1. Introduction

The revolution in portable electronic devices has been powered by rechargeable lithium-ion batteries. Alternative electrode materials for new generations of lithium batteries are generating considerable research activity, particularly for large-scale applications (such as electric vehicles and grid storage).\(^1\)–\(^9\) Graphite is currently the dominant anode material in Li-ion batteries. Metal oxide anodes such as TiO\(_2\)(B) are attracting interest since they can offer twice the volumetric energy density of graphite.\(^10\)–\(^12\) However, the anode voltage for titanium oxides of ~1.6 V vs. Li\(^+/\)Li compared to ~0.1 V for graphite compromises the cell voltage and hence energy storage. Recent studies have shown that Li can be intercalated into the layered oxide Li\(_{1+x}\)V\(_{1-x}\)O\(_2\) at an unusually low voltage of ~0.1 V vs. Li\(^+/\)Li,\(^13\)–\(^20\) with a theoretical volumetric capacity of 1360 mA h cm\(^{-3}\) compared to graphite at 790 mA h cm\(^{-3}\). Previously we investigated the intercalation process for Li\(_{1+x}\)V\(_{1-x}\)O\(_2\) and in particular the key role that non-stoichiometry or excess lithium (x > 0) plays in switching on intercalation.\(^16\) Lithium does not intercalate into stoichiometric layered LiVO\(_2\) (Fig. 1). However, substituting a small amount of the V on the transition metal sites by Li (typically Li\(_{1.0+y}\)V\(_{0.9}\)O\(_2\)) is sufficient to promote a two-phase intercalation process at a potential of ~0.1 V.

Other recent studies on this system\(^17\) include an investigation of doping on the V site with Cr or Fe leading to improved rate capabilities and cyclability. A combination of solid state NMR, pair distribution function analysis and density functional theory calculations has provided further insights into the crystal and electronic structures of Li\(_{1+x}\)V\(_{1-x}\)O\(_2\), indicating magnetically-induced distortions of the V sublattice to form trimers.\(^18\)

To fully understand the factors influencing the electrochemical behaviour of the Li\(_{1+x}\)V\(_{1-x}\)O\(_2\) anode material it is clear that greater insight into the underlying lithium transport properties is needed at the atomic scale. Indeed, a major puzzle is what is the atomistic mechanism controlling lithium-ion diffusion in this new oxide anode? Such transport features are important factors for charge/discharge rates and high power, but are often difficult to determine from experimental methods. Here, we extend our previous electrode work with a combination of energy minimization and molecular dynamics (MD) simulation techniques to probe, for the
first time, the lithium-ion diffusion mechanisms in the vanadate material. In particular, the results comparing stoichiometric LiVO₂ and Li-rich Li₁.₀₇V₀.₉₃O₂ from long time-scale MD provide new insights into the mechanistic features of interstitial lithium-ion transport.

2. Methods

Atomic modellling techniques are well suited to the investigation of defect and transport properties and have been applied successfully to a variety of studies on lithium battery materials. In the present study, potentials-based energy minimization and molecular dynamics (MD) were employed. The GULP code was used for the interatomic potential refinement, and the Mott–Littleton method was used to investigate the isolated point defects. The interactions between ions were represented in terms of a long-range Coulombic term plus an analytical function representing short-range repulsive and van der Waals forces. The empirically-derived potential parameters for Li-O, V-O and O-O were transferred from our previous study of the LiVO₂ system. The Buckingham shell-model potentials used in this study are presented in ESI, Table S1.

The MD technique consists of an explicit dynamical simulation of the ensemble of ions for which Newton's equations of motion are solved and were carried out using the DL POLY 2.20 code. For this work two key structural compositions were compared: stoichiometric LiVO₂ and the lithiated non-stoichiometric Li₁.₀₇V₀.₉₃O₂ (where y = 0.09). The LiVO₂ simulation box was constructed using a 10 × 10 × 2 P1 supercell consisting of 2400 atoms. Our previous work showed that Li intercalation into the Li-rich Li₁.₀₇V₀.₉₃O₂ phase was energetically more favourable and that the Li interstitials preferred to go on a tetrahedral site adjacent to a Li on a vanadium site. The initial Li₁.₀₇V₀.₉₃O₂ configuration contained 10% Li interstitial ions placed on these tetrahedral sites leading to a total of 2454 atoms in the supercell. The charge-compensation for Li on the V sites and Li interstitials was delocalised across all the V ions to make the supercell charge neutral. More than three initial configurations of the lithiated vanadium oxide were explored via full bulk optimisations; their energetic stabilities were compared and the lowest energy configuration was used for the subsequent MD simulations.

After initial equilibration (100 000 steps), MD simulations were performed with a 0.5 fs time step for long runs of 1.1 ns at temperatures in the range 200–600 K (Nose–Hoover thermostat) at intervals of 100 K. The NPT ensemble was used to allow for any thermal expansion after which the NVT ensemble was employed for the full production runs of 1.1 ns, which are important for good statistics. Such potentials-based MD techniques have been applied to other lithium battery materials and to oxide-ion conductors for solid oxide fuel cells. It is worth remarking that we are employing much larger supercells and an order of magnitude longer timescales than the majority of ab initio MD simulations.

3. Results and discussion

3.1 Structures and defect chemistry

LiVO₂ and Li₁.₀₇V₀.₉₃O₂ are both ccc structures (space group R₃m) with alternating LiO₆ and VO₆ layers shown schematically in Fig. 1; the lithium present in the transition metal layers in Li₁.₀₇V₀.₉₃O₂ is highlighted. The modelling study first attempted to reproduce the observed crystal structures. A comparison between the calculated unit cell parameters based on effective potentials and those of the experimental structure is given in Table 1. The calculated unit cell parameters deviate from experiment by at most 1.9%, and in most cases much less; the same is found for the Li–O and V–O bond lengths. This reproduction of the structures of both LiVO₂ and Li₁.₀₇V₀.₉₃O₂ compositions gives us confidence that the interatomic potential model can be used reliably in the defect and migration calculations. In ESI, † we have listed the calculated elastic and dielectric constants for LiVO₂ and Li₁.₀₇V₀.₉₃O₂. Although there are no experimental data for the LiVO₂ system for direct comparison, our calculated values are consistent with observed and DFT values for similar layered oxides including static dielectric constants for LiCoO₂.

A series of isolated point defect (vacancy and interstitial) energies were then calculated, and combined to give the relative energies of formation of the Li Frenkel defect. We also examined the Li/M “anti-site” pair defect, which involves the exchange of a V ion (radius 0.64 Å) with a Li ion (radius 0.76 Å); this type of defect is worth investigating since cation exchange effects have been observed in other layered oxide electrodes.

Table 2 lists the formation energies of Li Frenkel and anti-site defects in the two compositions. The high unfavourable energies suggest that the inability to intercalate into stoichiometric LiVO₂ is not due to the presence of site-exchange disorder involving V ions in the alkali metal layers pinning them together; this result is in agreement with previous structural studies indicating that there is no V in the Li layers of

| Table 1 Comparison of experimental and calculated structural parameters for LiVO₂ and Li₁.₀₇V₀.₉₃O₂. Calculated elastic and dielectric properties have been presented in ESI, Table S2. |
|-------------------------------------------------|-------------------|------------------|
| (a) LiVO₂ (R₃m) | Expt. | Calc. | Δ |
| a/Å | 2.8377 | 2.8608 | 0.023 |
| b/Å | 2.8377 | 2.8608 | 0.023 |
| c/Å | 14.8230 | 14.5516 | −0.271 |
| γ/deg | 90.0 | 90.0 | 0.0 |
| Li–O/Å | 2.102 | 2.103 | 0.001 |
| V–O/Å | 2.004 | 2.058 | 0.054 |
| O–O/Å | 2.830 | 2.905 | 0.075 |
| (b) Li₁.₀₇V₀.₉₃O₂ (R₃m) | | | |
| a/Å | 2.8430 | 2.9370 | 0.094 |
| b/Å | 2.8430 | 2.8920 | 0.049 |
| c/Å | 14.7675 | 14.6355 | −0.132 |
| γ/deg | 90.0 | 90.0 | 0.0 |
| Li–O/Å | 2.046 | 2.030 | −0.016 |
| V–O/Å | 2.037 | 2.030 | −0.007 |
| O–O/Å | 2.834 | 2.832 | 0.002 |
LiVO$_2$. The site exchange energy in Li$_{1.07}$V$_{0.93}$O$_2$ is the most favourable, although the magnitude still suggests that intrinsic concentrations will not be significant. The calculated defect energies also suggest that intrinsic lithium vacancies and interstitials are unlikely to be found in stoichiometric LiVO$_2$.

### 3.2 Li ion diffusion

Examination of the Li-ion transport properties of Li$_{1+x}$V$_{0.93}$O$_2$ is of vital importance when considering electrode kinetics. Of primary interest here is information on the atomistic mechanism of lithium-ion diffusion, which is difficult to probe purely by experimental methods. Molecular dynamics (MD) techniques are well suited to probing transport mechanisms, especially cooperative or correlated ion motion. Here, MD calculations over long simulation time scales were carried out at temperatures more than covering typical battery operating temperatures for the two compositions for direct comparison: stoichiometric LiVO$_2$ and the lithiated non-stoichiometric Li$_{1.07}$V$_{0.93}$O$_2$ ($y = 0.09$).

First, the mean squared displacements (MSDs), $\langle [r(t)]^2 \rangle$, of lithium ions have been resolved and shown in Fig. 2; the results clearly show that there is significant lithium-ion diffusion only in the Li-rich composition. For LiVO$_2$ the MSD of the Li-ions tends rapidly to a constant value and confirms that there is no ion diffusion in this stoichiometric composition.

The Li-ion diffusion coefficient ($D_{li}$) can be derived from the MSD data given by $D = (1/6t) \langle [r(t)]^2 \rangle$. We calculate a $D_{li}$ value of about 10$^{-9}$ cm$^2$ s$^{-1}$ for Li$_{1.07}$V$_{0.93}$O$_2$ ($y = 0.09$) at 300 K. Although there are currently no measured diffusion data for direct comparison, the magnitude is comparable to other electrode materials; for example, graphite has lithium diffusivity of about 10$^{-9}$ to 10$^{-8}$ cm$^2$ s$^{-1}$ and experimental diffusion coefficients of 10$^{-8}$ to 10$^{-11}$ cm$^2$ s$^{-1}$ have been reported$^{32}$ for Li$^+$ diffusion in layered oxide cathodes such as LiCoO$_2$ and LiNi$_{x}$Mn$_{0.5}$Co$_{0.5}$O$_2$.

An Arrhenius plot (ln$D$ versus 1/$T$) for lithiated Li$_{1.16}$V$_{0.93}$O$_2$ is presented in Fig. 3. Analysis of such data provides an estimate of the migration activation energy ($E_{act}$) using the standard Arrhenius relation:

$$D = A \exp(-E_{act}/kT) \tag{1}$$

A migration activation energy of 0.32 eV is derived, indicating high Li ion mobility in this Li-rich oxide anode, which is important for good rate capability. Despite the lack of Li ion conductivity data for direct comparison, our calculated migration energy is compatible with low activation energies for other layered oxides such as Li$_2$Co$_{0.95}$Mg$_{0.05}$O$_2$,$^{34}$ Li$_2$CoO$_2$,$^{26}$ and Li$_x$NiO$_2$,$^{33}$ albeit for Li vacancy migration.

Fig. 2 Mean squared displacement (MSD) plots for LiVO$_2$ (blue) and Li$_{1.07}$V$_{0.93}$O$_2$ (red) for 1.1 ns at (a) 400 K and (b) 500 K.

![Fig. 2 Mean squared displacement (MSD) plots for LiVO$_2$ (blue) and Li$_{1.07}$V$_{0.93}$O$_2$ (red) for 1.1 ns at (a) 400 K and (b) 500 K.](image-url)

**Table 2** Formation energies of lithium Frenkel and anti-site defects (The reaction equations can be found in the ESI.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Frenkel defect energy (eV)</th>
<th>Antisite defect energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiVO$_2$</td>
<td>3.58</td>
<td>3.44</td>
</tr>
<tr>
<td>Li$<em>{1.07}$V$</em>{0.93}$O$_2$</td>
<td>1.67</td>
<td>1.36</td>
</tr>
</tbody>
</table>

**Fig. 3** Arrhenius plot (ln$D$ vs. 1/$T$) for Li$_{1.07+y}$V$_{0.93}$O$_2$. 

A major thrust of fundamental transport studies has been the examination of the atomistic mechanisms controlling bulk transport phenomena. Indeed, the unravelling of mechanistic...
detail at the microscopic level is a powerful feature of the MD technique. Fig. 5 shows a series of snapshots of the lithium ions as they migrate within the alkali-ion layer and via the Li ions in the vanadium layers. This illustration suggests that lithium-ion diffusion takes place by a cooperative interstitialcy or knock-on type mechanism in which the migrating interstitial Li-ion displaces the Li in the V layer into a neighbouring interstitial position in the alkali-metal layer. Such a cooperative type mechanism facilitates lithium-ion diffusion despite the lack of open conduction pathways. Similar cooperative mechanisms have been discussed in connection with lithium migration in LiMgSO₄F³⁴ and with interstitial oxide-ion conduction in electrolytes for solid oxide fuel cells,³⁰ but have not been widely elucidated in Li-rich layered oxides.

4. Conclusions

Atomic-scale mechanistic features of Li-ion transport in vanadium oxide anode materials have been investigated, revealing three main results.

First, the defect formation energies indicate that the inability to intercalate into stoichiometric LiVO₂ is not due to the presence of cation exchange disorder involving V ions in the lithium ion layers pinning them together, which is in agreement with structural studies. It is known that the Li-rich composition Li₁₀V₀₉₃O₂ with lithium on the vanadium layers switches on lithium intercalation.

Second, the MD simulations indicate facile Li⁺ diffusion in the lithiated composition, Li₁₀.₀₇₉V₀₉₃O₂, with a low activation barrier (0.32 eV) for interstitial Li⁺ transport, and diffusion coefficients (D_li) of ca. 10⁻⁹ cm² s⁻¹; these values are consistent with other layered oxide electrodes and suggest favourable rate performance. Finally, long-range Li⁺ diffusion is found to be highly anisotropic, largely restricted to within the lithium layers adjacent to vanadium layers that contain lithium ions. Interestingly, there is also evidence of interlayer diffusion via the lithium ions on the vanadium sites, and involving a cooperative interstitial mechanism.

These insights into transport mechanisms and electrode kinetics are valuable in developing strategies for optimizing this low voltage oxide anode.

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Notes and references

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