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](image)

Figure 1. Crystal structure of the Wadsley–Roth crystallographic shear phase NaNb$_{13}$O$_{33}$.


**Keywords:** shear structures; Wadsley–Roth; X-ray absorption spectroscopy; solid-state NMR, neutron diffraction