Supplementary Information for:

Li trapping in nanolayers of cation 'disordered' rock-salt cathodes

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Supplementary Figures:

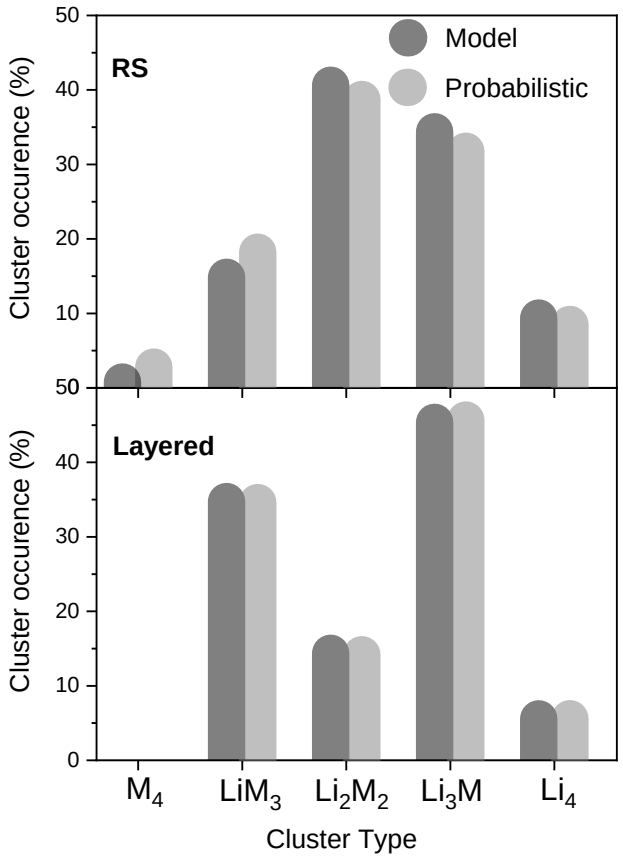

Figure S1. Comparison between the cluster occurrences in the models used in this study and the probabilistic limit.

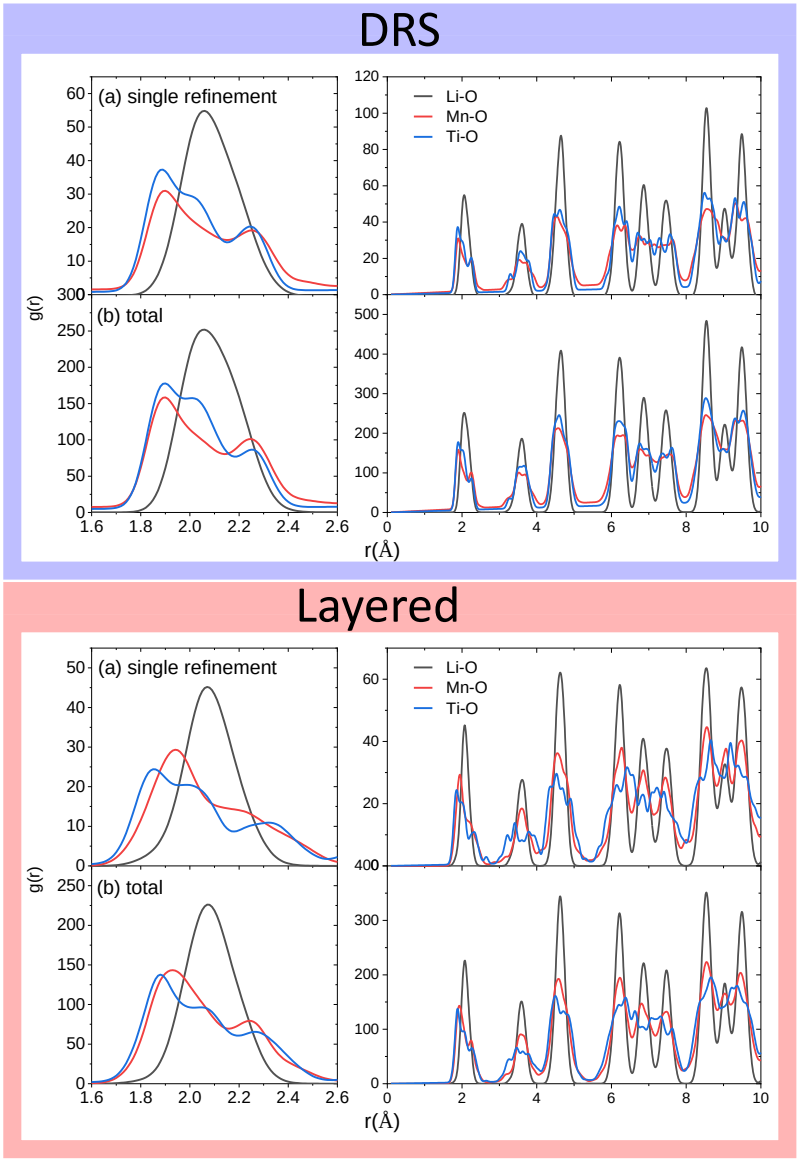

Figure S2. Partial atomic g(r)s of the DRS (top) and layered (bottom) models for a single refinement (a) and the sum of 5 (b).

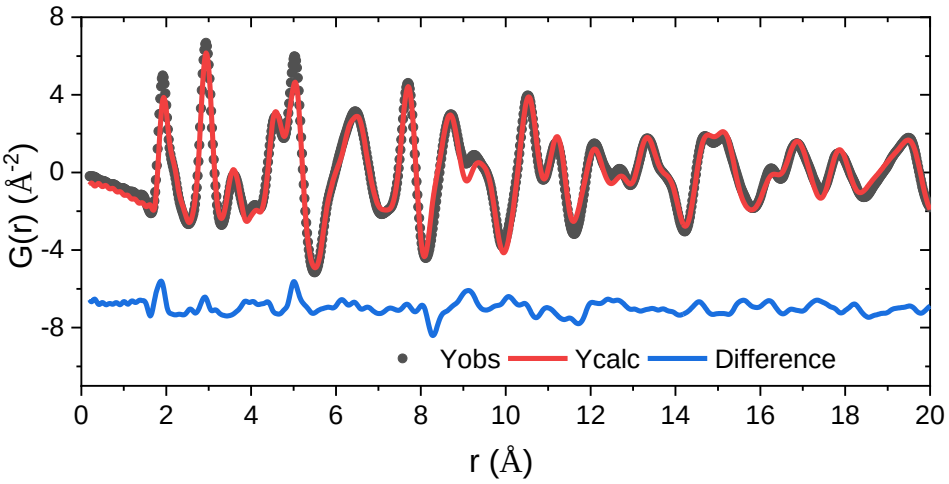

Figure S3. PDF fit of the disordered supercell showing the whole r-range used in the refinement.

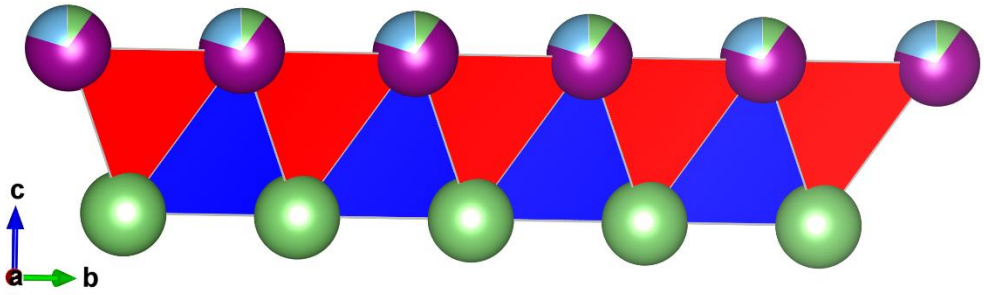

Figure S4. Representation of the two more predominant types of tetrahedral sites LiM3 (red) and Li3M (blue) in the layered model.

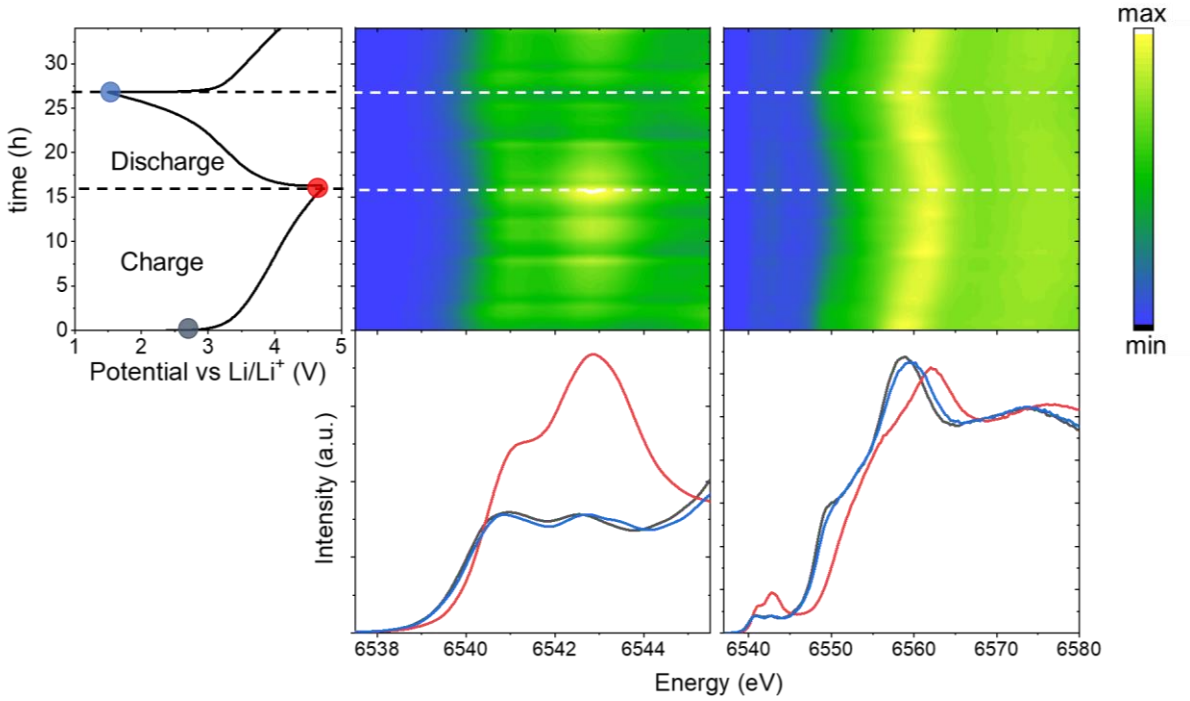

Figure S5. LMTO evolution with cycling characterized by HERFD-XANES. From left to right: electrochemical performance and contour plots of the magnified pre-edge region and HERFD-XANES. Bottom figures show superimposed spectra at highlighted potentials.

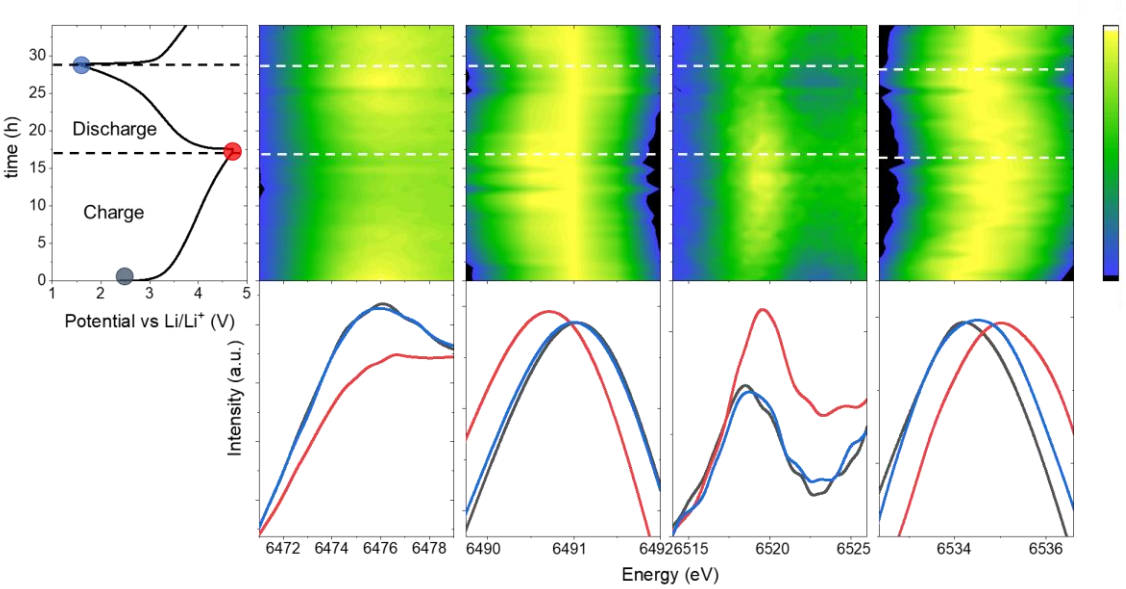

Figure S6. LMTO charge evolution with cycling characterized by operando XES. From left to right: electrochemical performance and contour plots of kβ′, $kβ_{1,3}$, kβ′′ and $kβ_{2,5}$ transitions.

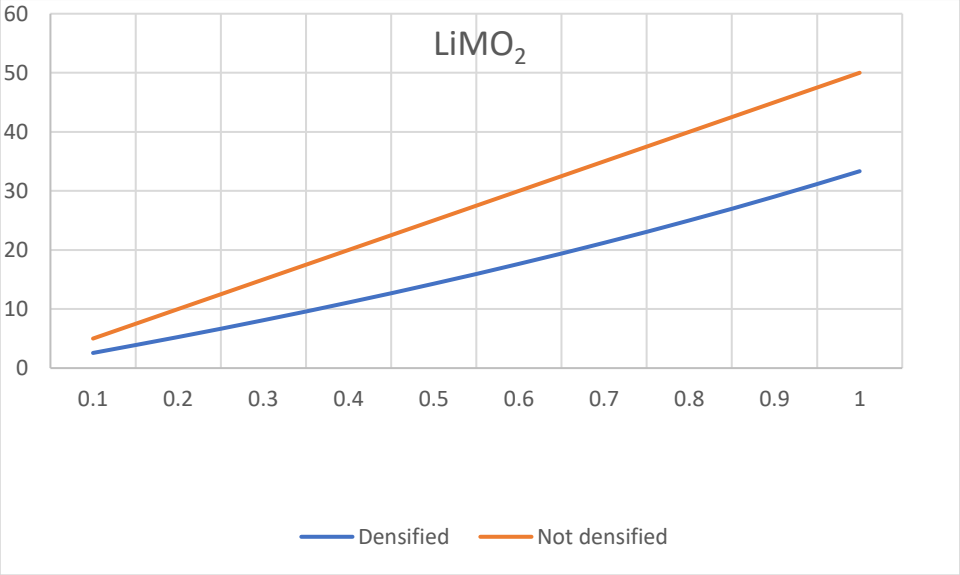

Figure S7. Cation vacancy concentration as a function of delithiation for other cathode materials and DRS undergoing densification. X-axis is y in densified $Li_{1+x-y}\square_{y/2}Mn_{1-x}O_{2-y/2}$ (blue) and 'undensified' $Li_{1+x-y}Mn_{1-x}O_2$ (orange) compositions. Y-axis is the concentration of vacancies.

Lattice densification during delithiation in DRS decreases the concentration of cation vacancies in the material in the charged state following the reaction:

$$Li_{1+x}Mn_{1-x}O_2 \rightarrow \square_{y/2}Li_{1+x-y}M_{1-x}O_{2-y/2} + y/2\ Li_2O$$

Note Li_2O is not detected as a secondary phase, as it forms Li^+ and oxide ions. The oxide ions have been reported to undergo redox to form molecular oxygen which can either be released at the surface of the particles or trapped in 'cavities' resulting from the clustering of cation vacancies.[1–3] Other hypothesis include the formation of peroxides that can be stabilized by the liquid electrolyte at the surface of the cathode material.

Lattice densification is not an irreversible process in DRS.[4] The O_2 molecules are cleaved on discharge reforming O^{2-}, this drives in turn the migration of transition metals into new vacancies and the reincorporation of Li^+-ions on discharge. During such lattice redistribution, layered domains continue to grow as shown in Figure 2.c. $M_3\square$ sites within layered domains could become disconnected from the pathways for Li^+-reincorporation rendering cation vacancies that can no longer be accessed by Li^+. The trapping of cation vacancies in the layered domains could explain the irreversible oxidation to Mn^{4+} during the first charge observed by XES.

References:

[1] R. Sharpe, R. A. House, M. J. Clarke, D. Fo, J. Marie, G. Cibin, K. Zhou, H. Y. Playford, P. G. Bruce, M. S. Islam, *J. Am. Chem. Soc.* **2020**.

[2] R. A. House, H. Y. Playford, R. I. Smith, I. Griffiths, K. Zhou, P. G. Bruce, *Energy Environ. Sci.* **2021**.

[3] R. A. House, U. Maitra, M. A. Pérez-osorio, J. G. Lozano, L. Jin, J. W. Somerville, L. C. Duda, A. Nag, A. Walters, K. Zhou, M. R. Roberts, P. G. Bruce, *Nature* **2020**, *577*, 502.

[4] M. Diaz-lopez, P. A. Chater, Y. Joly, O. Proux, J. Hazemann, V. Pralong, *J. Mater. Chem. A* **2020**, *2*, 10998.