Operando PXRD and PDF Investigations of Disordering in $NaCrO_2$-CrO_2

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The Li-ion battery technology completely revolutionized the portable electronic market and today it has become almost impossible to imagine a world without laptops, cell phones, etc.[1] This imposes a great challenge for the Li-ion battery industry, as demands for storing renewable energy and self-sufficiency in private homes are becoming more attractive.[2, 3] This will inevitably put pressure on the demand for both Li and Co, which are very limited resources.2 Despite elimination of toxic transition metals, like Co, has become a general aim for researchers and industry the Li extraction problem is yet to be solved.[4, 5] Here, Na-ion batteries are a great alternative to Li-ion batteries. Two types of materials are especially interesting, namely the O3 and P2 material, first discovered by Delmas and co-workers.[6, 7] Here O3-type has the highest capacity, as this material is synthesized with a higher Na content.[8]

From previous studies, the O3-type material is known to go through several phase transitions going from rhombohedral to monoclinic symmetry. In the beginning of 1980 Na intercalation was established for several O3-materials herein O3-$NaCrO_2$. The O3-$NaCrO_2$ is relatively, as great cycling stability and thermal stability has been shown, though upon complete charge, this material becomes disordered, and reversibility is lost.[9, 10] The material has been proposed to form Cr^{6+}, via a disproportionation from the formation of Cr^{4+}, during charge which migrates into the interslab forming a tetrahedral environment with oxygen. At end of charge, Cr^{4+} is reformed via a comproportionation which is suggested to arrange in a rock-salt structure.[11]

In this work, we set out to follow the structural behavior during charge and discharge in $NaCrO_2$. We have via operando PXRD confirmed that the material undergoes 3 phase transitions during charge, before the disorder is introduced in the material. Furthermore, we aim to trace the formation of tetrahedral Cr^{6+} with both ex situ and operando pair distribution function analysis (PDF) as this is directly linked to Cr-migration This is believed to be the source to the disordering of the material and the misfunctioning as positive electrode material in Na-ion batteries.

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