Out of order – Unravelling structural disorder in intercalation battery electrodes

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Rechargeable ion batteries rely on electrode materials that can reversibly host both ions and electrons during electrochemical cycling. The performance and lifetime of these materials are therefore closely linked to their structural evolution during operation. While crystallographic descriptions of well-ordered phases have historically dominated the understanding of battery electrodes, it is increasingly recognized that ion intercalation often induces significant structural disorder, including defect formation via e.g. transition-metal migration and stacking faults formation, and in some cases partial amorphization [1].

Understanding such order–disorder transformations is challenging because the structural evolution often occurs across multiple length scales and may involve the coexistence of crystalline phases, defect-rich states, and disordered components. Powder diffraction provides the essential structural framework for tracking these changes, while synergy with complementary probes is required to fully disentangle the relationships between phase evolution, local disorder, and redox processes.

In this contribution, we demonstrate how operando synchrotron powder X-ray diffraction, combined with total scattering analysis and X-ray absorption spectroscopy, can be used to track the structural evolution of battery electrode materials that undergo varying degrees of disorder during electrochemical cycling. The approach is exemplified through recent studies of layered Na_xMO_2 (M = transition metal) Na-ion battery electrodes, which show complex phase evolution during Na intercalation, including changes in layer stacking sequence, transition-metal migration from the transition-metal layers into the alkali layers, and extensive stacking-fault formation [2-5]. By combining diffraction and spectroscopic probes, we identify correlations between disorder formation and the redox chemistry of both transition metals and oxygen, and we follow the long-term structural evolution to provide insight into the mechanisms of electrode aging.

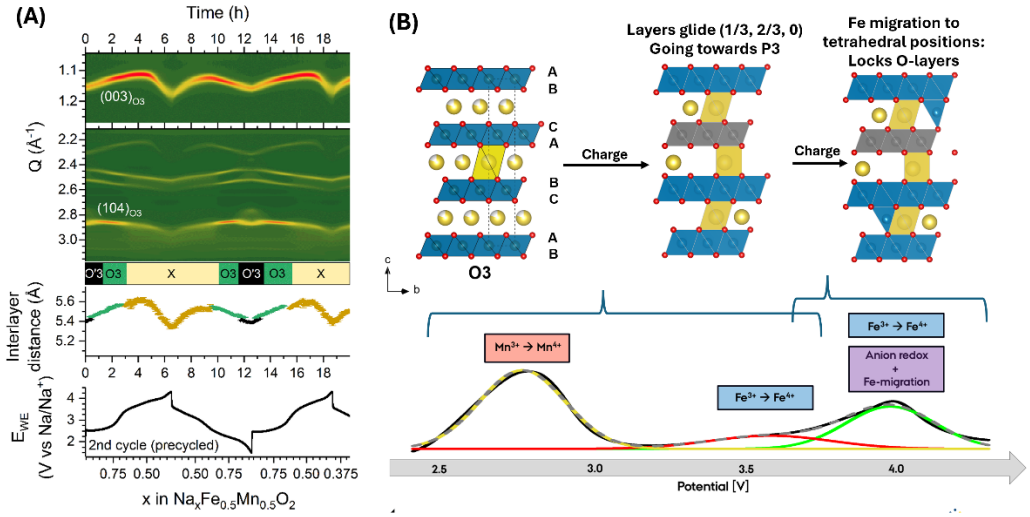


Figure 1. *(A) Operando powder X-ray diffraction collected during Na-ion extraction and intercalation in an O3-$Na_xFe_{0.5}Mn_{0.5}O_2$ electrode during 2nd cycle battery charge and discharge at constant current (C/10-rate). (B) Schematic illustration of correlation between the structural evolution of the O3-$Na_xFe_{0.5}Mn_{0.5}O_2$ electrode (top) and redox potentials from cyclic voltammetry (bottom).*

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