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). 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. However, the anode voltage for titanium oxides is of interest since they can offer twice the volumetric energy density anode material for lithium-ion batteries. A greater understanding of the lithium-ion transport mechanisms is important in optimising such oxide anodes. Here, stoichiometric LiVO_2 and Li-rich Li_{0.07}V_{0.93}O_2 are investigated using atomistic modelling techniques. Lithium-ion migration is not found in LiVO_2, which has also previously shown to be resistant to lithium intercalation. Molecular dynamics simulations of lithiated non-stoichiometric Li_{0.07}V_{0.93}O_2 suggest cooperative interstitial Li⁺ diffusion with favourable migration barriers and diffusion coefficients (D_L), which are facilitated by the presence of lithium in the transition metal layers; such transport behaviour is important for high rate performance as a battery anode.

Layered Li_{1+x}V_{1-x}O_2 has attracted recent interest as a potential low voltage and high energy density anode material for lithium-ion batteries. A greater understanding of the lithium-ion transport mechanisms is important in optimising such oxide anodes. Here, stoichiometric LiVO_2 and Li-rich Li_{1.07}V_{0.93}O_2 are investigated using atomistic modelling techniques. Lithium-ion migration is not found in LiVO_2, which has also previously shown to be resistant to lithium intercalation. Molecular dynamics simulations of lithiated non-stoichiometric Li_{0.07}V_{0.93}O_2 suggest cooperative interstitial Li⁺ diffusion with favourable migration barriers and diffusion coefficients (D_L), which are facilitated by the presence of lithium in the transition metal layers; such transport behaviour is important for high rate performance as a battery anode.
first time, the lithium-ion diffusion mechanisms in the vanadate material. In particular, the results comparing stoichiometric LiVO₂ and Li-rich Li₁₀.₇V₁.₃O₂ from long time-scale MD provide new insights into the mechanistic features of interstitial lithium-ion transport.

2. Methods

Atomistic modelling 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 successful study of the LiVO₂ system. The Buckingham shell-model potentials used in this study are presented in 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 DLPOLY 2.20 code). For this work two key structural compositions were compared: stoichiometric LiVO₂ and the lithiated non-stoichiometric Li₁₀.₇V₁.₃O₂ (where y = 0.09). The LiVO₂ simulation box was constructed using a 10 \times 10 \times 2 P1 supercell consisting of 2400 atoms. Our previous work showed that Li intercalation into the Li-rich Li₁₀.₇V₁.₃O₂ 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 Li₁₀.₇V₁.₃O₂ 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 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 Li₁₀.₇V₁.₃O₂ are both csp³ structures (space group R₃m) with alternating LiO₆ and VO₆ layers shown schematically in Fig. 1; the lithium present in the transition metal layers in Li₁₀.₇V₁.₃O₂ 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 Li₁₀.₇V₁.₃O₂ 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 Li₁₀.₇V₁.₃O₂. 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 ionic dislocations 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 LiVO₂.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Comparison of experimental and calculated structural parameters for LiVO₂ and Li₁₀.₇V₁.₃O₂. Calculated elastic and dielectric properties have been presented in ESI, Table S2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) LiVO₂ (R₃m)</td>
<td>Expt.</td>
</tr>
<tr>
<td>a/Å</td>
<td>2.8377</td>
</tr>
<tr>
<td>b/Å</td>
<td>2.8377</td>
</tr>
<tr>
<td>c/Å</td>
<td>14.8230</td>
</tr>
<tr>
<td>γ/deg</td>
<td>90.0</td>
</tr>
<tr>
<td>Li–O/Å</td>
<td>2.102</td>
</tr>
<tr>
<td>V–O/Å</td>
<td>2.004</td>
</tr>
<tr>
<td>O–O/Å</td>
<td>2.830</td>
</tr>
<tr>
<td>(b) Li₁₀.₇V₁.₃O₂ (R₃m)</td>
<td>Expt.</td>
</tr>
<tr>
<td>a/Å</td>
<td>2.8430</td>
</tr>
<tr>
<td>b/Å</td>
<td>2.8430</td>
</tr>
<tr>
<td>c/Å</td>
<td>14.7675</td>
</tr>
<tr>
<td>γ/deg</td>
<td>90.0</td>
</tr>
<tr>
<td>Li–O/Å</td>
<td>120.0</td>
</tr>
<tr>
<td>Li–V–O/Å</td>
<td>2.046</td>
</tr>
<tr>
<td>V–O/Å</td>
<td>2.037</td>
</tr>
<tr>
<td>O–O/Å</td>
<td>2.834</td>
</tr>
</tbody>
</table>
LiVO₂. The site exchange energy in Li₁₀.07V₀.93O₂ 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 LiVO₂.

3.2 Li ion diffusion

Examination of the Li-ion transport properties of Li₁₋ₓV₀.93O₂ 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 LiVO₂ and the lithiated non-stoichiometric Li₁₀.07V₀.93O₂ (y = 0.09).

First, the mean squared displacements (MSDs), ⟨⟨r(t)⟩⟩², 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 LiVO₂, 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 (Dᵢ) can be derived from the MSD data given by D = 1/6τ ⟨⟨r(t)⟩⟩². We calculate a Dᵢ value of about 10⁻⁹ cm² s⁻¹ for Li₁₀.07V₀.93O₂ (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 10⁻¹⁰ cm² s⁻¹ and experimental diffusion coefficients of 10⁻⁸ to 10⁻¹¹ cm² s⁻¹ have been reported for Li⁺ diffusion in layered cathodes such as LiCoO₂ and Li[Ni₀.5Mn₀.5Co₀.5]O₂.

An Arrhenius plot (lnD versus 1/T) for lithiated Li₁₋ₓV₀.93O₂ is presented in Fig. 3. Analysis of such data provides an estimate of the migration activation energy (Eₘaₓ) using the standard Arrhenius relation:

\[ D = A \exp\left(-\frac{E_{\text{act}}}{kT}\right) \] (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 Li₁₀.07Mg₀.05O₂, LiCoO₂ and Li₁₋ₓNi₀.5Mn₀.5O₂, albeit for Li vacancy migration.

Scatter or density plots of the accumulated density of lithium ion trajectories over the simulated time scale enables useful visualization of the migration pathways and the lattice regions most frequently traversed by the mobile Li-ions. Fig. 4a shows the starting configuration of the Li₁₀.07V₀.93O₂ (y = 0.09) structure where the Li⁺ ions are in the vanadium layers and the interstitial lithiums are on tetrahedral sites. As shown previously, substitution of Li for V on the octahedral transition metal sites renders tetrahedral sites in the alkali metal layers energetically accessible by Li.

The lithium diffusion density plots and final configuration of ions in Li₁₀.07V₀.93O₂ (y = 0.09) at the end of the MD simulation are shown in Fig. 4b. The diffuse distribution and overlapping of different lithium positions indicate that numerous different lithium ions are moving between octahedral lattice and tetrahedral interstitial sites. These results show that long-range lithium-ion migration is highly anisotropic, restricted to within the lithium layers adjacent to vanadium layers that contain a small amount of lithium ions. Interestingly, there is also evidence of ion migration between adjacent layers via the lithium ions on the V sites. In contrast, the lithium layers that are not adjacent to Li on V sites, do not exhibit diffusion within or across the layers. A key feature is that the Li-rich composition with Li on V sites plays a vital role in not only switching on the lithium intercalation process, but also in aiding facile lithium-ion diffusion.

A major thrust of fundamental transport studies has been the examination of the atomistic mechanisms controlling bulk transport phenomena. Indeed, the unravelling of mechanistic
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 LiVO$_2$ 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 Li$_{1.07}$V$_{0.93}$O$_2$ with lithium on the vanadium layers switches on lithium intercalation.

Second, the MD simulations indicate facile Li$^+$ diffusion in the lithiated composition, Li$_{1.07}$V$_{0.93}$O$_2$, with a low activation barrier (0.32 eV) for interstitial Li$^+$ transport, and diffusion coefficients ($D_{Li}$) of ca. $10^{-9}$ cm$^2$ 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.

Acknowledgements

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Notes and references

14 S.-S. Kim, J. Kim, M. Koike and N. Kobayashi, 14th International Meeting on Lithium Batteries, Tianjin, Abstract #20, 2008.