Complex early transition metal oxides have emerged as leading candidates for fast charging lithium-ion battery anode materials. 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. In this work, we focus on advanced characterization techniques to explore the relationship between composition, crystal structure, and reduction pathway in a variety of mixed transition metal and alkali or main group oxides. The electrochemical properties of a series of sodium and lithium niobates are studied as new fast-charging lithium-ion battery electrode materials. High-resolution neutron diffraction and $^{23}$Na solid-state NMR spectroscopy (Figure 1) are used to resolve structural questions in the host materials related to sodium disorder, space group subtleties, lithium positions, and second-order Jahn–Teller distortions of the d$^0$ Nb$^{5+}$ redox centers. Structural evolution is followed in real-time at rapid discharge/charge rates with operando synchrotron X-ray diffraction, collecting high-resolution diffraction patterns in a few seconds. The structure models from diffraction are further informed by the local structure perspective from solid-state NMR spectroscopy and X-ray absorption spectroscopy (XANES and EXAFS), while the structural (meta)stability and ionic properties are probed through density functional theory (DFT) calculations. A comprehensive picture of the charge storage mechanisms in these complex oxides are described. Prospects for tunability and implications for charge rate and structural stability will be discussed.