Ab Initio Molecular Dynamics Study of Garnet-Type Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$ (0≤x≤2)

Randy Jalem[1], Masanobu Nakayama[1,2,3], Toshihiro Kasuga[4], Kiyoshi Kanamura[5]

[1]Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso, Showa, Nagoya, Aichi 466-8555, Japan

[2]Japan Science and Technology Agency, PRESTO, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

[3]Unit of Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Katsura, Saikyo-ku, Kyoto, 615-8520, Japan

[4]Department of Frontier Materials, Nagoya Institute of Technology, Gokiso, Showa, Nagoya, Aichi 466-8555, Japan

[5]Department of Applied Chemistry, Tokyo Metropolitan University, 1-1 minami Oosawa, Hachioji, Tokyo 192-0397, Japan

Introduction

The recent surge in research related to developing and optimizing solid electrolytes has been catalyzed by the increasing demand for new generation of Li ion batteries with no toxic and combustible components. This study investigates by *ab initio* molecular dynamics (MD) calculation the Li ionic conduction property of one of the most promising group of materials up to date, the garnet-type cubic Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_2$O$_{12}$ (0≤x≤2), in order to gain crucial insights for chemical design and optimization that would eventually lead towards large scale application.

Computational details

First principles calculations were carried out within the density functional theory (DFT) framework as implemented in Vienna Ab Initio Simulation Package (VASP). Parametrization of the exchange correlation energy was made using generalized gradient approximation by Perdew–Burke–Ernzernhof for solids (GGA-PBEsol). Several compositions were considered which were based primarily on varying Zr/Ta within the Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$ composition: x = 0, 0.5, 0.75, 1.25, 1.5, and 2. The lattice parameter was first optimized by a random sampling approach of Li/Li vacancy and Zr/Ta arrangements before carrying out constant NVT MD runs at T = 873 K, 1073 K, 1273 K, 1473 K, and 1773 K.

Results and discussion

Figure 1a shows the cubic LLZO structure with the Wyckoff positions of atoms and connectivity of Li sites (dashed lines) forming a 3D conduction pathway. Fig. 1b displays the result from structural optimization of several Li/Li vacancy configurations in the cubic Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$ composition. In here, the calculated values are systematically lower than the experimental ones but with only < 1% difference and thus, are considered to be negligibly small to have any significant impact on the outcome of MD sampling run. The incremental substitution on Zr sites by Ta atoms leads to Li vacancies following the charge neutrality requirement. Strong agreement with literature data is also observed in the present calculation.
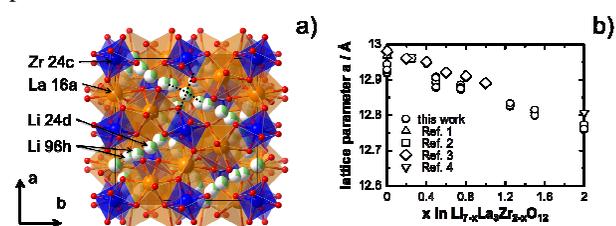

Figure 1. a) Crystal structure of cubic Li$_7$La$_3$Zr$_2$O$_{12}$. b) Optimized lattice parameters of cubic Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$. Experimental data are included for comparison.

Fig. 2a shows the Arrhenius plot for end members Li$_{7-x}$La$_3$Zr$_2$O$_{12}$ (LLZO) and Li$_5$La$_3$Ta$_2$O$_{12}$ (LLTO). At 300 K, the estimated bulk Li ionic conductivities are 1.06 x 10^{-4} and 1.63 x 10^{-3} S / cm with activation barrier energies of 0.33 and 0.26 eV, respectively. The calculated values for LLZO agree well with experiments. However, a surprising result is noted for LLTO, wherein the experimental value is lower by three orders of magnitude. Two possible reasons may explain this dramatic difference: i) a high temperature Li conduction process exists in cubic LLTO or ii) the severe effect of Al contamination in LLTO found in experiments which is not accounted the present MD calculation. This opens up new strategies for optimizing LLTO during experiments. Figure 2b shows the average Li site occupancy for the two materials. In here, Li ions in LLZO prefer 48g/96h sites more than the 24d sites. A slight preference for 24d is seen in LLTO.
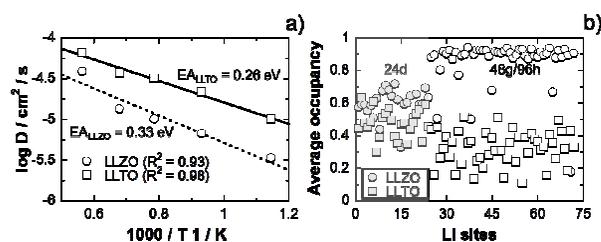

Figure 2. a) Arrhenius plots calculated from calculated diffusion coefficients at different temperatures and b) average Li site occupancy collected over 30 ps of MD run for LLZO and LLTO, respectively.

Fig. 3a shows the evolution of mean square displacement (MSD) plots at different at 1273 K. As x increases, Li ion diffusion coefficient also increases. For the occupancy at the two distinct Li sites, it is visible in Fig. 3b that 48g/96h site decreases linearly while 24d site decreases in an almost monotonic-like manner. These site relationships are strongly linked to the trend of the diffusion property in Fig. 3a.
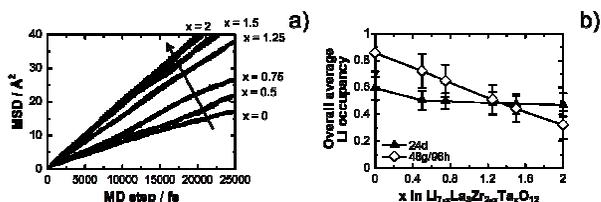

Figure 3. a) Evolution of the mean square displacement (MSD) plot with respect to x in Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$. b) Variation in Li site occupancy at different values of x.

Conclusions

The Li ion conduction property in cubic Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$ was successfully investigated by *ab initio* MD calculation. Good agreement with experimental results was determined for LLZO while interesting new observations are revealed for LLTO. The findings here offer useful insights for use during design and optimization of these solid electrolyte materials.

References

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