

Elucidating the phase, composition and structural evolution of layered positive electrodes for battery applications using in situ diffraction

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Electrodes account for a significant proportion of battery function, where atomic-scale perturbations or changes in the crystal structure during an electrochemical process permit the reversible insertion/extraction of charge carriers. In both lithium- and sodium-ion batteries, positive electrodes featuring a layered structure, with alternating charge carrier and transition-metal containing layers are found to deliver very good performance over a wide range of the electrochemical parameters. Our work has been focused on rationalizing the diverse range of the phases present, e.g. P2, O3, the compositions used, e.g. varied transition metal ratios, and the structural evolution, e.g. solid solution, two-phase, temperature and current-rate dependence, using a combination of *in situ* neutron and X-ray diffraction methods.

In this contribution, we focus on aspects such as current dependence in P2 $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$, and LiCoO_2 , polymorphic influences on structure and properties in O3 and P2 $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$, charged state stability in $\text{Li}(\text{Ni}_{0.42}\text{Mn}_{0.42}\text{Co}_{0.16})\text{O}_2$, and the role of the composition in $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$ on structural evolution. Highlighted in Figure 1 are representations of the evolution of the layered stacking axis of $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$ with varying Ni:Mn:Co ratios and of P2 $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$ at different current rates. Both the magnitude of change and the appearance/disappearance of reflections detail the result of charge-carrier insertion/extraction. Such studies allow us to explore the structural and electrochemical parameter space that underpin performance.

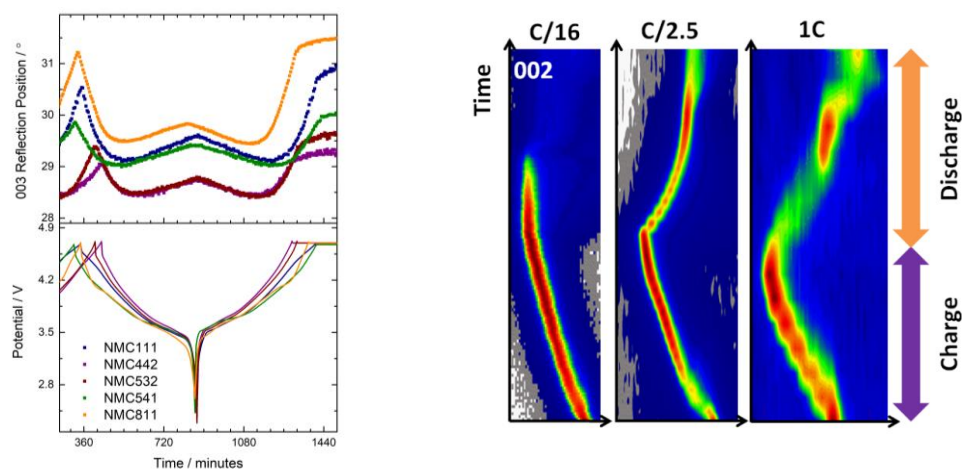


Figure 1. The 2θ position of the 003 stacking axis reflection of $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$ during discharge-charge as the Ni:Mn:Co ratio is varied (left) and a waterfall-type plot of the 002 reflection of P2 $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$ at different current rates.