

Supplementary Information

Lithium-Ion Diffusion Mechanisms in the Battery Anode Material $\text{Li}_{1+x}\text{V}_{1-x}\text{O}_2$

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Table S1. Interatomic Buckingham potentials used in this study.

Interaction	A (eV)	ρ (Å)	C (eVÅ ⁶)	γ (e)	k (eVÅ ⁻²)
$\text{Li}^+ \dots \text{O}^{2-}$	632.1018	0.2906	0.0	1.00	99999
$\text{V}^{4+} \dots \text{O}^{2-}$	1380.82	0.30170	0.0	3.04	196.30
$\text{V}^{3+} \dots \text{O}^{2-}$	1380.82	0.30170	0.0	2.04	196.30
$\text{O}^{2-} \dots \text{O}^{2-}$	22764.30	0.1490	20.0	-2.96	30.0

The interatomic potentials are based on the Born model for polar solids where the interactions between ions are represented in terms of a long-range Coulombic term plus an analytical function representing short-range repulsive and van der Waals interactions. For this study, the short-range interactions were modelled using the Buckingham potential:

$$V_{ij}(r) = A_{ij} \exp\left(-r/\rho_{ij}\right) - \frac{C_{ij}}{r^6}$$

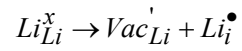
where r is the interatomic distance and A , ρ and C are empirically derived parameters. Charged defects will polarise nearby ions in the lattice and therefore, to calculate the defect energies accurately we included the electronic polarisability in the model, which is incorporated via the shell model.

Table S2. Calculated elastic and dielectric properties of LiVO_2 and $\text{Li}_{1.07}\text{V}_{0.93}\text{O}_2$.

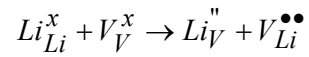
Property	Structural composition	
	LiVO_2	$\text{Li}_{1.07}\text{V}_{0.93}\text{O}_2$
Elastic Constant (10^{11} dyne cm^{-2})		
c_{11}	47.44	47.91
c_{12}	17.79	19.14
c_{13}	6.63	6.82
c_{33}	28.75	30.34
c_{44}	6.26	6.57
c_{66}	14.28	14.39
Dielectric Constant		
$\langle \epsilon_{\text{static}} \rangle$	5.82	6.09
$\langle \epsilon_{\text{high freq}} \rangle$	4.39	4.45

Defect Reactions:

Li Frenkel defect:



Antisite defect:



Using these defect reaction equations, the energies of the isolated point defects (vacancy, interstitial, substitutional) were combined to derive the total Frenkel and anti-site defect formation energies.

The point defects were modelled using the Mott-Littleton approach, in which a defect is introduced into the energy minimised lattice, and the surrounding ions partitioned into two regions. An inner sphere of ions immediately surrounding the point defect (region 1) is then relaxed explicitly whilst the crystal bulk (region 2) is treated by computationally less expensive quasi-continuum methods.