Defects and dopant properties of Li$_3$V$_2$(PO$_4$)$_3$

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Polyanion phosphate based Li$_3$V$_2$(PO$_4$)$_3$ material has attracted considerable attention as a novel cathode material for potential use in rechargeable lithium ion batteries. The defect chemistry and dopant properties of this material are studied using well-established atomistic scale simulation techniques. The most favourable intrinsic defect process is the Li Frenkel (0.45 eV/defect) ensuring the formation of Li vacancies required for Li diffusion via the vacancy mechanism. Long range lithium paths via the vacancy mechanism were constructed and it is confirmed that the lowest activation energy of migration (0.60 eV) path is three dimensional with curved trajectory. The second most stable defect energy process is calculated to be the anti-site defect, in which Li and V ions exchange their positions (0.91 eV/defect). Tetravalent dopants were considered on both V and P sites in order to form Li vacancies needed for Li diffusion and the Li interstitials to increase the capacity respectively. Doping by Zr on the V site and Si on the P site are calculated to be energetically favourable.

The increased need for electrical energy storage for static and mobile applications in conjunction with the demand for higher capacity, better safety, increased cycle performance, and durability made the solid-state lithium batteries technologically important$^{1-3}$. The research is focusing mainly on the electrolyte and cathode trying to identify more efficient materials$^{3-17}$. In particular, electrode materials require should satisfy safety requirements, be low cost, and critically have a higher energy density (i.e. large density of Li$^+$ ions).

The state of the art cathodes for solid-state lithium batteries include polyanion-type oxides, layered lithiated transition metal oxides and Mn-based spinels$^{18}$. Monoclinic Li$_3$V$_2$(PO$_4$)$_3$ has gained the interest of the community as a cathode material for solid-state lithium batteries due to its low cost, safety, low environmental impact, appropriate cycling stability, and high theoretical capacity (197 mAh$^{-1}$)$^{18-25}$. Fu et al.$^{26}$ synthesized this material using mixed lithium precursors with particles high surface area leading to good electrochemical performance. Solid state $^7$Li NMR together with two-dimensional exchange study of Lithium was used to determine the temperature dependent Li hoping process to understand the Li dynamics on the microscopic scale suggesting that their methodology can be applied to the cycled materials and other lithium metal phosphates$^{27}$. Lee and Park$^{22}$ employed molecular dynamics simulation to calculate the vacancy migration energy of Li at different temperatures and confirmed the mobility of Li$^+$ ions is anisotropic. Though these separate studies show different properties in this material, fundamental understating of this material is needed to optimize its performance.

Electrochemical behaviour of an electrode material is important to assess its applicability in batteries. This behaviour can be studied theoretically by performing defect calculations and we note that such studies are absent in the literature. Atomistic modelling based on the classical pair potentials is a powerful method and can provide useful information about the defect processes, cation doping behavior and ion migration mechanism. This methodology has been applied to a variety of oxides including Li containing materials and excellent agreement in trends and energetics of defect processes was observed between calculation and the experiment$^{10-17,28,29}$. Here, we extend our recent modelling of electrode materials$^{30-34}$ where we examined the defects, ion diffusion and dopants. In the present study, we employ established atomistic modeling techniques to investigate the intrinsic defect chemistry, the impact of doping on the formation of lithium interstitials and lithium ion diffusion pathways in Li$_3$V$_2$(PO$_4$)$_3$. We consider the solution of a range of oxides in Li$_3$V$_2$(PO$_4$)$_3$ including aliovalent dopants (e.g. Si, Ge and Ti) and isovalent dopants (e.g. Al, Ga and Sc).

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Results and Discussion

**Li₃V₂(PO₄)₃ structure.** The crystal structure of Li₃V₂(PO₄)₃ exhibits a monoclinic crystallographic structure with space group P2₁/n (lattice parameters a = 8.5978 Å, b = 8.5933 Å, c = 12.0327 Å, α = 90.0°, β = 90.496° and γ = 90.0°) as reported by Fu et al. Fig. 1 shows this structure and the chemical environment of P (forming tetrahedral unit with four O atoms) and V (forming octahedral unit with six O atoms). The starting point for the present study was to reproduce the experimentally observed monoclinic crystal structure to enable an assessment of the quality and efficacy of the classical pair potentials (refer to Table S1 in the supplementary information for the potentials parameters used and method section for the detailed description of the methodology) used here. The calculated equilibrium lattice constants (refer to Table 1) are in excellent agreement with experiment.

| Parameter | Calc    | Expt ¹¹ | |Δ| (%) |
|-----------|---------|---------|---|----|
| a (Å)     | 8.431424| 8.597800| 1.94|
| b (Å)     | 8.548920| 8.593300| 0.52|
| c (Å)     | 12.076179| 12.032700| 0.36|
| α (°)     | 90.0000 | 90.0000 | 0.00|
| β (°)     | 90.070  | 90.496  | 0.47|
| γ (°)     | 90.0000 | 90.0000 | 0.00|

Table 1. Calculated and Experimental Structural Parameters for Monoclinic (P2₁/n) Li₃V₂(PO₄)₃.

**Intrinsic defect processes.** To understand the electrochemical behavior of an electrode material, intrinsic defect processes are crucial. A series of isolated point defect (vacancy and interstitial) energies were calculated, which were combined to determine the formation energies for Frenkel and Schottky-type defects in Li₃V₂(PO₄)₃. The following equations represent the reactions involving these defects as written using Kröger-Vink notation ²⁵:

\[
\text{Li Frenkel: } \text{Li}_{Li}^{X} \rightarrow V_{Li}^{\alpha} + \text{Li}_{i}^{\alpha}
\]

(1)

\[
\text{O Frenkel: } \text{O}_{O}^{X} \rightarrow V_{O}^{\ell} + \text{O}_{i}^{\ell}
\]

(2)

\[
\text{V Frenkel: } V_{V}^{X} \rightarrow V_{V}^{\prime} + V_{i} \cdot \cdot \cdot
\]

(3)

\[
\text{P Frenkel: } P_{P}^{X} \rightarrow V_{P}^{\prime} + P_{i} \cdot \cdot \cdot 
\]

(4)
The reaction energies for these intrinsic defect processes are reported in Fig. 2 and Table S2. The most favourable intrinsic disorder is Li Frenkel and the formation of other Frenkel and Schottky defects is less energetically favourable. The second most favourable defect process is calculated to be Li-V anti-site. This indicates that there will be a small percentage of Li on V sites and P on Li sites particularly at higher temperatures. In the relaxed configuration, there is insignificant changes observed in the cation-oxygen bond distances. Antisite defects have been observed experimentally and theoretically in a variety of Li ion cathode battery materials. In the experimental study of as-prepared Li$_2$MnSiO$_4$, a small amount of Li-Mn anti-site defect was observed. During cycling of Li$_2$FeSiO$_4$, Nyten et al. observed structural rearrangement in the crystal structure responsible for the Li-Fe anti-site. The difference between the isolated and cluster defect energies is calculated to be $-1.06$ eV suggesting that the anti-site cluster is stable compared to its isolated form. The formation enthalpy of Li$_2$O via the Li$_2$O Schottky-like reaction (relation 6) is a process that requires an energy of $3.07$ eV per defect (refer to Table S2, supplementary information). This is a process that can lead to further VO, however, at elevated temperatures. The trend calculated for Li and V Frenkel and Li-V antisite defects is in agreement with the theoretical calculations performed by Lee et al., though there is a difference in defect energetics. Such difference is dependent on the choice of classical pair potentials used.

**Lithium ion-diffusion.** As the intrinsic lithium ion diffusion of Li$_3$V$_2$(PO$_4$)$_3$ material is of crucial importance when assessing its use as a possible high-rate cathode material in lithium batteries, we used the present static atomistic simulation to examine various possible diffusion paths responsible for Li ion conduction, which are often difficult to explore on the atomic scale by experiment alone. For the Li vacancy migration, we identified four lower activation energy local hops (A, B, C and D) and constructed long range paths connecting local Li hops (refer to Fig. 3). There are many long range three dimensional paths present. The lowest overall migration energy (0.60 eV) was calculated for the $D \rightarrow A \rightarrow B \rightarrow A$ path. Other possible long range paths were considered. However, the overall activation energy was calculated to be 0.87 eV due to the local hop C involved in the long range path. Here the activation energy of migration is defined as the position of the highest potential energy along the migration path. Migration energies are reported in Table 2 together with the Li-Li separation, whereas energy profile diagrams are shown in Fig. 4. Lee et al. calculated the one dimensional lithium ion diffusion mechanism in Li$_3$V$_2$(PO$_4$)$_3$ and their values deviates with our study. This is because in the present study we calculated three dimensional Li migration paths, which are the lowest energy migration paths (refer to Fig. 3 for detailed migration
path). Migration paths calculated in this study exhibit curved trajectories while in other studies, the paths are linear. Cahill et al. performed Li NMR measurements to estimate the activation energy for Li ion migration. The reported range of activation energies (0.73–0.83 eV) agrees reasonably with our calculated values of 0.46–0.87 eV.

**Tetravalent doping.** The Li Frenkel is calculated to be only 0.45 eV/defect; however, an increase in the concentration of Li will further increase the applicability of Li$_3$V$_2$(PO$_4$)$_3$ as a cathode material for rechargeable lithium batteries. A way to increase the content of intrinsic defects in oxides is by the solution of aliovalent dopants as it was previously demonstrated in CeO$_2$ (for example ref. and references therein). Here we considered the solution of RO$_2$ ($R$ = Ce, Zr, Ti, Si and Ge) via the following process (in Kröger-Vink notation):

$$2RO_2 + 2V^+_\text{Li} + 2\text{Li}^{x\text{X}}_\text{Li} \rightarrow 2R^+_\text{W} + 2V^+_\text{Li} + V_2\text{O}_3 + \text{Li}_2\text{O} \quad (9)$$

Figure 5 reports the solution energies of RO$_2$ and it can be observed that ZrO$_2$ has the lowest solution energy of 2.18 eV. Solution energies of CeO$_2$ and GeO$_2$ are 2.31 eV and 2.35 eV respectively meaning that Ce and Ge are also promising candidate dopants. As these solution energies are higher compared to the Li Frenkel process, the solution of ZrO$_2$, GeO$_2$ and CeO$_2$ during synthesis should be examined experimentally as they can increase the Li vacancy concentration (via relation (9)).

Incorporation of additional lithium into the as-prepared material will enhance the capacity and further increase the applicability of Li$_3$V$_2$(PO$_4$)$_3$ as a viable cathode material for rechargeable sodium batteries. A defect engineering way to increase the amount of lithium is by doping tetravalent cations on P site through creating Li interstitials. The efficacy of the approach has been previously demonstrated experimentally and theoretically inLi battery cathode materials. Here we considered the solution of RO$_2$ ($R$ = Si, Ge, Ti, Zr and Ce) via the following process (in Kröger-Vink notation):

### Table 2. Calculated Li-Li separations and activation energies for the sodium ion migration between two adjacent Li sites refer to Fig. 3.

| Migration path | Li-Li separation (Å) | Activation energy (eV) |
|---------------|----------------------|------------------------|
| A             | 2.9561               | 0.53                   |
| B             | 3.2091               | 0.46                   |
| C             | 3.2676               | 0.87                   |
| D             | 3.3501               | 0.60                   |

**Figure 3.** Possible long range sodium vacancy migration paths considered. Local Li migration paths are shown in blue, yellow, white and light purple atoms. PO$_4$ and VO$_6$ units are shown brown and violet colors respectively.
Figure 5 reports the solution energies of RO₂ (R = Si, Ge, Ti, Zr and Ce) and it can be observed that the most favorable dopant solution energy is found for Si⁴⁺. This suggests that a possible synthesis-doping strategy of introducing additional lithium into Li₃V₂(PO₄)₃, although the exact amount of Si incorporation cannot be predicted. The second most favorable dopant is Ge⁴⁺. The solution energy increases further with the dopant size.

$$2RO_2 + 2P_{\text{O}_5} + Li_2O \rightarrow 2R^{4+} + 2Li^+ + P_{\text{O}_5}$$  \hspace{1cm} (10)
Concentration of Li ions will be dominated by tetravalent doping via two processes as shown in equations 9 and 10. The formation Li interstitials will be favored by Si and Ge dopants (eqn 10) on the P site whereas Ti, Zr and Ce on the V site will favor the formation of Li vacancies (eqn 9). Solution of these tetravalent dopants will create the corresponding Li defects.

Trivalent doping. A wide range of isovalent substitutions on V sites were considered. The dopant incorporation mechanism does not require the creation of vacancies or interstitials for charge-compensation. Here we considered the solution of R₂O₃ (R = Al, Ga, Sc, In, Y, Gd and La) via the following process (in Kröger-Vink notation):

\[ R_2O_3 + 2V^{\text{V}}_\text{Li} \rightarrow 2V^*_R + V_\text{Li}O_3 \]  

In Fig. 6 the solution energies as a function of the dopant ionic radius are reported. The results reveal that the formation enthalpies for the dopants Sc³⁺, In³⁺, Y³⁺, Gd³⁺ and La³⁺ are exoergic suggesting that they are ideal candidates for substitution at the isovalent V site. The solution enthalpy for La³⁺ is highly negative meaning that it is worth investigating the formation of Li₃(V,La)₂(PO₄)₃ experimentally and its electrochemical performance.

Summary. In the present study, the atomistic simulation techniques have been used to provide detailed insights into intrinsic defects, lithium ion mobility and trivalent doping, which are relevant to the general electrochemical behavior of Li₃V₂(PO₄)₃. The dominant energy defect process is Li Frenkel. The Li-V anti-site defect is calculated to be the second most stable defect process suggesting that there would be small intrinsic concentration of Li on V sites at operating temperatures. The long range Li ion diffusion path with lowest migration energy was calculated to be three dimensional with the migration energy of 0.60 eV. Solution energies of RO₂ (R = Al, Ga, Sc, In, Y, Gd and La) were calculated to increase Li vacancies and extra Li ions in Li₃V₂(PO₄)₃. Zr on V site and Si on P site were found to be the efficient strategies to increase Li vacancies and extra Li ions respectively. Promising candidates for isovalent substitution on V site are Sc, In, Y, Gd and La. The present study aims to inspire further experimental work on doped Li₃V₂(PO₄)₃.

Methods
To calculate the energetics for the formation of intrinsic defects and the Li ion diffusion pathways, the classical pair potential method as implemented in the GULP package was employed. This method is based on the classical Born model description of the ionic crystal lattice. All systems were treated as crystalline solids with interactions between ions consisting of the long-range attractions and short-range repulsive forces representing electron-electron repulsion and van der Waals interactions. The short-range interactions were modelled using Buckingham potentials (refer to Table S1, supplementary information). Simulation boxes and the corresponding atom positions were relaxed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm. The Mott-Littleton method was used to investigate the lattice relaxation about point defects and the migrating ions. It divides the crystal lattice into two concentric spherical regions, where the ions within the inner spherical region (on the order of >700 ions) immediately surrounding the defect relaxed explicitly. Li ion diffusion was calculated considering two adjacent vacancy sites as initial and final configurations. Seven interstitial Li ions were considered in a direct linear route and they were fixed while all other ions were free to relax. The local maximum energy along this diffusion path is calculated and reported as activation energy of migration. As the present model assumes a full charge ionic model with the calculations corresponding to the dilute limit the defect enthalpies will be overestimated, however, relative energies and trends will be consistent.
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