MS19-O2

Operando neutron diffraction study of crystal structure changes in $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode material

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$LiNi_{1-x-y}Co_xAl_yO_2$ ($x \approx 0.15$, $y \approx 0.05$) 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 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.

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MS19-O3

Neutron diffraction studies of oxygen disorder in Nd_2NiO_{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 (R_2NiO_{4+d}) emerged as promising materials in which oxygen transport is driven by oxygen disorder and non-stoichiometry. Their crystal structure consists of $RNiO_3$ 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 rack salt layer. However, close to room temperature, diffusion is non-Aarhenius 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 $Nd_2NiO_{4.25}$ 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 (exclusing incommensurate superstructure reflections) of the compound can be described in orthorhmbic F*mmm* space group. However, these incommensurate oxygen superstructure reflections start to lose intensity around 400 K and arround 823 K, loss of 3d-oxygen ordering occurs which is accompanied by a orthorhmbic 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 $Nd_2NiO_{4.25}$ compound. In conclusion, with neutron diffraction studies up to high momentum transfers, we show that excess oxygens are essential to activate large apical oxygen displacemnts toward nearest vacant interstital site allowing oxygen diffussion in the intermediate tempearture range.

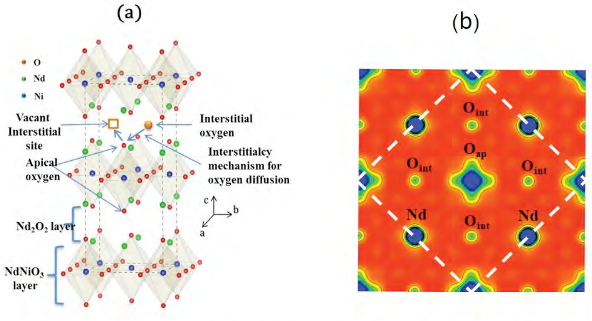

Fig. 1. (a) Crystal structure of $Nd_2NiO_{4.25}$ in F*mmm* space group (b)Anharmonic displacements of apical oxygen atoms at room temperature for $Nd_2NiO_{4.25}$ obtained with MEM. White lines represent F-cell.

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MS19-O4

The aluminium-ion battery

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The expansion of renewable energies and the growing number of electric vehicles and mobile devices demand for improved and low-price electrochemical energy storage. In order to meet the future needs for energy storages novel material systems with highest energy densities, readily available raw materials, and safety are required. Currently, especially lithium and lead dominate the battery market, but beside cobalt and phosphorous, in particular lithium may show substantial supply challenges in the future. Therefore, the search for new chemistries will become increasingly important in the future in order to diversify battery technologies.

Due to its high abundance and triple charge, aluminium is a highly interesting candidate for high-valent, *post*-lithium batteries, since for stationary application large quantities of active mass are necessary.

Within the crystalline structure of potential solid aluminium-ion conductors, the high charge of the trivalent aluminium ion poses the challenge of high attraction towards anions and high repulsion from cations. In this context, an optimised crystal structure is of paramount importance. By analysing the necessities for good ionic transport and applying this knowledge to large crystallographic databases by means of high-throughput crystal-chemical analyses, we address the identification of promising materials candidates for a future all-solid-state aluminium-ion battery technology.

Traditionally, the search for Al-conductors was started with oxygen-containing materials. We opened up the chemical space of potential aluminium-ion conductor materials by first analysing bonding differences in aluminium and oxygen, sulphur, or selenium-containing materials. Due to the decreasing electronegativity and increasing size, we found an increasing polarisation of the chalcogenides and a better shielding of charge from the aluminium-ions. We have studied varying ternary spinel-like structures by means of density functional theory (DFT) calculations to quantitatively evaluate the chemical bonding in aluminium-chalcogenides.

Eventually, this knowledge was applied to the ICSD to filter out promising materials for the conduction of aluminium-ions. We applied Voronoi-Dirichlet partitioning to first geometrically filter for materials with interconnected interstitial voids that are large enough to host aluminium-ions. Secondly, bond-valence site-energies were calculated to estimate respective activation energies for the percolation of aluminium-ion conduction paths. As a last step, DFT will is be used to simulate a full, dynamic diffusion process for the most interesting candidates *ab initio*.

We will present the current state of the aluminium-ion battery, including theoretical and first experimental results. This work is funded by the German BMBF (R2RBattery: 03SF0542A), the Russian Megagrant (14.B25.31.0005), and the RSF (16-13-10158).