

## MS19-O2

## Operando neutron diffraction study of crystal structure changes in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode material

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$\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$  ( $x \approx 0.15$ ,  $y \approx 0.05$ ) oxide (NCA) is one of the most common cathode materials used for the Li-ion batteries production. Its advantages include high practical capacity (~200 mA·h/g) and discharge voltage (~3.8 V), rather low cost, structural stability during electrochemical cycling and a relatively low capacity loss per cycle. NCA material was intensively studied during the last decade, but abnormal behavior of NCA crystal structure (phase separation, nonlinear changes of interlayer distances) during the first and consequent cycles had not been clearly explained until recently. We have applied *operando* neutron diffraction, combined topological analysis as well density functional theory modeling to study NCA crystal structure changes [1-3]. Due to high penetration possibility of neutrons a part of experiments has been made on a commercial 18650 battery with NCA cathode [1]. For crystal structure study of NCA during the first cycle a new electrochemical cell has been developed [3]. Measured dependencies of interatomic spacing and interlayer spacing of the cathode structure on the lithium content are explained by several factors, such as variations of oxidation state of cation in oxygen octahedra, Coulomb repulsion of oxygen layers, changes of average effective charge of oxygen layers and van der Waals interactions between  $\text{MeO}_2$ -layers at high level of NCA delithiation. The phase-separated state at the first cycle is caused by the morphology of NCA material. These observations could be expanded to layered cathode materials with similar microstructures.

References:

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## MS19-O3

## Neutron diffraction studies of oxygen disorder in $\text{Nd}_2\text{NiO}_{4+d}$

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Better understanding of oxygen diffusion in non-stoichiometric oxides becomes essential for further development of intermediate temperature solid oxide fuel cells. In this prospect, rare earth nickelates ( $\text{R}_2\text{NiO}_{4+d}$ ) emerged as promising materials in which oxygen transport is driven by oxygen disorder and non-stoichiometry. Their crystal structure consists of  $\text{RNiO}_3$  perovskite layers sandwiched between RO-type rock salt layers and extra oxygens are intercalated in tetrahedral sites inside the rock salt layer. Oxygen diffusion, in these materials, is highly anisotropic and described by interstitialcy mechanism [1] in which excess oxygens diffuse via apical oxygens inside the rock salt layer. However, close to room temperature, diffusion is non-Arrhenius type but a lattice activated process [2]. In this talk, I will address structural studies which are performed with neutron diffraction on polycrystalline and single crystal  $\text{Nd}_2\text{NiO}_{4.25}$  compound as a function of temperature, are essential to get experimental evidences on oxygen migration mechanism in these oxides. High resolution neutron diffraction studies show the evidence of 3d-ordering of excess oxygens in below 823 K, confirming the pinning of excess oxygens to the crystal lattice which makes the real structure incommensurate. The average structure (excluding incommensurate superstructure reflections) of the compound can be described in orthorhombic  $Fmmm$  space group. However, these incommensurate oxygen superstructure reflections start to lose intensity around 400 K and around 823 K, loss of 3d-oxygen ordering occurs which is accompanied by a orthorhombic to tetragonal structural transition. With scattering density studies of average structure using the Maximum Entropy Method, we observed unusually high anharmonic displacement factors both for equatorial and apical oxygen atoms showing large displacement amplitudes (fig. 1) towards [001] and [110] with respect to the F-symmetry cell, respectively which are getting amplified in the tetragonal phase. This result confirms the proposed interstitialcy diffusion mechanism for these oxides and supports previously reported molecular dynamics simulated results [3] on  $\text{Nd}_2\text{NiO}_{4.25}$  compound. In conclusion, with neutron diffraction studies up to high momentum transfers, we show that excess oxygens are essential to activate large apical oxygen displacements toward nearest vacant interstitial site allowing oxygen diffusion in the intermediate temperature range.