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## Failure mechanism of solid-state electrolyte $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ in a moist atmosphere: a first-principles study

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All-solid-state lithium-ion batteries (ASSLIBs) have commercial potential for industrial applications in long-range electric vehicles. The chemical properties of solid-state electrolytes (SSEs) play a key role in the performance of ASSLIBs. Among all kinds of SSEs, sulfide solid-state electrolytes are advantageous to ASSLIBs due to their high ionic conductivity and excellent electrochemical stability. However, sulfide electrolytes have poor stability in air due to their propensity to react with  $\text{H}_2\text{O}$  to generate toxic  $\text{H}_2\text{S}$  gas. Herein to understand the specific failure mechanism, we use first-principles calculations to study the kinetic and thermodynamic mechanism of the reaction between  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ , which is a typical sulfide electrolyte, and  $\text{H}_2\text{O}$  in the atmosphere. We find that the  $\text{H}_2\text{O}$  molecules preferentially react with the sulfur atoms of the  $\text{PS}_4$  tetrahedra to produce  $\text{H}_2\text{S}$ . As the sulfur atoms of the  $\text{PS}_4$  tetrahedra in the bulk continuously emerge towards the surface, this reaction occurs repeatedly. Meanwhile, the oxygen atoms from  $\text{H}_2\text{O}$  molecules can also diffuse into the bulk. These reactions continue until the sulfur atoms of the  $\text{PS}_4$  tetrahedra in  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  are completely replaced by oxygen atoms. Furthermore, we study the influence of Sb doping on  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ , and kinetically explain the mechanism of hydrolysis inhibition when doping Sb in  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ .

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## Introduction

With the growing demand for low-carbon technologies, lithium-ion batteries with a higher energy density, longer cycle life and better safety have become much more desirable to compete with gasoline vehicles. Traditional commercial lithium-ion batteries with a liquid organic electrolyte have the advantages of high theoretical specific capacity, environmental friendliness, etc.<sup>1–5</sup> However, the organic electrolyte in lithium-ion batteries is flammable, and has a lower thermal stability and lower safety compared with inorganic solid-state electrolytes.<sup>6–8</sup> The solid-state electrolytes used in solid-state lithium-ion batteries consist mainly of polymers,<sup>9,10</sup> oxides<sup>11–13</sup> and sulfides.<sup>14,15</sup> Among them, sulfides have a relatively high ionic conductivity, and some are comparable to organic liquid electrolytes.<sup>16</sup> However, sulfide solid-state electrolytes react easily with  $\text{H}_2\text{O}$  in moist air to generate toxic  $\text{H}_2\text{S}$  gas, which limits their practical applications. A great deal of experimental

work has been done to solve the air-stability problem. Maramatsu *et al.*,<sup>17</sup> have studied the structural changes of  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  glass structures in the atmosphere. This study found that  $\text{PS}_4^{3-}$  can reduce  $\text{H}_2\text{S}$  gas for binary  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  glass or glass ceramics. 75Li<sub>2</sub>S–25P<sub>2</sub>S<sub>5</sub> has been found to have better water stability. Tin sulfides ( $\text{Li}_4\text{SnS}_4$ ,<sup>18,19</sup> and  $\text{Li}_4\text{SnS}_4\text{-LiI}$ <sup>20</sup>), As-substituted  $\text{Li}_4\text{SnS}_4$ ,<sup>21</sup> and Sb-substituted  $\text{Li}_4\text{SnS}_4$ <sup>22,23</sup> also show better stability in air. Based on the hard and soft acids and bases (HSAB) theory,<sup>24</sup> P is a hard acid, Sn, Sb, and As are soft acids, and S is a soft base, Thus, the Sn-, Sb-, and As-S bonds are harder than the P-S bond. Hayashi *et al.*<sup>25</sup> inhibited the production of  $\text{H}_2\text{S}$  by doping  $\text{M}_x\text{O}_y$  (M = Fe, Zn, and Bi) in the  $\text{Li}_3\text{PS}_4$  electrolyte, which can absorb  $\text{H}_2\text{S}$ . Although metal oxide doping improves the air stability of sulfide solid-state electrolytes, it also reduces the ionic conductivity. In addition, Sun *et al.*<sup>26</sup> improved the air stability of the sulfide solid-state electrolyte through introducing soft acid metals. The air stability is improved *via* Sb doping of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ , where the  $\text{Li}_{10}\text{Ge}(\text{P}_{1-x}\text{Sb}_x)_2\text{S}_{12}$  ionic conductivity is  $17.3 \pm 0.9 \text{ mS cm}^{-1}$ . After air exposure, the ionic conductivity can remain between 12.1 and 15.7  $\text{mS cm}^{-1}$ .

Kamaya *et al.* reported a superionic conductor  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  with high ionic conductivity ( $12 \text{ mS cm}^{-1}$ ) at room temperature.<sup>27</sup> Compared with most sulfide solid-state electrolytes,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  has been more extensively studied. Its space

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group is  $P42/nmc$ , and consists of  $(\text{Ge}_{0.5}\text{P}_{0.5})\text{S}_4$  tetrahedra,  $\text{PS}_4$  tetrahedra,  $\text{LiS}_4$  tetrahedra and  $\text{LiS}_6$  octahedra. It has three-dimensional lithium-ion channels.<sup>27–29</sup> The diffusion paths along the  $c$  direction are considered as the dominant transport channel with the activation barrier of 0.16 eV, which is much lower than the diffusion barrier in the  $ab$  plane (0.26 eV).<sup>30</sup> In addition,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  also has a wide electrochemical stability window ( $>5$  V against  $\text{Li}/\text{Li}^+$ ) at room temperature. Mo *et al.*<sup>29</sup> proposed that this is due to the decomposition of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  into  $\text{Li}_2\text{S}$  and  $\text{P}_2\text{S}_5$  passivation layers when  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  comes into contact with the electrode, which then protects the solid-state electrolyte, resulting in a wide electrochemical window. However, as with other sulfide compounds,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  is sensitive to atmospheric moisture, which can react with  $\text{H}_2\text{O}$  to produce the air pollutant  $\text{H}_2\text{S}$ ,<sup>31,32</sup> and lead to a decreased ionic conductivity for  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ . These drawbacks limit the practical applications of sulfide solid electrolytes in industry. Although a lot of research into  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  air stability has been carried out experimentally, few theoretical studies have been performed to explore the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  air stability. In this work, we systematically study the specific chemical reactions between  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  and  $\text{H}_2\text{O}$  in air based on first-principles calculations, and explore the failure mechanism of the solid-state electrolyte in a moist atmosphere.

## Computational details

All calculations are performed based on density functional theory (DFT) using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional.<sup>33</sup> The interactions between ion cores and valence electrons are treated using the projector augmented wave (PAW)<sup>34,35</sup> method as implemented in the Vienna *ab initio* simulation package (VASP).<sup>36</sup> The kinetic energy cutoff is set as 450 eV. In addition, the climbing image nudged elastic band (CI-NEB) method<sup>37</sup> is used to obtain the specific chemical reaction paths. A  $4 \times 4 \times 1$  Monkhorst–Pack  $k$ -point grid is used to calculate the reaction coordinates and surface energies. All structures are fully relaxed until the residual forces are less than  $0.01 \text{ eV } \text{\AA}^{-1}$  with the spin-polarized calculations. The crystal structure of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  is shown in Fig. 1. The calculated lattice constants are  $a = b = 8.74 \text{ \AA}$ , and  $c = 12.86 \text{ \AA}$ , which are consistent with an earlier report.<sup>38</sup>

## Results and discussion

In order to find the dominant surface of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ , we first obtain the surface energies ( $E_s$ ) of various surfaces, which are calculated using eqn (1),

$$E_s = \frac{1}{2S}(E_{\text{slab}} - nE_{\text{bulk}}) \quad (1)$$

where  $S$  is the surface area,  $E_{\text{slab}}$  is the total energy of the surface structure,  $n$  is the number of unit cells, and  $E_{\text{bulk}}$  is the total energy of bulk  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ . As listed in Table 1, we find that the most stable surface is the (110) surface, which has

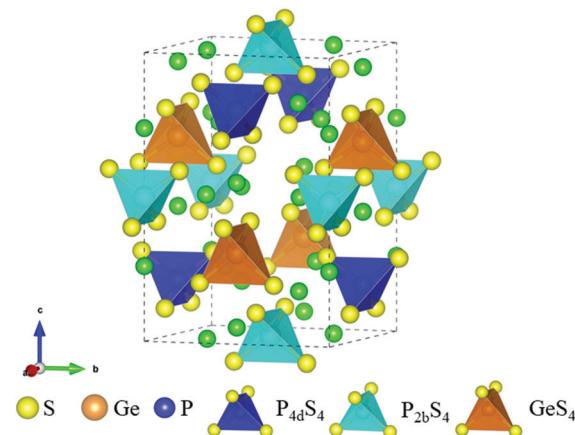


Fig. 1 Crystal structure of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ .

Table 1 Surface energy ( $E_s$ ) values of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$

Surface	$E_s$ (eV $\text{\AA}^{-2}$ )
(001)	0.033
(010)	0.075
(100)	0.059
(110)	0.029
(011)	0.055
(101)	0.064
(111)	0.040

lowest energy of  $0.029 \text{ eV } \text{\AA}^{-2}$ . According to the results of the surface energies, the (001) and (110) surfaces are more likely to be exposed to the air. However, we find that there are both  $\text{PS}_4$  tetrahedra and  $\text{GeS}_4$  tetrahedra on the exposed (110) surface (see Fig. 2), which is more representative.

As can be seen in Fig. 2, there are four possible sites that can be adsorption sites for  $\text{H}_2\text{O}$  molecules: these are S sites on the  $\text{PS}_4$  tetrahedron (site ① in Fig. 2), S sites on the  $\text{GeS}_4$  tetrahedron (site ② in Fig. 2), and Li sites between the  $\text{PS}_4$  and  $\text{GeS}_4$

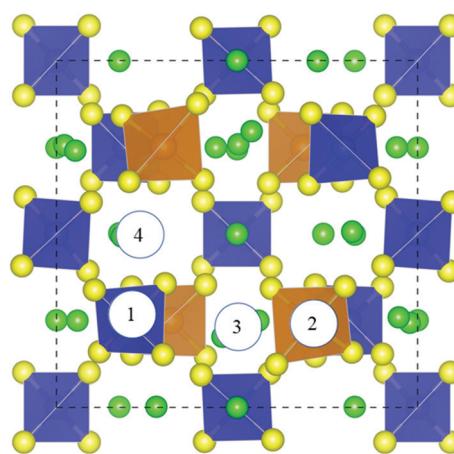


Fig. 2  $\text{H}_2\text{O}$  adsorption site on the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}(110)$  surface. Site ① is the adsorption site on the  $\text{PS}_4$  tetrahedron, site ② is the adsorption site on the  $\text{GeS}_4$  tetrahedron, and sites ③ and ④ are the adsorption sites on  $\text{Li}^+$ .

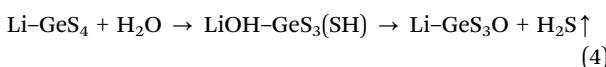


tetrahedra (sites ③ and ④ in Fig. 2). The adsorption energy ( $E_{\text{ads}}$ ) is calculated as *via* eqn (2),

$$E_{\text{ads}} = E_{\text{tot}} - E_{\text{H}_2\text{O}} - E_{\text{surface}} \quad (2)$$

where the  $E_{\text{tot}}$  is the total energy of the  $\text{H}_2\text{O}$ -adsorbed surface,  $E_{\text{H}_2\text{O}}$  is the energy of the  $\text{H}_2\text{O}$  molecule, and  $E_{\text{surface}}$  is the total energy of the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  slab. As listed in Table 2, we find that, compared with the S atoms in  $\text{PS}_4$  tetrahedra and the S atoms in  $\text{GeS}_4$  tetrahedra,  $\text{H}_2\text{O}$  molecules are more likely to be adsorbed on  $\text{Li}^+$ . For site ③, the adsorption energy of  $\text{H}_2\text{O}$  is  $-0.43$  eV. This is because  $\text{O}$   $\text{sp}^3$  hybridization in  $\text{H}_2\text{O}$  has an unshared electron pair, which can be combined with the vacant 2s orbital of the outermost layer of  $\text{Li}^+$ , thus forming the  $\text{Li}-\text{O}$  bond with greater adsorption energy.

We now investigate the decomposition of  $\text{H}_2\text{O}$  on the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}(110)$  surface. According to the theoretical calculations of Mo *et al.*,<sup>39</sup> the reaction between the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}(110)$  surface and  $\text{H}_2\text{O}$  is as follows:



We show the reaction processes in Fig. 3. The adsorbed  $\text{H}_2\text{O}$  molecules can be decomposed into  $\text{H}^+$  and  $\text{OH}^-$  on the surface, where  $\text{H}^+$  reacts with the S atom on the  $\text{PS}_4/\text{GeS}_4$  tetrahedra to form the  $\text{H}-\text{S}$  bond, and  $\text{OH}^-$  can be further decomposed to form  $\text{O}^{2-}$  and  $\text{H}^+$ . The latter  $\text{H}^+$  reacts with  $\text{S}-\text{H}$  to form  $\text{H}_2\text{S}$ , which is desorbed from the (110) surface.

Fig. 4(a and b) depict the energy profile of the hydrolysis reaction between  $\text{H}_2\text{O}$  molecules and S of the  $\text{PS}_4$  tetrahedra and the relative intermediate reaction products. IS0 stands for the (110) surface with no  $\text{H}_2\text{O}$  molecules adsorbed. IS1 stands for the (110) surface-adsorbed  $\text{H}_2\text{O}$  molecules. TS1 stands for the transition state and MS1 stand for the intermediate state of  $\text{H}_2\text{O}$  decomposed into  $\text{H}^+$  and  $\text{OH}^-$ . MS2 stands for the second intermediate state, which relaxes the position of the H atom of  $\text{OH}^-$ , and MS3 stands for the third intermediate state of  $\text{OH}^-$  decomposition into  $\text{H}^+$  and  $\text{O}^{2-}$ . FS stands for the final state of  $\text{H}_2\text{S}$  desorbing from the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}(110)$  surface. From the results of Table 2,  $\text{H}_2\text{O}$  adsorbs on  $\text{Li}^+$  and the adsorption energy is  $-0.43$  eV. For the process from IS1 to MS1,  $\text{H}_2\text{O}$  decomposes into  $\text{H}^+$  and  $\text{OH}^-$ , where  $\text{H}^+$  combines with S to form the  $\text{H}-\text{S}$  bond and the related energy barrier is  $0.41$  eV.  $\text{OH}^-$  decomposes into  $\text{H}^+$  and  $\text{O}^{2-}$  from MS2 to MS3, where  $\text{H}^+$  combines with the SH group in MS1 to generate  $\text{H}_2\text{S}$ , which is adsorbed on the surface. Meanwhile,  $\text{O}^{2-}$  combines with S of  $\text{GeS}_4$  to form the  $\text{S}-\text{O}$  bond, and the energy barrier for this is  $0.65$  eV. The process from MS3 to FS is the desorption of  $\text{H}_2\text{S}$ .

Table 2 Adsorption energies of  $\text{H}_2\text{O}$  at different sites on the (110) surface

Site	①	②	③	④
$E_{\text{ads}}$ (eV)	0.15	-0.12	-0.43	-0.28

from the surface, where the desorption energy is  $0.27$  eV. In addition, we also consider the similar reaction between  $\text{H}_2\text{O}$  and the  $\text{GeS}_4$  tetrahedra on the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}(110)$  surface, shown in Fig. 4(c and d). By comparing the energy profiles with different sulfur sources, we find that the reaction energy barrier of  $\text{H}_2\text{O}$  decomposition on the  $\text{GeS}_4$  tetrahedra ( $0.80$  eV,  $0.72$  eV) is higher than the reaction energy barrier on  $\text{PS}_4$  tetrahedra ( $0.41$  eV,  $0.65$  eV). This suggests that  $\text{H}_2\text{O}$  is more likely to react with S in the  $\text{PS}_4$  tetrahedra in  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  to produce  $\text{H}_2\text{S}$ . FS in Fig. 4(b and d) also shows the result of an adsorbed oxygen atom and a sulfur vacancy. Since the reaction on the  $\text{PS}_4$  tetrahedron is much easier than that on the  $\text{GeS}_4$  tetrahedron, we now study the existence of S vacancies on the  $\text{PS}_4$  tetrahedra.

As experiments have shown that the degradation of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  releases a large amount of  $\text{H}_2\text{S}$ ,<sup>26</sup> this process inevitably involves the sulfur atoms in the bulk. This means that S in  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  will migrate to the surface. As shown in Fig. 5, three diffusion paths of the S atom are considered: S atom diffusion on the surface, S atom diffusion from a  $\text{GeS}_4$  tetrahedron to a  $\text{PS}_4$  tetrahedron, and S atom diffusion from a  $\text{PS}_4$  tetrahedron to a  $\text{PS}_4$  tetrahedron, and Fig. 5(a) shows the energy barriers of  $0.45$  eV,  $1.07$  eV and  $0.82$  eV, respectively. Fig. 5(b) shows the initial and final structures for the diffusion of an S atom on the (110) surface. We find the presence of the  $\text{Li}^+$  vacancy could be conducive to the diffusion of the S atom. This is because when the S atom diffuses from one tetrahedron to another tetrahedron, it could use the  $\text{Li}^+$  channel along the *c* direction. Fig. 5(c and d) show the S atom diffusion path from a  $\text{PS}_4$  tetrahedron to a  $\text{PS}_4$  tetrahedron and from a  $\text{GeS}_4$  tetrahedron to a  $\text{PS}_4$  tetrahedron, respectively. The diffusion barriers shows that the diffusion of the S atom from a  $\text{PS}_4$  tetrahedron to a  $\text{PS}_4$  tetrahedron is relatively facile. This is also consistent with HSAB theory, where the bond of the soft base S and soft acid Ge is stronger than the bond of the soft base S and the hard acid P, and the bond energy of Ge-S is higher than that of P-S.

The decomposition of  $\text{H}_2\text{O}$  also leaves an oxygen atom on the surface, while experimental results of the continuous release of  $\text{H}_2\text{S}$  also show that those oxygen atoms do not form a protective layer on the surface to prevent  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  from contacting the air. This also means O atoms on the surface can diffuse into the bulk. Since Fig. 5 shows that a S atom can diffuse from a  $\text{GeS}_4$  tetrahedron to a  $\text{PS}_4$  tetrahedron in the bulk, S vacancies will concentrate on the  $\text{GeS}_4$  tetrahedra. Therefore, oxygen atoms can diffuse from the surface to the bulk through the  $\text{GeS}_4$  tetrahedra. Fig. 6(a) shows the energy barriers during the process of O diffusing from the surface to the bulk, an O atom diffusing from  $\text{GeS}_3\text{O}$  to  $\text{PS}_3\text{O}$ , and an O atom diffusing from  $\text{PS}_3\text{O}$  to  $\text{PS}_3\text{O}$ , for which the energy barriers are  $0.21$  eV,  $1.99$  eV and  $2.72$  eV, respectively. Fig. 6(b) shows the diffusion path of an oxygen atom from the surface to the bulk. The path through the  $\text{GeS}_4$  tetrahedron into the bulk is found to have the lowest energy barrier ( $0.21$  eV). However, the energy barriers for O atom diffusion in the bulk are  $1.99$  eV and  $2.72$  eV, which are too high for O atoms in the pristine  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  crystal. Thus, it is hard for O ions to diffuse in



S diffuse from bulk to surface

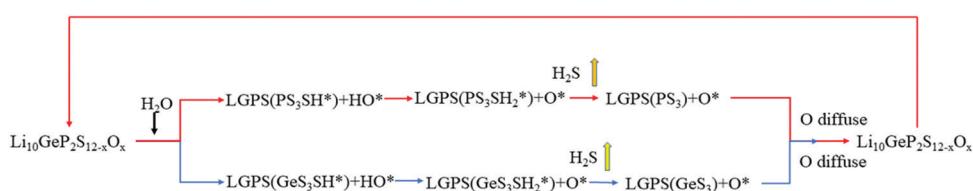


Fig. 3 Reaction paths of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  surfaces and  $\text{H}_2\text{O}$ , where the red path represents  $\text{H}_2\text{O}$  reacting with S in the  $\text{PS}_4$  tetrahedra, and the blue one represents  $\text{H}_2\text{O}$  reacting with S in the  $\text{GeS}_4$  tetrahedra.

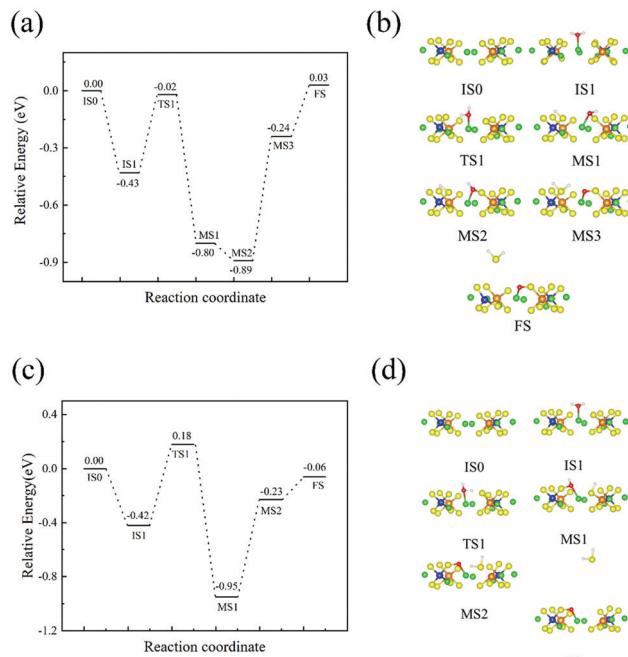


Fig. 4 Reaction path profiles of  $\text{H}_2\text{O}$  reactions on the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}(110)$  surface. (a)  $\text{H}_2\text{O}$  reaction energies related to the  $\text{PS}_4$  tetrahedra; (b) structural diagram of the minimum energy path for the  $\text{H}_2\text{O}$  reaction with  $\text{PS}_4$  tetrahedra; (c)  $\text{H}_2\text{O}$  reaction energy related to the  $\text{GeS}_4$  tetrahedra; and (d) structural diagram of the minimum energy path for the double  $\text{H}_2\text{O}$  reaction with the  $\text{GeS}_4$  tetrahedra. (IS, initial state; TS, transition state; MS, meta-stable state; FS, final state). Color code: green, Li atoms; yellow, S atoms; blue, P atoms; orange, Ge atoms; red, O atoms; white, H atoms.

the bulk. However, it will lead O ions being deposited in the same area, which will destroy the structure of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ , and this is also the cause of the miscellaneous peaks in the XRD pattern of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  after exposure to air.<sup>25</sup>

According to the XRD patterns obtained by Sun *et al.*,<sup>26</sup>  $\text{PO}_4^{3-}$  is found in the product of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  decomposition in the atmosphere. Mo *et al.*<sup>29</sup> also claimed that  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  is thermodynamically unstable. Considering the thermodynamic stability, we also calculated the thermodynamic stability of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  after being exposed to the air and the degree to which it reacts with  $\text{H}_2\text{O}$ . Mo *et al.*<sup>29</sup> also found that  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  can be decomposed into  $\text{Li}_3\text{PS}_4$  and  $\text{Li}_4\text{GeS}_4$ . The phase decomposition energy ( $\Delta E_{\text{pd}}$ ) of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$  is calculated with

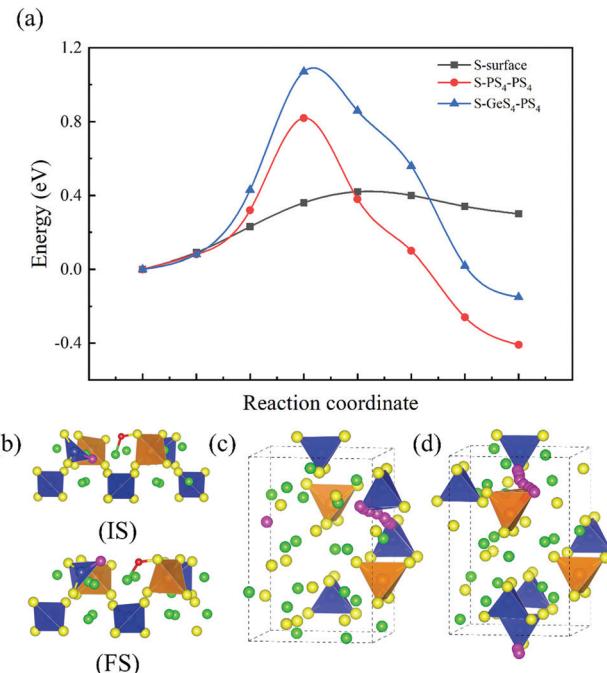


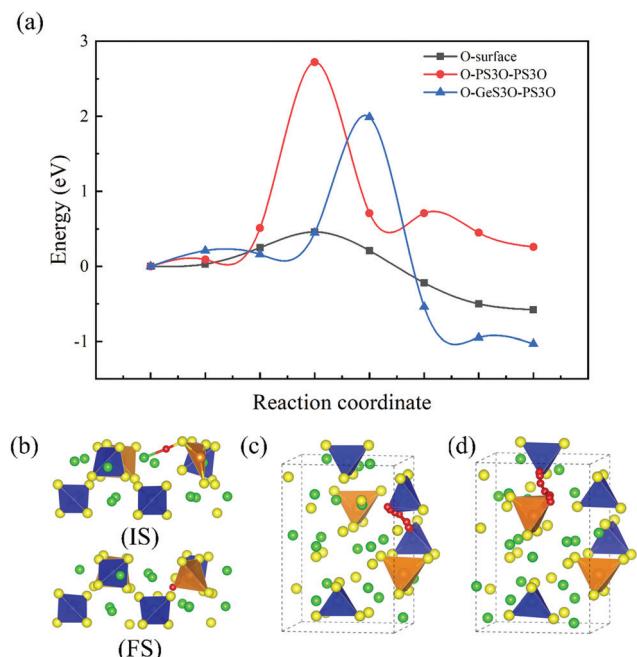
Fig. 5 Minimum energy paths for sulfur diffusion. (a) Energy profiles of S atom diffusion. (b) Structural diagram of S atom diffusion on the surface (IS, initial state; FS, final state). (c) Structural diagram of S atom diffusion in the bulk from a  $\text{PS}_4$  tetrahedron to a  $\text{PS}_4$  tetrahedron. (d) Diagram of S atom diffusion in the bulk from a  $\text{GeS}_4$  tetrahedron to a  $\text{PS}_4$  tetrahedron. Color code: green, Li atoms; yellow, S atoms; blue, P atoms; orange, Ge atoms; pink, the diffusing S atom.

respect to the most stable ternary compounds ( $\text{Li}_3\text{PS}_4$ ,  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_4\text{GeS}_4$ , and  $\text{Li}_4\text{GeO}_4$ ) to further check the phase stability. The  $\Delta E_{\text{pd}}$  is defined as follows:

$$\Delta E_{\text{pd}}(x=0) = E(\text{Li}_3\text{PS}_4) + \frac{E(\text{Li}_4\text{GeS}_4)}{2} - E(\text{Li}_{10}\text{GeP}_2\text{S}_{12}) \quad (5)$$

$$\Delta E_{\text{pd}}(0 < x < 8) = \frac{[(8-x)E(\text{Li}_3\text{PS}_4) + xE(\text{Li}_3\text{PO}_4)]}{8} + \frac{E(\text{Li}_4\text{GeS}_4)}{2} - E(\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x) \quad (6)$$





**Fig. 6** Minimum energy paths for O atom diffusion. (a) Energy profiles for O atom diffusion. (b) Structural diagram of O atom diffusion from the surface into the bulk. (c) Structural diagram of O atom diffusion in the bulk from a  $\text{PS}_3\text{O}$  tetrahedron to a  $\text{PS}_3\text{O}$  tetrahedron. (d) Diagram of O atom diffusion in the bulk from a  $\text{GeS}_3\text{O}$  tetrahedron to a  $\text{PS}_3\text{O}$  tetrahedron. Color code: green, Li atoms; yellow, S atoms; blue, P atoms; orange, Ge atoms; red, O atoms.

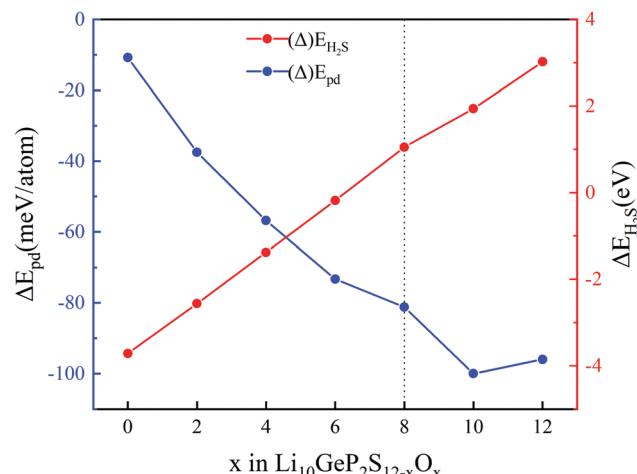
$$\Delta E_{\text{pd}}(8 < x < 12) = \frac{[(12-x)E(\text{Li}_4\text{GeS}_4) + (x-8)E(\text{Li}_4\text{GeO}_4)]}{8} + 2E(\text{Li}_3\text{PO}_4) - E(\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x) \quad (7)$$

$$\Delta E_{\text{pd}}(x=12) = 2E(\text{Li}_3\text{PO}_4) + E(\text{Li}_4\text{GeO}_4) - E(\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x) \quad (8)$$

A negative value of  $\Delta E_{\text{pd}}$  indicates thermodynamic phase stability against decomposition. For the degree of reaction with  $\text{H}_2\text{O}$  in air, according to the reaction equilibrium  $\text{Li}_{10}\text{GeP}_2\text{S}_{12} + \text{H}_2\text{O} \rightarrow \text{Li}_{10}\text{GeP}_2\text{O}_{12} + \text{H}_2\text{S}$ , we define the energy of the generation of  $\text{H}_2\text{S}$  as  $\Delta E_{\text{H}_2\text{S}}$ :

$$\Delta E_{\text{H}_2\text{S}} = E(\text{Li}_{10}\text{GeP}_2\text{O}_{12})/12 + E(\text{H}_2\text{S}) - E(\text{Li}_{10}\text{GeP}_2\text{S}_{12})/12 - E(\text{H}_2\text{O}) \quad (9)$$

A positive value of  $\Delta E_{\text{H}_2\text{S}}$  indicates thermodynamic stability against  $\text{H}_2\text{S}$  generation. As shown in Fig. 7, we find that the value of  $\Delta E_{\text{pd}}$  decreases as O atoms successively replace the S atoms in  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ . This indicates that the thermal stability of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  is continuously improved with the reaction. When  $x$  reaches 8 ( $\Delta E_{\text{H}_2\text{S}} = 1.05$  eV),  $\text{Li}_{10}\text{GeP}_2\text{S}_4\text{O}_8$  is inert to  $\text{H}_2\text{O}$  molecules in the air. At the same time,  $\text{Li}_{10}\text{GeP}_2\text{S}_4\text{O}_8$  could be decomposed to  $\text{Li}_3\text{PO}_4$  and  $\text{Li}_4\text{GeS}_4$ . This indicates that the S



**Fig. 7** Phase decomposition (pd) stability ( $\Delta E_{\text{pd}}$ , reaction equilibrium in eqn (5)–(8)) and moisture stability with  $x$  in the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ .

atoms of a  $\text{PS}_4$  tetrahedron are completely replaced by O atoms, proving that S in  $\text{H}_2\text{S}$  comes from the  $\text{PS}_4$  tetrahedra.

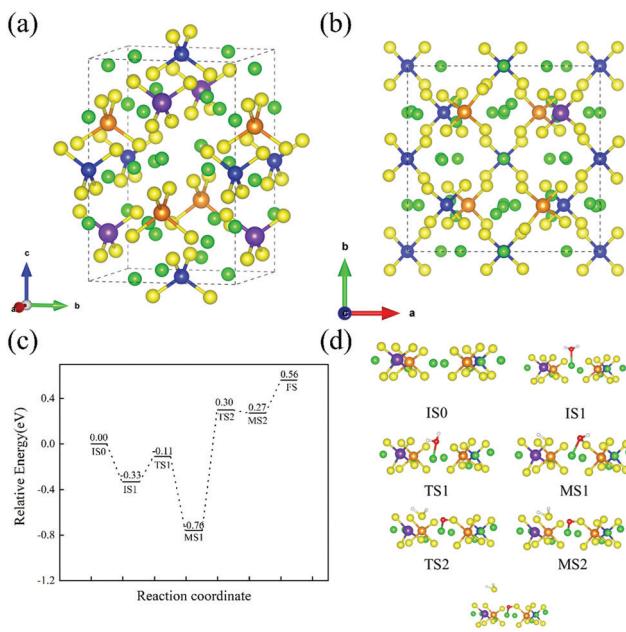
By doping with Sb, Sun *et al.* successfully inhibited  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  hydrolysis.<sup>26</sup> To analyze the mechanism, we investigated how Sb doping inhibits the hydrolysis of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ . For the possible doping locations of Sb *via* thermodynamic calculations, the  $\text{Sb}_P$  formation energy ( $E$ ) was calculated using eqn (10):

$$E = E_{(x\text{Sb-LGPS})} + x \cdot E_{\text{P}} - E_{(\text{LGPS})} - x \cdot E_{\text{Sb}} \quad (10)$$

We considered two Sb doping sites (on  $\text{P}_{2\text{b}}$  or  $\text{P}_{4\text{d}}$  sites) and five types of substitution (no Sb substitution, 100% on  $\text{P}_{2\text{b}}$  substitution, 100% on  $\text{P}_{4\text{d}}$  substitution, 50%  $\text{P}_{2\text{b}}$  + 50%  $\text{P}_{4\text{d}}$  substitution, and full substitution). The results of the formation energy when Sb occupies different P sites are shown in Table 3. We find that Sb is more inclined to occupy the  $\text{P}_{4\text{d}}$  sites. Fig. 8(a) shows the structure of  $\text{Li}_{10}\text{Ge}(\text{P}_{1-x}\text{Sb}_x)_2\text{S}_{12}$  with Sb occupying  $\text{P}_{4\text{d}}$  sites. According to the previous calculation of surface energies, the (110) surface is more easily exposed. Fig. 8(b) shows the new surface when Sb is substituted on a surface  $\text{P}_{4\text{d}}$  site. Fig. 8(c) shows the energy profile of  $\text{H}_2\text{O}$  adsorption and reaction with an  $\text{SbS}_4$  tetrahedron on the  $\text{Li}_{10}\text{Ge}(\text{P}_{1-x}\text{Sb}_x)_2\text{S}_{12}(110)$  surface. Fig. 8(d) depicts the structures of the intermediates and the corresponding transition states during the reaction of  $\text{H}_2\text{O}$  and a  $\text{SbS}_4$  tetrahedron on the  $\text{Li}_{10}\text{Ge}(\text{P}_{1-x}\text{Sb}_x)_2\text{S}_{12}(110)$  surface. In the process from IS0 to IS1,  $\text{H}_2\text{O}$  molecules are adsorbed at the Li site, and the adsorption energy is  $-0.33$  eV. For the process from IS1 to MS1, the  $\text{H}_2\text{O}$  molecule is decomposed to form  $\text{H}^+$  and  $\text{OH}^-$ , while  $\text{H}^+$  is bonded to the S on an  $\text{SbS}_4$  tetrahedron forming  $\text{SH}$ . The decomposition barrier is 0.22 eV; meanwhile, it releases

**Table 3** Relative energy with Sb doping at different P sites

Sb	No doping	100% $\text{P}_{2\text{b}}$	100% $\text{P}_{4\text{d}}$	50% $\text{P}_{2\text{b}}$ + 50% $\text{P}_{4\text{d}}$	Full doping
$E$ (eV)	0	5.16	4.64	4.65	9.96



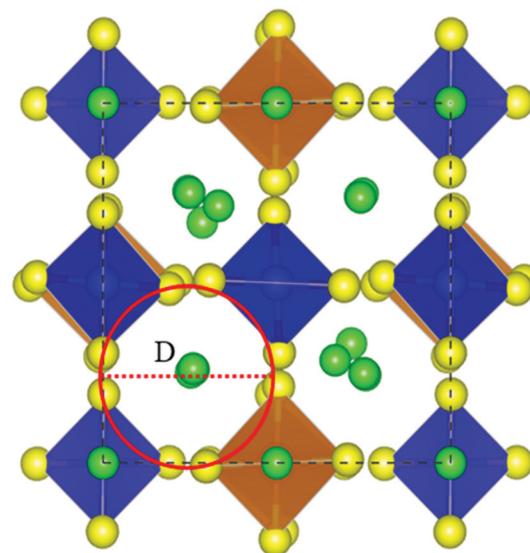
**Fig. 8** (a) Crystal structure of Sb substitution on  $P_{4d}$  sites; (b) crystal structure of Sb substitution on a  $P_{4d}$  site on the (110) surface; (c)  $H_2O$  reaction energy profile on an  $SbS_4$  tetrahedron of the  $Li_{10}Ge(P_{1-x}Sb_x)_2S_{12}(110)$  surface; and (d) structural diagram of the minimum energy path for the reaction of  $H_2O$  with an  $SbS_4$  tetrahedron on the  $Li_{10}Ge(P_{1-x}Sb_x)_2S_{12}(110)$  surface. Color code: green, Li atoms; yellow, S atoms; blue, P atoms; orange, Ge atoms; red, O atoms; white, H atoms; purple, Sb atoms.

0.65 eV for this step. For the process from MS1 to MS2,  $OH^-$  is decomposed to form  $H_2S$  with HS adsorbed on the surface, while the remaining O atoms are adsorbed on Li atoms. The barrier of this step is 1.06 eV. MS2 to FS is the  $H_2S$  desorption process, which needs 0.29 eV. From the decomposition of  $H_2O$  molecules on  $SbS_4$  tetrahedra, the maximum reaction barrier required for the reaction of an  $H_2O$  molecule with S in a  $SbS_4$  tetrahedron to produce  $H_2S$  gas is 1.06 eV. In the previous calculation, the maximum energy barrier required for  $H_2O$  molecules to react with S in  $PS_4$  tetrahedra to form  $H_2S$  gas was 0.65 eV. With the increased barrier of  $OH^-$  decomposition, the substitution of Sb can prevent the hydrolysis of  $Li_{10}GeP_2S_{12}$ .

In addition, we studied the effect of Sb doping on  $Li_{10}GeP_2S_{12}$ . The data in Table 4 show that with an increase in Sb doping, the lattice constants of  $Li_{10}GeP_2S_{12}$  will also increase. Furthermore, the diffusion barrier of Li ions along the  $c$  direction will also increase, which is consistent with the

**Table 4** Lattice constants ( $a$ , and  $c$ ), Li ion channel width  $D$  and Li diffusion barrier  $E_b$  in  $Li_{10}Ge(P_{1-x}Sb_x)_2S_{12}$  related to the amount of Sb doping  $x$

$x$	0	0.125	0.250	0.375	0.50
$a$ (Å)	8.75	8.78	8.79	8.81	8.82
$c$ (Å)	12.88	12.93	12.99	13.04	13.09
$D$ (Å)	4.47	4.45	4.43	4.42	4.42
$E_b$ (eV)	0.25	0.27	0.30	0.31	0.32



**Fig. 9** Lithium-ion diffusion channel in the  $c$ -direction (red circle), where the channel radius is  $D$ . Color code: green, Li atoms; yellow, S atoms; blue, P atoms; orange, Ge atoms.

experimental findings of Sun *et al.*<sup>26</sup> that the conductivity of the Li ion decreases with Sb doping. The diffusion channel diameter ( $D$ ) is defined as the average value of the minimum distances between tetrahedra along the  $c$  direction, as shown Fig. 9. From Table 4, we find that diffusion barrier ( $E_b$ ) increases as  $D$  decreases.

## Conclusion

Based on first principles calculations, we have unveiled the kinetic and thermodynamic mechanism in the reaction of  $Li_{10}GeP_2S_{12}$  with  $H_2O$  molecules in air to produce  $H_2S$  gas. The surfaces of  $Li_{10}GeP_2S_{12}$  exposed to the air are (001), (110) and (111), and  $H_2O$  molecules are adsorbed on  $Li^+$  sites. The rate-determining step for the  $H_2S$ -releasing reaction is the decomposition of  $OH^-$  with an energy barrier of 0.65 eV. The S atoms can diffuse between  $PS_4$  tetrahedra, and the diffusion barrier is 0.82 eV. Moreover, S can diffuse from the bulk to the surface with a diffusion energy barrier of 0.45 eV. The O atoms can diffuse from the surface into the bulk, and the diffusion energy barrier is 0.21 eV. According to the thermodynamic analysis, the formation of  $Li_{10}GeP_2S_4O_8$  will inhibit the reaction with  $H_2O$  molecules and prevent the release of  $H_2S$  gas. Sb doping could also prevent the hydrolysis of  $Li_{10}GeP_2S_{12}$  due to the increased energy barrier (1.06 eV) for the decomposition of  $H_2O$  on the  $SbS_4$  tetrahedra. The diffusion barrier of the Li ions in  $Li_{10}Ge(P_{1-x}Sb_x)_2S_{12}$  will also increase with the amount of Sb doping.

## Conflicts of interest

There are no conflicts to declare.



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