Boosting Li-Ion Transport in Transition Metal-Doped Li$_2$SnO$_3$

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ABSTRACT

Lithium stannate (Li$_2$SnO$_3$) is currently being considered as a material for electrode and electrode coating applications in Li-ion batteries. The intrinsic defect formation and Li-ion transport properties of Li$_2$SnO$_3$ doped with divalent and trivalent transition metal dopants (Mn, Fe, Co and Ni) are explored in this work using atomistic simulations. Defect formation simulations reveal that all divalent dopants occupy the Li site with charge compensation through Li vacancies. For trivalent doping, occupation of the Sn site is energetically preferred with charge compensation from Li interstitials. Molecular dynamics simulations reveal that divalent and trivalent dopants increase Li-ion diffusion and reduce its activation energy compared with the undoped system. We show that Li$_2$SnO$_3$ with Li excess or deficiency as a result of doping has improved lithium transport properties. This study highlights the substantial improvement in Li-ion diffusion of Li$_2$SnO$_3$ for both current commercial and next-generation Li-ion battery technologies that can be achieved through transition-metal doping.
1. Introduction

The Li-ion battery has been instrumental in powering the surge in portable electronics as a result of its high energy density and advantageous chemistry. However, high-performance materials with the potential to increase the energy and power densities of next-generation Li-ion batteries are becoming ever more important for the electrification of transport and grid-scale energy storage.1–3

One particular family of materials of interest in the search for new high-performance battery materials is $\text{Li}_2\text{MO}_3$ (where $\text{M} = \text{Ti, Sn or Si}$). These materials are of interest in battery applications because of their high Li content, thermodynamic stability, capacity and Li-ion conductivity.4–16 $\text{Li}_2\text{MO}_3$ (where $\text{M} = \text{Ti, Sn or Si}$) materials are currently being considered as cathodes, anodes and electrode coatings for Li-ion batteries.4–16 For instance, $\text{Li}_2\text{SnO}_3$ coatings improve the rate capability, thermal stability and cycling of graphene supported $\text{Li}_2\text{SiO}_3/\text{Li}_2\text{SnO}_3$, as well as graphene-$\text{Li}_2\text{SiO}_3$ composite anodes in LIBs.10,11 A $\text{Li}_2\text{SiO}_3@\text{Li}_2\text{SnO}_3/\text{SnO}_2$ composite was shown to induce volume change inhibition, thereby improving the rate and cycling properties of the electrode.12 $\text{Li}_2\text{SnO}_3$ acts as effective protection as a Li-ion conductive coating material for high-voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes.13 Considering that $\text{Li}_2\text{SnO}_3$ and $\text{Li}_2\text{MnO}_3$ both have a monoclinic structure, the synergy required at the cathode ($\text{Li}_2\text{MnO}_3$)–electrolyte (pure, coated or doped $\text{Li}_2\text{SnO}_3$) interphase is guaranteed.13,15

A variety of atomistic simulations have previously been used to explore the physicochemical properties of $\text{Li}_2\text{SnO}_3$.15–17 Based on a force-field approach, Kuganathan et al.17 studied defect formation and ion migration in $\text{Li}_2\text{SnO}_3$ and showed that $\text{Al}^{3+}$ is the optimal dopant of those tested, with the lowest formation energy, to be incorporated at the
Sn$^{4+}$ site to increase the Li content in the sample. However, the Li Frenkel defect type is the most favorable in terms of energetics in this structure.\textsuperscript{17}

In this work, intrinsic defect formation and ion migration in Li$_2$SnO$_3$ doped with divalent and trivalent dopants (Mn, Fe, Co and Ni) are investigated using lattice statics and molecular dynamics (MD) simulations. The results show that all divalent dopants occupy the Li site, creating Li vacancies as a result. In contrast, trivalent dopants reside at the Sn site with Li interstitials as the charge compensating defects. Both divalent and trivalent doping of Li$_2$SnO$_3$ improve its Li-ion transport properties by dramatically increasing Li-ion diffusion and reducing its activation energy.

2. Methodology

Defect calculations were performed using GULP.\textsuperscript{18} The interatomic potential parameters to model the ion-ion interactions were taken from the literature and are also provided in the Supplementary Information (SI).\textsuperscript{17,19–21} The long-range interactions are treated Coulombically while short-range interactions are represented by Buckingham potentials. The shell model\textsuperscript{22} is included to consider ion polarization for the O–O interactions. The shell model considers each ion as a positively core and negatively shell charged joined by a spring with spring constant, with the sum of the core-shell charge leading to the overall charge of each species.

The Mott–Littleton approach is used to calculate the defect and dopant energetics.\textsuperscript{23} This method subdivides the crystal structure into two spherical regions with radii R1 and R2 (R1<R2). The isolated defect or defect cluster is located at the inner sphere R1, where the interaction between the defect/cluster and the local structure is strong. The outer region
R2 is treated by a quasi-continuum approximation. For optimum accuracy, values of R1 = 13 Å and R2 = 21 Å were utilized after convergence testing. The Broyden–Fletcher–Goldfarb–Shanno algorithm was adopted to update the cell parameters and fractional positions during the defect energetics and geometry optimization calculations. These methods have been used to explore ion migration and defect formation in a variety of solid-state materials.

MD simulations are used to determine the long-range diffusion of Li ions. All MD simulations are carried out using LAMMPS. The simulation boxes were created using a 5×5×4 supercell of Li2SnO3, equivalent to 4800 ions in the stoichiometric cell. For the Li2O Schottky scheme, 10% and 5% of Li and O ions, respectively, were removed. The divalent and trivalent doping concentrations were 6.25%. The temperature range for the MD simulations is 500–1100 K. We consider undoped Li2SnO3 with Li2O Schottky defects to promote Li-ion diffusion and Li2SnO3 doped with transition metals as additional sources of Li vacancies or interstitials. The cells were first relaxed using an NPT ensemble until equilibrium was reached. Production runs were then carried out with an NVT ensemble, while recording the mean square displacement (MSD) for the Li ions. The slope of the expected straight line of MSD plots was then used to calculate the diffusion coefficients (D) using:

\[ \Delta \text{MSD} = 6Dt \]  

where \( t \) is the simulation time. Given the significant number of defect concentrations, each production run was limited to 2 ns with a time step of 2 fs. An example LAMMPS input file is provided in the SI for reference. The computational techniques adopted in this work have been successfully applied to a wide range of materials for battery applications.
3. Results and discussion

3.1. Structure and defect energetics of Li$_2$SnO$_3$

The monoclinic Li$_2$SnO$_3$ (C2/c space group) structure consists of lithium layers sandwiched between LiSn$_2$ layers forming honeycombs (six Sn ions surrounding a Li ion to create a Li-centered hexagon).\textsuperscript{15,33} The calculated cell parameters are $a = 5.303$ Å, $b = 9.257$ Å, $c = 10.061$ Å and $\beta = 100.852^\circ$, which agree well with the experimental and simulated values reported in the literature ($a = 5.8229$–$5.303$ Å, $b = 91872$–$9.257$ Å, $c = 10.026$–$10.061$ Å and $\beta = 100.348$–$100.852^\circ$).\textsuperscript{15,17,33}

Various defect formation mechanisms are considered in this study. The first mechanism describes Li$_2$O Schottky defect formation and is used for undoped Li$_2$SnO$_3$:

$$2\text{Li}_{\text{Li}} + \text{O}_\text{O} \rightarrow 2V'_{\text{Li}} + V''_\text{O} + \text{Li}_2\text{O} \quad (2)$$

where $\text{Li}_{\text{Li}}$ is a Li ion at a Li site, $\text{O}_\text{O}$ is an oxygen ion at an oxygen site, $V'_{\text{Li}}$ represents a Li vacancy and $V''_\text{O}$ represents an oxygen vacancy.

The second scheme represents the incorporation of a divalent dopant (M$^{2+}$) at the Li site with a Li vacancy to ensure charge neutrality:

$$\text{MO} + 2\text{Li}_{\text{Li}} \rightarrow M^*_{\text{Li}} + V'_{\text{Li}} + \text{Li}_2\text{O} \quad (3)$$

where $M^*_{\text{Li}}$ denotes a divalent dopant occupying a Li site in Li$_2$SnO$_3$. Alternatively, the substitution of M$^{2+}$ at the Sn site is described by:

$$\text{MO} + \text{Sn}_{\text{Sn}} + \text{O}_\text{O} \rightarrow M''_{\text{Sn}} + V''_\text{O} + \text{Sn}_2\text{O}_2 \quad (4)$$

where $M''_{\text{Sn}}$ represents a divalent dopant at a Sn site.
The other three incorporation mechanisms feature trivalent dopants ($M^{3+}$) at Li sites with Li vacancy compensation, Sn sites with oxygen vacancy compensation and Sn sites with Li interstitial ($Li^i$) charge compensation, respectively:

\[
M_2O_3 + 6Li_{Li} \rightarrow 2M_{Li}^{**} + 4V_{Li}^{'} + 3Li_2O
\]  
(5)

\[
M_2O_3 + 2Sn_{Sn} + O_o \rightarrow 2M_{Sn}^{'} + V_{O}^{**} + 2SnO_2
\]  
(6)

\[
M_2O_3 + 2Sn_{Sn} + Li_2O \rightarrow 2M_{Sn}^{'} + 2Li^i + 2SnO_2
\]  
(7)

The creation of Li interstitials was previously tested for Al$^{3+}$ doping,\(^{17}\) revealing that it is a reasonable doping modification to improve the Li-ion transport properties of Li$_2$SnO$_3$.

The binding energy between oppositely charged defects, e.g., Li and oxygen vacancies in the case of a Li$_2$O Schottky defect, is defined as the difference between the calculated defect cluster energy for neighboring defects and the sum of the energies of the isolated defects. A negative value for the binding energy represents an attraction between the defects. By combining the solution and binding energies, the combined (final) solution energy for each defect formation mechanism can be achieved.\(^{25,34}\) The calculated Li$_2$O Schottky defect energy, taking binding into account, is calculated to be 2.02 eV/defect, in agreement with the literature.\(^{17}\)

Figure 1 shows the calculated solution, binding and final solution energies for transition metal-doped Li$_2$SnO$_3$. The solution energies for M$^{2+}$ doping at a Li site with Li vacancy formation are far lower than for the same dopants at a Sn site with oxygen vacancy formation (Figure 1(a)). This is not unexpected given the increased energetic penalty of forming an oxygen vacancy compared to a Li vacancy. For trivalent doping, the opposite is true, with doping at the Sn site with the creation of compensating Li interstitials.
proceeding with remarkably low solution energies of \(~0.5\) eV for all four dopants (Figure 1(b)). There are minimal solution energy differences between the four dopants for each doping mechanism.

Figures 1(c) and (d) show the calculated binding energies for divalent and trivalent transition-metal doping of Li$_2$SnO$_3$, respectively. All the binding energies are negative for divalent dopants, suggesting strong favorable interactions between the dopants and charge compensating defects. Significantly stronger binding energies are found between divalent dopants and oxygen vacancies (~2.2 eV) than between the same dopants and Li vacancies (<0.2 eV), in agreement with simple Coulombic arguments. For the trivalent dopants, all binding energies are again negative, with the exception of small positive values for Co$^{3+}$ and Ni$^{3+}$ doped at Sn sites with Li interstitials for charge compensation. Again, the strongest binding energies (~2.1–2.6 eV) are for the scheme involving oxygen vacancies as charge compensating defects. Low binding energies are observed for all dopant incorporations schemes involving Li vacancies and interstitials, which is an important factor for fast Li-ion diffusion throughout the Li$_2$SnO$_3$ structure.

The calculated final solution energies, representing the combination of the solution and binding energies, are presented in Figures 1(e) and (f) for divalent and trivalent doping, respectively. From these figures, it is clear that the inclusion of binding energies does not change the most energetically preferred dopant incorporation mechanisms, i.e., Li site doping with Li vacancies is preferred for divalent dopants while Sn site doping with Li interstitials dominates for trivalent dopants. On the basis of these low calculated defect energies, we propose that transition-metal doping of Li$_2$SnO$_3$ should be an effective and
low energy method for the creation of additional lithium charge carriers (vacancies or interstitials) to boost long-range Li-ion diffusion in this material.
**Figure 1.** (a, b) Solution, (c, d) binding and (e, f) final solution energies of $M^{2+}$ (left) and $M^{3+}$ (right) doping of $Li_2SnO_3$ at Li and Sn sites with a range of possible charge compensation schemes.

3.2. *Li-ion transport in undoped and transition metal-doped Li$_2$SnO$_3$*

Large-scale MD simulations are carried out to determine the Li-ion diffusion in undoped and doped Li$_2$SnO$_3$ as a function of temperature and dopant. The calculated MSDs are given in Figures S1–S3 for the undoped system, divalent doping at Li sites with Li vacancy formation and trivalent doping at Sn sites with Li interstitial formation, respectively. Only these two dopant incorporation mechanisms were considered for the calculation of Li-ion diffusion as they are the lowest energy schemes for all tested dopants, as discussed in the previous section. All the MSDs increase linearly with simulation time, indicating long-range Li-ion diffusion. Three-dimensional Li-ion diffusion in this material is demonstrated in Figure S1, which shows the $x$, $y$ and $z$ direction components of the MSD for undoped Li$_2$SnO$_3$ at 1000 K.

Li-ion diffusion coefficients are derived from these MSDs using Eq. (1) and are presented using Arrhenius plots in Figure 2. For the undoped system, a Li-ion diffusion coefficient of $8.65\times10^{-9}$ cm$^2$ s$^{-1}$ at 500 K is found. When we extrapolate our results to 300 K, we obtain a Li-ion diffusion coefficient of $5.63\times10^{-12}$ cm$^2$ s$^{-1}$. This value is over an order of magnitude greater than the value of $2.14\times10^{-13}$ cm$^2$ s$^{-1}$ obtained experimentally via the Randles-Sevcik equation at room temperature. The reasons for this discrepancy are likely related to the differences between the experimental sample and the model used in this study. For example, the experimental sample used in Ref. 12 is polycrystalline and it has been shown that the overall Li-ion diffusion of Li$_2$SnO$_3$ is
inhibited by grain boundaries, whereas our model can effectively be considered as single crystal. To our knowledge there are no available reports of Li-ion diffusion in single-crystal Li$_2$SnO$_3$ samples. Similar differences between computational and experimental results have been reported for solid electrolytes for solid-state batteries.

(a) $M^{2+}_\text{Li} + V_{\text{Li}}$

(b) $M^{3+}_\text{Sn} + Li_i$

![Graph (a)](image_url_a)

![Graph (b)](image_url_b)
**Figure 2.** Arrhenius plots of Li-ion diffusion for undoped and (a) M$_{2+}$ and (b) M$_{3+}$ doping of Li$_2$SnO$_3$ at Li and Sn sites with Li vacancy and interstitial charge compensation, respectively.

The Arrhenius plots in Figures 2(a) and (b) for divalent and trivalent doping, respectively, show a clear enhancement in Li-ion diffusion through the introduction of transition-metal dopants compared to the undoped material. This is particularly true for the trivalent dopants at the Sn site with compensating Li interstitials, with increases of over an order of magnitude for Mn$_{3+}$, Co$_{3+}$ and Ni$_{3+}$ at 500 K. Fe$_{3+}$ exhibits the smallest increase in diffusivity, but even this increase is close to one order of magnitude. Furthermore, it is noteworthy that Li interstitial diffusion mechanisms have been reported for a variety of related materials,\(^{36-38}\) including the isostructural Li$_2$TiO$_3$.\(^{39}\) The enhancement in Li-ion diffusion for divalent doping is also substantial with four- to sevenfold increases at 500 K compared to the undoped system. We are not aware of any experimental reports concerning the Li-ion transport properties of transition metal-doped Li$_2$SnO$_3$. While these promising results suggest that transition-metal doping of this material may be a viable method for dramatically enhancing its Li-ion transport via the creation of extra Li charge carriers, we must also consider its effect on the activation energy for Li-ion diffusion.

We derive an activation energy of 0.48 eV for undoped Li$_2$SnO$_3$. This value is in excellent agreement with the values of ~0.45 eV obtained using $^7$Li spin-alignment echo NMR and $^7$Li NMR relaxometry.\(^{40}\) The impact of grain boundary resistance in Li$_2$SnO$_3$ is again confirmed by the larger activation energies of 0.6–0.9 eV reported for polycrystalline samples and determined using impedance spectroscopy.\(^{41}\) Kuganthan et al.\(^{17}\) used potentials-based methods to calculate activation energies of 0.16–0.65 eV depending on the individual Li migration pathways in Li$_2$SnO$_3$. 

The activation energies for Li-ion diffusion obtained from the Arrhenius plots for the doped systems are shown in Figure 3. The most important finding from these results is that all transition-metal dopants produce substantial reductions in activation energy (with values of 0.35–0.42 eV) compared with the undoped material (0.48 eV). The lowest overall value is found for Mn³⁺ doping while the largest is observed for Fe³⁺, although this still represents a reduction of 0.06 eV compared to the undoped system. The average activation energy for trivalent doping is 0.37 eV, which is marginally lower than the average value for divalent doping of 0.40 eV.

On the basis of our combined defect energetics and Li-ion diffusion results, the inclusion of transition-metal dopants into the Li₂SnO₃ structure can be deemed a viable and simple route to improving the properties of the material for its application as an electrode and electrode coating material in Li-ion batteries. This is particularly true for doping with Mn³⁺, which has both the lowest final solution energy (0.40 eV) and lowest activation energy (0.35 eV) of all dopants and schemes tested, as well as resulting in a significant enhancement in Li-ion diffusion.
Figure 3. Comparison of activation energies for Li-ion diffusion ($E_a$) for $M^{2+}$ and $M^{3+}$ doping of Li$_2$SnO$_3$ at Li and Sn sites with Li vacancy and interstitial charge compensation, respectively.

4. Conclusions

We have utilized atomic-scale simulations to study dopant incorporation and Li-ion diffusion in undoped and transition metal-doped Li$_2$SnO$_3$. Defect energy calculations reveal that divalent dopants occupy the Li site, leading to Li vacancy formation. In contrast, trivalent dopants have a strong energetic preference for doping at the Sn site, with charge compensation from Li interstitial formation.

Molecular dynamics simulations show that transition-metal doped Li$_2$SnO$_3$ can result in a Li-ion diffusion enhancement of over one order of magnitude with substantially lower activation energies. The activation energy for diffusion ranges between 0.35 and 0.42 eV, while a value of 0.48 eV is obtained for the undoped material. Mn$^{3+}$ is shown to be the most promising dopant considered as a result of its remarkably low solution and activation energies, as well as the significant increase in Li-ion diffusion that it produces.

Based on the results for the defect formation and transport properties explored in this work, we show that divalent and trivalent transition metal-doped Li$_2$SnO$_3$ has excellent potential as an electrode or coating material for Li-ion batteries and is therefore worthy of future experimental research.

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NOTES

The authors declare no competing financial interest.
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