Electrochemical stability and ionic conductivity of solid electrolytes based on Li$_{10}$GeP$_2$S$_{12-x}$A$_x$ (A=O, Se, x= 0, 0.2, 0.4, 0.6, 0.8, 1)

Shipai Song¹, Zongkai Yan¹, Fang Wu¹, Xiaokun Zhang¹ and Yong Xiang¹,*

¹School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu, 611731, China
*Corresponding author’s e-mail: xyg@uestc.edu.cn

Abstract. The compositions Li$_{10}$GeP$_2$S$_{12-x}$A$_x$ (A = O, Se) solid electrolytes were synthesized. As $x$ increases, the ionic conductivity of the Li$_{10}$GeP$_2$S$_{12}$ samples decreases from 2.8 mS/cm to 1.09 mS/cm. Li$_{10}$GeP$_2$S$_{11.8}$Se$_{0.2}$ has the highest ionic conductivity, 3.43 mS/cm, and the activation energy of 0.143 eV. The electrochemical stability is Li$_{10}$GeP$_2$S$_{11.6}$O$_{0.4}$ > Li$_{10}$GeP$_2$S$_{12}$ > Li$_{10}$GeP$_2$S$_{11.8}$Se$_{0.2}$, and the electrochemical window of Li$_{10}$GeP$_2$S$_{11.8}$O$_{0.4}$ is about 1.40 – 3.00 V. The difference in electrochemical properties of Li$_{10}$GeP$_2$S$_{12-x}$A$_x$ (A = O, Se) can be used as a way to improve the interface of Li$_{10}$GeP$_2$S$_{12}$-type solid batteries.

1. Introduction

Lithium-ion batteries are used in all aspects of our lives. However, because of using flammable organic electrolytes, there is a serious safety issue, especially for the large-format battery packs in EVs. Solid-state lithium-ion batteries with solid electrolytes are considered to completely solve the safety problems. The solid electrolyte needs to satisfy the following three conditions: ① ≥1 mS/cm high lithium ion conductivity and low electron conductivity; ② wide electrochemical working window; ③ good chemical compatibility between positive and negative electrodes [1-4].

Sulfur-based solid electrolytes have received extensive attention due to their relatively high ionic conductivity (≥ 1 mS/cm) and low grain boundary resistance [3-7]. Especially, Li$_{10}$GeP$_2$S$_{12}$ (LGPS) has a high ionic conductivity (12 mS/cm), and a wide electrochemical window (up to 5 V, vs. Li/Li$^+$) [5]. That is because the Li$_{10}$GeP$_2$S$_{12}$ solid electrolytes have a high number of lithium ions, and process a large migration tunnel for lithium ions. However, LGPS is not stable against Li metal, because of the reduction of Ge at the low voltage, resulting that LGPS decomposes [17,24]. The existing research mainly focuses on the replacement of Ge sites, and the cost of noble metal Ge is reduced by the doping substitution of Si and Sn [8-15,23]. Li$_{10}$SnP$_2$S$_{12}$ is highly electrochemically unstable at potentials lower than 1.5 V vs. Li/Li$^+$ [16]. The experimental electrochemical window of LGPS solid electrolyte is up to 5V [8-15]. However, the theoretical calculation of LGPS solid electrolyte is only 1.7-2.1 V [18-19], and the electrochemical stability is poor, which cannot coexist stably with lithium metal anode. The chemical bond energy of Ge/P-O is much stronger than that of Ge/P-S [8,23]. The results from first-principles calculations predict that LiMPO has higher redox stability than LiMPS, and the complete substitution of selenium will increase the conductivity of LGPS by a factor of two [8]. It has been reported that the addition of oxides for sulfide solid electrolytes have high electrochemical stability at low voltage [23-26,30-32,34-35], and the addition of seleniums could improve the ionic
conductivity [27-29]. However, there is no comparative report on the electrochemical window of O-doped and Se-doped for Li$_{10}$GeP$_2$S$_{12-x}$A$_x$ (A = O, Se) solid electrolyte. In this study, the compositions Li$_{10}$GeP$_2$S$_{12-x}$A$_x$ (A = O, Se, $x = 0$, 0.2, 0.4, 0.6, 0.8, 1.0) solid electrolytes which are the substitute products of oxygen or selenium for sulfur in the Li$_{10}$GeP$_2$S$_{12}$ structure were synthesized. The effects of ionic radius and anionic polarizability on the crystal structure, electrochemical stability, and ionic conductivity of Li$_{10}$GeP$_2$S$_{12}$-type solid electrolyte are investigated. The crystal structure of Li$_{10}$GeP$_2$S$_{12}$-type solid electrolyte are measured by X-ray powder diffraction (XRD). The effects of O and Se single doping on ionic conductivity, activation energy and electrochemical window are systematically compared by the electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV).

2. Experiment

2.1 The preparation of Li$_{10}$GeP$_2$S$_{12-x}$A$_x$

The preparation of Li$_{10}$GeP$_2$S$_{12-x}$A$_x$ samples was realized by traditional high temperature solid phase method. The raw materials are Li$_2$S (Alfa, 99.9%), GeS$_2$ (BT reagent, 99.99%), GeO$_2$ (BT reagent, 99.99%), GeSe$_2$ (BT reagent, 99.9%), and P$_2$S$_5$ (Aladdin, 99%). In the Argon-filled glove-box (GGP25D, Dellix, China), the above raw materials were weighed proportionally, and the mixtures were sealed in a stainless steel zirconium tank fitted with a zirconium ball, and followed by grounding in a planetary ball mill (Pulverisette 7, FRITSCH, Germany) for 3 hours at 600 rpm to obtain the powder. In the glove-box, the stainless-steel zirconium tank was opened and the mixtures were pressed into tablets at 400 MPa. The tablets were sealed in the quartz tube and vacuum sintered at 570 °C for 8 hours, in which the heating rate is 1.5 °C/min and the cooling rate is 1 °C/min [20-21].

2.2 X-ray diffraction test

The crystallinity of the Li$_{10}$GeP$_2$S$_{12-x}$A$_x$ samples were investigated by X-ray diffraction method (XRD, D8advance, Bruker, Germany) with CuKα radiation. The X-ray diffraction data was collected in a 0.02° step width over the 2θ range of 10° to 80°. The Li$_{10}$GeP$_2$S$_{12-x}$A$_x$ powders were placed in a grooved quartz grinder and sealed with a polyester film in a glove box to prevent the material from reacting to the oxygen and water in the air.

2.3 Electrochemical performance test

The ionic conductivity (σ) was calculated as following equation:

$$\sigma = \frac{d}{R \times A}$$

where $d$ is the thickness of the samples, $A$ is the effective area between electrode and electrolyte, and R is the electrolyte resistance of the samples that is determined by the value of Zre, when –Zim goes through in the electrochemical impedance spectra (EIS). The lithium-ion conductivity was achieved through EIS with applied frequencies in the 0.1 Hz-200 kHz range using a Princeton VersaSTAT 3F electrochemical analyzer. The electrochemical impedance spectroscopy (EIS) were tested through the two-electrode measurement system (stainless steel/Li$_{10}$GeP$_2$S$_{12-x}$A$_x$/stainless steel, SS), in which the solid electrolyte ceramic tablets were 18 mm in diameter and 1.5 mm in thickness, and SS (one piece with a diameter of 13 mm and another with a diameter of 16mm) were used as the blocking electrode. The electrochemical working windows were measured via cyclic voltammetry (CV) through the structure of Li/Li$_{10}$GeP$_2$S$_{12-x}$A$_x$/SS at the ranging from -0.5 V to 6 V with a scan rate of 10 mV/s.

3. Analysis and discussion

3.1 O doping

Figure 1 shows the XRD diffraction patterns of Li$_{10}$GeP$_2$S$_{12-x}$O$_x$ samples. It can be seen that the overall diffraction peak positions of the Li$_{10}$GeP$_2$S$_{12-x}$O$_x$ samples have not changed much, and the XRD peak
are shown as the Thio-LISICON II structure phase [12]. Compared with the characteristic peaks of the LGPS phase, the Li\textsubscript{10}Ge\textsubscript{3}P\textsubscript{12}S\textsubscript{12}O\textsubscript{x} samples appear impurity peaks due to Li\textsubscript{3}PO\textsubscript{4} near 22.5°, which is because according to the hard and soft acids and bases (HSAB) theory [22-23], oxygen is a hard base which reacts preferentially with hard bases, and the relatively small and non-polarizable P can be considered a hard acid. Therefore, most of the introduced oxygen atoms are contained in the PS\textsubscript{4} tetrahedra rather than the (Ge/P)S\textsubscript{4} and LiS\textsubscript{6} units [23-24]. In order to further confirm the O-doping into LGPS samples, the diffraction peaks near 29.7° are amplified. The diffraction peak around 29.7° obviously shift to the right with increasing \(x\), which indicates O substituting S are incorporated into the Li\textsubscript{10}Ge\textsubscript{3}P\textsubscript{12}S\textsubscript{12} crystal structure. [23-26]

Figure 1. XRD patterns of the Li\textsubscript{10}Ge\textsubscript{3}P\textsubscript{12}S\textsubscript{12}O\textsubscript{x} (\(x = 0, 0.2, 0.4, 0.6, 0.8, 1.0\)) samples. The magnified patterns around 29.7° are characteristic peaks for LGPS-type phases.

Figure 2 shows the Nyquist plots and the ionic conductivity of Li\textsubscript{10}Ge\textsubscript{3}P\textsubscript{12}S\textsubscript{12}O\textsubscript{x} samples at 25 °C. The ionic conductivity of the Li\textsubscript{10}Ge\textsubscript{3}P\textsubscript{12}S\textsubscript{12}O\textsubscript{x} samples decreases from 2.8 mS/cm to 1.09 mS/cm with increasing \(x\). This is mainly because the smaller radius O ions (\(r = 1.38 \text{ Å}\)) which is smaller than S (\(r = 1.84 \text{ Å}\)) incorporated into the crystal lattice narrow the ion diffusion channel. In addition, the electrostatic attraction between O atom and Li ion is much stronger than that between S atom and Li ion.

Figure 2. (a) The electrochemical impedance spectra and (b) the ionic conductivity of Li\textsubscript{10}Ge\textsubscript{3}P\textsubscript{12}S\textsubscript{12}O\textsubscript{x}.

The magnified patterns near the starting point are the impedance value of Li\textsubscript{10}Ge\textsubscript{3}P\textsubscript{12}S\textsubscript{12}O\textsubscript{x}.

3.2 Se doping

Figure 3 shows the XRD diffraction patterns of Li\textsubscript{10}Ge\textsubscript{3}P\textsubscript{12}S\textsubscript{12}Se\textsubscript{x} samples. The XRD peaks are shown as the Thio-LISICON II structure phase [29]. In order to further confirm the Se-doping into LGPS samples, the diffraction peaks near 29.7° are amplified. As \(x\) increased, the diffraction peaks around 29.7° obviously are shifted to the left, indicating that the crystal lattice is expanded which is result from a larger ionic radius of Se\textsuperscript{2-} ion (1.98 Å) than S\textsuperscript{2-} ion (1.84 Å) [28-30]. The XRD peak shift indicates Se substituting S are incorporated into the LGPS crystal structure.
Figure 3. XRD patterns of Li$_{10}$GeP$_2$S$_{12-x}$Se$_x$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) samples. The magnified patterns around 29.7° are characteristic peaks for LGPS-type phases.

Figure 4 shows the Nyquist plots and the ionic conductivity of Li$_{10}$GeP$_2$S$_{12-x}$Se$_x$ samples at 25 °C. The highest ionic conductivity of 3.43 mS/cm was achieved for Li$_{10}$GeP$_2$S$_{11.8}$Se$_{0.2}$. When $1 \geq x > 0.2$, the ionic conductivity decreases from 3.43 mS/cm to 1.32 mS/cm with increasing $x$. We know that doping causes lattice distortion, and the larger polarization characteristics of Se can reduce the ion migration energy. A small amount of Se incorporated into the crystal lattice can broaden the ion diffusion channel and increase ionic conductivity. However, many studies have shown that with increasing in the number of Se, the strong Raman peak at 421 cm$^{-1}$ attributed to the $PS_3^{3-}$ units decrease sharply, which indicate that excessive doping may damage the high conductive phase structure of $PS_3^{3-}$[20-22]. Therefore, with the change of Se doping, the ionic conductivity shows a trend of increasing first and then decreasing.

Figure 4. (a) The electrochemical impedance spectra and (b) the ionic conductivity of Li$_{10}$GeP$_2$S$_{12-x}$Se$_x$.

The magnified patterns near the starting point are the impedance value of Li$_{10}$GeP$_2$S$_{12-x}$Se$_x$.

The Arrhenius plots of Li$_{10}$GeP$_2$S$_{11.6}$O$_{0.4}$, Li$_{10}$GeP$_2$S$_{12}$ and Li$_{10}$GeP$_2$S$_{11.8}$Se$_{0.2}$ are displayed in Figure 5. Impedance spectra were collected at the temperature range of 25 °C to 125 °C in 25 °C increments for the Li$_{10}$GeP$_2$S$_{11.6}$O$_{0.4}$, Li$_{10}$GeP$_2$S$_{12}$ and Li$_{10}$GeP$_2$S$_{11.8}$Se$_{0.2}$ samples to assess the temperature dependence of conductivity. The ionic conductivity of the samples at various temperatures are shown in Figure 5. The temperature dependence of conductivity is found to follow an Arrhenius equation

$$\sigma_T = A \exp\left(-\frac{E_a}{kT}\right)$$

(2)

where $k$ is Boltzmann constant, $A$ is pre-exponential factor, and $E_a$ is the activation energy of the sample. The difference of the activation energy ($E_a$) of the three samples (Li$_{10}$GeP$_2$S$_{11.6}$O$_{0.4}$, Li$_{10}$GeP$_2$S$_{12}$, and Li$_{10}$GeP$_2$S$_{11.8}$Se$_{0.2}$) is not big, and the activation energy ($E_a$) of Li$_{10}$GeP$_2$S$_{11.8}$Se$_{0.2}$ reached a minimum value of 0.143 eV. All of them are the fast-ionic conductor.
Figure 5. The temperature dependence of the ionic conductivity of Li$_{10}$GeP$_2$S$_{11.6}$O$_{0.4}$, Li$_{10}$GeP$_2$S$_{12}$ and Li$_{10}$GeP$_2$S$_{11.8}$Se$_{0.2}$ at various temperatures.

Figure 6 shows the current-voltage curves for Li$_{10}$GeP$_2$S$_{11.6}$O$_{0.4}$, Li$_{10}$GeP$_2$S$_{12}$, and Li$_{10}$GeP$_2$S$_{11.8}$Se$_{0.2}$. No significant current change were observed when the voltage was as high as 5 V. To further confirm the electrochemical window, the curves in the range of -4 $\mu$A to 4 $\mu$A are magnified. It can be seen that the electrochemical stability is Li$_{10}$GeP$_2$S$_{11.6}$O$_{0.4}$ $>$ Li$_{10}$GeP$_2$S$_{12}$ $>$ Li$_{10}$GeP$_2$S$_{11.8}$Se$_{0.2}$, and the electrochemical window of Li$_{10}$GeP$_2$S$_{11.6}$O$_{0.4}$ is about 1.40 – 3.00 V. The electrochemical window experiment result of Li$_{10}$GeP$_2$S$_{12}$ is 1.45 – 2.85 V, which is close to the theoretical calculation result (1.0 – 3.0 V, vs. Li/Li$^+$) [19,30]. This is mainly because the bonding strength between the oxygen and lithium ions is the largest among them (the oxygen and lithium ions, the sulfur and lithium ions, the selenium and lithium ions), resulting that the Li atoms could be pulled close to the electrolyte structure [19,23-25,30]. In addition, much work so far has indicated that the way to the addition of oxides to sulfide solid electrolytes could improve their stability to the moisture [3,31-35].

4. Conclusion
In this study, the compositions Li$_{10}$GeP$_2$S$_{12-x}$A$_x$ (A = O, Se. x = 0, 0.2, 0.4, 0.6, 0.8, 1.0) solid electrolytes which are the substitute products of oxygen or selenium for sulfur in the Li$_{10}$GeP$_2$S$_{12}$ structure were synthesized. The ionic conductivity of the Li$_{10}$GeP$_2$S$_{12-x}$O$_x$ samples decreases from 2.8 mS/cm to 1.09 mS/cm with increasing x. The highest ionic conductivity of 3.43 mS/cm was achieved for Li$_{10}$GeP$_2$S$_{11.8}$Se$_0.2$. When 1 $\geq$ x > 0.2, the ionic conductivity decreases from 3.43 mS/cm to 1.32 mS/cm with increasing x. Doping to improve material properties is generally a very small amount of doping, and excessive doping may damage the high conductive phase structure of the raw material. The electrochemical stability is Li$_{10}$GeP$_2$S$_{11.6}$O$_{0.4}$ $>$ Li$_{10}$GeP$_2$S$_{12}$ $>$ Li$_{10}$GeP$_2$S$_{11.8}$Se$_{0.2}$, and the electrochemical window of Li$_{10}$GeP$_2$S$_{11.6}$O$_{0.4}$ is about 1.40 – 3.00 V. Due to the change of anion radius and interaction force with Li ion, the trend of the conductivity and electrochemical stability are observed. The difference in electrochemical properties of Li$_{10}$GeP$_2$S$_{12-x}$A$_x$ (A = O, Se) can be used as a way to improve the interface of Li$_{10}$GeP$_2$S$_{12}$-type solid batteries.
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