Sodium layered oxides were first examined for use as positive electrode materials in the early 1980s but become overshadowed in following years by more commercially successful Li-ion based technologies. However, lately there is again renewed focus on the Na layered oxide systems (\(\text{Na}_{x}\text{M}O_2\), where \(\text{M}\) can be a single 3d cation, a mixture of several 3d cations, or a mixture of a 3d cation and magnesium) both for their unusual electronic properties and for potential energy storage applications, where the low cost and abundance of sodium makes them attractive candidates for economical largescale batteries. In the context, we studied the structural rearrangement occurring in \(\text{Na}_{x}\text{VO}_2\) materials used in a sodium-battery as positive electrode materials.

Phase diagrams and structural transformations in the complex \(\text{Na}_{x}\text{VO}_2\) system have been studied using electrochemical (de)intercalation and in situ and operando high resolution synchrotron powder diffraction. Starting from \(\text{O}'3-\text{Na}_{1/2}\text{VO}_2\) obtained by sodium electrochemical deintercalation of \(\text{O}'3-\text{NaVO}_2\) (ABCA oxygen stacking, \(\text{Na}^+\) in octahedral interstitial sites), the structural details of irreversible and reversible thermally driven transformations to \(\text{P}'3\) and \(\text{P}3\) type structures are presented (ABBCCA oxygen stacking, \(\text{Na}^+\) in trigonal prismatic interstitial sites). Subsequently, these \(\text{P}'3\)- \(\text{Na}_{x}\text{VO}_2\) phases provide a platform for operando studies exploring the \(\text{Na}_{x}\text{VO}_2\) phase diagram as a function of sodium electrochemical (de)intercalation. In this system, three single phase domains have been found: a line phase \(\text{P}'3-\text{Na}_{1/2}\text{VO}_2\), one solid solution for \(0.53 \leq x \leq 0.55\) characterized by an incommensurate modulated structure and a second solid solution for \(0.63 \leq x \leq 0.65\) with a defective structure resulting from a random stack of \(\text{O}'3\) and \(\text{P}'3\) layers. With further sodium intercalation \((x > 0.65)\), the structure irreversibly transforms to the starting parent phase \(\text{O}'3-\text{NaVO}_2\). This work reveals new details about the diverse structural prototypes found in sodium layered oxides used as electrode battery materials and the transitional pathways between them as a function of temperature and composition.

**Keywords:** Sodium battery, Sodium layered oxide, Structural transitions