


## Letter

# Air exposure towards stable Li/Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> interface for all-solid-state lithium batteries

Wei Weng<sup>1,2</sup>, Dong Zhou<sup>1</sup>, Gaozhan Liu<sup>1</sup>, Lin Shen<sup>1,2</sup>, Mengqi Li<sup>1</sup>, Xinshuang Chang<sup>1</sup> and Xiayin Yao<sup>1,2,\*</sup> 

<sup>1</sup> Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, People's Republic of China

<sup>2</sup> Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

E-mail: [yaoxy@nimte.ac.cn](mailto:yaoxy@nimte.ac.cn)

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## Abstract

Moist air is a great challenge for manufacturing sulfide-based all-solid-state lithium batteries as the water in air will lead to severe decomposition of sulfide electrolytes and release H<sub>2</sub>S gas. However, different with direct reaction with water, short-period air exposure of Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> sulfide electrolyte with controlled humidity can greatly enhance the stability of Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> against lithium metal, thus realizing stable Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> based all-solid-state lithium metal batteries. During air exposure, partial hydrolysis reaction occurs on the surface of Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> pellets, rapidly generating a protective decomposition layer of Li<sub>4</sub>P<sub>2</sub>S<sub>6</sub>, GeS<sub>2</sub> and Li<sub>2</sub>HPO<sub>3</sub> in dozens of seconds. This ionically conductive but electronically insulation protecting layer can effectively prevent the severe interface reaction between Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> and lithium metal during electrochemical cycling. The Li/40s-air-exposed Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>/Li cell shows long cycling stability for 1000 h. And the LiCoO<sub>2</sub>/40s-air-exposed Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>/Li batteries present good rate capability and long cyclic performances, showing capacity retention of 80% after 100 cycles.

Supplementary material for this article is available [online](#)

Keywords: Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>, lithium metal, interface stability, air-exposure treatment, all-solid-state lithium batteries

\* Author to whom any correspondence should be addressed.



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### Future perspectives

$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  is a promising solid electrolyte with high ionic conductivity and good lithium dendrite inhibition for application in all-solid-state lithium metal batteries. However,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  can be easily reduced by lithium metal with formation of mixed conductive decomposition products including  $\text{Li}_2\text{S}$ ,  $\text{Li}_3\text{P}$  and Ge/Li-Ge alloy, resulting in continuously increased interfacial impedance until cell failure. Interestingly, a stable  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ /Li metal interface can be constructed simply by exposing the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellet in air for dozens of seconds, and the insight reason comes from the formed ionically conductive but electronically insulated decomposition products from  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  and water in air, making the fabrication process for  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  solid electrolyte in the low-dew-point drying room possible in the future. Inspired by the air treatment strategy, further works can focus on the reactions between solid electrolytes and various gas sources to generate stable interface layers with high ionic conductivity, and thus realizing high-performance all-solid-state lithium batteries with excellent rate capability and cycling stability.

## 1. Introduction

All-solid-state lithium batteries exhibit increased safety due to the employment of nonflammable inorganic solid electrolytes [1–3]. To date, various inorganic solid electrolytes, especially sulfide solid electrolytes, possessing high ionic conductivity have been developed [4–8], potentially achieving high-rate capability of all-solid-state lithium batteries. However, sulfide solid electrolytes exhibit extremely poor air stability and long-time air exposure leads to severe decomposition of sulfide electrolytes with destroyed structure and release of toxic  $\text{H}_2\text{S}$  gas [9, 10]. The accumulated decomposition products with poor ionic conductivity deteriorate the bulk and interface ion transfer, and finally resulting in rapid battery decay [10, 11].

Compared with commercial lithium-ion batteries, the employment of lithium metal anodes is an essential prerequisite to realize higher energy density all-solid-state batteries [2, 3, 12]. Among sulfide electrolytes,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  possesses high ionic conductivity of  $12 \text{ mS cm}^{-1}$ , which exceeds to that of organic liquid electrolytes [4]. However, the sulfide solid electrolyte  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  strongly reacts with lithium metal and decomposes to  $\text{Li}_{15}\text{Ge}_4$ ,  $\text{Li}_3\text{P}$  and  $\text{Li}_2\text{S}$  [13–15]. The large fraction of metallic  $\text{Li}_{15}\text{Ge}_4$  at the Li/ $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  interface can create electronically conducting pathways, which will continuously consume the bulk  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  and increase impedance until cell failure. Thus, a passivating layer without electronic conductivity is crucial to suppress the highly reactive Li/ $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  interface. Modification of lithium metal through chemical reaction is an appealing strategy to stabilize the Li/ $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  interface. Zhang *et al* [16] identified the *in-situ* formation of the  $\text{LiH}_2\text{PO}_4$  by reacting the lithium metal with  $\text{H}_3\text{PO}_4$ . This  $\text{LiH}_2\text{PO}_4$  layer is ionically conducting but electronically insulating, which can prevent the direct contact between  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  and lithium metal and passivate the interface reaction. A more effective approach

is introducing an electronic insulating layer with high interface energy against lithium. Wan *et al* [17] constructed a bifunctional layer at Li/ $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  interface by reacting the lithium metal with  $\text{Mg}(\text{TFSI})_2$ -LiTFSI-DME liquid electrolyte. The sequential reduction of salts and solvent generates a gradient solid electrolyte interface  $\text{Li}_x\text{Mg}/\text{LiF}/\text{polymer}$ , resulting in a stabilized interface and demonstrating effective protection for  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ . In addition, using bilayer composite electrolyte can also passivate the Li/ $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  interface [18–20]. The cells employing Li-argyrodites  $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$  or  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  exhibit distinct failure behavior toward lithium metal due to short circuit by lithium dendrite penetration for  $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$  and increased overpotential by electrolyte decomposition for  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ . The bilayer construction of Li/ $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  shows excellent interface stability even at high current density, in which the  $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$  layer as buffer layer is to isolate  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  from lithium metal and the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  can prevent the lithium dendrite penetration [20]. Clearly, designing an artificial passivation interface layer by more convenient method is crucial to stabilize Li/ $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  interface, while the reported approaches generally involve complicated reaction process or electrolyte multilayer structures.

Considering the severe reaction between sulfide electrolytes and moisture in air, interestingly, it is found that short-period air exposure of sulfide electrolytes with controlled humidity could provide effective passivation against lithium metal. The dramatically improved interface stability between  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  solid electrolyte and lithium metal is achieved by simply exposing the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellet into air for dozens of seconds. This air-exposure treatment could rapidly generate a protective layer of  $\text{Li}_4\text{P}_2\text{S}_6$ ,  $\text{GeS}_2$  and  $\text{Li}_2\text{HPO}_3$  coated on the surface of the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellets. This protecting layer is ionically conductive but electronically insulation, which can not only physically isolate the contact between  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  and lithium metal but also effectively suppress the continuous decomposition of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  reduced by lithium metal.

## 2. Methods

### 2.1. Preparation of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ pellets with and without air-exposure treatment

The synthesis of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  solid electrolytes can be found elsewhere [21]. The room temperature ionic conductivity of  $6.13 \times 10^{-3} \text{ S cm}^{-1}$  and its X-ray diffraction (XRD) pattern is shown in figure S1 (available online at [stacks.iop.org/MF/1/021001/mmedia](https://stacks.iop.org/MF/1/021001/mmedia)). The  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellet (10 mm diameter,  $\sim 1$  mm thickness) was prepared by cold pressing  $\sim 150$  mg of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  powder under 180 MPa. For the air-exposure treatment of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  electrolytes, both side of the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellet were separately exposed to air in a constant temperature of  $30^\circ\text{C}$  and humidity chamber with 45% humidity for different durations. Before one side of the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellet was exposed to air, the other side was sealed to avoid secondary exposure. Air-exposed

$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  electrolytes with duration of 40 s is labeled as 40 s air-exposed  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ .

## 2.2. Materials characterization

To identify the composition of interfacial layer of the air-exposed  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellets, XRD measurements were performed on Bruker D8 Advance Diffractometer with  $\text{Cu } K\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The EIS measurements for the symmetric cells were tested using Solartron 1470E electrochemical workstation (Solartron Public Co., Ltd) from 1 MHz to 0.1 Hz under 10 mV at 25 °C. Surface and cross-section morphology of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellet before and after air exposure were investigated by a scanning electron microscope (Regulus-8230, Hitachi).

## 2.3. Electrochemical performance measurements

The lithium metal foils with thickness of 80  $\mu\text{m}$  were used as electrode to assemble the symmetric cells and solid-state lithium metal batteries. To prepare the Li metal symmetric cells, two pieces of metallic lithium foils were attached on both sides of the electrolyte pellet and vacuum sealed in a pouch bag. Then the cells were isostatically pressed under 50 MPa for 5 min. The stainless steel attached with nickel tag was used as current collector. For testing the impedance of the symmetric cells after cycling tests, the galvanostatic Li plating/stripping was performed at 0.1  $\text{mA cm}^{-2}$  and 0.1  $\text{mAh cm}^{-2}$  under 25 °C. To fabricate the all-solid-state lithium metal batteries, the composite cathode was prepared by mixing  $\text{LiNbO}_3$ -coated  $\text{LiCoO}_2$  and  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  powders with 70:30 weight ratio. The composite cathode ( $\sim 2 \text{ mg cm}^{-2}$ ) powder was spread on one side of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellet and pressed at 180 MPa to obtain the integrated cathode-electrolyte pellet. The lithium metal was attached on the other side of electrolyte pellet and sealed in pouch bag. Before assembling the air-exposed  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  based solid-state batteries, the side of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellet integrated with cathode powder was sealed to avoid exposing to air. Charge/discharge measurements were conducted between 3.0 and 4.2 V at 25 °C using a multichannel battery test system (LAND CT-2001A, Wuhan Rambo Testing Equipment Co., Ltd).

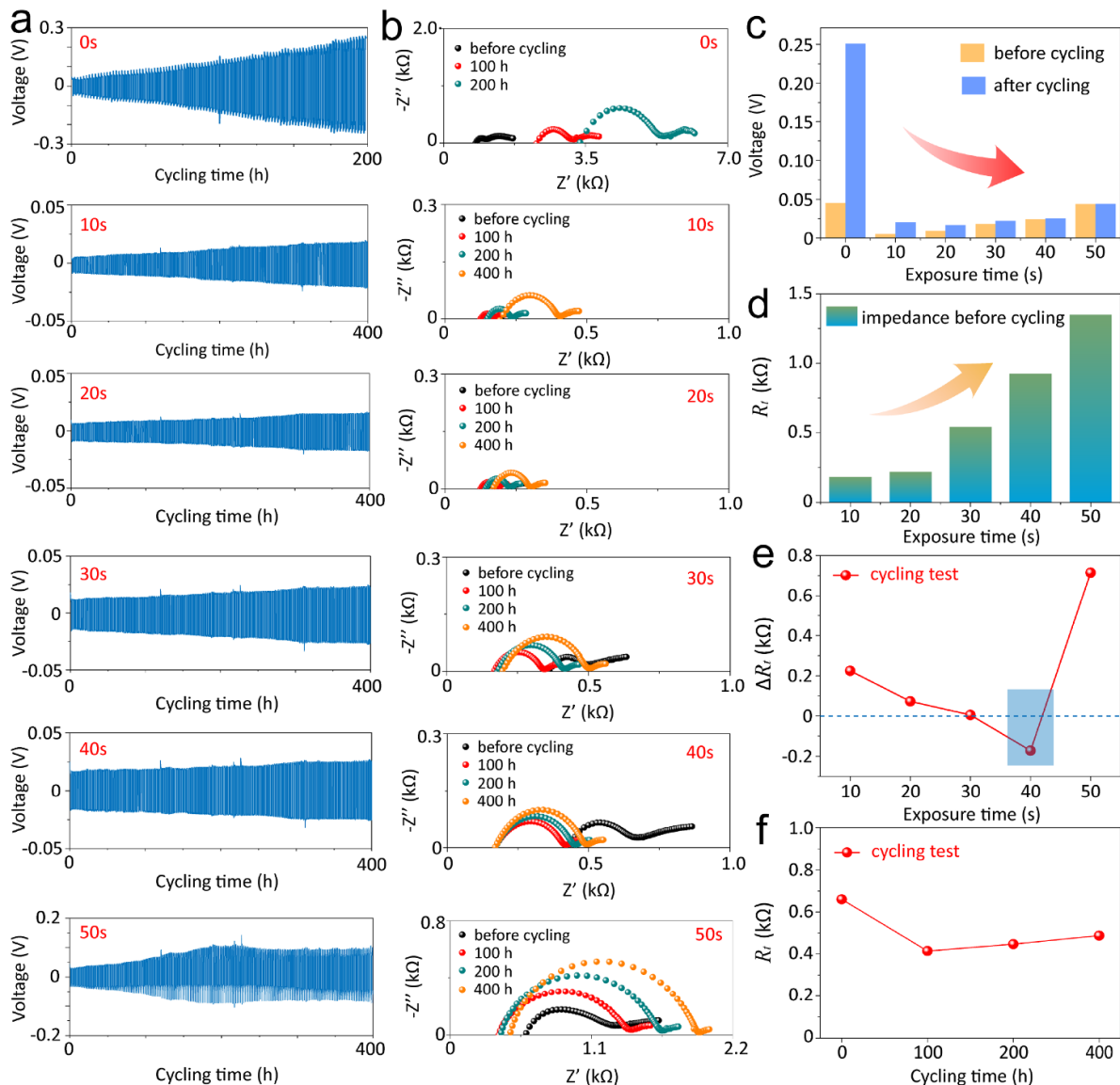
## 3. Results

As shown in figure 1(a), in contrast with the nearly linear increasing Li plating/stripping voltage for the symmetric  $\text{Li}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cell without air-exposure treatment, the  $\text{Li}/\text{air-exposed } \text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cells show obviously sluggish increase of the potential. The air-exposure durations were set at 10, 20, 30, 40, and 50 s. In addition, the suppressed increase of impedance for the  $\text{Li}/\text{air-exposed } \text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cells was directly observed during the electrochemical cycling. Figure 1(b) presents the impedance of the  $\text{Li}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  or air-exposed  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cells for

the cycling tests. It can be clearly found that the continuously increasing impedance arising from strong reaction at  $\text{Li}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  interface was dramatically suppressed when the air-exposure treatment for  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellets was employed. Figure 1(c) presents the voltage of the symmetric  $\text{Li}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  or air-exposed  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cells before and after cycling. The  $\text{Li}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  symmetric cell shows much higher polarization voltage than that of air-exposed  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  based symmetric cells before cycling, which is due to the decomposition reaction occurred once the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  solid electrolytes contact with Li metal during assembling the symmetric cells. However, the obviously suppressed increase of the voltage after cycling was detected after short-time exposure of 10 s. With increased air-exposure durations, such as 40 s and 50 s, the Li plating/stripping voltages perform negligible increase even after 400 h cycling, which clearly demonstrates that the air-exposure treatment can effectively stabilize the  $\text{Li}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  interface. Whereas, the impedance of the  $\text{Li}/\text{air-exposed } \text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  symmetric cells nearly linearly increases with the air-exposure durations (figure 1(d)), which implies that the air-exposure treatment introduced a low ionically conducting layer at the interface. Moreover, the difference value of the impedance of the  $\text{Li}/\text{air-exposed } \text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cells for cycling tests ( $\Delta R_t = R_{t, (400 \text{ h})} - R_{t, (0 \text{ h})}$ ) were evaluated. As presented in figure 1(e), the symmetric cells using  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  with an optimal exposure duration of 40 s exhibit the smallest value of the impedance changes, showing the decreased impedance for the  $\text{Li}/40 \text{ s air-exposed LGPS}/\text{Li}$  symmetric cell after cycling. Specifically, compared with the impedance of around 660  $\Omega$  before cycling, the impedance decreases to around 487  $\Omega$  after 400 h cycling (figure 1(f)). The decreased impedance could be attributed to the improved interfacial contact between the decomposition layer and Li metal due to the volume expansion of lithium metal during repeat plating/stripping processes [18].

Figure 2(a) shows the galvanostatic Li plating/stripping of the  $\text{Li}/40 \text{ s air-exposed } \text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  and the  $\text{Li}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cells. The  $\text{Li}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cell shows a rapid increase in polarization voltage due to the continuous and deteriorative  $\text{Li}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  interface reaction. In contrast, the  $\text{Li}/40 \text{ s air-exposed } \text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cell presents improved interface stability with small polarization voltage of 26 mV after 1000 h cycling. Moreover, the rate capability of the  $\text{Li}/40 \text{ s air-exposed } \text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cell was evaluated in figure 2(b). When the current densities are set at 0.2 or 0.4  $\text{mA cm}^{-2}$ , the polarization voltage is steady. However, gradual rise of polarization voltage was observed with increasing of current density to 0.6 and 0.8  $\text{mA cm}^{-2}$ . Nevertheless, the  $\text{Li}/40 \text{ s air-exposed } \text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cell can still stably cycle for 300 h at 0.2  $\text{mA cm}^{-2}$  under an areal capacity of 0.5  $\text{mAh cm}^{-2}$  (figure 2(c)).

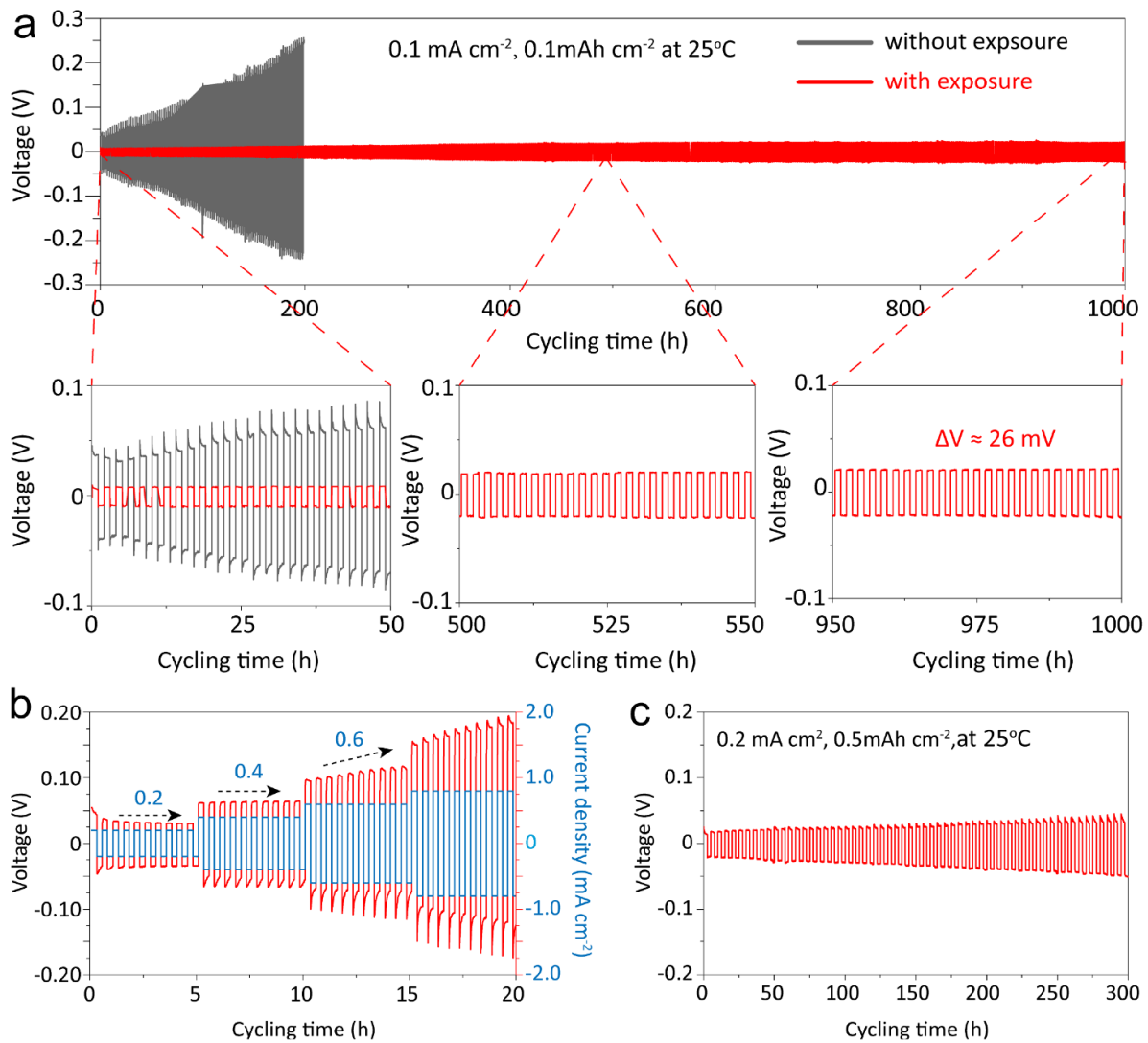
To understand the mechanism of the protective layer for improving the  $\text{Li}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  interface stability, the composition of the formed protective layer through air-exposure



**Figure 1.** Evaluation of the Li/Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> interface stability through Li plating/stripping experiments and evolution of impedance for the symmetric Li/Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> or air-exposed Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>/Li cells. (a) Cyclic performance of the Li/Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> or air-exposed Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>/Li cells at 0.1 mA cm<sup>-2</sup> and 0.1 mAh cm<sup>-2</sup>. (b) EIS plots of the symmetric Li/Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> or air-exposed Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>/Li cells before cycling and after different cycling time. (c) Li plating/stripping voltages of the Li/Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> or air-exposed Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>/Li cells before and after cycling. (d) Total impedance ( $R_t$ ) of the Li/air-exposed Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>/Li cells before cycling. (e) Difference value of the total impedance of the Li/air-exposed Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>/Li cells for cycling tests ( $\Delta R_t = R_{t(400h)} - R_{t(0h)}$ ). (f) Evolution of the total impedance ( $R_t$ ) of the Li/40 s air-exposed Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>/Li cells for cycling tests.

treatment was identified. Generally, most sulfide solid electrolytes are not stable to moisture because they easily react with H<sub>2</sub>O by release of toxic H<sub>2</sub>S gas [10, 22, 23]. Calpa *et al* [24] reported their DFT calculation results that the hydrolysis of Li<sub>3</sub>PS<sub>4</sub> would decompose into Li<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>S. Ohtomo *et al* [9] experimentally detected the Li<sub>3</sub>PO<sub>4</sub> phase after the 75Li<sub>2</sub>S-25P<sub>2</sub>S<sub>5</sub> electrolytes reacting with water. However, the reaction products of Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> and water are unclear. Through dissolving the Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> powder into water followed by vacuum drying at 150 °C for 3 h, the reaction

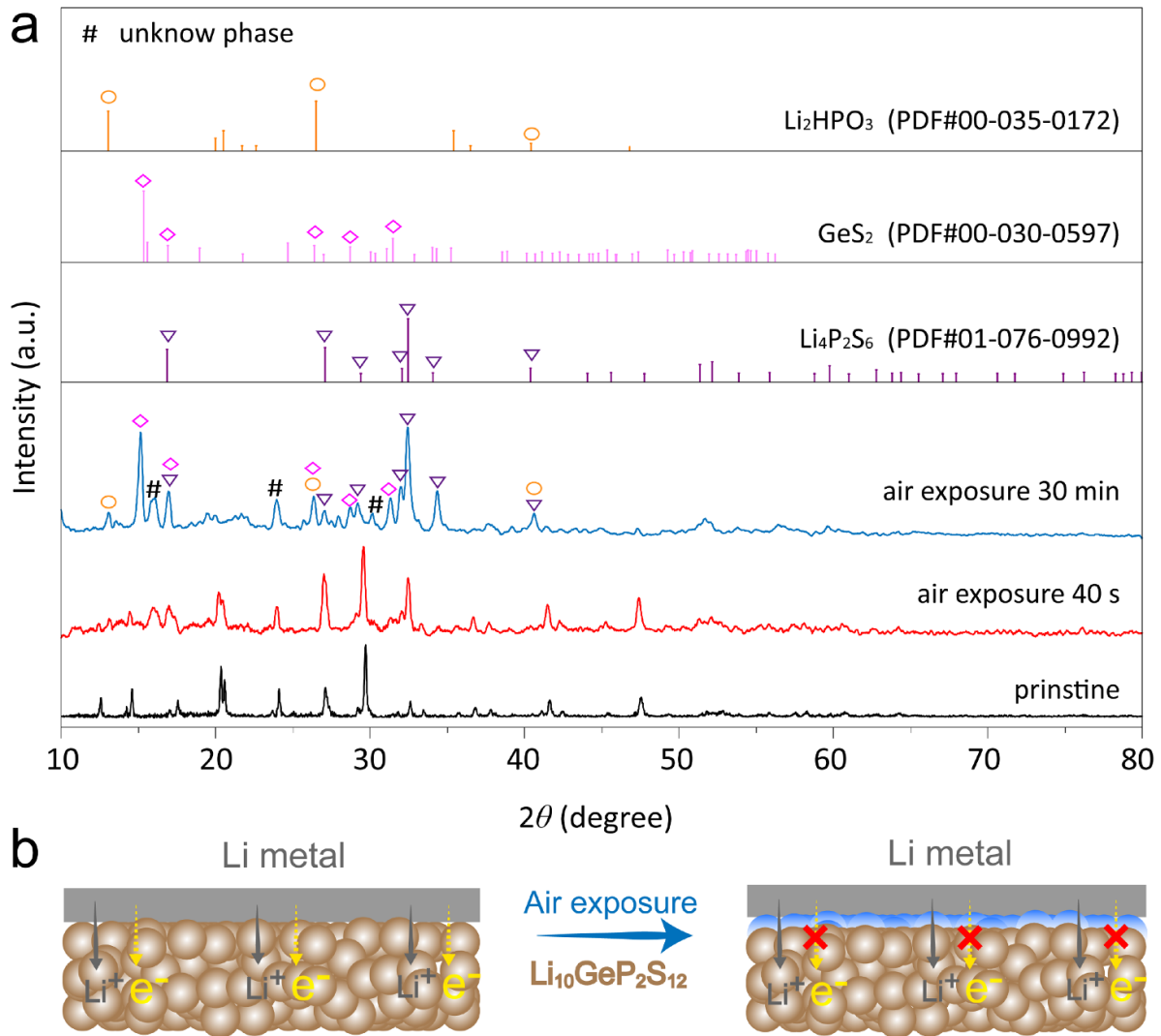
products are determined to be Li<sub>3</sub>PO<sub>4</sub> and Li<sub>4</sub>GeO<sub>4</sub>, as shown in figure S2. Noticeably, the Li<sub>3</sub>PO<sub>4</sub> and Li<sub>4</sub>GeO<sub>4</sub> were not observed on the surface of the air-exposed Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> pellet, indicating a different reaction process occur during the air-exposure treatment. As shown in figure 3(a), for the Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> pellet after 40 s air exposure, most of diffraction peaks can be indexed to Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> phase [25, 26]. Only three diffraction peaks at 12.58°, 14.60° and 17.56° belongs to Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> phase disappear and two new diffraction peaks at 16.07° and 16.99° were detected. After 30 min



**Figure 2.** Galvanostatic Li plating/stripping of the Li/40 s air-exposed  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cells. (a) Cyclic performance of the Li/40 s air-exposed  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cell at  $0.1 \text{ mA cm}^{-2}$  and  $0.1 \text{ mAh cm}^{-2}$ . The Li/Li $_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cell is also shown for comparison. (b) Rate capability at different current density and (c) cyclic performance at  $0.2 \text{ mA cm}^{-2}$  and  $0.5 \text{ mAh cm}^{-2}$  of the Li/40 s air-exposed  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cell.

air exposure, large amounts of new diffraction peaks were observed, indicating new phases formed on the surface of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellet. The diffraction peaks at  $16.94^\circ$ ,  $27.08^\circ$ ,  $29.24^\circ$ ,  $32.04^\circ$ ,  $32.46^\circ$ ,  $34.32^\circ$ ,  $40.62^\circ$  can be indexed to  $\text{Li}_4\text{P}_2\text{S}_6$  (PDF#01-076-0992), while  $15.48^\circ$ ,  $16.94^\circ$ ,  $26.42^\circ$ ,  $28.82^\circ$ ,  $31.38^\circ$  belong to  $\text{GeS}_2$  (PDF#00-030-0597) and  $13.04^\circ$ ,  $26.42^\circ$ ,  $40.62^\circ$  correspond to  $\text{Li}_2\text{HPO}_3$  (PDF#00-035-0172). The XRD results suggest that a partial hydrolysis reaction occurs on the surface of the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellet after air exposure with formation of the mixed phases of  $\text{Li}_4\text{P}_2\text{S}_6$ ,  $\text{GeS}_2$  and  $\text{Li}_2\text{HPO}_3$ , where the  $\text{Li}_4\text{P}_2\text{S}_6$  is main phase as majority of diffraction peaks belong to it. The compound,  $\text{Li}_4\text{P}_2\text{S}_6$ , have been reported to exhibit considerable ionic conductivity and good interface stability towards lithium metal [27–30], making it desirable for interface protection

for  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ . Besides, both  $\text{LiH}_2\text{PO}_4$  and  $\text{Li}_3\text{PO}_4$  have been proven to be efficient protective layers for Li/solid electrolyte interface [16, 31–34], indicating phosphide, such as  $\text{Li}_2\text{HPO}_3$ , can stabilize the Li/Li $_{10}\text{GeP}_2\text{S}_{12}$  interface. Figures S3 and S4 presents the surface and cross-section morphology of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellets before and after air exposure, showing the obvious decomposition layer coated on the surface of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellet. Figure 3(b) presents schematic illustrations of the mechanism of the protective layer formed by air exposure for stabilizing the Li/Li $_{10}\text{GeP}_2\text{S}_{12}$  interface. For the Li/Li $_{10}\text{GeP}_2\text{S}_{12}$  interface, a mixed conductive interface is formed when  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  attaches with lithium metal, leading to continuously consume inner  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  and increase the cell impedance. After exposing  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellet in air, a passivating layer rapidly generated. On

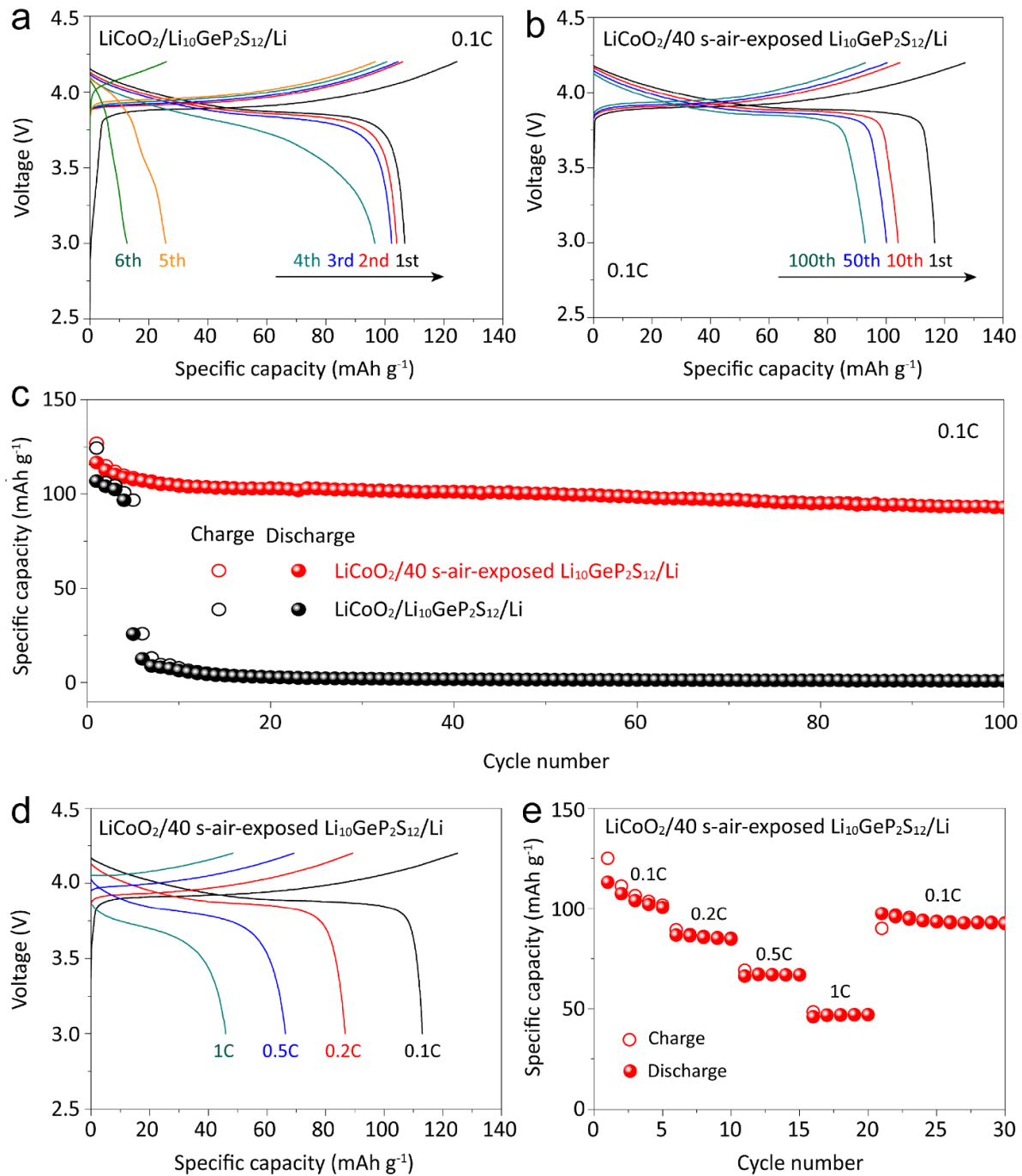


**Figure 3.** Improvement of the interface stability between  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  solid electrolytes and lithium metal through introducing a protective layer by air-exposure treatment. (a) XRD patterns of the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellets before and after 40 s and 30 min air exposure. (b) Schematic illustrations of the mechanism of the protective layer formed by air exposure for stabilizing the  $\text{Li}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  interface.

one hand, this layer can physically isolate the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  from lithium metal. On the other hand, this layer comprising of the  $\text{Li}_4\text{P}_2\text{S}_6$ ,  $\text{GeS}_2$  and  $\text{Li}_2\text{HPO}_3$  is lithium-ion permeable but electronic obstructed, which can effectively suppress the decomposition of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  during the Li metal plating/stripping.

To further demonstrate the effect of the protective layer on stabilizing the  $\text{Li}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  interface, the  $\text{LiCoO}_2$  based all-solid-state lithium metal batteries were fabricated by using both  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  and 40 s air-exposed  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  pellets as solid electrolyte. Figure 4(a) shows charge and discharge curves of the  $\text{LiCoO}_2/\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  battery, showing a rapid decay in specific capacity and large polarization after 5 cycles. In contrast, for the  $\text{LiCoO}_2/40$  s air-exposed

$\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  battery, high reversible specific capacity and low degree of polarization are delivered (figure 4(b)). The  $\text{LiCoO}_2/40$  s air-exposed  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  battery shows an initial charge specific capacity of  $127 \text{ mA h g}^{-1}$  with high initial Coulombic efficiency of 92% and delivered long cyclic stability for 100 cycles with capacity retention of 80%, as shown in figure 4(c). The good rate performances of the  $\text{LiCoO}_2/40$  s air-exposed  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  battery were also presented (figures 4(d) and (e)), exhibiting the discharge capacities of 113, 87, 66, 46  $\text{mAh g}^{-1}$  at 0.1, 0.2, 0.5 and 1 C, respectively. The high reversible specific capacity and long cyclic stability strongly support the rapid generated protective layer by simple air-exposure treatment can effectively stabilize the  $\text{Li}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  interface.



**Figure 4.** Electrochemical performances of all-solid-state lithium batteries. Charge and discharge curves of (a) the LiCoO<sub>2</sub>/Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>/Li battery and (b) the LiCoO<sub>2</sub>/40 s air-exposed Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>/Li battery at 0.1 C (1 C = 120 mA g<sup>-1</sup>) under 25 °C. (c) Cyclic performances of the LiCoO<sub>2</sub>/Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>/Li and LiCoO<sub>2</sub>/40 s-air-exposed Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>/Li batteries at 0.1 C under 25 °C. (d) Charge and discharge curves and (e) cyclic performances of the LiCoO<sub>2</sub>/40 s-air-exposed Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>/Li battery at different rates.

#### 4. Conclusion

In summary, the strong reactive Li/Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> interface was effectively passivated via a rapid formed protective layer through simply exposing the Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> pellet to air for dozens of seconds. The protective layer coated on the

surface of the Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> pellets is derived from the partial hydrolysis reaction of Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> in air, generating the decomposition products of Li<sub>4</sub>P<sub>2</sub>S<sub>6</sub>, GeS<sub>2</sub> and Li<sub>2</sub>HPO<sub>3</sub>. This lithium-ion permeable but electronic obstructed layer can both separate the contact and effectively suppress the decomposition reaction between Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> and lithium metal during

electrochemical cycling. After optimal air-exposure duration of 40 s, the Li/40 s air-exposed  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  symmetric cell presents long cyclic stability for 1000 h with small polarization voltage of 26 mV at  $0.1 \text{ mA cm}^{-2}$ . Compared with the  $\text{LiCoO}_2/\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  battery with rapid capacity decay after 10 cycles, the all-solid-state  $\text{LiCoO}_2/40 \text{ s}$  air-exposed  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  battery shows long cyclic performances for 100 cycles with capacity retention of 80%, and good rate capabilities of discharge capacity of 113, 87, 66, 46  $\text{mAh g}^{-1}$  at 0.1, 0.2, 0.5 and 1 C, respectively.

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## Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Authors contributions

Wei Weng: investigation, methodology, formal analysis, data curation, visualization, writing—original draft. Dong Zhou: visualization, validation. Gaozhan Liu, Lin Shen: methodology, visualization. Mengqi Li, Xinshuang Chang: validation. Xiayin Yao: conceptualization, supervision, project administration, funding acquisition, resources, writing—review and editing.

## ORCID iD

Xiayin Yao  <https://orcid.org/0000-0002-2224-4247>

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