First principle analysis of electrochemical stability of $Li_{10}GeP_2S_{12}$.

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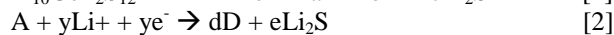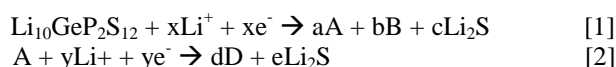
Introduction

All-solid-state lithium-ion batteries are expected to be one of next-generation energy devices because of its high energy density and non-flammability. Solid electrolytes are key materials of the solid-state batteries and required to have high ionic conductivity and electrochemical stability. $Li_{10}GeP_2S_{12}$ (LGPS), which exhibits a conductivity of 12 mS cm^{-1} at room temperature, is one of the promising solid electrolytes[1]. However, it has been reported that a solid electrolyte including Ge $(Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3)$ arises an irreversible reduction current at the 1st cycle[2]. In this study, we investigated the electrochemical stability of LGPS under the anodic environment from both experimental and theoretical aspects.
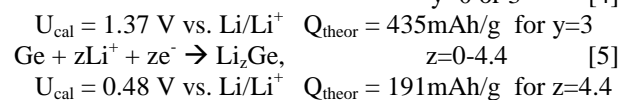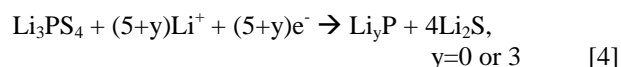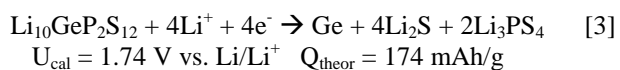
Method

Galvanostatic measurement for LGPS mixed with conductive agent was performed at a current density of 0.01 mA cm^{-2} to investigate the reduction potentials and capacities. Li-In alloy was used as a reference and a counter electrode. The samples before and after the measurement were analyzed by STEM, XAFS, XRD, and TEM-EELS. Theoretical reduction potentials were calculated by the DFT to specify the reduction reaction formulae. Furthermore, the intermediates at early process of the reaction were also discussed by DFT calculation to consider the reaction mechanism.

Results and discussion

From the galvanostatic analysis, the reduction currents were observed at the potentials of around 0.8 and 0.4 V vs. Li/Li$^+$ as plateaus. The STEM images showed the structural changes of LGPS near the conductive agent after the measurement. This result implied decomposition of LGPS. Li concentration at decomposed area of LGPS was high compared to that at non-decomposed area from TEM-EELS analysis. The formation of Li_2S was determined by XRD measurement. The XANES spectrum indicated the reduction of Ge. Based on these results, the reduction reaction formulae were assumed as follows.

$$Li_{10}GeP_2S_{12} + xLi^+ + xe^- \rightarrow aA + bB + cLi_2S \quad [1]$$
$$A + yLi+ + ye^- \rightarrow dD + eLi_2S \quad [2]$$

We supposed some candidates of the decomposition products; A, B, and D. Their reduction potentials were calculated by the DFT. Reaction products were determined by the comparing the calculated reduction potentials (U_{cal}) and their theoretical capacity (Q_{theor}) to experimental reduction potentials and capacity. The experimental potentials were determined by open circuit voltage (OCV) to exclude the overpotentials. As a result of evaluating fifteen electrochemical reaction formulae, it was identified that the following reactions occur at the LGPS/conductive agent interface.

$$Li_{10}GeP_2S_{12} + 4Li^+ + 4e^- \rightarrow Ge + 4Li_2S + 2Li_3PS_4 \quad [3]$$
$$U_{cal} = 1.74 \text{ V vs. Li/Li}^+ \quad Q_{theor} = 174 \text{ mAh/g}$$

$$Li_3PS_4 + (5+y)Li^+ + (5+y)e^- \rightarrow Li_yP + 4Li_2S,$$
$$y=0 \text{ or } 3 \quad [4]$$
$$U_{cal} = 1.37 \text{ V vs. Li/Li}^+ \quad Q_{theor} = 435\text{mAh/g} \text{ for } y=3$$
$$Ge + zLi^+ + ze^- \rightarrow Li_zGe, \quad z=0\text{-}4.4 \quad [5]$$
$$U_{cal} = 0.48 \text{ V vs. Li/Li}^+ \quad Q_{theor} = 191\text{mAh/g} \text{ for } z=4.4$$

These results were consistent with experimental ones. The first potential plateau at 0.8 V corresponds to the reaction [3] because the OCV of the first plateau (1.71 V) is close to the calculated reduction potential. The second plateau at 0.4 V corresponds to the mixture of reactions [4] and [5]. Reduction of P in formula [4] was also confirmed as the chemical shift in the XANES spectrum.

The intermediates of the reaction [3] were investigated by DFT calculation to clarify the structural changes of reduction process. LGPS has many lithium-ion sites and Li concentration was increased after galvanostatic measurement as mentioned above. Therefore, Li-excess structure is possibly the intermediate of LGPS. Thus the early process of the reduction was assumed as follows.

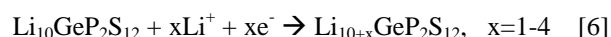$$Li_{10}GeP_2S_{12} + xLi^+ + xe^- \rightarrow Li_{10+x}GeP_2S_{12}, \quad x=1\text{-}4 \quad [6]$$

Figure 1 shows the relationship between the calculated potential and the energy changes of Li-excess structures. The equilibrium potentials of Li-excess structures, $Li_{11}GeP_2S_{12}$, $Li_{12}GeP_2S_{12}$, $Li_{13}GeP_2S_{12}$, and $Li_{14}GeP_2S_{12}$ were 1.26, 1.22, 1.05, and 0.35 V vs. Li/Li$^+$ respectively. The experimental reduction potential of the first plateau was around 0.8 V vs. Li/Li$^+$ due to mainly reaction overpotential though the equilibrium potential of decomposition reaction [3] is 1.74 V vs. Li/Li$^+$. We suppose that the reaction overpotentials of reaction [6] are low, compared to that of the reaction [3], because their structures hardly change. It was found that the charges of Ge atoms neighboring excess-Li were reduced and the Ge-S bonds were stretched in the structures. Thus it was suggested that Li-excess structures ($Li_{11}GeP_2S_{12}$, $Li_{12}GeP_2S_{12}$, and $Li_{13}GeP_2S_{12}$) were formed before decomposition of LGPS and Ge was reduced by excess-Li existence.
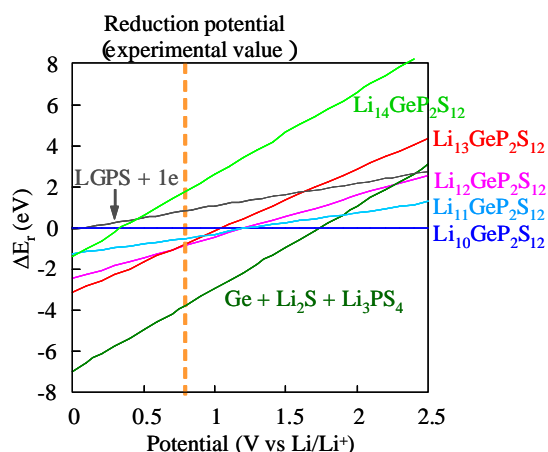

Figure 1. Relationship between the calculated potential and the energy changes of Li-excess structures, decomposition products of reaction [3], and reductant of LGPS without excess-Li from LGPS ($Li_{10}GeP_2S_{12}$).

References
1. N. Kayama, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, and A. Mitsui, *Nature materials*, **10(9)**, 682 (2011).
2. J. K. Feng, L. Lu, and M. O. Lai, *J. Alloys and Compounds*, **501**, 255 (2010).