



Materials Design Principles for Air-Stable Lithium/Sodium Solid Electrolytes

Yizhou Zhu* and Yifei Mo*

Abstract: Sulfide solid electrolytes are promising inorganic solid electrolytes for all-solid-state batteries. Despite their high ionic conductivity and desirable mechanical properties, many known sulfide solid electrolytes exhibit poor air stability. The spontaneous hydrolysis reactions of sulfides with moisture in air lead to the release of toxic hydrogen sulfide and materials degradation, hindering large-scale manufacturing and applications of sulfide-based solid-state batteries. In this work, we systematically investigate the hydrolysis and reduction reactions in Li- and Na-containing sulfides and chlorides by applying thermodynamic analyses based on a first principles computation database. We reveal the stability trends among different chemistries and identify the effect of cations, anions, and Li/Na content on moisture stability. Our results identify promising materials systems to simultaneously achieve desirable moisture stability and electrochemical stability, and provide the design principles for the development of air-stable solid electrolytes.

All-solid-state batteries based on inorganic solid electrolytes are one of the most promising candidates for next-generation energy storage systems with improved safety, higher energy density, and a longer cycle life. After decades of research, various lithium and sodium solid electrolytes with high ionic conductivity have been developed, including $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$, $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($0 \leq x \leq 3$), Na_3PS_4 , and Na_3SbS_4 .^[1] Among these materials, sulfide solid electrolytes show exceptionally high ionic conductivity (for example, 25 mS cm^{-1} at room temperature for $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ ^[1c]) and desirable mechanical properties of high deformability. In sulfide-based all-solid-state batteries, good physical contact at the electrolyte–electrode interfaces can be formed by cold pressing, and the interfacial compatibility with electrode materials is achieved by interfacial

coating or passivation.^[1a,c,2] Currently, sulfide-based all-solid-state batteries provide the best cell performance.^[1a,c]

However, a key challenge for the large-scale manufacturing of sulfide solid electrolytes is their poor stability against moisture in the air. Even trace amount of moisture in the ambient environment can initiate spontaneous hydrolysis reactions for many lithium thiophosphates, leading to materials degradation, deteriorated properties, and the release of toxic H_2S gas. Handling these moisture-sensitive sulfides is restricted to a dry inert-gas environment and is a great challenge for large-scale manufacturing and processing.^[3] Therefore, development of sulfide solid electrolytes with good air stability is urgently desired.

To address the issue of moisture stability, various design and modification approaches have been developed. Doping of oxides, such as P_2O_5 , Bi_2O_3 , ZnO , and Fe_2O_3 ,^[4] is reported to improve moisture stability and suppress the H_2S generation, but usually leads to compromised ionic conductivity. Another effective strategy is substituting or doping cations that exhibit better moisture stability. Successful examples $\text{Li}_{10}\text{Ge}(\text{P}_{1-x}\text{Sb}_x)_2\text{S}_{12}$, $\text{Li}_{4-x}\text{Sn}_{1-x}\text{As}_x\text{S}_4$, $\text{Li}_{3.85}\text{Sn}_{0.85}\text{Sb}_{0.15}\text{S}_4$, Li_3SbS_4 , Na_3SbS_4 , $\text{Na}_3\text{P}_{0.62}\text{As}_{0.38}\text{S}_4$, and $\text{Na}_{3.75}\text{Sn}_{0.75}\text{Sb}_{0.25}\text{S}_4$, have both improved moisture stability and good ionic conductivity.^[5] However, these substituting cations are usually derived from the empirical hard soft acid base (HSAB) theory or from the intuition and experience of chemists. Currently, only a limited number of the cation choices, such as Sn^{4+} , Ge^{4+} , As^{5+} , and Sb^{5+} are available. Cations such as Sn^{4+} and Ge^{4+} sacrifice the electrochemical stability under reduction, which is a critical issue for battery applications.^[1 f,3a,5f,6] Recently, lithium chlorides were demonstrated as an emerging class of solid electrolytes with high ionic conductivity and good electrochemical stability.^[7] In order to develop new solid electrolyte materials with good moisture stability while maintaining good electrochemical stability and ionic conductivity, the effects of different cations, anions, and compositions on moisture stability need to be systematically studied and understood.^[7c,e]

Thermodynamic analyses based on first principles computation databases have been demonstrated in the study of the electrochemical stability of solid electrolytes in different chemical systems.^[2,6a,8] In this study, we perform similar thermodynamic analyses to investigate the moisture stability of a wide range of lithium/sodium sulfides and chlorides. Although we confirm that most lithium-containing sulfides have limited moisture stability, promising cations with improved moisture and electrochemical stability were identified. In addition, chlorides and sodium sulfides show better moisture stability. Based on the identified stability trends, we provide strategies to design new solid electrolytes

[*] Dr. Y. Zhu, Prof. Y. Mo
Department of Materials Science and Engineering
University of Maryland
College Park, MD 20742 (USA)
E-mail: yizhou.zhu@northwestern.edu
yfmo@umd.edu

Dr. Y. Zhu
Department of Materials Science and Engineering
Northwestern University
Evanston, IL 60201 (USA)

Prof. Y. Mo
Maryland Energy Innovation Institute, University of Maryland
College Park, MD 20742 (USA)

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with improved moisture stability and electrochemical stability.

To study the moisture stability of sulfides, we focused on hydrolysis reactions that generate H_2S , which are observed as the major detrimental hydrolysis reactions from experiments. The energies of all solid phases are based on the formation energies from the Materials Project database,^[9] except for hydroxides. The energies of hydroxide phases and gaseous species, including H_2O , H_2S , and HCl , are based on experimental values^[10] (see the Methods section in the Supporting Information).

We first studied the moisture stability of simple binary compounds: Li_2S , Na_2S , LiCl , and NaCl . The major competing phases are hydroxides and oxides. Based on the calculated relative stability, we constructed the predominance diagrams under different H_2O and $\text{H}_2\text{S}/\text{HCl}$ chemical potentials (Figure 1). Lithium compounds exhibit poorer moisture stability than sodium compounds because Li_2S and LiCl occupy smaller stable ranges compared to Na_2S and NaCl . Chlorides are much more stable than sulfides.

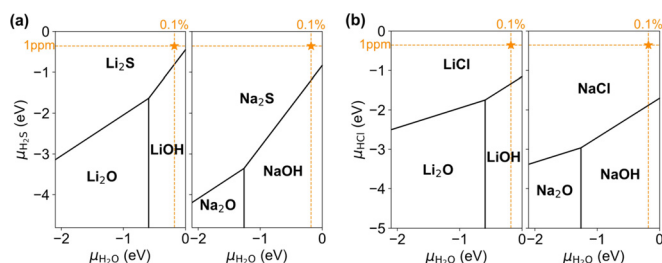
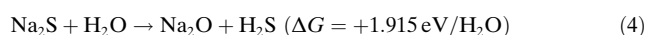
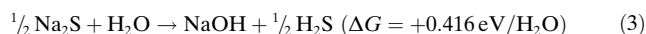
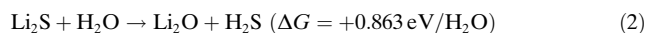
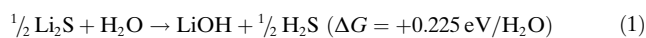


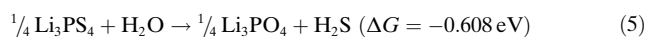
Figure 1. Predominance phase diagrams under different H_2O and H_2S chemical potentials. a) Li_2S – LiOH – Li_2O (left) and Na_2S – NaOH – Na_2O (right), b) LiCl – LiOH – Li_2O (left) and NaCl – NaOH – Na_2O (right). The orange stars correspond to the preset conditions: 0.1% H_2O and 1 ppm $\text{H}_2\text{S}/\text{HCl}$.

To make a consistent comparison among different materials, we selected the partial pressure of gaseous species to resemble the practical conditions of materials processing or battery manufacturing. The molar fraction of H_2O was set to 0.1%, and $\text{H}_2\text{S}/\text{HCl}$ was set to 1 ppm (orange stars in Figure 1). For Li_2S and Na_2S , the key hydrolysis reactions are:



The positive (unfavorable) reaction energy shows that both Li_2S and Na_2S are stable under the given conditions.

We then investigated the moisture stability of compounds with other cations, including M–X binaries and A–M–X ternaries ($\text{A} = \text{Li}, \text{Na}, \text{X} = \text{S}, \text{Cl}$). The calculation scheme of representative hydrolysis reactions and reaction normalization scheme are provided in the Supporting Information. For example, the representative hydrolysis reaction of Li_3PS_4 is:



This highly thermodynamically favorable reaction indicates the poor moisture stability of Li_3PS_4 .

Figure 2 shows the hydrolysis reaction energies for all sulfides (data in the Supporting Information). Metalloid ions in period 4, 5, and 6, including Ga^{3+} , Ge^{4+} , Sn^{4+} , Sb^{5+} , Pb^{4+} , and Bi^{3+} , show significantly better moisture stability than P^{5+} . This trend is consistent with the empirical HSAB theory and previous experiments.^[1f,g,4a,5a,b,d] Early-transition-metal ions including Zr^{4+} , Hf^{4+} , Ta^{5+} , Nb^{5+} , Cr^{6+} , and W^{6+} show poor moisture stability, and Y^{3+} , Cr^{3+} are relatively better. Most lanthanide ions show similar poor moisture stability. In

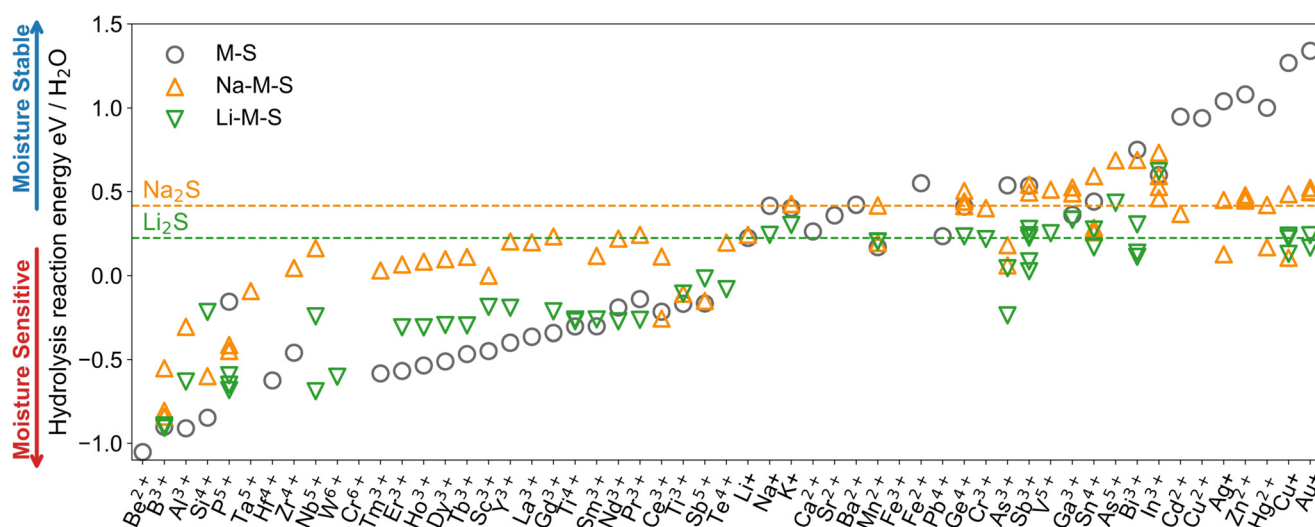


Figure 2. Hydrolysis reaction energy of sulfides, including 46 binary M–S (grey circles), 52 ternary Li–M–S (green triangles) and 65 Na–M–S (orange triangles), as a function of cation M. More-negative reaction energy indicates worse moisture stability (moisture sensitive), whereas more-positive reaction energy indicates better moisture stability (moisture stable). The horizontal dashed lines correspond to the hydrolysis reaction energy of Li_2S (green) and Na_2S (orange), respectively.

contrast, alkali and alkaline ions generally show decent moisture stability. Late-transition-metal ions, such as Zn^{2+} , Cd^{2+} , Cu^{2+} , and Ag^{+} exhibit the best moisture stability among the cations investigated. Previous experimental works reported that the addition of ZnO nanoparticles to phosphorus-based glass sulfide electrolytes can suppress the release of H_2S gas, this finding is consistent with our calculation.^[3d,4a,b,e] Some of these identified cations with better moisture stability are promising elements for doping and substitution to improve moisture stability of current sulfide solid electrolytes.

Compared to lithium compounds, sodium ternary sulfides Na-M-S generally show better moisture stability, while the overall stability trend with respect to cations is generally similar (Figure 2). Compounds with metalloid-like ions and early-transition-metal ions still exhibit poor moisture stability. Most lanthanide-related compounds are nearly stable under the given conditions. Similar to lithium compounds, sodium compounds with alkali, alkaline, and late-transition-metal ions show good moisture stability with a positive hydrolysis reaction energy.

We further compared the moisture stability of binary sulfides M-S with ternary sulfides Li/Na-M-S. The hydrolysis reaction energy of binaries Li_2S (+0.225 eV) and Na_2S (+0.416 eV) are marked as the dashed lines in Figure 2. For most ions on the left-hand side of Figure 2, Li-M-S ternary sulfides show moisture stability better than M-S but worse than that of Li_2S (below the green dashed line), and most ions on the right-hand side of Figure 2 show the opposite trend, i.e., moisture stability worse than M-S but better than that of Li_2S . This result can be explained because Li-M-S ternaries are intermediate compounds between M-S binaries and Li_2S , and thus have an “intermediate” moisture stability that lies between M-S binaries and Li_2S . The same trend also applies to sodium compounds, which explains their better moisture stability. Na_2S has better moisture stability than Li_2S , therefore Na-M-S ternaries as intermediates between Na_2S and M-S binaries in general exhibit better moisture stability than Li-M-S ternaries. As a notable exception, Li_3PS_4 and Na_3PS_4 show poorer moisture stability than their binary P_2S_5 . This exception is due to the formation of highly stable phosphates Li_3PO_4 and Na_3PO_4 in hydrolysis reactions, and is consistent with the hypersensitivity to moisture of thiophosphates as observed in experiments.^[4a,c] According to this stability trend, increasing the Li/Na content in the sulfides composition in general drives the moisture stability towards the moisture stability level of binary $\text{Li}_2\text{S}/\text{Na}_2\text{S}$.

In the case of the chlorides, most chlorides show positive hydrolysis reaction energy and are stable under the given conditions (Figure S1), except for P^{5+} and B^{3+} . These results suggest that moisture stability is much less of an issue for chlorides compared to sulfides. In addition, the stability trend among different cations in chlorides in general differs from that in sulfides. Cations that provide better moisture stability in chlorides are listed in the Supporting Information.

Our calculation provides guidance for selecting cations that can achieve better moisture stability. Herein, we provide guiding charts for cation selection considering the effect of both moisture stability and electrochemical stability (Figure 3). The moisture stability is quantified as the hydroly-

sis reaction energy (y-axis in Figure 3). The cations with best moisture stability such as In^{3+} and As^{5+} are shown on the top region of the chart. In addition, electrochemical stability is critical for solid electrolytes, and the cation is a key factor determining the reduction stability.^[6a] We calculated the reaction energy per Li/Na in the reduction reaction $\text{Li-M-X}/\text{Na-M-X}$ at 0 V (referenced to Li/Li^+ or Na/Na^+ respec-

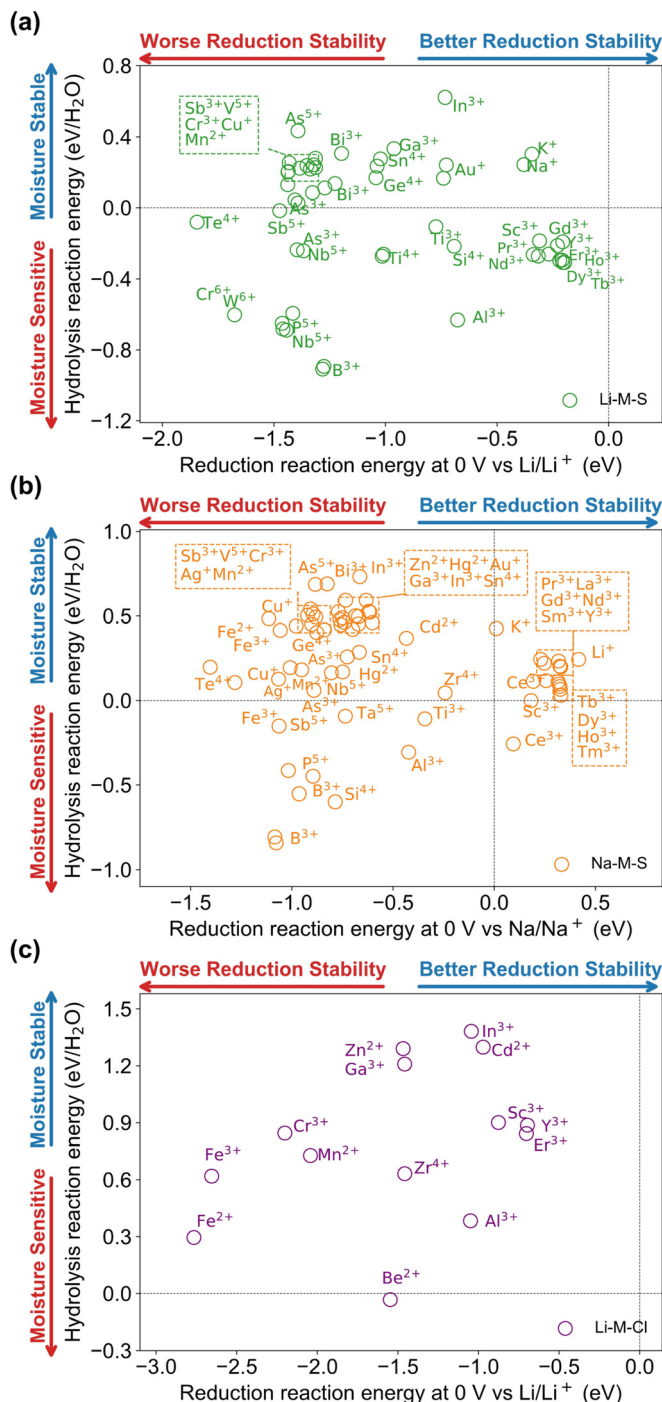


Figure 3. Guiding charts for cation selection. The moisture stability (hydrolysis reaction energy, y-axis) versus reduction stability (reduction reaction energy with alkali metal, x-axis) for a) 52 lithium ternary sulfides b) 65 sodium ternary sulfides, and c) 14 lithium ternary chlorides.

tively), using a similar scheme as in our previous studies.^[2] The reduction reaction energy at 0 V reflects the reduction stability of a material (x -axis of Figure 3). Figure 3 can serve as a practical guiding chart for cation selection to simultaneously achieve good moisture stability and reduction stability (towards top right corner). The calculated stability is based on thermodynamics, but kinetics such as the passivation on surfaces and interfaces also play important effects in stability^[2,8,11] and should be considered.

As shown in Figure 3a, lithium compounds with cations located at the lower left corner, such as P^{5+} , are highly reactive to moisture and are easily reduced by Li, in agreement with experiments.^[11a,12] Previously explored air-stable cations, such as Sn^{4+} , Ge^{4+} , As^{5+} , and Sb^{5+} , lie on the upper left, indicating decent moisture stability but limited reduction stability. The reduction reaction energies indicate approximate reduction potentials of 1.0–1.5 V (referenced to Li/Li^+), in agreement with previous studies.^[5a,e] The upper right corner contains the most desirable cations with both good moisture stability and reduction stability. Unfortunately, no lithium sulfide compounds are simultaneously stable against Li metal and moisture under the given conditions. Among lithium sulfides, rare-earth elements, including Sc^{3+} , Y^{3+} , and many lanthanides have the best reduction stability and moisture stability similar to that of Ti^{4+} and Sb^{5+} . In^{3+} shows the best moisture stability and relatively good reduction stability compared to commonly used Sn^{4+} or Ge^{4+} . These cations may be used as doping or substitution for materials design to improve reduction and moisture stability.

Sodium sulfide compounds have significantly better reduction stability and moisture stability than their lithium counterparts, and thus have a broader choice of cations. Sodium sulfide compounds with cations including Sc^{3+} , Y^{3+} , Zr^{4+} , and most lanthanides cations can achieve reduction stability and decent moisture stability (Figure 3b). These cations are promising for the development of air-stable sulfide solid electrolytes.

Ternary lithium chlorides are generally stable against moisture because most of them, except for Be^{2+} , show positive hydrolysis reaction energy (Figure 3c). However, they have poor reduction stability against Li metal. In general, the reduction stability, rather than the moisture stability, is more of a critical issue for lithium chloride compounds.

In summary, we performed systematic thermodynamic analyses on the moisture stability of alkali-metal sulfides and chlorides based on a first principles computation database. By systematically studying the hydrolysis reactions in a broad range of cations, anions, and compositions, we uncovered the general trends of moisture stability in the alkali-metal sulfides and chlorides. In addition to confirming previously reported air-stable sulfide cation chemistry, we identify a few new cations with good moisture stability and electrochemical stability. Materials design strategies to improve moisture stability and electrochemical stability include doping/substituting cations with better stability and tuning Li/Na content. Chlorides generally have much better moisture stability than sulfides, confirming their promising use in solid electrolyte chemistry with good moisture stability. Sodium compounds generally exhibit better moisture and electrochemical stabil-

ity than lithium compounds, suggesting the advantages of sodium solid-state batteries in enabling stable metal anodes and low-cost processing compared to that of lithium-metal batteries. Our work provides a comprehensive understanding of the moisture stability trend in sulfide and chloride chemistries, and proposes practical design and engineering strategies to achieve better electrochemical and moisture stability, paving the way for the development of air-stable solid electrolytes for solid-state batteries.

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Conflict of interest

The authors declare no conflict of interest.

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