# Congener Substitution Reinforced Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> Glass-Ceramic Electrolytes for All-Solid-State Lithium–Sulfur Batteries

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strengthened oxysulfide structural unit of  $POS_3^{3^-}$  and  $P_2OS_6^{4^-}$  with bridging oxygen atoms and a distorted lattice configuration of the Sb–S tetrahedron, the  $Li_7P_{2.9}Sb_{0.1}S_{10.75}O_{0.25}$  electrolyte exhibits prominent chemical stability and high ionic conductivity. Besides the improved air stability, the ionic conductivity of  $Li_7P_{2.9}Sb_{0.1}S_{10.75}O_{0.25}$  could reach  $1.61 \times 10^{-3}$  S cm<sup>-1</sup> at room temperature with a wide electrochemical window of up to 5 V (vs Li/Li<sup>+</sup>), as well as good stability against Li and Li–In alloy anodes. Consequently, the ASSLSB with the  $Li_7P_{2.9}Sb_{0.1}S_{10.75}O_{0.25}$  electrolyte shows high discharge capacities of 1374.4 mAh g<sup>-1</sup> (0.05C, 50th cycle) at room temperature and 1365.4 mAh g<sup>-1</sup> (0.1C, 100th cycle) at 60 °C. The battery also presents remarkable rate performance (1158.3 mAh g<sup>-1</sup> at 1C) and high Coulombic efficiency (>99.8%). This work provides a feasible technical route for fabricating ASSLSBs.

KEYWORDS: all-solid-state batteries, lithium-sulfur batteries, sulfide electrolyte, solid-state electrolyte, air stability

## 1. INTRODUCTION

High-energy lithium-metal batteries are gaining tremendous interest in recent years, among which the lithium-sulfur battery (Li-S) is believed as a promising candidate for nextgeneration power batteries.<sup>1-3</sup> However, lithium metal is highly active toward conventional liquid organic electrolytes and holds safety hazards of thermal runaway because of notorious lithium dendrites.<sup>4,5</sup> Compared to liquid electrolytes, solid-state electrolytes are intrinsically nonvolatile and nonflammable. More importantly, solid-state electrolytes could effectively inhibit the growth of lithium dendrites, which is beneficial for improving the battery safety.  $^{6-10}$  As for Li–S, the shuttling effect of polysulfides in organic liquid electrolytes is a severe limitation for reaching the long-term cyclic stability, whereas polysulfides are insoluble in solid-state electrolytes.<sup>11,12</sup> Besides, solid-state electrolytes can be prepared as ultrathin films and get rid of inactive diaphragm components, thus improving the energy density of batteries. In this way, high-performance all-solid-state batteries (ASSBs), especially all-solid-state lithium-sulfur batteries (ASSLSBs), are highly expected to be game changer in future energy storage systems.

Among a series of solid-state electrolytes, the polymer electrolyte has good stability against lithium but low conductivity of Li ions at room temperature, leading to the poor electrochemical and thermal stability in ASSBs.<sup>13,14</sup> The oxide electrolyte has good stability and compatibility with

commercial oxide cathode materials; however, the ionic conductivity is relatively low, and the poor electrode/ electrolyte interface and large grain boundary resistance are the primary defects to be resolved.<sup>15,16</sup> In recent years, the sulfide electrolyte has been one of the research focuses in the field of ASSBs owing to the high ionic conductivity (>1 mS cm<sup>-1</sup>),<sup>17,18</sup> wide electrochemical window (>5 V vs Li/Li<sup>+</sup>),<sup>19,20</sup> excellent mechanical properties, and negligible grain boundary resistance.<sup>21,22</sup> In particular, the sulfide electrolyte of metastable glass-ceramic  $\text{Li}_7\text{P}_3\text{S}_{11}$  holds a high ionic conductivity of 3.2 mS cm<sup>-1</sup>.<sup>23</sup> By further component optimization, Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub><sup>24</sup> and Li<sub>9.54</sub>Si<sub>1.74</sub>P<sub>1.44</sub>S1<sub>1.7</sub>Cl<sub>0.3</sub><sup>2</sup> have ionic conductivities of up to of 12 and 25 mS cm<sup>-1</sup> at room temperature, respectively, which are comparable to those of commercial liquid electrolytes. Therefore, among various types of solid-state electrolytes, the sulfide electrolytes and corresponding modification technologies are investigated with high prospect.

Received: June 4, 2021 Accepted: July 12, 2021



Although great progress has been made, most sulfide electrolytes have poor stability in air and must be operated in an argon-filled environment, which greatly increases the complexity and cost. In ambient air, the sulfide electrolyte hydrolyzes partially to generate toxic  $H_2S$  gas and the structure collapses during the hydrolysis process, resulting in sharply dropped ionic conductivity and latent safety problems.<sup>26,27</sup>

Therefore, improving the air stability of the sulfide electrolyte is an urgent issue for ASSBs. Some works have been reported to improve the air stability of sulfide electrolytes by partially replacing  $\text{Li}_2\text{S}$  with  $\text{Li}_2\text{O}^{28}$  and  $\text{ZnO}^{29}$  and partially replacing  $P_2\text{S}_5$  with  $P_2\text{O}_5^{30}$  to suppress the generation of  $H_2\text{S}$  gas. These successful attempts indicate that the substitution engineering of O to S could effectively improve the stability of sulfide electrolytes. Element substitution within the same main group would induce manageable structure deformation, which is also favorable for improving structural stability. In particular, based on the theory of hard and soft acid—base (HSAB),<sup>31,32</sup> the replacement of P and S elements with congeners, such as more polarizable Sb and more stable O, could improve the stability of sulfide electrolytes.

In this work, we propose a congener substitution strategy to optimize  $\text{Li}_7\text{P}_3\text{S}_{11}$  as  $\text{Sb}_2\text{O}_5$ -doped  $\text{Li}_7\text{P}_{3-x}\text{Sb}_x\text{S}_{11-2.5x}\text{O}_{2.5x}$  (x = 0, 0.04, 0.08, 0.1, 0.12, and 0.16) electrolytes by chemical bond and structure regulation through high-energy ball milling and subsequent heat treatment. It is demonstrated that with proper Sb and O replacement, not only the ionic conductivity but also the air stability of the optimized  $\text{Li}_7\text{P}_{2.9}\text{Sb}_{0.1}\text{S}_{10.75}\text{O}_{0.25}$  electrolyte could be significantly improved. Moreover, the  $\text{Li}_7\text{P}_{2.9}\text{Sb}_{0.1}\text{S}_{10.75}\text{O}_{0.25}$  electrolyte possesses better solid–solid interface compatibility in the assembled ASSLSBs as compared with  $\text{Li}_7\text{P}_3\text{S}_{11}$ , which is helpful to improve the capacity, rate performance, Coulombic efficiency, and cycle life of ASSLSBs.

## 2. EXPERIMENTAL SECTION

**2.1.** Preparation of Solid-State Electrolytes.  $Li_7P_{3-x}Sb_xS_{11-2,5x}O_{2,5x}$  (x = 0, 0.04, 0.08, 0.1, 0.12, and 0.16) solidstate electrolytes were prepared via a high-energy ball-milling technique and a further heat treatment strategy.  $Li_2S$  (99.9%, Alfa Aesar),  $P_2S_5$  (99%,  $p \ge 27\%$ , Macklin), and  $Sb_2O_5$  (99.995%, Aladdin) crystalline powders were used as raw materials, which were accurately weighed according to the stoichiometric ratio in an argonfilled glovebox. These powders were poured into a zirconia pot (50 mL in volume) containing ten zirconia balls (4 mm in diameter) and then were milled using a high-energy planetary ball mill apparatus at 550 rpm for 30 h at room temperature. Finally,  $Li_7P_{3-x}Sb_xS_{11-2,5x}O_{2,5x}$ solid-state electrolytes could be obtained by heating the ball-milled powder at 270 °C for 2 h in an argon-filled glovebox (H<sub>2</sub>O < 0.1 ppm,  $O_2 < 0.1$  ppm).

**2.2.** Preparation of the Sulfur–Carbon Composite Cathode. The composite cathode  $(S/C-Li_7P_{2.9}Sb_{0.1}S_{10.75}O_{0.25}-C$  and  $S/C-Li_7P_3S_{11}-C)$  of all-solid-state LSBs was composed of S/C (60% S), solid-state electrolytes  $(Li_7P_{2.9}Sb_{0.1}S_{10.75}O_{0.25}$  and  $Li_7P_3S_{11})$ , and carbon (Super-P) in a weight ratio of 3:5:2. First, the S/C (60% S) material was obtained by mixing sulfur powder and carbon powder in a mass ratio of 3:2 and then heat-treating in a muffle furnace at 155 °C for 12 h. Then, S/C (60% S) and carbon (Super-P) were mixed according to a mass ratio of 3:2 and subjected to mechanical ball milling at 350 rpm for 5 h at room temperature. Finally, a certain amount of the electrolyte was added to the ball-milling pot, and ball milling was continued at 350 rpm for 10 h to obtain the composite cathode of all-solid-state LSBs.

**2.3. Assembly of ASSLSBs.** For the assembly of the all-solid-state LSBs,  $Li_7P_{2,9}Sb_{0.1}S_{10.75}O_{0.25}$  and  $Li_7P_3S_{11}$  powders were used as solid electrolyte,  $S/C-Li_7P_{2,9}Sb_{0.1}S_{10.75}O_{0.25}-C$  and  $S/C-Li_7P_3S_{11}-C$  were used as the active material of the composite cathode, and the Li/In

alloy was used as the anode. First, 130 mg of solid-state electrolyte powders was poured into a mold with an inner diameter of 10 mm and cold-pressed at a pressure of 380 MPa. Then, 3.0 mg of composite cathode material was poured on top of the electrolyte, and the Li/In alloy (Li/In = 1:2) was placed under the electrolyte. This overall structure was cold-pressed under a pressure of 380 MPa. Finally, a three-layered pellet was finished by attaching two stainless steel (SS) disks as current collectors. All of the processes of assembling the batteries were carried out in a glovebox filled with argon gas.

2.4. Material Characterization. X-ray diffraction (XRD) was used to investigate the crystalline phase of the solid-state electrolytes using a Rigaku Mini Flex II instrument with Cu K radiation. Raman spectra were carried out using an SR-500I-A Raman microscope at an excitation of 532 nm. The amount of H<sub>2</sub>S gas released by the solidstate electrolytes was measured under the condition of 25 °C with a relative humidity of 25-30%. The test was carried out in a closed container about 5000 mL filled with moist air, which contains solidstate electrolyte powders, a H<sub>2</sub>S gas detector (HJ-BXA-H<sub>2</sub>S), and a small fan. Solid-state <sup>7</sup>Li and <sup>31</sup>P MAS-NMR (magic-angle spinning nuclear magnetic resonance) analysis was performed using a Bruker Avance III HDX 400 WB spectrometer. The morphological analysis and elemental mapping of the solid-state electrolytes were performed by SEM (JEOL-JSM7800F) and EDS (Bruker Quantax 200), respectively. The sulfur content in the composite cathode was confirmed by thermogravimetric analysis (TG, METTLER TOLEDO, TG/DSC1) from 50 to 800 °C under an argon atmosphere. X-ray photoelectron spectroscopy (XPS) measurements were conducted on Escalab 250Xi (Thermo Fisher Scientific).

2.5. Electrochemical Measurement. To measure the lithiumion conductivities of the solid-state electrolytes, the solid-state electrolyte samples were cold-pressed under 380 MPa into a mold with an inner diameter of 10 mm. Both sides of the electrolyte samples were coated with a SS plate as current collectors to form the symmetric blocking cells. Electrochemical impedance spectroscopy (EIS) using Zahner IM6e in a frequency range from 1 MHz to 1Hz with a 5 mV potential perturbation was performed at temperatures from 298 to 398 K. Cyclic voltammetry (CV) of asymmetric Li/SE/ SS batteries was carried out to analyze the electrochemical stability in the voltage window range from -0.5 to 5 V (Li/Li<sup>+</sup>) at a scan rate of 1 mV s<sup>-1</sup>. The electrochemical stability of the solid-state electrolytes with the Li and Li/In alloy was tested through constant direct current charge and discharge cycling (C2001A, LAND, China) at a current density of 0.1/0.2 mA cm<sup>-2</sup> at room temperature. The discharge and charge cycle performance of ASSLSBs was measured by a LAND battery test system (C2001A, LAND, China) at a current of 0.05C and the voltage range from 0.8 to 2.4 V. The rate performance of ASSLSBs was determined by testing under different current densities from 0.05 to 1C at room temperature and 60 °C.

## 3. RESULTS AND DISCUSSION

**3.1.** Preparation and Characterization of  $Li_7P_{3-x}Sb_xS_{11-2.5x}O_{2.5x}$  (x = 0, 0.04, 0.08, 0.1, 0.12, and 0.16) Electrolytes. As shown in Figure 1,  $Li_7P_{2.9}Sb_{0.1}S_{10.75}O_{0.25}$  is prepared from  $Li_2S$ ,  $P_2S_5$ , and  $Sb_2O_5$  dopants via a high-energy ball-milling method and subsequent



Figure 1. Preparation of the solid-state electrolyte and schematic of ASSLSBs.



Figure 2. (a) XRD patterns, (b) Raman spectra, (c) <sup>31</sup>P MAS-NMR spectra, and (d) <sup>7</sup>Li NMR spectra of  $\text{Li}_7\text{P}_{3-x}\text{Sb}_x\text{S}_{11-2.5x}\text{O}_{2.5x}$  (x = 0, 0.04, 0.08, 0.1, 0.12, and 0.16) electrolytes. (e) SEM image of  $\text{Li}_7\text{P}_{2.9}\text{Sb}_{0.1}\text{S}_{10.75}\text{O}_{0.25}$  and EDS mapping images of P, S, Sb, and O elements.

heat treatment. In the Sb<sub>2</sub>O<sub>5</sub>-doped sample, the Sb element could form SbS<sub>4</sub> tetrahedrons and the O element tends to act as bridging atoms, leading to the formation of chemical bonds and lattice distortions (detailed in the XPS spectrum of Sb 3d in Figure S1). The crystal phase and composition of the solidstate electrolytes are confirmed by powder XRD, Raman spectra, and MAS-NMR analyses. Figure 2a shows the XRD patterns of  $\text{Li}_7 P_{3-x} \text{Sb}_x S_{11-2.5x} O_{2.5x}$  (x = 0, 0.04, 0.08, 0.1, 0.12, and 0.16) electrolytes. In Figure 2a, the dispersed diffraction peaks indicate that the powders are composed of a glass phase and crystal phase. Herein, without element substitution, the pristine sample is mainly composed of Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> with the coexistence of trace Li<sub>4</sub>P<sub>2</sub>S<sub>6</sub> impurities as indicated in the diffraction patterns.<sup>33</sup> The appearance of Li<sub>4</sub>P<sub>2</sub>S<sub>6</sub> impurities is attributed to the decomposition of the  $Li_7P_3S_{11}$  metastable phase during heat treatment.<sup>34</sup> When adding different ratios of  $Sb_2O_5$ , no diffraction peaks of  $Sb_2O_5$  are observed, indicating that Sb and O are successfully incorporated into the crystal structure. With increasing  $Sb_2O_5$  content, the intensity of the diffraction peaks corresponding to Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> remains the same, while the diffraction peaks of  $\mathrm{Li}_4 \mathrm{P}_2 \mathrm{S}_6$  weaken and almost disappear when x = 0.1 and 0.12, showing a purified constituent. With increasing  $Sb_2O_5$  content to 0.16, a weak signal of Li<sub>4</sub>P<sub>2</sub>S<sub>6</sub> appears again due to the instability of the

intrinsic lattice structure by excessive substitution of Sb and O, showing destruction of the stable phase.<sup>35</sup>

Figure 2b displays Raman spectra of  $\text{Li}_7\text{P}_{3-x}\text{Sb}_x\text{S}_{11-2.5x}\text{O}_{2.5x}$ (x = 0, 0.04, 0.08, 0.1, 0.12, and 0.16) electrolytes. Clearly, three peaks at around 421, 408, and 386 cm<sup>-1</sup> could be observed. The peaks at 421 and 408 cm<sup>-1</sup> correspond to the symmetrical stretching vibrations of P–S bonds of PS<sub>4</sub><sup>3–</sup> and P<sub>2</sub>S<sub>7</sub><sup>4–</sup> groups, respectively, indicating the formation of a highly conductive  $\text{Li}_7\text{P}_3\text{S}_{11}$  phase,<sup>36,37</sup> while the peak at 386 cm<sup>-1</sup> corresponds to P<sub>2</sub>S<sub>6</sub><sup>4–</sup>, on behalf of a low conductive phase.<sup>38</sup> Obviously, the addition of Sb<sub>2</sub>O<sub>5</sub> can restrain the formation of the low conductivity phase of P<sub>2</sub>S<sub>6</sub><sup>4–</sup>. As a result, the pure  $\text{Li}_7\text{P}_3\text{S}_{11}$  phase electrolyte can be obtained when x > 0.1, in agreement with XRD analysis results. It indicates that the congener substitution strategy by doping Sb<sub>2</sub>O<sub>5</sub> could be effective to regulate the conductive phase preference of  $\text{Li}_7\text{P}_3\text{S}_{11}$ , thus inducing performance improvement.

As mentioned before, Sb and O elements could enter the lattice structure of  $\text{Li}_7\text{P}_3\text{S}_{11}$ , resulting in good crystallization of the as-prepared samples. More specifically, the O element tends to form bridging oxygen to displace bridging sulfur, while Sb<sup>5+</sup> ions with large radii can replace P<sup>5+</sup> and shield Coulombic repulsion among S<sup>2-</sup> ions, consequently improving the stability of the  $\text{Li}_7\text{P}_3\text{S}_{11}$  mother phase.<sup>39,40</sup> As seen from MAS-NMR



**Figure 3.** (a) Nyquist plots at room temperature and (b) corresponding Arrhenius plots of ionic conductivity of  $\text{Li}_7 P_{3-x} \text{Sb}_x S_{11-2.5x} O_{2.5x}$  (x = 0, 0.04, 0.08, 0.1, 0.12, and 0.16) electrolytes.

spectra (Figure 2c), when x = 0, two peaks with almost the same intensity can be observed at 86.3 and 90.5 ppm, corresponding to the tetrahedral unit of  $PS_4^{3-}$  and the unit of  $P_2S_7^{4-}$  with bridging sulfur, respectively.<sup>41,42</sup> It can also be observed that two peaks at 103.7 and 107.1 ppm correspond to the unit of  $P_2S_6^{-43}$  With the substitution of  $Sb_2O_5$ , the peak intensity corresponding to  $PS_4^{3-}$  and  $P_2S_7^{4-}$  changes obviously, showing an opposite tendency of increased PS<sub>4</sub><sup>3-</sup> and reduced  $P_2S_7^{4-}$ . This indicates that oxygen could replace the bridging sulfur in the  $PS_4^{3-}$  and  $P_2S_7^{4-}$  structural units, reconstructing new structural units ( $POS_3^{3-}$  and  $P_2OS_6^{4-}$ ) to stabilize the electrolyte lattice.<sup>44</sup> Meanwhile, the  $P_2S_6^-$  structural units would be weakened gradually along with Sb<sub>2</sub>O<sub>5</sub> doping, indicating the suppression of the low conductive phase, consistent with XRD and Raman analyses. As presented in <sup>7</sup>Li NMR spectra (Figure 2d) of the as-prepared samples, there is no obvious chemical environment change of the lithium element, and all of the electrolytes show sharp peaks in <sup>7</sup>Li NMR spectra. The size of the as-prepared  $Li_7P_{3-x}Sb_xS_{11-2.5x}O_{2.5x}$  electrolytes ranges from several micrometers to several tens of micrometers as aggregate-like morphology (Figure S1). The element distribution and particle size of the typical Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolyte on the SEM mode are shown in Figure 2e. A typical spherical powder morphology is observed with a diameter size of 8.24  $\mu$ m. In the spherical sample, P, S, Sb, and O elements are distributed uniformly, further demonstrating the desired substitution of Sb and O in the Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolyte.

The optimal doping amount of Sb<sub>2</sub>O<sub>5</sub> is screened by measuring the EIS of symmetrical SS/solid-state electrolyte/SS (SS/SE/SS) cells (Figure 3a) and Arrhenius curves (Figure 3b) of Li<sub>7</sub>P<sub>3-x</sub>Sb<sub>x</sub>S<sub>11-2.5x</sub>O<sub>2.5x</sub> (x = 0, 0.04, 0.08, 0.1, 0.12, and 0.16) electrolytes. In addition, Table 1 lists the corresponding ionic conductivity ( $\sigma$ ) and activation energy ( $E_a$ ). It can be clearly observed that the ionic conductivity of the pristine

Table 1. Conductivity and Activation Energy $E_a$ of	
Li <sub>7</sub> P <sub>3-x</sub> Sb <sub>x</sub> S <sub>11-2.5x</sub> O <sub>2.5x</sub> (x = 0, 0.04, 0.08, 0.1, 0.12, and 0.1	6)

X	conductivity ( $\sigma$ , S cm <sup>-1</sup> )	$E_{\rm a}~({\rm kJ}~{\rm mol}^{-1})$
X = 0	$7.26 \times 10^{-4}$	30.3
X = 0.04	$9.06 \times 10^{-4}$	28.5
X = 0.08	$1.04 \times 10^{-3}$	28.4
X = 0.10	$1.61 \times 10^{-3}$	26.6
X = 0.12	$1.22 \times 10^{-3}$	28.1
X = 0.16	$8.98 \times 10^{-4}$	29.3

Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> electrolyte is 7.26 × 10<sup>-4</sup> S cm<sup>-1</sup>. With increasing doping amount of Sb<sub>2</sub>O<sub>5</sub>, the ionic conductivity of the electrolytes increases in the first place. When x = 0.1, the ionic conductivity of the Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolyte reaches the maximum value of 1.61 × 10<sup>-3</sup> S cm<sup>-1</sup>. Then, the ionic conductivity of the electrolyte decreases to 8.98 × 10<sup>-4</sup> S cm<sup>-1</sup> on increasing the doping amount of Sb<sub>2</sub>O<sub>5</sub> to up to 0.16. By comparing the key parameters, it is demonstrated that the ionic conductivity of the as-prepared Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolyte is 2.2 times higher than that of the pristine Li<sub>7</sub>P<sub>3-x</sub>Sb<sub>x</sub>S<sub>11-2.5x</sub>O<sub>2.5x</sub> electrolytes can be calculated according to the Arrhenius equation:

$$\sigma = A \exp(-E_a/kT)$$

where  $\sigma$  is the ionic conductivity, *T* is the absolute temperature, *k* is the Boltzmann constant, and *A* is the preexponential factor.<sup>45</sup> According to Table 1, it can be concluded that the Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolyte presents the smallest activation energy  $E_{\rm a}$  of 26.6 kJ mol<sup>-1</sup>, while the pristine Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> electrolyte presents the largest  $E_{\rm a}$  value of 30.3 kJ mol<sup>-1</sup>.

Water in humid air can hydrolyze sulfide electrolyte and produce harmful  $H_2S$ , ultimately decomposing the electrolyte and reducing ionic conductivity.<sup>46</sup> Air exposure experiments are performed to compare the stability of solid-state electrolytes with different doping amounts of Sb<sub>2</sub>O<sub>5</sub>. As shown in Figure 4a, the amount of H<sub>2</sub>S gas generated is gradually increased during the exposure, and the pristine Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> electrolyte shows the fastest growing speed among all of the samples. After 4000 s, all of the samples are severely decomposed, but the total amount of H<sub>2</sub>S gas of the  $Li_7P_{2.9}Sb_{0.1}S_{10.75}O_{0.25}$  electrolyte is the lowest at  $1.02 \text{ cm}^3/\text{g}$ , which is  $\sim$ 2.83 times lower as compared to that of Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> (Figure 4b), showing significantly improved air stability. As discussed before, more Sb<sub>2</sub>O<sub>5</sub> doping might destruct the stable structure of the sulfide phase; thus, the amount of H<sub>2</sub>S would slightly increase when x > 0.1. Considering that the ionic conductivity is also the highest when x = 0.1, it can be concluded that the congener substitution strategy by incorporating Sb<sub>2</sub>O<sub>5</sub> can concurrently improve the chemical stability and ionic conductivity of the solid-state electrolytes.

When applied in lithium-metal batteries, the electrochemical stability is a decisive parameter. The electrochemical window of  $\text{Li}_7\text{P}_3\text{S}_{11}$  and  $\text{Li}_7\text{P}_{2.9}\text{Sb}_{0.1}\text{S}_{10.75}\text{O}_{0.25}$  solid-state electrolytes is tested at room temperature by CV in the potential range from

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Figure 4. (a) Quantity of H<sub>2</sub>S gas produced from  $Li_7P_{3-x}Sb_xS_{11-2.5x}O_{2.5x}$  (x = 0, 0.04, 0.08, 0.1, 0.12, and 0.16) electrolytes during air exposure and (b) amount of H<sub>2</sub>S gas generated after 4000 s air exposure tests.



Figure 5. (a,b) Cyclic voltammograms of the Li/Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>/SS and Li/Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub>/SS cells in the potential range from -0.5 to 5 V (vs Li/Li<sup>+</sup>) with a scan rate of 1 mV s<sup>-1</sup> at room temperature. (c) Galvanostatic charge/discharge curves of the Li/Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>/Li and Li/Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub>/Li symmetric cells under 0.1 mA cm<sup>-2</sup>. (d) Galvanostatic charge/discharge curves of the Li/Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>/Li/In and Li/In/Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub>/Li/In symmetric cells under 0.2 mA cm<sup>-2</sup> at room temperature.

-0.5 to 5 V (vs Li/Li<sup>+</sup>) at a scan rate of 1 mV s<sup>-1</sup>. In Figure 5a, a pair of obvious redox peaks of the Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> electrolyte is attributed to the electrochemical deposition (Li<sup>+</sup> + e<sup>-</sup>  $\rightarrow$  Li) and dissolution (Li  $\rightarrow$  Li<sup>+</sup> + e<sup>-</sup>) of lithium occurring on the SS electrode.<sup>47</sup> In addition, the small peak at 2.3 V (vs Li/Li<sup>+</sup>) is attributed to the oxidative decomposition of the unstable Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> electrolyte.<sup>48</sup> In contrast, in Figure 5b, there are no other redox peaks except for the electrochemical deposition/ dissolution of lithium in the potential range from -0.5 to 5 V (vs Li/Li<sup>+</sup>), which indicates that the Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolyte has a wide and stable electrochemical window of up to 5.0 V vs Li/Li<sup>+</sup>.

To further study the interfacial stability of the electrolyte to lithium metal, the galvanostatic charge/discharge tests of the  $Li/Li_7P_3S_{11}/Li$  and  $Li/Li_7P_{2.9}Sb_{0.1}S_{10.75}O_{0.25}/Li$  symmetric cells are carried out at 0.1 mA cm<sup>-2</sup> at room temperature (Figure 5c). It can be clearly seen that the  $Li/Li_7P_3S_{11}/Li$  cell shows a

higher overpotential (+0.034 and -0.035 V). After 24 h of cycling, the voltage curve suddenly drops due to short circuit caused by the formation of lithium dendrites in the cell with the Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> electrolyte.<sup>49</sup> In contrast, the stripping/plating behavior of the Li/Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub>/Li cell remains steady for 62 h and owns a lower overpotential (+0.023 and -0.022 V), which is due to the low interface resistance, good chemical/electrochemical stability of the Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolyte, and suppressed lithium dendrites. Additionally, to study the stability of the interface between the electrolyte and lithium-indium alloy (Li/In), Li/In/Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>/Li/In and Li/ In/Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub>/Li/In symmetric cells are assembled for galvanostatic charge/discharge tests. Figure 5d displays the galvanostatic curves of the Li/In/Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>/Li/In and Li/In/ Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub>/Li/In symmetric cells at 0.2 mA cm<sup>-2</sup> (room temperature). Clearly, the  $\text{Li}/\text{In}/\text{Li}_7\text{P}_{2.9}\text{Sb}_{0.1}\text{S}_{10.75}\text{O}_{0.25}/\text{Sb}_{0.1}$ Li/In symmetric cell exhibits stable electrochemical dissolu-



Figure 6. (a) Initial discharge/charge cycles of Li–In/Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>/S–C and Li–In/Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub>/S–C batteries at 0.05C rate. (b) Rate performance of ASSLSBs with Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> and Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolytes at 0.05C, 0.1C, 0.2C, 0.5C, and 1C rates. (c) Cycling performance and Coulombic efficiency of ASSLSBs with Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> and Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolytes at 0.05C rate.

tion/deposition behavior at 0.2 mA cm<sup>-2</sup>. Significantly, the overpotential of the Li/In/Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub>/Li/In symmetric cell remains relatively low (+0.018 and -0.017 V) during 1500 h tests. In contrast, the voltage curve of the Li/In/Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>/Li/In symmetric cell displays a higher overpotential (+0.073 and -0.075 V), almost twice that of the Li/In/Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub>/Li/In symmetric cell. The main reason for such differences is the decreased interfacial resistance between the Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolyte and the Li/In anode. Consequently, through the congener substitution strategy of Sb and O, the ionic conductivity, air stability, interface stability, and compatibility of the solid-state electrolyte are improved simultaneously, thus making it possible to fabricate high-performance ASSLSBs.

3.2. Electrochemical Performance of ASSLSBs. ASSLSBs are fabricated by a composite sulfur cathode, a solid electrolyte  $(Li_7P_3S_{11} \text{ or } Li_7P_{2.9}Sb_{0.1}S_{10.75}O_{0.25})$ , and a Li or Li/In anode. It can be calculated that the weight losses of the Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolyte and Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub>based composite cathode at 50-800 °C are 16.4% and 27.3%, respectively. According to the TG analysis, the content of sulfur loading in the composite sulfur cathode is 19.1%. (Figure S2a-d). The electrochemical performances of ASSLSBs with Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> and Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolytes at room temperature are measured and presented in Figure 6. The initial discharge/charge cycles of ASSLSBs based on  $Li_7P_3S_{11}$  and  $Li_7P_{2.9}Sb_{0.1}S_{10.75}O_{0.25}$  electrolytes at 0.05C in the range of 0.8-2.4V (vs Li-In) at room temperature are shown in Figure 6a. Obviously, ASSLSBs have only one discharge and charge voltage plateau, corresponding to the reversible electrochemical reaction of S/Li2S without polysulfide intermediates.<sup>50,51</sup> The discharge capacity of ASSLSBs with

the  $\text{Li}_7\text{P}_3\text{S}_{11}$  electrolyte is 957.5 mAh g<sup>-1</sup>, while that of the one with the  $Li_7P_{2,9}Sb_{0,1}S_{10.75}O_{0.25}$  electrolyte can reach 1309.7 mAh g<sup>-1</sup> because of the improved low interface resistance and ionic conductivity. Figure 6b demonstrates the rate performance of ASSLSBs with Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> and Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolytes at various rates. The discharge capacities of ASSLSBs with Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> are 1435.7, 1360.8, 1235.6, 1002.9, and 634.0 mAh  $g^{-1}$  at discharge rates of 0.05C, 0.1C, 0.2C, 0.5C, and 1C, respectively. In comparison, ASSLSBs with Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> exhibit inferior discharge capacities of 944.4, 866.5, 722.1, 408.3, and 69.2 mAh g<sup>-1</sup> at 0.05C, 0.1C, 0.2C, 0.5C, and 1C rates, respectively. When the rate is switched to 0.05C, the capacities of ASSLSBs with  $\text{Li}_7\text{P}_3\text{S}_{11}$ and  $Li_7P_{2.9}Sb_{0.1}S_{10.75}O_{0.25}$  electrolytes could recover to 919.2 and 1417.8 mAh g<sup>-1</sup>, indicating good reversibility. The cyclic performances of ASSLSBs with Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> and Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolytes at 0.05C are demonstrated in Figure 6c. In the first cycle of ASSLSBs, the solid-solid interface between the cathode/anode and sulfide electrolyte is unstable. In particular, in the charge process, the interfacial reaction based on the partial oxidation of the sulfide electrolyte could be the main reason for the large initial charge capacity and low initial Coulombic efficiency. After the activation process, the battery can be charged/discharged normally with high Coulombic efficiency. It is demonstrated that ASSLSBs assembled with the Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolyte exhibit stable cyclic performance during 50 discharge and charge cycles, and their capacity remains 1374.4 mAh  $g^{-1}$  with a Coulombic efficiency of 99.86%. In contrast, the ASSLSBs assembled with the Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> electrolyte showed a fast capacity decline. After 50 discharge and charge cycles, the capacity is decreased sharply to 614.1 mAh  $g^{-1}$ , only 64.2% of the initial



Figure 7. (a) Initial discharge/charge cycles of  $\text{Li}-\text{In}/\text{Li}_7P_3S_{11}/\text{S}-\text{C}$  and  $\text{Li}-\text{In}/\text{Li}_7P_{2.9}\text{Sb}_{0.1}S_{10.75}O_{0.25}/\text{S}-\text{C}$  batteries under 0.05C rate at 60 °C. (b) Rate performance of ASSLSBs with  $\text{Li}_7P_3S_{11}$  and  $\text{Li}_7P_{2.9}\text{Sb}_{0.1}S_{10.75}O_{0.25}$  electrolytes under 0.05C, 0.1C, 0.2C, 0.5C, and 1C rates at 60 °C. (c) Cycling performance and Coulombic efficiency of ASSLSBs with  $\text{Li}_7P_3S_{11}$  and  $\text{Li}_7P_2S_{11}$  and  $\text{Li}_7P_2S_{12}$  electrolytes (0.05C rate) at 60 °C.

capacity. The EIS spectra of ASSLSBs with  $\rm Li_7P_3S_{11}$  and  $\rm Li_7P_{2.9}Sb_{0.1}S_{10.75}O_{0.25}$  electrolytes are shown in Figure S3. With the substitution of Sb and O, the impedance of the battery decreases from 204 to 88  $\Omega$  (Figure S3a). In particular, for the Li–In/Li<sub>7</sub>P\_2.9Sb\_{0.1}S\_{10.75}O\_{0.25}/S-C battery, the impedance changes are moderate as compared to those for the Li–In/Li\_7P\_3S\_{11}/S-C battery.

To investigate the performance of the ASSLSBs at high temperatures, the batteries are tested at 60 °C. As shown in Figure 7a, there is also only one battery discharging and charging voltage platform. The initial discharge capacity of the  $Li-In/Li_7P_{2,9}Sb_{0,1}S_{10,75}O_{0,25}/S-C$  battery is 1333.3 mAh g<sup>-1</sup>, which is much higher than that of the Li-In/Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>/S-C battery (897.8 mAh  $g^{-1}$ ) at 0.1C rate. In addition, ASSLSBs with Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> and Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> display high discharge capacities of 1063.1/1612.7, 1037.5/1513.6, 937.1/1390.0, 790.6/1261.8, and 623.6/1158.3 mAh g<sup>-1</sup> at 0.05C, 0.1C, 0.2C, 0.5C, and 1C rates, respectively (Figure 7b). Furthermore, when the current density is adjusted to the 0.05C rate, the discharge capacity of the battery increases to 1080.9 and 1518.2 mAh g<sup>-1</sup>. After cycling for 100 cycles, the discharge capacities of the battery are maintained at 934.1 and 1365.4 mAh  $g^{-1}$ , respectively, with a stable Coulombic efficiency (Figure 7c). A low Coulombic efficiency is still observed for the battery in the first cycle at 60 °C. It seems that the interfacial reaction from the partial oxidation of the sulfide electrolyte is more serious at 60 °C, leading to the poorer initial Coulombic efficiency. Generally, the performance of ASSLSBs with different electrolytes at higher temperatures is improved, including the capacity and cyclic stability. Especially, the  $Li_7P_{2,9}Sb_{0,1}S_{10.75}O_{0.25}$  electrolyte shows the obvious advantage for enhancing the electrochemical performance of

ASSLSBs. It means that the congener substitution strategy of the all-solid-state electrolytes holds a great promise for developing high-performance next-generation power batteries.

#### 4. CONCLUSIONS

In summary, in this work, we propose a congener substitution strategy to prepare  $\text{Li}_7 P_{3-x} \text{Sb}_x S_{11-2.5x} O_{2.5x}$  (x = 0, 0.04, 0.08, 0.1, 0.12, and 0.16) solid-state electrolytes for high-performance ASSLSBs. Owing to the partial substitution of Sb to P and O to S, the low conductivity phase is eliminated and the labile structure is strengthened by chemical bond regulation and lattice distortion. When x = 0.1, the ionic conductivity of the Li<sub>7</sub>P<sub>2.9</sub>Sb<sub>0.1</sub>S<sub>10.75</sub>O<sub>0.25</sub> electrolyte reaches to the maximum value of  $1.61 \times 10^{-3}$  S cm<sup>-1</sup>, with a minimum activity energy  $E_a$  of 26.6 kJmol<sup>-1</sup>. At the same time, the  $Li_7P_{2,9}Sb_{0,1}S_{10,75}O_{0,25}$ electrolyte also exhibits good stability in air (~2.83 times lower  $H_2S$  output as compared to that of pristine  $Li_7P_3S_{11}$ ), reduced interface resistance, and good electrochemical stability against Li and Li-In alloy anodes. When fabricating ASSLSBs with the Li7P2.9Sb0.1S10.75O0.25 electrolyte, the discharge capacity is 1374.4 mAh  $g^{-1}$  with a high Coulombic efficiency of 99.86% at room temperature after 50 cycles. When tested at higher temperatures, the capacity could be maintained at 1365.4 mAh g<sup>-1</sup> after 100 cycles at 60 °C. On increasing the current density to 1C rate, the battery still shows excellent discharge capacities of 634.0 mAh g<sup>-1</sup> at room temperature and 1158.3 mAh  $g^{-1}$  at 60 °C. This work provides a feasible attempt for preparing practical ASSLSBs through proper electrolyte modification.

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#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c10238.

SEM images of  $Li_7P_{3-x}Sb_xS_{11-2.5x}O_{2.5x}$ ; TG curves of TG curves of  $Li_7P_3S_{11}$  electrolyte,  $Li_7P_{2.9}Sb_{0.1}S_{10.75}O_{0.25}$  electrolyte,  $Li_7P_3S_{11}$  cathode, and  $Li_7P_{2.9}Sb_{0.1}S_{10.75}O_{0.25}$  cathode; EIS spectra of  $Li_7P_3S_{11}$  electrolyte with different preparation conditions; and XPS spectrum of Sb 3d (PDF)

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#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

Financial support from the Science and Technology Support Plan of Tianjin (no. 19YFZCGX00220), the National Natural Science Foundation (no. 21935006) of China, and Fundamental Research Funds for the Central Universities, Nankai University (no. 63211043) is gratefully acknowledged.

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