Analysis of Lithium-Ion Conduction in LISICON-based Solid Electrolytes by First-Principles Molecular Dynamics Simulation

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Toward the development of next-generation all solid rechargeable batteries, it is essential to further improve ionic conductivity of solid electrolytes. LISICON is a solid solution system of Li2+2 GeO4 (0≤x≤1) and is one of the classical Li+ ion conductors. This system has relatively high ionic conductivity among oxide compounds. The crystal structure of γ-Li2+xZn1-xGeO4 (x=0.5) is shown in Figure 1. Oxide ions are arrayed as distorted hexagonal close packing. Cations occupy one-half of tetrahedral sites. Excess Li+ ions partially occupy interstitial octahedral sites when x changes from 0 to 1. There are γ, β and Li2+2 GeO4-phase as crystalline polymorphs depending on temperature and composition. Difference among these polymorphs is characterized by a direction of the apexes of a GeO4 tetrahedron. The γ-form was reported as low-temperature phase for Li1+xZn0.5GeO4 (x=0.5) and Li1+xZn2-xGeO4 (x=0.75) [3,4]. The ionic conductivity increases significantly with increasing x. The solid solutions for x = 0.25, 0.50 and 0.75 have 0.009, 0.059 and 0.235 S cm-1 at 400°C, respectively. It is supposed that high ionic conductivities of the LISICON systems are attributed to the number of Li+ ions. In this work, diffusion behavior of Li+ ions in LISICON-based ionic conductors was studied by first principles molecular dynamics (FPMD) simulations.

All calculations in this work were performed using the projector augmented wave method with generalized gradient approximation as implemented in the VASP code. The FPMD simulations were performed within NVT ensemble. The volume and shape of the cell were fixed during the FPMD simulation. We adopted a crystal structure of γ-form as our simulation models. Simulation cells are composed of Li1+xZn0.5GeO4 and Li2+2 GeO4 (2×1×2 expansion of the γ-type unit cell). The time step was chosen to be 2 fs. The FPMD simulations were performed for 12500 steps, i.e. 25 ps. Initial 5 ps are removed from the analysis as thermal equilibration time.

Figure 2 shows the computational diffusion coefficients of Li+ ions for Li1+xZn0.5GeO4 and Li1+xGeO4 based on the Nernst-Einstein equation. The computational diffusion coefficients are twice as large as the experimental values of both Li-Zn-Ge-O and Li-Ge-P-S. The reason of this difference may be grain boundary resistivity effects included in experimental measurement. However, the calculated activation energy for Li1+xZn0.5GeO4, 0.34 eV, is in good agreement with the experimental one, 0.31 eV. The comparable result is shown for Li-Ge-P-S. Moreover, ratios between the diffusion coefficients of Li-Ge-P-S and Li-Zn-Ge-O were almost reproduced. These results imply that the model in the FPMD simulation can represent the ionic conduction mechanism in the actual compounds.

From analysis of trajectory for Li+ ions in the FPMD simulation, we found Li+ ion diffusion via an interstitialcy mechanism. In this mechanism, excess Li+ ion at an octahedral site jumps to a tetrahedral site and the Li+ ion at the tetrahedral site simultaneously jumps to another octahedral site. We also found that Li+ ions diffuse via the octahedral sites sharing an edge with a GeO4 tetrahedron. Calculated diffusion coefficients for γ-Li1+xZn1-xGeO4 (0≤x≤1) at 1600 K are shown in Figure 3. The diffusion coefficients increase with increasing the number of excess Li+ ions at interstitial octahedral sites. This result is in agreement with the experimental trend and is consistent with the interstitialcy mechanism caused by excess Li+ ions.