Short Communication

Li$_{9.54}$Si$_{1.74}$(P$_{1-x}$Sb$_x$)$_{1.44}$Si$_{11.7}$Cl$_{0.3}$: A functionally stable sulfide solid electrolyte in air for solid-state batteries

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A R T I C L E   I N F O

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A B S T R A C T

The air stability of a new family of sulfide solid state electrolytes of Li$_{9.54}$Si$_{1.74}$(P$_{1-x}$Sb$_x$)$_{1.44}$Si$_{11.7}$Cl$_{0.3}$ (LS(Sb)PS) is reported. The Sb doping further improves the ionic conductivity and cycling stability of the Li$_{9.54}$Si$_{1.74}$(P$_{1-x}$Sb$_x$)$_{1.44}$Si$_{11.7}$Cl$_{0.3}$ (LSPS). The air stability of LS(Sb)PS is tested by both material characterization and electrochemical techniques. The structure and electrochemical property of LS(Sb)PS are maintained after 1-hour air exposure in an extreme humidity environment. The lithium metal anode solid-state battery with LiNi$_{0.83}$Mn$_{0.11}$O$_{2.06}$Co$_{0.11}$O$_2$(NMC811) as the cathode and LS(Sb)PS as the electrolyte delivers a high specific capacity and shows a high capacity-retention after cycling.

1. Introduction

Solid state electrolytes have demonstrated certain compatibility with high voltage cathode and Li metal anode by various interface designs [1–4]. Sulfide solid electrolytes have attracted considerable attention due to its high ionic conductivity and unique mechanical properties [5,6]. Among them, Li$_{9.54}$Si$_{1.74}$(P$_{1-x}$Sb$_x$)$_{1.44}$Si$_{11.7}$Cl$_{0.3}$ delivers an extremely high conductivity of 25 mS/cm and enables a solid-state battery with ultrafast charge and discharge [7]. However, in comparison to oxide electrolytes, sulfide solid electrolytes often exhibit a lower air-stability. Moisture in the air can in principle always react with sulfides, leading to degraded performance [8,9]. Here in this paper, we report the air-stability of a new family of sulfide electrolytes with high ionic conductivity by doping Sb element in the parent material of Li$_{9.54}$Si$_{1.74}$(P$_{1-x}$Sb$_x$)$_{1.44}$Si$_{11.7}$Cl$_{0.3}$ (LSPS). A lithium metal solid-state battery was made using LiNi$_{0.83}$Mn$_{0.11}$O$_{2.06}$Co$_{0.11}$O$_2$ (NMC811) as the cathode. The battery with Sb doped LSPS (LS(Sb)PS) delivers a high capacity even after the air-exposure in an environment with a high humidity.

2. Experimental

Li$_{9.54}$Si$_{1.74}$(P$_{1-x}$Sb$_x$)$_{1.44}$Si$_{11.7}$Cl$_{0.3}$ of compositions ranging from 0 $\leq$ x $\leq$ 12.5% were prepared by ball milling and solid-state reaction. Stoichiometric amounts of Li$_2$S (>99.9% purity, Alfa Aesar), SiS$_2$ (American elements), P$_2$S$_5$ (S > 99% purity, Sigma Aldrich), Sb$_2$S$_3$ (Sigma Aldrich), and LiCl (>99% purity, Alfa Aesar) were weighted and milled for 40 h at 370 rpm in a planetary ball mill PM200 (Retsch GmbH, Germany). The whole milling process was carried out under a protective Ar atmosphere to avoid the oxidation of the materials. The milled powder were subsequently transferred into quartz tubes, which were sealed and heated at 5 ℃/min up to 460 ℃ for 8 h. Finally, the powder was cooled down naturally to room temperature. The power was left in an environmental chamber (Memmert HPP) for 1 h for the air-stability test, in which the relative humidity was set at 15% at 35 ℃.

X-Ray Diffraction (XRD) patterns were taken on a Rigaku Miniflex 600 diffractometer (CuK$_\alpha$ radiation, $\lambda$ = 0.15405 nm) working at 40 kV and 15 mA. Measurements were collected within a 20 range from 10 to 70°, with a 0.02° step and a scan speed of 1.5 s per step. Kapton films were employed to seal sample holders in Ar-filled glovebox in order to avoid the air exposure during XRD measurements. Celerf software was used to determine the lattice parameters of the samples with different antimony contents.

Impedance spectroscopy was employed to evaluate the ionic conductivity of the samples. Measurements were collected on a Solartron electrochemical potentiostat 1455A over the frequency range from 100 Hz to 1 MHz, with an amplitude of 0.01 V at room temperature (22 ℃). Cells with the configuration C-SE|SE|C-SE were used, where the electrodes (C-SE) were composed of 90 wt% of Li$_{9.54}$Si$_{1.74}$(P$_{1-x}$Sb$_x$)$_{1.44}$Si$_{11.7}$Cl$_{0.3}$ (LSPS) and 10 wt% of conductive carbon black (C). Cells were previously cold pressed at 500 MPa, while 150 MPa approximately
was maintained during the impedance measurement.

A lithium metal solid state battery was made with the structure of Li/graphite[LiS|Sb)PS|NMC811. A 25 µm lithium metal is covered by a graphite film with the capacity ratio of Li: graphite (5 wt%) PTFE. This protection layer prevents the direct contact between lithium metal and solid electrolyte [10]. 140 mg LS(Sb)PS powder was applied as the electrolyte. 70 wt% LiNi0.83Co0.11O2 was maintained during the impedance measurement. Batteries were cycled on a LAND battery testing station at 0.5C-rate at 55 ˚C. Fig. 1 a) represents the XRD patterns of the as-synthesized compounds, with the general formula, Li9.5xS17.4(1-x)Sb0.1++1.74S11.7Cl0.3 (0 ≤ x ≤ 12.5%) as a function of Sb content. All XRD patterns have been identified as a LGPS-type structure with a tetragonal unit cell and the P4/2/nmc space group (ICSD code 248307) [1,7].

3. Results and discussion

Fig. 1a) represents the XRD patterns of the as-synthesized compounds, with the general formula, Li9.5xS17.4(1-x)Sb0.1++1.74S11.7Cl0.3 (x = 0, 2.8, 5.5, 9.7 and 12.5%), as a function of Sb content. All XRD patterns fit well with the phase of the parent compound at x = 0%, which can be indexed using a tetragonal unit cell (P4/2/nmc). In order to provide more details, Fig. 1b) shows an expanded region of the collected XRD data in the 20 range from 25˚ to 32˚. It can be observed that at low Sb content (x = 0 and 2.8%), some small peaks of impurities at 25.9˚ and 30.4˚ are present, which may be related to Li1.74Sb3 and Li1.74Sb2, respectively, as suggested by the comparison with the XRD database. Further substitution of Sb in Li9.5xS17.4(1-x)Sb0.1++1.74S11.7Cl0.3 contributes to the suppression of the two peaks of secondary phases. Hence, samples can be considered as phase-pure compounds from approximately 5.5% to 9.7% of Sb content. As marked in Fig. 1a), additional peaks started to appear at 12.5% Sb substitution up to approximately 9.7%. A

<table>
<thead>
<tr>
<th>Sb Content (%)</th>
<th>a (Å)</th>
<th>c (Å)</th>
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<tbody>
<tr>
<td>x = 0</td>
<td>8.7087 (0.0019)</td>
<td>12.5601 (0.0002)</td>
</tr>
<tr>
<td>x = 2.8</td>
<td>8.7065 (0.0027)</td>
<td>12.5622 (0.0001)</td>
</tr>
<tr>
<td>x = 5.5</td>
<td>8.7075 (0.0025)</td>
<td>12.5677 (0.0001)</td>
</tr>
<tr>
<td>x = 9.7</td>
<td>8.7048 (0.0030)</td>
<td>12.5612 (0.0002)</td>
</tr>
<tr>
<td>x = 12.5</td>
<td>8.7065 (0.0023)</td>
<td>12.5690 (0.0001)</td>
</tr>
</tbody>
</table>

Impedance spectroscopy was employed to measure the ionic conductivity of the samples. Fig. 1c) depicts the impedance complex plane of materials with different Sb compositions at room temperature, where just the spike of the blocking electrodes can be distinguished due to the highly conductive nature of the samples, and therefore, the charge transfer contributions do not fall within the frequency range. The ionic conductivity values were obtained from the interception of these Nyquist plots on the real Z' axis, whose details can be observed from the inset of Fig. 1c). Fig. 1d) shows the conductivity values from the impedance measurement as a function of Sb composition. They all show high values in the range from 5 to 9 mS/cm, comparable with reported values for Li9.5xS17.4(1-x)Sb0.1++1.74S11.7Cl0.3 (1,7,12). Moreover, the ionic conductivity increases with Sb substitution up to approximately 9.7%.
similar behavior has been previously reported for other Sb-substituted sulfide solid electrolytes [8,13]. Note that the cold press method used in our experiment gives a weaker interface contact than hot press, leading to lower ionic conductivity than the highest reported value of 25 mS/cm at $x = 0\%$ [7]. The relative increase of ionic conductivity with Sb doping for $x > 0\%$ here thus indicates that the actual ionic conductivity of materials can be very high in Sb doped Li$_{9.54}$Si$_{1.74}$(P$_{1-x}$Sb$_x$)$_{1.44}$S$_{11.7}$Cl$_{0.3}$ ($0 \leq x \leq 12.5\%$). Substitutions beyond 9.7% give rise to Sb-rich secondary phases, as it can be observed from the XRD data (Fig. 1a). These secondary phases may be responsible for the decrease of the ionic conductivity, which drops from 8.8 mS/cm at 9.7% of Sb substitution to 5.8 mS/cm for 12.5% of Sb. In practice, the mechanism to improve the ionic conductivity of solid electrolyte is complicated, which can be influenced by many factors and is not necessarily directly related to the lattice parameters [14,15]. The simplest argument is that with the substitution of a larger atom than the original atomic site (such as Sb here), the lithium diffusion pathway can be broadened, enhancing the overall ionic conductivity. In addition to the cell volume, other factors such as the existence of impurities, local modification of diffusion pathways and different microstructures can also affect the ionic conductivity of solid electrolytes.

The air stability of solid electrolytes is of great interest as it would give more flexibility in handling sulfide-based solid electrolytes, thus it is critical to promote a much more affordable mass production in industrial applications. Li$_{9.54}$Si$_{1.74}$(P$_{1-x}$Sb$_x$)$_{1.44}$S$_{11.7}$Cl$_{0.3}$ ($x = 0, 2.8, 5.5, 9.7$ and 12.5%) samples of different compositions were exposed to air at 35°C, 15% humidity for 1 h.
35 °C with 15% humidity for 1 h. XRD patterns of the samples were collected before (solid lines) and after (dots) the air exposure in Fig. 2. For comparison the XRD patterns were overlapped, which includes an expanded region in the 2θ range from 25° to 32° for further details (Fig. 2b). A close examination to the XRD data reveals that air exposure did not induce any significant changes in the XRD patterns with respect to the as-synthesized compounds for any compositions. No additional peaks or peak broadening have been observed, suggesting that samples did not suffer from severe decompositions and their structures remain unchanged.

The ionic conductivity values of the samples after air exposure were also evaluated and compared with the pristine one before the exposure in Fig. 3. The impedance complex plane of the different samples are depicted in Fig. 3a and 3b. The extracted ionic conductivity in Fig. 3c shows that most samples can retain more than 60% of their initial ionic conductivity after the air exposure. The air stability of pristine LSPS might be originated from the moisture stability of Si$_{1.74}$Cl$_{0.3}$, as indicated by the computational study [16]. In spite of the conductivity drop, it is worth mentioning that the conditions under which these air stability experiments (35 °C, 15% humidity) were carried out here are much harsher than those reported in literatures for other solid electrolytes with improved air stability [8,17]. Moreover, the conductivity is still high enough to allow the operation of a cell assembled from the air-exposed solid electrolyte. The increased ionic conductivity by Sb doping also gives additional flexibilities to accommodate the conductivity drop that is inevitable after the air exposure.

To further understand the electrochemical performance of the as-synthesized LS(Sb)PS, a solid-state battery was made with lithium metal as the anode and single crystal NMC811 as the cathode. It is known that sulfide solid electrolytes are not electrochemically stable with lithium metal. Direct contact with lithium metal can decompose sulfides and disable its electrochemical conductivity [18]. Here, a graphite film as a protection layer was added to separate LS(Sb)PS from lithium metal [10]. The cycling performance of batteries with Li/graphite-LS(Sb)PS-NMC811 is shown in Fig. 4. The pristine LS(Sb)PS shows a high capacity of 174.4 mAh/g and 92% retention after 30 cycles. In comparison, the LS(Sb)PS after 1-hour air exposure shows a slightly improved specific capacity of 182.4 mAh/g (Fig. 4a). X-ray photoelectron spectroscopy (XPS) measurements in Fig. 4d and 4e further show that after air exposure, P and S are only slightly oxidized in LS(Sb)PS at a similar level for varying Sb compositions.

After cycling with bare NMC811, the electrolyte shows a further oxidation in XPS Fig. 4d3 and 4e3. However, the batteries with 9.7% Sb doped LS(Sb)PS does not show detectable capacity fading with such decompositions, while the batteries with undoped LSPS does within 10 cycles (Fig. 4c). The battery performance and XPS measurement of LS(Sb)PS before and after air exposure first indicates that the electrolyte is a good candidate for solid-state batteries, and potentially suitable for a more manufacturing-friendly condition. The function of cathode interface decomposition is partly described in our previous work [3]. In comparison, the worse cycling performance of LSPS without Sb doping even before air exposure suggests that the faster degradation is most probably due to a worse interface electrochemical stability of LSPS than the Sb doped version. As indicated by the drop of voltage plateau in Fig. 4b, the stronger instability level between LSPS and lithium metal may play an important role, which includes but not limited to the interface decomposition energies [19].

4. Conclusion

A new sulfide solid electrolyte with the composition of Li$_{0.54}$Si$_{1.74}$Cl$_{0.3}$ is synthesized. It is found that the ionic conductivity of the sulfide is improved after Sb doping. The crystal structure of the solid electrolyte is maintained after exposing the powder in an environment with a high moisture of 15% relative humidity. The good battery performance of LS(Sb)PS before and after air exposure indicates that it is a promising solid electrolyte with functional air-stability for solid-state battery applications.
CRediT authorship contribution statement

Luhan Ye: Conceptualization, Methodology, Investigation, Writing – original draft. Eva Gil-González: Methodology, Investigation, Writing – original draft. Xin Li: Conceptualization, Writing - review & editing, Supervision.

Declaration of Competing 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.

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References


