

Supplementary Information

Here, further details of the results obtained from the numerical optimisation procedure are given. In Figure S1, plots of dx/dV and dS/dx are shown for all the experimentally evaluated defect fractions. In Figure S2, visualisations of the parameter values by the parallel coordinates method are shown in detail. The green lines in Figure S1 correspond to simulations with the optimised energy parameters, i.e. the parameters shown in the right hand column of Figure S2.

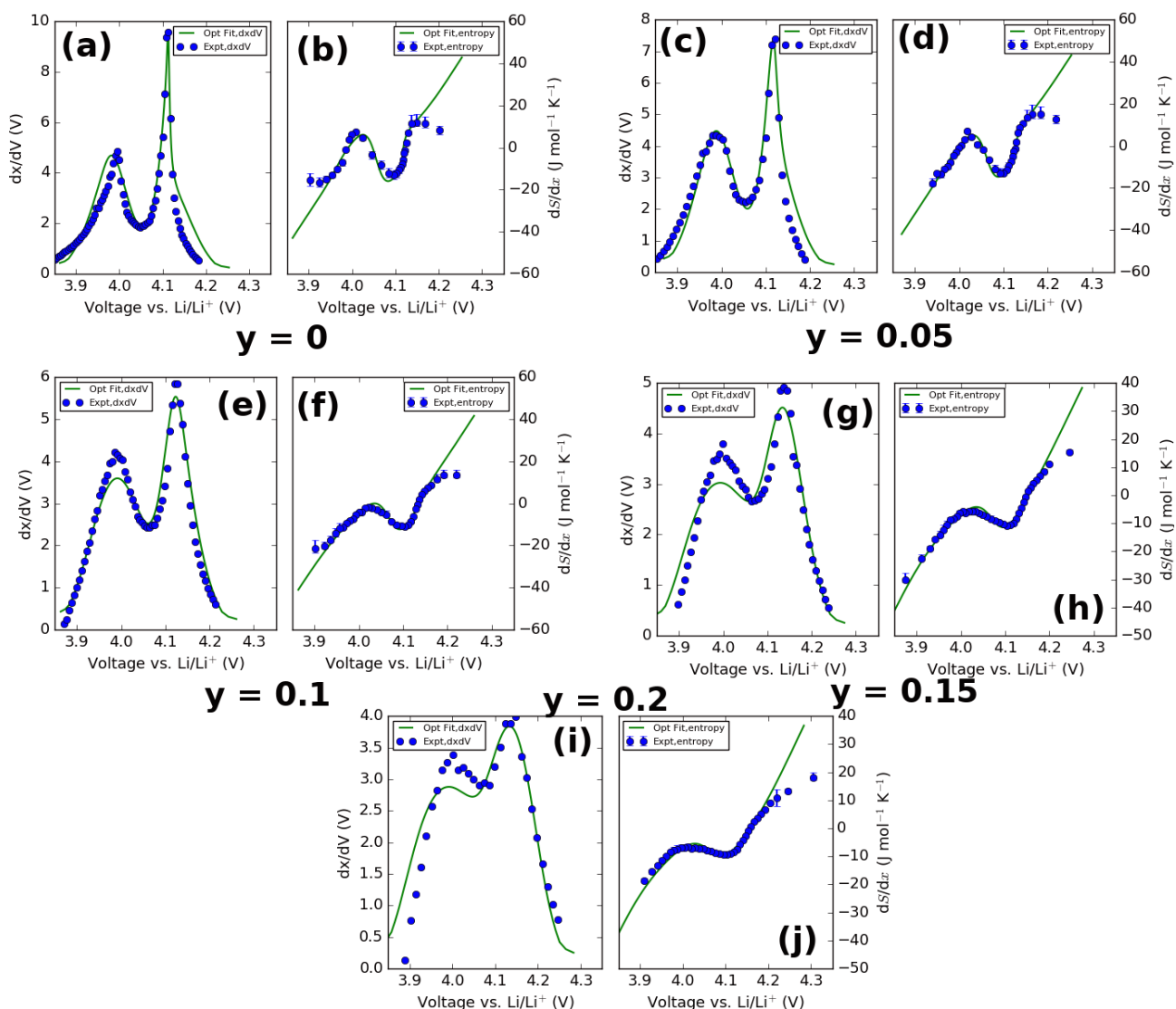


Figure S1. Experimental data (blue points) overlaid with simulated results (green lines). Results for dx/dV (a,c,e,g,i) are shown together with entropy profiling results, dS/dx (b,d,f,h,j). The relevant defect concentration, y , is indicated on the figure. The results correspond to those of model 2B in the main paper, i.e. all interaction parameters were optimised with respect to the defect concentration.

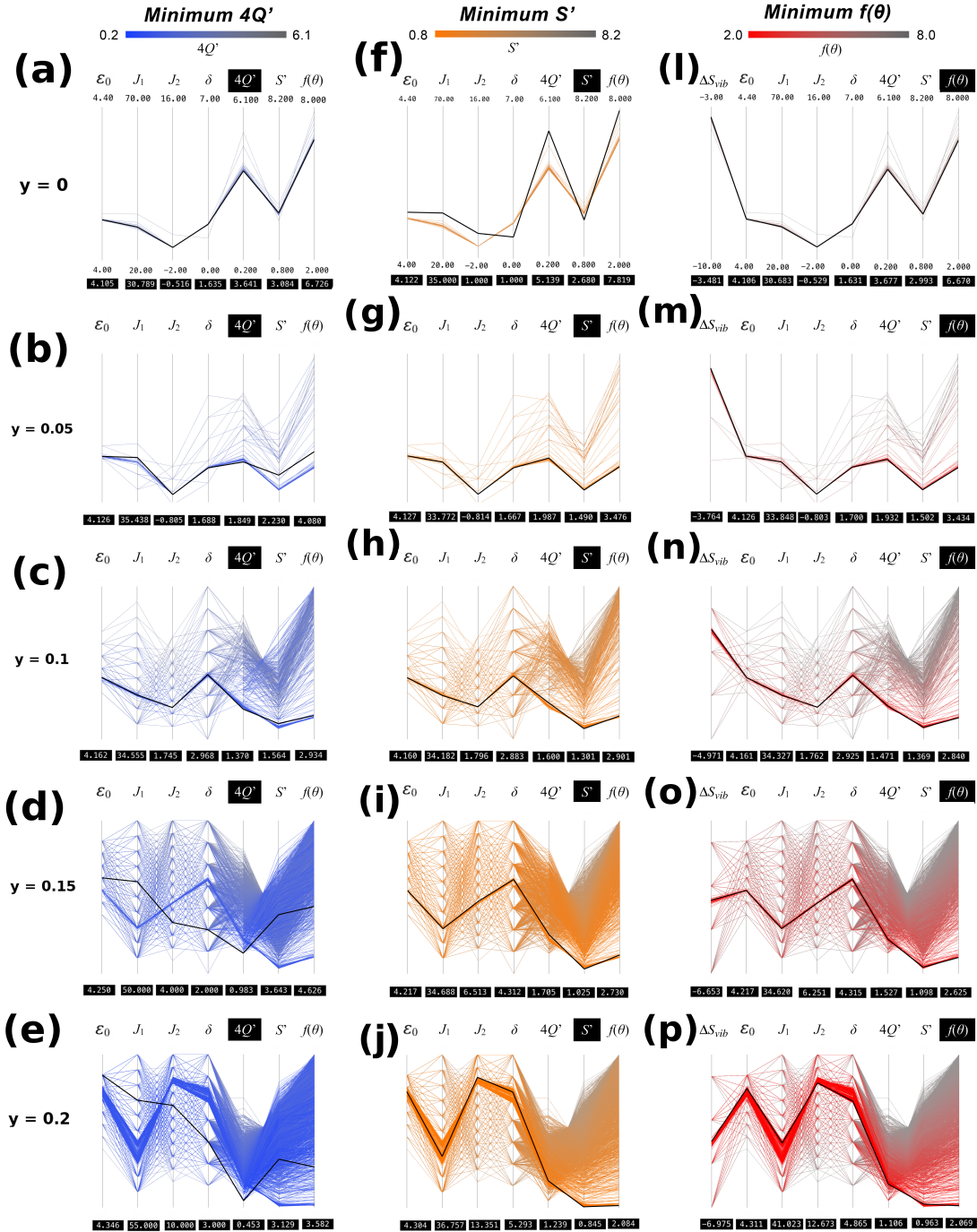


Figure S2. Visualisation of the optimisation procedure by the parallel coordinates method. (a-e): optimisation values considering only the $4Q'$ score (optimisation with respect to the dx/dV curves only); (f-j): optimisation values considering only the S' score (with respect to the dS/dx curves); (l-p): optimisation based on the overall objective, $f(\theta)$, based on the weighted sum of the scores from the optimisation of dx/dV and dS/dx (c.f. green lines in Figure S1). The axis limits are indicated in the top row of figures and are the same for all the plots. In the two leftmost columns, the vibrational entropy parameter ΔS_{vib} was kept constant and was set to the optimal value from the corresponding overall optimisation; in the right hand column it was one of the arguments of the minimisation, θ . The relevant defect concentration in each case is indicated on the left hand side. The optimal argument values obtained in each case are highlighted in black. In each case the black line shows the overall minimum from each optimisation procedure.

Figure S2, rows 2 and 3, corresponding to defect concentrations $y = 0.05$ and $y = 0.1$, indicate that the argument values obtained by optimising with respect to $4Q'$ or S' are nearly the same. Hence these values were also obtained in the overall optimisation (right hand column of Figure S1). For $y = 0$, the optimisation with respect to $4Q'$ and $f(\theta)$ resulted in nearly the same parameter values, but there is a slight discrepancy for S' . The likely reason for this discrepancy is the relatively poor agreement between simulated and experimental entropy profiles at high and low state of charge, as shown in Figure S1b. The flattened regions in the entropy profile could arise due to the presence of an inactive phase in the stoichiometric compound. Bianchini et al. also inferred the presence of inactive phase(s) in stoichiometric LMO by in-situ neutron diffraction measurements [1].

On the other hand, for high defect concentrations $y = 0.15$ and $y = 0.2$, the S' and overall optimisations are in good agreement, while there is a different optimal set of parameters for $4Q'$. The origin of this difference can be seen in Figure S1g and Figure S1i. The optimisation method allows high quality fits to the entropy profiles, but the dx/dV peak separation with this parameter set is overestimated. In both cases a higher J_1 value and lower J_2 value than obtained during the overall optimisation procedure provide the optimal fit to experimental dx/dV data, as shown in Figure S2d and Figure S2e. This parameter set favours the order/disorder transition, and therefore would result in entropy peak amplitudes greater than the experimentally observed ones. This is why the value of $f(\theta)$ highlighted by the black lines in Figures S2d and S2e is significantly greater than the global minimum (c.f. Figures S2o and S2p).

We don't know the full reasons for the discrepancies between entropy and voltage profiles obtained with high defect fraction but it is possible that the mean field approximation, assuming rigid pinning of a certain fraction of Li sites, is deficient in this regime. Alternatively it is possible that the simple approximation to evaluate the vibrational entropy contribution requires additional parameters when the contribution to the configurational entropy from the order/disorder transition is small. These aspects are beyond the scope of the present work and will be investigated further in our future work.

References

- [1] M. Bianchini *et al.*, *J. Phys. Chem. C* **118** (2014) 25947–25955