfides and particularly the selenides display very narrow windows, which is in line with the relatively low electronegativity of the chalcogen anions and the versatility of their valence electron shell with oxidation states from −2 to +6. None

![Fig. 2](image-url)
of the chalcogenides is stable against Na metal, in agreement with previous reports. Moreover, a reduction product of the phosphorus selenides and sulfides is Na$_3$P, which is a mixed ionic and electronic conductor and prohibits the passivation of the electrolyte. This is in contrast to Li$_2$P that is an electronic insulator and can therefore passivate P-containing chalcogenide conductors.

The voltage stability ranges of the oxides are much wider than those of the chalcogenides. In particular, oxides with relatively high Na content such as Na$_4$SiO$_4$, Na$_3$BO$_3$, Na$_3$PO$_4$, and Na$_3$SbO$_4$ are all stable down to 0 V versus Na/Na$^+$. The cathodic stability becomes more limited in the presence of easily reducible species, e.g., C$^{4-}$, Sb$^{5+}$, or condensed polyanions such as [PO$_4$]$^{3-}$ and [NbO$_4$]$^{3-}$. The latter, however, boost the oxidation limits to somewhat higher voltages (3–5 V).

Among the NaSICONs, the P-containing compounds exhibit excellent anodic stability, resisting oxidation up to approximately 5 V. At low voltage, all the explored NaSICON compositions are predicted to decompose. However, we compute a much lower driving force for reduction for the pure silicate Na$_4$Zr$_2$(SiO$_4$)$_3$ (decomposition energy $|\Delta E| = 0.15$ eV/atom) than for the phosphates ($|\Delta E| = 0.54$ eV/atom for NaZr$_2$(PO$_4$)$_3$ and 0.86 eV/atom for NaTi$_2$(PO$_4$)$_3$). This finding is consistent with previous experimental assessments suggesting that silicates are kinetically stabilized. Fig. S2† shows the relative decomposition energies as a function of the voltage versus Na metal. We also note that the cathodic stability of the NaSICON-type phosphates is considerably worse than that of Na$_3$PO$_4$, which is predicted to be stable. By looking at the reduction products of NaZr$_2$(PO$_4$)$_3$ and NaTi$_2$(PO$_4$)$_3$, which always involve a metal oxide and a reduced phosphide, one may deduce that the presence of a high content of Na$^+$ stabilizes the PO$_4$ group more than the transition metals do.

In contrast to the NaSICONs, the Na aluminates are thermodynamically stable against Na metal. The only exception is the β-alumina phase NaAl$_{11}$O$_{17}$: the 0 K enthalpy calculations indicate that this phase is unstable with respect to the decomposition into NaAlO$_2$ + Al below 0.14 V. However, the reaction energy for the β-alumina decomposition is less than 25 meV/atom. Moreover, commonly found excess sodium induces structural disorder which makes it possible that β-alumina is stabilized by the Na-ion configurational entropy at higher temperatures. The β-alumina phase is oxidized at approximately 4 V. This is the maximum anodic stability attained by the Na aluminates, whose oxidation voltage progressively shifts to lower potentials with increasing Na content, approaching the limit of the sodium oxide binary. The antiperovskites Na$_3$O$_2$ and Na$_3$OBr also have oxidation limits close to that of the Na$_2$O binary, consistent with the presence of fully reduced anions in all of these structures. In contrast, the borohydrides are characterized by remarkable covalent stabilization with respect to the NaH binary: the oxidation voltage increases from 0.58 V for NaH to 3.46 V for Na$_2$B$_{12}$H$_{12}$. The latter is also stable in contact with Na metal.

### 3.2.2 Kinetic anodic voltage limit

In our analysis, the thermodynamic anodic limit is calculated as the voltage (the Na chemical potential) at which the electrolyte is expected to decompose into other phases, accompanied by Na extraction. Such decomposition into distinct phases may not always be possible at RT until a sufficient driving force for the reaction is achieved at higher potentials. Tian et al. defined the absolute limit of kinetic stabilization as the voltage at which Na is extracted topotactically from the electrolyte. This kinetic limit is shown for a few compounds in Table 2. As anticipated, the predicted kinetic voltage limit is always higher than the thermodynamic one, and the real anodic potential is expected to fall in between these two extremes. Large Na extraction voltages hint at the potential for substantial kinetic stabilization, especially for sodium borohydride NaBH$_4$, whose computed voltage for Na extraction is more than twice the thermodynamic anodic voltage limit.

### 3.3 Chemical reactivity at the cathode/electrolyte interface

Using eqn (3), we calculated the maximum driving force for the reaction between the solid-state electrolytes and different cathodes. Positive electrodes such as common layered TM oxides (TM = Cr, Mn, Fe, Co) and fluorine-doped vanadium phosphates were considered in both fully discharged and half-charged (i.e., more oxidizing) states. Fig. 3 presents heat maps of the corresponding predicted reaction energies. The energy values and reaction products are listed in Tables S2–S5 of the ESI†.

We first consider the chemical reactivity against layered TM oxides. All the P-containing chalcogenide electrolytes are predicted to undergo O for Se/S anion exchange, in agreement with previous reports. However, the predicted reaction products may slightly vary because of differences in datasets used to construct the high-dimensional phase diagrams. For instance, Tang et al. predicted that the reaction at the Na$_3$PS$_2$/NaCrO$_2$ interface would produce Na$_3$PO$_4$ + NaCrS$_2$, whereas we predict Na$_3$PS$_2$O$_5$ to be an additional intermediate phase, similar to the findings of Tian et al.

In line with ref. 14 and 15, the substitution of P with other cations (e.g., Si and Sb) in the conductor generally improves the chemical stability of the interface with the TM oxide cathodes.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermodynamic window (V)</th>
<th>Kinetic limit (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_3$PSe$_4$</td>
<td>1.57–1.87</td>
<td>2.75$^a$</td>
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<tr>
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<td>3.05$^a$</td>
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<tr>
<td>Na$_4$Zr$_2$(SiO$_4$)$_3$</td>
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<td>4.13</td>
</tr>
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<td>NaAl$<em>{11}$O$</em>{17}$</td>
<td>0.14–3.79</td>
<td>4.79</td>
</tr>
<tr>
<td>NaAlCl$_4$</td>
<td>1.78–4.42</td>
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</tr>
<tr>
<td>Na$_3$AlF$_6$</td>
<td>0.46–6.19</td>
<td>6.35</td>
</tr>
<tr>
<td>NaBH$_4$</td>
<td>0.02–2.07</td>
<td>4.91</td>
</tr>
<tr>
<td>Na$<em>2$B$</em>{12}$H$_{12}$</td>
<td>0.00–3.46</td>
<td>4.31</td>
</tr>
</tbody>
</table>

$^a$ Data from ref. 14.
by switching from $\mathrm{Na}_3\mathrm{PS}_4$ to $\mathrm{Na}_3\mathrm{SbS}_4$, the reaction energies decrease by approximately 40–90% against the fully discharged TM oxide cathodes and by ~20–50% against the half-charged cathodes. In moving from the early to the late TMs in the cathode ($\mathrm{Cr} \rightarrow \mathrm{Ni}$), an increasing tendency toward TM reduction by the chalcogen anions is observed. In contrast to the chalcogenides, the oxide electrolytes display negligible ($\Delta E < 25$ meV/atom) or rather low reaction energies. Among the oxides, the most reactive interfaces are those of the Na-rich aluminates and antiperovskites against the half-charged cathodes; however, the breakdown energies ($\Delta E$) are still lower than 150 meV/atom and thus much lower than the $\Delta E$ values of up to 580 meV/atom calculated for the chalcogenides. The chloride $\mathrm{NaAlCl}_4$ behaves quite differently from the fluorides $\mathrm{Na}_3\mathrm{AlF}_6$ and $\mathrm{Na}_5\mathrm{Al}_3\mathrm{F}_{14}$. In fact, whereas $\mathrm{Cl}^-$ is easily oxidized to $\mathrm{Cl}^{\mathrm{4+}}$ and/or displaced into TM-based compounds, the fluorides are much less reactive: $\Delta E$ is on the order of 10–80 meV/atom, to be compared with ~200–300 meV/atom for the chloride. Finally, the borohydrides are confirmed to be strong reducing agents, especially when coupled with Co- and Ni-containing cathodes. Overall, $\mathrm{NaCrO}_2$ appears to be the TM oxide that is most widely compatible with the different types of electrolytes. Experimental findings by Tian $et$ al.\textsuperscript{14} support this conclusion for pairings with $\mathrm{Na}_3\mathrm{PX}_4$ ($X = \mathrm{S}, \mathrm{Se}$) electrolytes.

Polyanionic cathodes such as fluorophosphates appear to be somewhat compatible with various solid-state electrolytes, including sulfides and selenides. Among the oxides, NaSICON electrolytes are particularly stable against vanadium fluorophosphate cathodes. Some reactivity ($\Delta E \approx 50–80$ meV/atom) is predicted only for the Si-containing NaSICONs in contact with the partially desodiated electrodes, whose average potential (~3.5 V vs. Na/Na$^+$) is close to the intrinsic oxidation limits of such electrolytes (see Fig. 2). We also predict fairly low reactivity for $\mathrm{NaAl}_2\mathrm{O}_{17}$ ($\Delta E \approx 50$ and 70 meV/atom against discharged and half-charged cathodes, respectively), whereas aluminates with higher Na content show an increasing driving force for chemical reactions, which is consistent with their lowered anodic stability limit (Fig. 2). The halo-aluminates are relatively stable against the fluorophosphate cathodes, particularly the fluorides $\mathrm{Na}_3\mathrm{AlF}_6$ and $\mathrm{Na}_5\mathrm{Al}_3\mathrm{F}_{14}$ which are substantially inert ($\Delta E < 10$ meV/atom). The borohydrides instead react by reducing $\mathrm{P}^{5+}$ to $\mathrm{P}^{3+}$ and releasing protons or $\mathrm{H}_2$.

4 Discussion

With the discovery of numerous solid-state ion conductors that have conductivities capable of competing with those of liquid electrolytes, the critical issue for the development of SSB devices has shifted to achieving optimal (electro)chemical compatibility at the interfaces. The thermodynamic stability of these interfaces can be evaluated by construction of (grand potential) phase diagrams based on DFT calculations. The predictive capability and scalability of this approach has been demonstrated in previous work examining a wide range of chemical systems relevant for Li SSBs.\textsuperscript{11–13} In the field of Na SSBs, computational and experimental investigations have mainly focused on chalcogenide electrolytes and their interactions with the electrodes, also providing insight into important kinetic effects.\textsuperscript{14,15}

In this work, we have extended the previous analysis to consider a wide selection of Na solid-state electrolytes and coating candidates. In line with the literature, we find that the chalcogenide conductors exhibit poor chemical and electrochemical stabilities. The oxides display much larger voltage stability windows and generally lower reactivity against the cathode. Comparison of the calculated thermodynamic stability windows for polyanionic Na and Li compounds (see Fig. S3$^\ddagger$) reveals two substantial differences. The first difference is that the cathodic (reduction) limits against Na/Na$^+$ are lower than those for similar lithiated materials, with several Na polyanion compounds being stable against Na metal. For instance, $\mathrm{Na}_3\mathrm{PO}_4$, $\mathrm{Na}_3\mathrm{SiO}_4$, and $\mathrm{NaAlO}_2$ are all stable down to 0 V $\textit{versus}$ Na/Na$^+$, whereas the corresponding lithiated compounds are reduced at 0.74, 0.26, and 0.15 V against Li/Li$^+$, respectively. The other difference is that the anodic (oxidation) voltage limits of the Li compounds are generally higher than those of the Na compounds. While these observations are consistent with the standard redox potential of Na being higher than that of Li,
significant structural effects can modify this expectation. For example, the higher compatibility of Na⁺ with very large anions such as I⁻, Br⁻ or [B₃H₁₂]³⁻ stabilizes the corresponding electrolyte structures and raises their oxidation potentials with respect to the equivalent Li compounds. In addition, by considering pairs such as MP₂O₃/MP₃O₇ or MNB₂O₆/MNB₇O₉ (M = Li, Na), we observe that with increasing alkali chemical potential $\mu_M$ (and content), both Na and Li compounds exhibit improved cathodic stability but reduced anodic stability. The latter is problematic as high alkaline content seems to correlate with high ionic conductivity.

The lower reducing capability of Na (vs. Li) broadens the selection of stable electrolyte/anode interfaces that are predicted to have either no decomposition or a very small driving force for reduction by Na. These interfaces are type A interfaces according to the classification scheme proposed by Wenzel et al. and later adopted by Zhu et al., and in our analysis they are primarily formed by some oxides and borohydrides. Among these, Tang et al. identified binaries such as $\text{Se}_2\text{O}_3$, $\text{ZrO}_2$, and $\text{H}_2\text{O}_2$ as promising coating materials for the anode. To these materials, we add Na-based ternaries such as Na₃P₀₄, Na₃NbO₄, and Na₃SiO₄, antiperovskites, and aluminum oxides. The Na aluminum oxides, in particular, are remarkably stable against reduction by Na metal, whereas Li aluminates in contact with Li metal have Al reduced and form Li–Al alloys (see Fig. S3†).

Somewhat surprisingly, the stability of the [SiO₄]³⁻ and [PO₄]³⁻ groups in contact with Na metal as observed in the ternary salts Na₃SiO₄ and Na₃PO₄ does not hold for the NaSICONs: our results indicate that no composition is thermodynamically stable against Na metal, which reduces the polyoxions when they are in a structure with Zr or Ti metal. The presence of these TM ions providing charge compensation for the polyoxions instead of Na⁺ diminishes the sodium content of the NaSICONs and the lower Na content appears to correlate with a diminished cathodic stability. Likewise, pure phosphate NaSICONs are less stable against Na metal than Si-containing NaSICONs whose chemistry allows for a higher Na content. The interphase products Na₃P and Na₃Si (see Table S1†) provide mixed electronic and ionic conduction, matching the NaSICON/Na pair with interfaces of type B according to the classification scheme of Wenzel et al. The simultaneous ion and electron transport provided by these reaction products can lead to the progressive consumption of the solid-state electrolyte.

The interfaces generated by decomposition of most of the chalcogenides against Na metal are also type B interfaces (Table S1†). In contrast, the electronically insulating and therefore passivating interphases Li₃P and Li₃S produced by reduction of lithium thiophosphates against Li constitute interfaces of type C. This difference points towards the use of oxides that are stable in contact with Na metal as protective layers to enable Na metal cycling. An example of an eligible anode coating candidate is orthophosphate Na₃P₀₄. Indeed, the higher ionic character of the covalent bonds between phosphorus and oxygen, as compared to P–S or P–Se, widens the calculated energy gap of Na₃P₀₄ ($E_g = 4.01$ eV) and prevents its reduction by Na metal, in contrast to the analogous chalcogenides Na₃PSe₄ ($E_g = 2.68$ eV) and Na₃PSe₄ ($E_g = 1.56$ eV). Moreover, Na₃P₀₄ displays a very low driving force for the reaction with superionic conductors such as Na₃P₀₄ ($|\Delta E| \leq 20$ meV/atom), Na₃PSe₄ ($|\Delta E| \leq 17$ meV/atom) or Na₃SbS₄ (no reaction predicted). Hence, the combination of Na/Na₃PO₄/Na₃PSe₄ may allow stable cycling of Na metal, with the thiophosphate undergoing only minimal anion-exchange reactions at the interface with the buffer layer (the calculated reaction energy is <25 meV/atom). In addition, the use of Na-containing protective oxides instead of the Na-free binaries suggested by Tang et al., should, in principle, provide better diffusion of Na⁺ through the buffer.

Because the cations in the electrolytes are fully oxidized, the anodic limits are typically controlled by oxidation of the anion. In general, higher anion electronegativity correlates with a larger oxidation voltage. This trend explains the excellent stability of fluorides (>6 V) and poor performance of sulfides and selenides, whose oxidative breakdown is predicted to occur well before 3 V vs. Na/Na⁺. The oxides show remarkable variability in terms of anodic stability. Structures governed mainly by ionic interactions, such as the antiperovskites, display somewhat low oxidation limits, comparable to that of the simple binary oxide Na₂O. The oxidation limit increases in polyanionic compounds by virtue of the covalent interaction of the highly electronegative O with main group elements such as P, Si or B. As suggested by the parallel with the molecular orbital theory, this covalent bonding lowers the energy of the valence states and protects them from oxidation. Exemplary cases include the phosphates Na₃P₀₄/Na₃PO₄ and the NaSICONs. The latter also benefit from the positive Madelung potential exerted by Ti⁴⁺ and Zr⁴⁺ on the polyanion, which further opposes the anion oxidation. The covalent stabilization of the valence states is most dramatically observed when comparing the binary NaH with the borohydrides, particularly the borane Na₃B₁₂H₂₀, where the B–B skeletal bonding that builds up the [B₁₂H₁₂]³⁻ cluster framework results in extended electron delocalization. For the borohydrides, the anodic stability can also be greatly enhanced by kinetic factors, as indicated by the calculated potential for desodiation. If superionic conduction could be achieved at RT, e.g., by doping NaBH₄ into Na₃B₁₂H₂₀, the borane would become an eligible electrolyte candidate for SSBs. Among the positive electrodes, the fluorophosphates show good chemical compatibility with a wide range of solid electrolytes. In fact, the fluorophosphates display limited reactivity even with the chalcogenides. Sulfides and selenides are highly reactive in contact with Co and Ni layered oxides and would be progressively consumed by the formation of interphases with a metallic character, e.g., Co$_2$Se$_3$ (ref. 86) or NiS₂ (ref. 87) (type B interfaces), thereby requiring the application of a buffer layer. Again, similar to the electrolyte/Na anode interface, a viable solution could be the use of Na₃PO₄ (or Na₃P₀₄) as a cathode coating.

NaSICON ceramics and Na–β-alumina are the Na superionic conductors with the highest resilience to variations in cathode chemistry, forming essentially stable interfaces with all the positive electrodes considered here. Na–β[β⁺]-alumina is also stable against sodium metal and can now be processed into flexible ceramic membranes (≤50 μm), which makes it usable as a solid-state electrolyte separator for stable Na metal cycling in
a full solid-state cell. Using NaSICON ceramics instead of Na- 
alumina would enable the working potential of the SSB to be 
increased if a compositional gradient from silicate (stable at low 
voltage) to phosphate (at high voltage) could be implemented or if 
the two electrolytes could be combined in a single cell. However, 
the high co-sintering temperatures currently needed to deliver 
highly conductive NaSICONs impose serious processing chal- 
 lenges. Finally, concerning the cathode composite, our results 
suggest the possibility of combining a high-energy-density 
cathode such as Na3PS4, provided that a protective buffer 
layer (e.g., Na2PO4 or NaPO3) is applied. Given that chalcogenides are 
notably characterized by a higher degree of plasticity than oxides, 
this solution would ensure interparticle contact in addition to 
efficient ionic and electronic transport at the positive electrode, 
thus completing an optimized full solid-state cell design.

5 Conclusion

We have addressed the question of interfacial stability in solid-
state sodium batteries by assessing the electrochemical stability 
and thermodynamic phase equilibria of numerous potential 

solid-state electrolyte/electrode combinations using DFT 
calculations. In addition, a direct comparison between Na- 
and Li-containing materials revealed differences in electrochemical 
which are critical for tailoring the design of SSBs. More 
specifically, we observed that Na compounds generally display 
lower reduction and oxidation potentials than their Li coun-
termates. The enhanced cathodic stability of Na-based oxides 
provides multiple options to enable stable Na metal cycling, 
including their use as buffer layers to protect chalcogenide 
conductors from reduction or their direct use as solid-state 
electrolytes (e.g., Na- 
alumina). On the other hand, the 
anodic stability of sodium compounds can be improved over 
their lithium equivalents by structure stabilization factors such 
as the higher compatibility of Na+ with large anions, e.g., I- or 
[B12H12]2-. High voltage stability (>4-5 V) was predicted for sodium 
halides and oxides (especially phosphate NaSICONs), 
the borohydride superionic conductor NaB12H12 where covalent 
stabilization plays a major role. Finally, we identified 
several promising electrolyte/cathode combinations, demonstrat- 
ing, among other things, the limited chemical reactivity of the 
layered TM oxide NaCrO2 and polyaniionic fluorophosphate 
cathodes with many potential solid electrolytes. Our findings 
will provide valuable guidance for the effective design of future 
solid-state sodium batteries as well as other technologically 
relevant electrochemical systems.

Conflicts of interest

There are no conflicts to declare.

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References

1 H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka and 
G. Adachi, Ionic Conductivity of Solid Electrolytes Based on 
Lithium Titanium Phosphate, J. Electrochem. Soc., 1990, 
137(4), 1023–1027.

2 J. W. Fergus, Ion transport in sodium ion conducting solid 

3 S. Ohta, T. Kobayashi and A. Takahiko, “High lithium ionic 
conductivity in the garnet-type oxide Li7–X La3(Zr2–X, 
NbX)O12 (X = 0–2),” J. Power Sources, 2011, 196(6), 3342–3345.

4 V. Thangadurai, D. Pinzaru, S. Narayanan and A. K. Baral, 
Fast Solid-State Li Ion Conducting Garnet-Type Structure 
6(2), 292–299.

5 N. Kamaya, et al., A lithium superionic conductor, Nat. 
Mater., 2011, 10(9), 682–686.


58 K. Takahashi, et al., All-solid-state lithium battery with LiBH4 solid electrolyte, J. Power Sources, 2013, 226, 61–64.


