論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Synthesis of crystalline lithium ion conductors based on the Li-Ge-P-S-O and Li-Sn-Si-P-S systems: phase relationships, structures and electrochemical properties
著者(和文)	SunYulong
Author(English)	Yulong Sun
出典(和文)	学位:博士（理学）, 学位授与機関:東京工業大学, 報告番号:甲第10296号, 授与年月日:2016年9月20日, 学位の種別:課程博士, 審査員:菅野 了次,平山 雅章,原 正彦,川路 均,松下 伸広,中村 二朗
Citation(English)	Degree:, Conferring organization: Tokyo Institute of Technology, Report number:甲第10296号, Conferred date:2016/9/20, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

博士論文要約

論文題目

Synthesis of crystalline lithium ion conductors based on the Li-Ge-P-S-O and Li-Sn-Si-P-S systems: phase relationships, structures and electrochemical properties

物質電子化学専攻　菅野・平山研究室

13D53065　Yulong Sun

1. Introduction

All-solid-state systems with solid electrolytes are potential candidates for next generation batteries and are expected to provide a high power and energy density with reliable and improved safety characteristics. Sulfide-based lithium ion conductors have the advantages of high conductivities together with suitable electrochemical windows and mechanical properties; thus, they are intensively studied as promising solid electrolytes. Especially, $Li_{10}GeP_2S_{12}$ (LGPS) shows high ionic conductivity comparable to the conventional organic liquid electrolytes. However, There are two disadvantages for LGPS. (1) LGPS is not stable against Li metal, which provides the highest battery voltage, because it decomposes at the low voltage. (2) Ge is a relatively expensive element and could limit the widespread use of LGPS materials. Therefore, in order to realize the high energy all-solid-state battery, searching new solid electrolytes is significant, especially for those solid electrolytes with high ionic conductivity, high electrochemical stability and low cost.

In this thesis, material searches based on quasi-ternary phase diagram in Li_2S-MS_2-P_2S_5 system (M=Si, Sn) are carried out. As the beginning point of this study, original LGPS composition is focused. Using the high ionic conductive property and structure of LGPS, enhancement of electrochemical stability is demonstrated by partial oxygen substitution for sulfur; $Li_{10}GeP_2S_{1-x}O_x$. Given that the chemical bonds between Ge/P–O are stronger than those of Ge/P–S, oxygen substitution would be expected to enhance thermodynamic stability. In addition, in term of cost, ion conductors constructed by cheap and earth-abundant elements might be promising as solid electrolytes for practical application. Therefore, Li_4MS_4-Li_3PS_4 tie line is examined as following composition of $Li_{10+\delta}[Sn_ySi_{1-y}]_{1+\delta}P_{2-\delta}S_{12}$, which could provide LGPS type solid solution. Finally, unexplored region in the phase diagram, deviated from the tie line, is investigated with a composition of $(Li_{3.45+\beta-4\alpha}Sn_\alpha)(Si_{0.36}Sn_{0.09})(P_{0.55-\beta}Si_\beta)S_4$. The structures, electrochemical properties and phase relationship of obtained crystalline lithium ion conductors in in the Li-Ge-P-S-O and Li-Sn-Si-P-S systems were also investigated.

2. Experimental

Crystalline ion conductors in Li-Ge-P-S-O and Li-Sn-Si-P-S systems were synthesized by solid-state reactions. Powder samples were subjected to X-ray diffraction (CuKα) and synchrotron X-ray diffraction for phase identification and structural analysis. Synchrotron X-ray diffraction data was analyzed by Rietveld refinement method using RIETAN-FP programs. The ionic conductivity was measured by the AC impedance method with an applied voltage of 20 mV and a frequency range from 10 Hz to 15 MHz using frequency response analyzers (NF Corp. FRA5097 and Solartron 1260). The electrochemical stability was evaluated by cyclic voltammetry on Li/solid electrolytes/Au cells at a scan rate of 1 mV s^{-1} between −0.5 and 5 V using a Solartron 1287 electrochemical interface. All-solid-state batteries were fabricated using the prepared solid electrolytes, $LiNbO_3$-coated $LiCoO_2$ cathode and In-Li alloy/Li metal anode under an Ar atmosphere. The electrochemical properties of the cells were evaluated using a TOSCAT-3100 (Toyo system).

3. Oxygen substitution effects in $Li_{10}GeP_2S_{12}$ solid electrolyte

For the lithium super-ionic conductor $Li_{10}GeP_2S_{12}$, the partial substitution of sulfur by oxygen is achieved *via* a solid-state reaction. The solid-solution range of oxygen is found to be $0 \leq x < 0.9$ in $Li_{10}GeP_2S_{12-x}O_x$. Structure refinements using synchrotron X-ray diffraction data confirm the preference for oxygen substitution in the PS_4 tetrahedra. The local structural change in the $P(S/O)_4$ tetrahedra upon substitution is also indicated by Raman spectroscopy. High ionic conductivities are maintained even after the oxygen substitution in $Li_{10}GeP_2S_{12}$; the ionic conductivity of $Li_{10}GeP_2S_{12-x}O_x$ ($0.3 \leq x \leq 0.6$) ranges from 1.03×10^{-2} to 8.43×10^{-3} S cm^{-1} at 298 K. No redox current is observed by cyclic voltammetry from nearly 0 to 10 V versus Li/Li^+ except for that due to the lithium deposition/dissolution reactions. All-solid-state batteries using $Li_{10}GeP_2S_{12-x}O_x$ (x = 0.3 and 0.6) as solid electrolytes with Li metal anodes show discharge capacities exceeding 100 mAh g^{-1} and better cycling performance compared to batteries using the original $Li_{10}GeP_2S_{12}$. The partial substitution of oxygen for sulfur in $Li_{10}GeP_2S_{12}$ affords a novel solid electrolyte, $Li_{10}GeP_2S_{12-x}O_x$, with high conductive properties and electrochemical stability.

4. Superionic conductors: $Li_{10+\delta}[Sn_ySi_{1-y}]_{1+\delta}P_{2-\delta}S_{12}$ with a $Li_{10}GeP_2S_{12}$-type structure in the Li_3PS_4-Li_4SnS_4-Li_4SiS_4 quasi-ternary system

Solid solutions of Sn-Si derivatives with the LGPS-type structure were synthesized by a solid-state reaction in the Li_3PS_4-Li_4SnS_4-Li_4SiS_4 quasi-ternary system. The monophasic region of the LGPS-type structure deviated from the tie line between $Li_{10}SiP_2S_{12}$ and $Li_{10}SnP_2S_{12}$, and the composition of the solid solution was determined to be $-0.1 \leq \delta \leq 0.5$

and $0 \le y \le 1.0$ in $Li_{10+\delta}[Sn_ySi_{1-y}]_{1+\delta}P_{2-\delta}S_{12}$ ($0.50 \le x \le 0.7$ and $0 \le y \le 1.0$ in $Li_{4-x}[Sn_ySi_{1-y}]_{1-x}P_xS_4$). The solid solution was formed by a double substitution that changed the Sn/Si ratio and the M^{4+} (Sn^{4+} and Si^{4+})/P^{5+} ratio, which adjusted the sizes of the lithium conduction tunnels and the lithium concentration, and contributed to the optimal conductivity value. The highest ionic conductivity value of 1.1×10^{-2} S cm^{-1} was achieved for the composition of $Li_{10.35}[Sn_{0.27}Si_{1.08}]P_{1.65}S_{12}$ ($Li_{3.45}[Sn_{0.09}Si_{0.36}]P_{0.55}S_4$) at 298 K, which is close to the value for the original LGPS compound (1.2×10^{-2} S cm^{-1}). The Ge-free solid electrolyte could be suitable for practical applications in all-solid-state batteries.

5. Phase relationship in the Li_2S-SnS_2-SiS_2-P_2S_5 system

Crystalline lithium ionic conductors were explored in the Li_2S-SnS_2-SiS_2-P_2S_5 system. LGPS-type phase, $Li_{3.25}Sn_{0.19}Si_{0.56}P_{0.35}S_4$, deviating conventional $Li_{4-x}M_{1-x}PS_4$ (M = Si, Ge, Sn) formula and argyrodite phases and $Li_{3.14}[Sn_{0.74}Si]P_{0.38}S_6$ were discovered. Interestingly, the compositions of $Li_{3.14}[Sn_{0.74}Si]P_{0.38}S_6$ far deviateed from the conventional Li_7PS_6 argyrodite, and the $Li_{3.14}[Sn_{0.74}Si]P_{0.38}S_6$ argyrodite was stable at room temperature.

6. Summary

The results and conclusions of this work are summarized as follows.

1) The partial oxygen substitution for sulfur in $Li_{10}GeP_2S_{12}$ affords a novel solid electrolyte, $Li_{10}GeP_2S_{12-x}O_x$, with high conductive properties and electrochemical stability.
2) Through finely changing the Sn/Si ratio to adjust the sizes of the lithium conduction tunnels and the lithium concentration to the optimal values, the highest ionic conductivity of 1.1×10^{-2} S cm^{-1} was achieved in $Li_{10+\delta}[SnySi_{1-y}]_{1+\delta}P_{2-\delta}S_{12}$.
3) LGPS-type phase deviating conventional $Li_{4-x}M_{1-x}PS_4$ (M = Si, Ge, Sn) formula and argyrodite phases were discovered in the Li-Sn-Si-P-S system.

Material search based on LGPS structure and the quasi-ternary phase diagram in Li_2S-MS_2-P_2S_5 system (M=Si, Sn) provided novel materials with various structure, composition and electrochemical properties. Detailed tuning of the composition, which contribute to ionic conductivity and electrochemical stability, for the developed materials is expected to achieve solid-electrolyte materials for practical use in the all-solid-state battery system.