Density Functional Theory Studies on Li Metal Electrode/Garnet-Type Li$_7$La$_3$Zr$_2$O$_{12}$ Solid Electrolyte Interfaces for Application in All-Solid-State Batteries

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Garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ) and its analogs are considered potential candidates as solid electrolytes for all-solid-state Li metal batteries because their fast Li-ion conductivity and chemical stability against Li metal anodes result in both safe and large energy densities. To date, several computational and experimental studies have been performed to obtain a more detailed understanding of the nonreactivity of garnet-type LLZ with Li metal and related phenomena. Herein, first-principles calculations based on the density functional theory approach are performed for Li metal/LLZ interfaces to elucidate the electronic and atomistic level aspects. It is confirmed that the valence band maximum and the conduction band minimum for the LLZ phase do not cross the Fermi level corresponding to the Li 2s band. In addition, it is found that the defect formation energies associated with both Li vacancy formation and interstitial Li formation are largely reduced. In particular, the formation energy associated with interstitial Li sites, i.e., Li$^+$ insertion into the LLZ phase, is negative, indicating that spontaneous Li insertion is likely to proceed in the vicinity of the Li/LLZ interface. This new suggestion may help further elucidation of the reported interfacial behavior.

1. Introduction

The development of fast Li-ion conductive oxides is vital owing to their practical application as solid electrolytes for all-solid-state Li metal batteries. In this context, the use of solid electrolytes is expected to solve the safety concerns arising from flammable conventional liquid electrolytes, particularly in large-scale usage, such as in the power sources of electric vehicles.[11–13] In addition, a large increase in capacity can be achieved by adopting a Li metal anode,[14] on the condition that the solid electrolytes do not react with the Li metal and that they can suppress dendrite growth.

To date, various inorganic Li-ion conductive materials,[15–27] including nitrides,[28] sulfides,[29–32] halogenides,[33–35] and oxides,[36] have been investigated to replace conventional liquid electrolytes. Among them, oxide-based Li-ion conductors are advantageous because of their nonflammable nature, good chemical stability, and mechanical strength. Although several oxide-based compounds, such as β-alumina-type,[37] LISICON,[38,39] NASICON[40–44] perovskite-type,[45,46] and garnet-type oxides,[47,48] possess fast ionic conductivities, the majority of these compounds react with Li metal.

Since the first report by Murugan et al. in 2007,[49] garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ) compounds have gained increasing attention due to their fast Li-ion conductivity (i.e., $>10^{-4}$ S cm$^{-1}$ at room temperature) and their nonreactivity with molten Li metal.

In recent years, such nonreactivity with Li metal has been investigated both experimentally and computationally.

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DOI: 10.1002/pssb.202100546
For example, our previously reported density functional theory (DFT) calculations\cite{29} indicated that the stability of garnet-type oxides against Li metal is largely dependent on the choice of cation occupying the octahedral site. In addition, the structural features of the isolated octahedron, i.e., ZrO$_6$, were found to be important in determining the stability due to the suppressed hybridization between Zr 4d orbitals.\cite{29} Furthermore, electron energy loss spectroscopy studies have shown that a phase transition from the cubic to the tetragonal LLZ phase takes place in the vicinity of the Li metal/LLZ phase, which results in a high interfacial resistance for the tetragonal LLZ interlayer.\cite{30} Moreover, partial reduction of the Zr ions in the vicinity of the interface has been suggested by Zhu et al.\cite{31} Recently, DFT and structural optimization studies on the Li metal/LLZ interface have been performed by Bo et al.,\cite{32} who confirmed that undercoordinated Zr ions exist around the interfacial region. These undercoordinated Zr ions are reduced upon contact with Li metal, which leads to an unstable Li/Llz interface. During these studies, the wettability of Li on the LLZ was found to be strongly dependent on the termination structures.

Thus, we herein report our computation of 132 Li metal/LLZ interfaces to elucidate the relationship between the electrochemical stability and the interfacial structure. In addition, the electronic structures and the formation energies of vacancies and interstitial defects are computed for the most stable interface model.

2. Results and Discussion

We selected 3 and 89 surface models for the Li metal and LLZ species, respectively, and 132 interface models were computed by considering the total number of atoms (>300 atoms), preservation of the stoichiometry of LLZ, and the periodic boundary conditions (PBCs). More specifically, the LLZ phase consists of 8 formula units of Li$_5$La$_3$Zr$_2$O$_{12}$ (i.e., Li$_{56}$La$_{27}$Zr$_{16}$O$_{96}$), while the Li metal phase consists of 102 or 104 Li atoms for all computed interface models. The slab thickness of Li ranges from 10 to 15 Å, while that of LLZ ranges from 12 to 18 Å. It should be noted here that only the Li(001)/LLZ(001) and Li(111)/LLZ(111) interfaces were considered in this study because of the PBC restrictions within the limitation of the total number of atoms in the model. However, the selection of surface termination and in-plane translational operations resulted in a large variety of surface models. Figure 1a presents the variation in the formation energies for the 132 interface models between LLZ and Li metal obtained according to Equation (3) in the Computational Section. As can be seen, the interfacial energy was widely scattered from ~0.02 to 0.54 eV Å$^{-2}$ to ensure that the surface wettability was largely dependent on the surface structure. Figure 1b shows the dependence of the interface formation energy on the selection of the Li(001)/LLZ(001) or Li(111)/LLZ(111) models. The obtained results show no significant difference between the two models, thereby indicating that the local arrangement of ions at the interface may affect the interface formation energy. Figure S1, Supporting Information, displays the adhesion energies calculated by Equation (4), Computational Section, for selected interface models as a function of the interface formation energy. The adhesion energy changes from negative to positive (i.e., ~$-0.15 < W_{ad} < 0.15$ eV Å$^{-2}$) upon increasing the interface formation energy, which was comparable to previously reported values.\cite{32} Thus, both adhesion and exfoliation of the Li metal to and from the LLZ surface are possible depending on the interfacial local structure. As reported by Basappa et al.\cite{33} and Motoyama et al.\cite{34} the Li/LLZ contact critically affects the battery performance, including the charge-discharge kinetics and capacity, thereby indicating that an optimized design of the contact surface may improve the battery performance.

To identify the dominant factors affecting the interface formation energy between Li metal and LLZ, machine learning (ML) regression analysis was performed using structure descriptors, differential histograms of the radial distribution function (RDF), the angular distribution function (ADF), and Voronoi tessellation-derived features, as reported in a previous study.\cite{35} The root mean square errors (RMSEs) were also obtained using eight ML regression algorithms, namely, the partial least squares (PLS) regression, ridge regression, the least absolute shrinkage and selection operator (LASSO), elastic-net regression, linear support vector regression (SVR), kernel SVR, random forest regression, and gradient boosting regression (GBR).\cite{36} In this study, 80% of the dataset was randomly selected for training.
that distortion of the ZrO$_6$ octahedron at the interface causes an
structure appeared to be more signif-
 affects the interface energy (i.e., $\approx$0.04 eV Å$^{-2}$) for the test data, which is significantly smaller than the variation in the interface formation energies (i.e., $\approx$0.04–0.55 eV Å$^{-2}$). Thus, the fitted function using differential histogram descriptors has sufficient predictive power for determining the interface formation energy of the arbitrary interface model, and this approach should be generally applicable to the other solid–solid interface models.

In addition, feature importance analysis indicated that the differential histogram of the ADF-derived descriptors, in particular, those including Zr ions in the bond angle, largely affects the interface energy (Table 1). Furthermore, deviation of the bond angles at the Li metal/LLZ interface from the bulk structure appeared to be more significant in determining the interface energy than the bond distances. We therefore inferred that distortion of the ZrO$_6$ octahedron at the interface causes an increase in the interfacial energy, as reported by Bo et al.\cite{32}

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Figure 2. Comparison of the RMSE using various ML regression algorithms for the test datasets. The difference between the interface model and the bulk model structural features are used as descriptors, consisting of the RDF, the bond ADF, and the Voronoi tessellation-derived features.

Table 1. Top ten important descriptors obtained by importance analysis for the GBR algorithm. Histogram-type descriptors are used for the ML regression.\cite{35}

| Descriptor | Importance |
|------------|------------|
| ADF for $\angle$Li–Zr–O (bond angle $\approx$130°) | 674 |
| Number of vertices for La-centered Voronoi polyhedron | 576 |
| ADF for $\angle$Li–Zr–O (bond angle $\approx$123°) | 487 |
| ADF for $\angle$O–Li–O (bond angle $\approx$15°) | 439 |
| ADF for $\angle$Zr–La–Zr (bond angle $\approx$111°) | 354 |
| ADF for $\angle$Zr–O–Zr (bond angle $\approx$96°) | 229 |
| Order of facets of La-centered Voronoi polyhedron (order = 8, octagon) | 193 |
| Number of facets of Li-centered Voronoi polyhedron (number $\approx$16) | 193 |
| ADF for $\angle$O–Zr–O (bond angle $\approx$75°) | 191 |
| ADF for $\angle$O–La–O (bond angle $\approx$111°) | 187 |

and test predictions were performed on the remaining 20%. Hyperparameter tuning was performed using a ten-partition cross-validation method. Figure 2 shows the determined RMSEs, wherein the GBR algorithm gave the lowest RMSE (i.e., $\approx$0.04 eV Å$^{-2}$) for the test data, which is significantly smaller than the variation in the interface formation energies (i.e., $\approx$0.04–0.55 eV Å$^{-2}$). Thus, the fitted function using differential histogram descriptors has sufficient predictive power for determining the interface formation energy of the arbitrary interface model, and this approach should be generally applicable to the other solid–solid interface models.

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The deviation index of ZrO$_6$ represents the difference from
the ideal Zr–O coordination number of 6 divided by the interface area. It was found that the interface formation energy exhibited a positive correlation with an increase in the deviation index for the low deviation index region, thereby indicating that the diversion from octahedral coordination may affect the stability of the interface. However, the plots are largely scattered, indicating that multiple factors affect the Li/LLZ interface formation energies.

Figure 3a shows the projected density of states (PDOS) for the La, Zr, and O ions in the LLZ bulk model. The valence bands are mainly composed of an oxide 2p orbital, while the conduction bands are La 4f and Zr 4d orbitals. The bandgap in this calculation is $\approx$4 eV. Figure 4a displays the most stable Li(001)/LLZ(001) interface model among the 132 DFT-calculated models. The corresponding electronic structure, i.e., the density of states, is displayed in Figure 4b using the heat map style as a function of the energy level versus the Fermi level (horizontal axis) and the fractional z-axis of the structure model (vertical axis). It should be noted here that $z < \approx$0.45 and $z > \approx$0.45 correspond to the Li metal and LLZ phases, respectively. In the Li metal phase ($z < \approx$0.45), a typical metallic band structure is indicated, where the Li band crosses the Fermi level owing to the half-filled electronic configuration (2$s^2$) of Li. On the other hand, a rather wide bandgap lies at the center of the LLZ slab ($z > \approx$0.75). The valence band maximum (VBM) and conduction band minimum (CBM) are located at $\approx$3.3 and 0.8 eV, respectively, and thus the bandgap is $\approx$4 eV, which is in accordance with the calculated bandgap in the bulk structure (Figure 3a). Accordingly, the LLZ phase is chemically stable when in contact with Li metal because the electrons present in the Li phase are not energetically transferred to the CBM of the LLZ phase. This agrees with a previous report, where the voltage for Li insertion into the LLZ phase was negative.\cite{29} However, the band with a dilute density of states crosses the Fermi level in the vicinity of the interface ($z \approx$0.45 or $\approx$1.0), which is similar to the band bending behavior observed at the p–n junction of semiconductor materials. Therefore, a partial reduction of the LLZ-derived elements is indicated. However, the corresponding density of states at the interface is very dilute, and we confirmed that the local net spin for all the atoms was $\approx$0. Therefore, the degree of reduction is negligibly small in this study, although the partial reduction of Zr ions...
undercoordinated with oxide ions has been reported.\textsuperscript{32} As all Zr ions were coordinated with six oxide ions (i.e., through the formation of octahedral $\text{ZrO}_6$) in the most stable interfacial model, the coordination structure of Zr ions at the interface is clearly one of the most important factors in determining the stability against Li metal.

\text{The Li defect formation energies in the LLZ phase, i.e., those associated with Li vacancy formation and interstitial Li formation, were calculated for both the bulk and interface models. The Li vacancy formation energy, $E_{\text{vac}}$, and the interstitial Li-ion formation energy, $E_{\text{itst}}$, are defined as follows}

$$E_{\text{vac}} = nE_0(\text{Li}_{7-x/8}\text{La}_3\text{Zr}_2\text{O}_{12}) + E_0(\text{Li metal})$$

$$-nE_0(\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12})$$

(1)

$$E_{\text{itst}} = nE_0(\text{Li}_{7+x/16}\text{La}_3\text{Zr}_2\text{O}_{12}) - nE_0(\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12})$$

$$-E_0(\text{Li metal})$$

(2)

where $E_0(X)$ represents the calculated total electron energy of compound X. Equation (1) and (2) correspond to the Li removal and Li insertion reactions, respectively.

The red plots shown in Figure 5 display the Li vacancy formation energies (Equation (1)) of selected Li ions in the LLZ phase as a function of the depth from the Li metal/LLZ interface. The Li vacancy formation energy for the bulk model was determined to be $\approx 4.0$ eV, as indicated by the red hatched line in the figure. PDOS analysis of the bulk of the delithiated LLZ indicates that the oxidation reaction generally occurs at the O 2p band that mainly forms at the top of the valence band, as shown in Figure 3b. On the other hand, Li vacancy formation was largely reduced to $\approx 0.5$–1.0 eV in the interface model, and no significant dependence on the depth from the interface was indicated (Figure 5). Figure 6b shows the corresponding DOS as a function of the energy level and z-coordinates, indicating no significant change in the location of the CBM or the VBM of the LLZ phase. Hence, the delithiated LLZ phase maintained a sufficient electrochemical window against Li metal. Furthermore, spin integration analysis indicated the lack of a large spin polarization for all constituent elements. Hence, Li metal is responsible for charge compensation during delithiation, i.e., elevation of the Fermi

Figure 3. a) PDOS for the bulk model of Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ) compounds. Panels (b) and (c) represent the PDOS for the delithiated and lithiated LLZ, respectively (see also Equation (1) and (2) in the main text). The inset shows the magnification around the Fermi level ranging from $-0.5$ to 0.5 eV.

Figure 4. a) Model of the Li metal/LLZ interfacial structure. The upper and lower halves show the LLZ and Li metal phases, respectively. The green spheres, orange polyhedra, and dark blue polyhedra correspond to Li, LaO$_x$, and ZrO$_x$, respectively. b) Heat map of the density of states featuring horizontal and vertical axes corresponding to the Fermi level and the z-axis as shown in (a), respectively.

Figure 5. Calculated defect formation energies in the vicinity of the Li metal/LLZ interface as a function of the depth from the interface. The red and blue plots correspond to Li vacancy and interstitial Li site formation, respectively. The hatched lines show the defect formation energies for the bulk LLZ phase. The arrows indicate the calculation results shown in Figure 6 and 7.
1.2 eV, showing a good agreement with a previous report (blue/C25).

The interstitial Li-ion formation energies, $E_{\text{inst}}$, for both the bulk and interfacial LLZ phases were also calculated using Equation (2). The $E_{\text{inst}}$ for the bulk LLZ model is positive, i.e., $\approx$1.2 eV, showing a good agreement with a previous report (blue hatched line in Figure 5). Thus, the reduction of the LLZ phase is unlikely to occur only by contact with Li metal. The DOS analysis for the Li-inserted bulk LLZ model indicates that electrons partially occupy the Zr 4d and O 2p bands (Figure 3c).

The blue plots shown in Figure 5 display the interstitial Li formation energies in the LLZ phase as a function of depth from the Li metal/LLZ interface. Unlike the $E_{\text{inst}}$ for the bulk LLZ, the formation energies are negative ($\approx$–2.5 eV), regardless of the depth from the interface. This indicates that the Li atom in the metal phase was spontaneously inserted into the LLZ phase. Nevertheless, the electronic structure after Li insertion, as shown in Figure 7, clearly indicates that the VBM and the CBM of the LLZ phase do not cross the Fermi level; thus, the Li-inserted LLZ phase is electrochemically stable. This stems from the fact that charge compensation for the electrons released upon ionization of Li atoms in the metal phase to Li ions in LLZ (Li$^+$) occurred in the Li metal with a slight increase in the Fermi level, as was also the case for Li vacancy formation at the interface (Figure 7).

Further, it can be seen that the CBM and VBM shown in Figure 7 are slightly shifted to lower energy levels, which supports a rise in the Fermi level of the Li metal. Accordingly, an increase in the Li-ion concentration is indicated at the LLZ phase close to the Li/LLZ interface without any reduction-induced decomposition reaction taking place. The insertion reaction continued until the interstitial Li formation energy became zero, and so we inferred that the tetragonal phase transition in the vicinity of the Li/LLZ interface reported in the literature stems from a lithiation-induced off-stoichiometry.

3. Conclusions

DFT studies into the interfacial model for Li metal/LLZ solid electrolytes (LLZ = garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$) were performed in our study. Various interface structure models were generated, the interface formation energies were exhaustively evaluated, and the electronic structure of the most stable interface model was investigated. It was confirmed that the VBM and the CBM do not cross the Fermi level originating from half occupation of the Li 2s band, thereby resulting in LLZ being electrochemically stable against Li metal. Moreover, the defect formation energies relating to Li vacancies and interstitial Li formation were found to be lower for the interfacial model than for the bulk model.
In particular, we confirmed that the formation energy of interstitial Li sites was negative, thereby resulting in the concentration of Li ions in the LLZ phase being locally increased in the vicinity of the interface, ultimately leading to an off-stoichiometric composition of Li$_{7-x}$La$_x$Zr$_2$O$_{12}$. This was attributed to charge compensation involving two phases, namely, a rise in the Fermi level of the Li metal and the formation of interstitial Li$^+$ in the LLZ phase. Finally, we confirmed that the defect formation energy remained relatively unchanged even at a charge separation distance of 10 Å between the two phases. These observations may help to further understand the interfacial behavior and promote the application of LLZ species as solid electrolytes for all-solid-state Li metal batteries.

4. Computational Section

In this study, we created a large number of Li metal/LLZ interface models to investigate the comprehensive effect of the interface using in-house software.[33] Initially, we cut the crystal structure with various Miller indices and terminated the slab model. Subsequently, after checking the periodicity of each slab model, the interface model was created by selecting two slab models with lattice fit and minor deformation. The atoms on the surface were shifted in the direction of the interface surface as the Coulomb interactions locally are minimized, where the charges of the La, Nb, and O ions in the LLZ phase were assigned as +3, +5, and −2, respectively, and the Li atoms derived from both LLZ and metal Li were virtually assigned as +1. This treatment can remove structural candidates with unphysically short bonded configurations. The thickness of the slab model was set at 10 Å to avoid interactions between the interfaces. Among the obtained structures, we selected interface structures that contained <300 atoms to complete the calculation within a reasonable amount of time.

The interface formation energy ($\gamma_{int}$) was then calculated to evaluate the stability of the interfacial structure, as follows

$$\gamma_{int} = \frac{E_{int} - n_{Li}E_{LLZ} - n_{Li}E_{Li}}{2S}$$

where $S$, $E_{int}$, $E_{LLZ}$, and $E_{Li}$ are the area of the interface surface, the total energy of the interface model, the total energy of the bulk LLZ model, and the total energy of the bulk Li, respectively. $n$ is a correction term used to adjust the number of atoms. The adhesion energy ($W_{ad}$) was calculated as follows

$$W_{ad} = \frac{E_{int} - (E_{LLZ}^{sub} + E_{Li}^{sub})}{2S}$$

where $E_{LLZ}^{sub}$ and $E_{Li}^{sub}$ are the total energies of the corresponding slab models of LLZ and Li metal, respectively.

All first-principles calculations were performed using the Vienna ab initio simulation package (VASP).[34-36] A spin-polarized generalized gradient approximation (GGA) + PBEsol[41] was used to approximate the electron exchange interactions. The dipole corrections were not considered in the surface and/or interface calculations because the difference in the interface formation energies in the presence and absence of dipole corrections in the representative interface models was <0.02 eV Å$^{-2}$, thereby indicating that it does not affect the following discussion.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The computations reported in this article were performed using the facilities of the Supercomputer Centre at the Institute for Solid State Physics at the University of Tokyo, Japan. English language editing was performed by Editage (www.editage.com). The figures illustrating the crystal structures were drawn using VESTA software.[42] This work was partially supported by a Grant-in-Aid for Scientific Research (grant numbers 19H05815, 19K15657, 20H02436, 21H01625, 21J14422, and 21K14715) of the Ministry of Education Culture, Sports, Science and Technology (MEXT), Japan; the Elements Strategy Initiative to Form Core Research Center of MEXT (grant number JPMXP0121101003), the Program for Promoting Research on the Supercomputer Fugaku (Fugaku Battery & Fuel Cell Project) of MEXT (grant number JPMXP1020200301), and a CREST grant from the Japan Science and Technology Agency (JST), Japan (grant number JPMJCR12106). Part of this work was carried out under the Interdisciplinary Research Project Program of the Nagoya Institute of Technology.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

density functional theory, garnet-type Li$_7$La$_x$Zr$_2$O$_{12}$, Li metal electrode, solid electrolytes, solid–solid interface

Received: October 26, 2021
Revised: December 12, 2021
Published online: January 17, 2022

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