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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.¹⁻⁵ However, the organic electrolyte in lithiumion batteries is flammable, and has a lower thermal stability and lower safety compared with inorganic solid-state electrolytes.⁶⁻⁸ The solid-state electrolytes used in solid-state lithium-ion batteries consist mainly of polymers,^{9,10} oxides¹¹⁻¹³ and sulfides.^{14,15} Among them, sulfides have a relatively high ionic conductivity, and some are comparable to organic liquid electrolytes.¹⁶ However, sulfide solid-state electrolytes react easily with H₂O in moist air to generate toxic H₂S gas, which limits their practical applications. A great deal of experimental

Failure mechanism of solid-state electrolyte Li₁₀GeP₂S₁₂ 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-sate electrolytes (SSEs) play a key role in the performance of ASSLIBs. Among all kinds of SSEs, sulfide solid-sate 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 H₂O to generate toxic H₂S gas. Herein to understand the specific failure mechanism, we use first-principles calculations to study the kinetic and thermodynamic mechanism of the reaction between Li₁₀GeP₂S₁₂, which is a typical sulfide electrolyte, and H₂O in the atmosphere. We find that the H₂O molecules preferentially react with the sulfur atoms of the PS₄ tetrahedra to produce H₂S. As the sulfur atoms of the PS₄ tetrahedra in the bulk continuously emerge towards the surface, this reaction occurs repeatedly. Meanwhile, the oxygen atoms from H₂O molecules can also diffuse into the bulk. These reactions continue until the sulfur atoms of the PS₄ tetrahedra in Li₁₀GeP₂S₁₂, and kinetically explain the mechanism of hydrolysis inhibition when doping Sb in Li₁₀GeP₂S₁₂.

work has been done to solve the air-stability problem. Muramatsu et al.,¹⁷ have studied the structural changes of Li₂S-P₂S₅ glass structures in the atmosphere. This study found that PS_4^{3-} can reduce H₂S gas for binary Li₂S-P₂S₅ glass or glass ceramics. 75Li₂S-25P₂S₅ has been found to have better water stability. Tin sulfides (Li₄SnS₄,^{18,19} and Li₄SnS₄-LiI²⁰), As-substituted Li₄SnS₄,²¹ and Sb-substituted Li₄SnS₄,^{22,23} also show better stability in air. Based on the hard and soft acids and bases (HSAB) theory,²⁴ 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.25 inhibited the production of H_2S by doping M_rO_v (M = Fe, Zn, and Bi) in the Li₃PS₄ electrolyte, which can absorb H₂S. Although metal oxide doping improves the air stability of sulfide solid-state electrolytes, it also reduces the ionic conductivity. In addition, Sun et al.26 improved the air stability of the sulfide solid-state electrolyte through introducing soft acid metals. The air stability is improved via Sb doping of Li10GeP2S12, 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 mS cm⁻¹. After air exposure, the ionic conductivity can remain between 12.1 and 15.7 mS cm^{-1} .

Kamaya *et al.* reported a superionic conductor $Li_{10}GeP_2S_{12}$ with high ionic conductivity (12 mS cm⁻¹) at room temperature.²⁷ Compared with most sulfide solid-state electrolytes, $Li_{10}GeP_2S_{12}$ has been more extensively studied. Its space



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Paper

group is P42/nmc, and consists of $(Ge_{0.5}P_{0.5})S_4$ tetrahedra, PS_4 tetrahedra, LiS₄ tetrahedra and LiS₆ octahedra. It has threedimensional lithium-ion channels.27-29 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).³⁰ In addition, Li₁₀GeP₂S₁₂ also has a wide electrochemical stability window (>5 V against Li/Li⁺) at room temperature. Mo *et al.*²⁹ proposed that this is due to the decomposition of Li₁₀GeP₂S₁₂ into Li₂S and P₂S₅ passivation layers when Li₁₀GeP₂S₁₂ comes into contact with the electrode, which then protects the solidstate electrolyte, resulting in a wide electrochemical window. However, as with other sulfide compounds, Li₁₀GeP₂S₁₂ is sensitive to atmospheric moisture, which can react with H₂O to produce the air pollutant $H_2S_1^{31,32}$ and lead to a decreased ionic conductivity for Li₁₀GeP₂S₁₂. These drawbacks limit the practical applications of sulfide solid electrolytes in industry. Although a lot of research into Li₁₀GeP₂S₁₂ air stability has been carried out experimentally, few theoretical studies have been performed to explore the Li₁₀GeP₂S₁₂ air stability. In this work, we systematically study the specific chemical reactions between Li₁₀GeP₂S₁₂ and H₂O 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.³³ The interactions between ion cores and valence electrons are treated using the projector augmented wave (PAW)^{34,35} method as implemented in the Vienna ab initio simulation package (VASP).³⁶ The kinetic energy cutoff is set as 450 eV. In addition, the climbing image nudged elastic band (CI-NEB) method³⁷ 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 eV Å⁻¹ with the spinpolarized calculations. The crystal structure of Li₁₀GeP₂S₁₂ is shown in Fig. 1. The calculated lattice constants are a = b = 8.74 Å, and c = 12.86 Å, which are consistent with an earlier report.38

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),

$$E_{\rm s} = \frac{1}{2S} (E_{\rm slab} - nE_{\rm bulk}) \tag{1}$$

where *S* is the surface area, E_{slab} is the total energy of the surface structure, *n* is the number of unit cells, and E_{bulk} is the total energy of bulk Li₁₀GeP₂S₁₂. As listed in Table 1, we find that the most stable surface is the (110) surface, which has



Fig. 1 Crystal structure of $Li_{10}GeP_2S_{12}$.

Table 1 Surface energy ($E_{\rm S}$) values of Li₁₀GeP₂S₁₂

Surface	$E_{\rm S} \left({\rm eV} \ {\rm \AA}^{-2} \right)$
(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 eV Å⁻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 PS_4 tetrahedra and 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 H_2O molecules: these are S sites on the PS₄ tetrahedron (site \bigcirc in Fig. 2), S sites on the GeS₄ tetrahedron (site \bigcirc in Fig. 2), and Li sites between the PS₄ and GeS₄



Fig. 2 H_2O adsorption site on the Li₁₀GeP₂S₁₂(110) surface. Site O is the adsorption site on the PS₄ tetrahedron, site O is the adsorption site on the GeS₄ tetrahedron, and sites O and O are the adsorption sites on Li⁺.

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

$$E_{\rm ads} = E_{\rm tot} - E_{\rm H_2O} - E_{\rm surface}$$
(2)

where the E_{tot} is the total energy of the H₂O-adsorbed surface, E_{H_2O} is the energy of the H₂O molecule, and $E_{surface}$ is the total energy of the Li₁₀GeP₂S₁₂ slab. As listed in Table 2, we find that, compared with the S atoms in PS₄ tetrahedra and the S atoms in GeS₄ tetrahedra, H₂O molecules are more likely to be adsorbed on Li⁺. For site ③, the adsorption energy of H₂O is -0.43 eV. This is because O sp³ hybridization in H₂O has an unshared electron pair, which can be combined with the vacant 2s orbital of the outermost layer of Li⁺, thus forming the Li–O bond with greater adsorption energy.

We now investigate the decomposition of H_2O on the $Li_{10}GeP_2S_{12}(110)$ surface. According to the theoretical calculations of Mo *et al.*,³⁹ the reaction between the $Li_{10}GeP_2S_{12}(110)$ surface and H_2O is as follows:

$$\text{Li-PS}_4 + \text{H}_2\text{O} \rightarrow \text{LiOH-PS}_3(\text{SH}) \rightarrow \text{Li-PS}_3\text{O} + \text{H}_2\text{S}\uparrow$$
 (3)

$$\text{Li-GeS}_4 + \text{H}_2\text{O} \rightarrow \text{LiOH-GeS}_3(\text{SH}) \rightarrow \text{Li-GeS}_3\text{O} + \text{H}_2\text{S}\uparrow$$
(4)

We show the reaction processes in Fig. 3. The adsorbed H_2O molecules can be decomposed into H^+ and OH^- on the surface, where H^+ reacts with the S atom on the PS_4/GeS_4 tetrahedra to form the H–S bond, and OH^- can be further decomposed to form O^{2-} and H^+ . The latter H^+ reacts with S–H to form H_2S , which is desorbed from the (110) surface.

Fig. 4(a and b) depict the energy profile of the hydrolysis reaction between H₂O molecules and S of the PS₄ tetrahedra and the relative intermediate reaction products. IS0 stands for the (110) surface with no H₂O molecules adsorbed. IS1 stands for the (110) surface-adsorbed H₂O molecules. TS1 stands for the transition state and MS1 stand for the intermediate state of H₂O decomposed into H⁺ and OH⁻. MS2 stands for the second intermediate state, which relaxes the position of the H atom of OH⁻, and MS3 stands for the third intermediate state of OH⁻ decomposition into H⁺ and O²⁻. FS stands for the final state of H_2S desorbing from the $Li_{10}GeP_2S_{12}(110)$ surface. From the results of Table 2, H₂O adsorbs on Li⁺ and the adsorption energy is -0.43 eV. For the process from IS1 to MS1, H₂O decomposes into H^+ and OH^- , where H^+ combines with S to form the H-S bond and the related energy barrier is 0.41 eV. OH⁻ decomposes into H⁺ and O²⁻ from MS2 to MS3, where H⁺ combines with the SH group in MS1 to generate H₂S, which is adsorbed on the surface. Meanwhile, O^{2-} combines with S of GeS₄ to form the S-O bond, and the energy barrier for this is 0.65 eV. The process from MS3 to FS is the desorption of H_2S

Table 2	Adsorption energies	of H ₂ O at diffe	rent sites on the (110) surface
Site	1	2	3	4
$E_{\rm ads}$ (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 H₂O and the GeS₄ tetrahedra on the Li₁₀GeP₂S₁₂(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 H₂O decomposition on the GeS₄ tetrahedra (0.80 eV, 0.72 eV) is higher than the reaction energy barrier on PS₄ tetrahedra (0.41 eV, 0.65 eV). This suggests that H₂O is more likely to react with S in the PS₄ tetrahedra in Li₁₀GeP₂S₁₂ to produce H₂S. 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 PS₄ tetrahedron is much easier than that on the GeS₄ tetrahedra.

As experiments have shown that the degradation of Li₁₀GeP₂S₁₂ releases a large amount of H₂S,²⁶ this process inevitably involves the sulfur atoms in the bulk. This means that S in Li₁₀GeP₂S₁₂ 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 GeS₄ tetrahedron to a PS₄ tetrahedron, and S atom diffusion from a PS_4 tetrahedron to a 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 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 Li^+ channel along the c direction. Fig. 5(c and d) show the S atom diffusion path from a PS4 tetrahedron to a PS4 tetrahedron and from a GeS4 tetrahedron to a PS4 tetrahedron, respectively. The diffusion barriers shows that the diffusion of the S atom from a PS₄ tetrahedron to a PS₄ 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 H₂O also leaves an oxygen atom on the surface, while experimental results of the continuous release of H₂S also show that those oxygen atoms do not form a protective layer on the surface to prevent Li10GeP2S12 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 GeS₄ tetrahedron to a PS₄ tetrahedron in the bulk, S vacancies will concentrate on the GeS₄ tetrahedra. Therefore, oxygen atoms can diffuse from the surface to the bulk through the 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 GeS₃O to PS₃O, and an O atom diffusing from PS₃O to PS₃O, 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 GeS₄ 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 Li₁₀GeP₂S₁₂ crystal. Thus, it is hard for O ions to diffuse in



Fig. 3 Reaction paths of $Li_{10}GeP_2S_{12}$ surfaces and H_2O , where the red path represents H_2O reacting with S in the PS₄ tetrahedra, and the blue one represents H_2O reacting with S in the GeS₄ tetrahedra.



Fig. 4 Reaction path profiles of H₂O reactions on the Li₁₀GeP₂S₁₂(110) surface. (a) H₂O reaction energies related to the PS₄ tetrahedra; (b) structural diagram of the minimum energy path for the H₂O reaction with PS₄ tetrahedra; (c) H₂O reaction energy related to the GeS₄ tetrahedra; and (d) structural diagram of the minimum energy path for the double H₂O reaction with the GeS₄ 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.



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 PS_4 tetrahedron to a PS_4 tetrahedron. (d) Diagram of S atom diffusion in the bulk from a GeS₄ tetrahedron to a PS_4 tetrahedron. Color code: green, Li atoms; yellow, S atoms; blue, P atoms; orange, Ge atoms; pink, the diffusing S atom.

the bulk. However, it will lead O ions being deposited in the same area, which will destroy the structure of $Li_{10}GeP_2S_{12}$, and this is also the cause of the miscellaneous peaks in the XRD pattern of $Li_{10}GeP_2S_{12}$ after exposure to air.²⁵

According to the XRD patterns obtained by Sun *et al.*,²⁶ PO₄³⁻ is found in the product of Li₁₀GeP₂S₁₂ decomposition in the atmosphere. Mo *et al.*²⁹ also claimed that Li₁₀GeP₂S₁₂ is thermodynamically unstable. Considering the thermodynamic stability, we also calculated the thermodynamic stability of Li₁₀GeP₂S₁₂ after being exposed to the air and the degree to which it reacts with H₂O. Mo *et al.*²⁹ also found that Li₁₀GeP₂S₁₂ can be decomposed into Li₃PS₄ and Li₄GeS₄. The phase decomposition energy (ΔE_{pd}) of Li₁₀GeP₂S_{12-x}O_x is calculated with

respect to the most stable ternary compounds (Li₃PS₄, Li₃PO₄, Li₄GeS₄, and Li₄GeO₄) to further check the phase stability. The ΔE_{pd} is defined as follows:

$$\Delta E_{\rm pd}(x=0) = E({\rm Li}_{3}{\rm PS}_{4}) + \frac{E({\rm Li}_{4}{\rm GeS}_{4})}{2} - E({\rm Li}_{10}{\rm GeP}_{2}{\rm S}_{12})$$
(5)

$$\Delta E_{\rm pd}(0 < x < 8) = \frac{\left[(8 - x)E({\rm Li}_3{\rm PS}_4) + xE({\rm Li}_3{\rm PO}_4)\right]}{8} + \frac{E({\rm Li}_4{\rm GeS}_4)}{2} - E({\rm Li}_{10}{\rm GeP}_2{\rm S}_{12-x}{\rm O}_X)$$
(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 PS_3O tetrahedron to a PS_3O tetrahedron. (d) Diagram of O atom diffusion in the bulk from a GeS₃O tetrahedron to a PS_3O tetrahedron. Color code: green, Li atoms; yellow, S atoms; blue, P atoms; orange, Ge atoms; red, O atoms.

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

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

A negative value of ΔE_{pd} indicates thermodynamic phase stability against decomposition. For the degree of reaction with H₂O in air, according to the reaction equilibrium Li₁₀GeP₂S₁₂ + H₂O \rightarrow Li₁₀ GeP₂O₁₂ + H₂S, we define the energy of the generation of H₂S as ΔE_{H_2S} :

$$\Delta E_{\rm H_2S} = E({\rm Li}_{10}{\rm GeP_2O_{12}})/12 + E({\rm H_2S}) - E({\rm Li}_{10}{\rm GeP_2S_{12}})/12 - E({\rm H_2O})$$
(9)

A positive value of $\Delta E_{\rm H_2S}$ indicates thermodynamic stability against H₂S generation. As shown in Fig. 7, we find that the value of $\Delta E_{\rm pd}$ decreases as O atoms successively replace the S atoms in Li₁₀GeP₂S₁₂. This indicates that the thermal stability of Li₁₀GeP₂S₁₂ is continuously improved with the reaction. When *x* reaches 8 ($\Delta E_{\rm H_2S} = 1.05$ eV), Li₁₀GeP₂S₄O₈ is inert to H₂O molecules in the air. At the same time, Li₁₀GeP₂S₄O₈ could be decomposed to Li₃PO₄ and Li₄GeS₄. This indicates that the S



Fig. 7 Phase decomposition (pd) stability (ΔE_{pd} , reaction equilibrium in eqn (5)–(8)) and moisture stability with *x* in the Li₁₀GeP₂S_{12-x}O_x.

atoms of a PS_4 tetrahedron are completely replaced by O atoms, proving that S in H_2S comes from the PS_4 tetrahedra.

By doping with Sb, Sun *et al.* successfully inhibited $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ hydrolysis.²⁶ 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 Sb_P formation energy (*E*) was calculated using eqn (10):

$$E = E_{(xSb-LGPS)} + x \cdot E_P - E_{(LGPS)} - x \cdot E_{Sb}$$
(10)

We considered two Sb doping sites (on P_{2b} or P_{4d} sites) and five types of substitution (no Sb substitution, 100% on P_{2b} substitution, 100% on P_{4d} substitution, 50%P_{2b} + 50%P_{4d} 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 P_{4d} sites. Fig. 8(a) shows the structure of $Li_{10}Ge(P_{1-x}Sb_x)_2S_{12}$ with Sb occupying P4d 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 P_{4d} site. Fig. 8(c) shows the energy profile of H₂O adsorption and reaction with an SbS4 tetrahedron on the $Li_{10}Ge(P_{1-x}Sb_x)_2S_{12}(110)$ surface. Fig. 8(d) depicts the structures of the intermediates and the corresponding transition states during the reaction of H₂O and a SbS₄ tetrahedron on the $Li_{10}Ge(P_{1-x}Sb_x)_2S_{12}(110)$ surface. In the process from IS0 to IS1, H₂O molecules are adsorbed at the Li site, and the adsorption energy is -0.33 eV. For the process from IS1 to MS1, the H₂O molecule is decomposed to form H^+ and OH^- , while H^+ is bonded to the S on an SbS₄ tetrahedron forming 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	$100\% P_{2b}$	100% P _{4d}	50% P_{2b} + 50% P_{4d}	Full doping
$\overline{E(eV)}$	0	5.16	4.64	4.65	9.96

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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.

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 SbS₄ tetrahedron of the $Li_{10}Ge(P_{1-x}Sb_x)_2$ S₁₂(110) surface; and (d) structural diagram of the minimum energy path for the reaction of H_2O with an SbS₄ 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 SbS₄ tetrahedra, the maximum reaction barrier required for the reaction of an H_2O molecule with S in a SbS₄ 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 PS₄ 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 ion diffusion barrier $E_{\rm b}$ in Li₁₀Ge(P_{1-x}Sb_x)₂S₁₂ 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

experimental findings of Sun *et al.*²⁶ 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 ($E_{\rm b}$) increases as *D* decreases.

Conclusion

Based on first principles calculations, we have unveiled the kinetic and thermodynamic mechanism in the reaction of Li₁₀GeP₂S₁₂ with H₂O molecules in air to produce H₂S 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 H2S-releasing reaction is the decomposition of OH⁻ with an energy barrier of 0.65 eV. The S atoms can diffuse between PS4 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 Li₁₀GeP₂S₄O₈ will inhibit the reaction with H₂O molecules and prevent the release of H₂S 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 H₂O on the SbS₄ 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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