Parallel and serial reduction pathways in complex oxide lithium-ion battery anodes

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Complex early transition metal oxides have emerged as leading candidates for fast charging lithium-ion battery anode materials [1,2]. Framework crystal structures with frustrated topologies are good electrode candidates because they may intercalate large quantities of guest ions with minimal structural response. Starting from the empty perovskite (ReO_3) framework, shear planes and filled pentagonal columns are examples of motifs that decrease the structural degrees of freedom. As a consequence, many early transition metal oxide shear and bronze structures do not readily undergo the tilts and distortions that lead to phase transitions and/or the clamping of lithium diffusion pathways that occur in a purely corner-shared polyhedral network [1].

In this work, we explore the relationship between composition, crystal structure, and reduction pathway in a variety of recently synthesized mixed alkali, transition metal, and main group oxides (Fig. 1), moving beyond the archetypal Ti-Nb-O and W-Nb-O phase spaces. Solid-state NMR spectroscopy, X-ray absorption spectroscopy (XANES and EXAFS), synchrotron and neutron diffraction, and DFT are combined with electrochemical experiments to present a comprehensive picture of the charge storage mechanisms. Prospects for tunability and implications for charge rate and structural stability will be discussed.

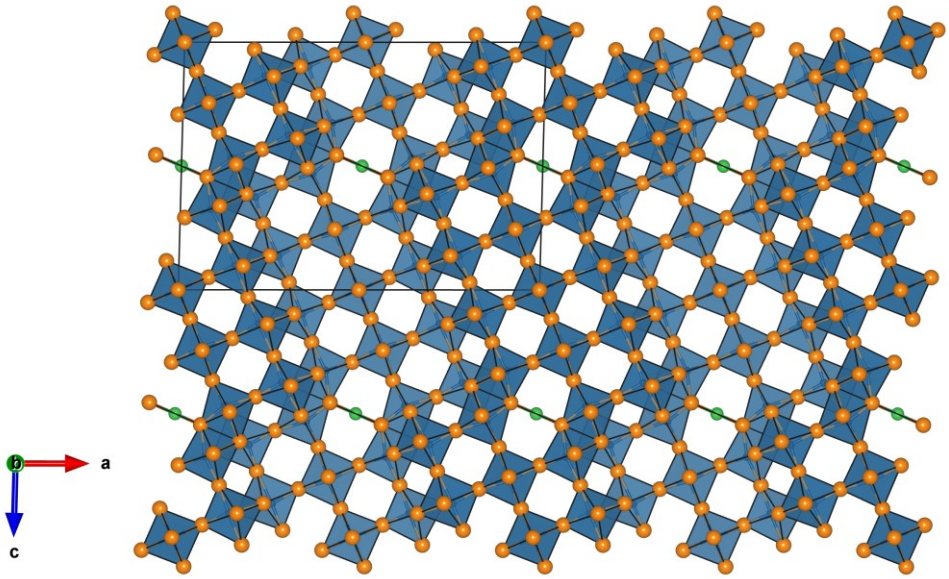

Figure 1. Crystal structure of the Wadsley–Roth crystallographic shear phase $NaNb_{13}O_{33}$.

[1] Griffith, K. J., Wiaderek, K., Cibin, G., Marbella, L. M. Grey, C. P. (2018). *Nature* **559**, 556.

[2] Griffith, K. J., Harada, Y., Egusa, S., Ribas, R. M., Monteiro, R. S., Von Dreele, R. B., Cheetham, A. K., Cava, R. J., Grey, C. P., Goodenough, J. B. (2021). *Chem. Mater.* **33**, 4.

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