

operaXX

Clarification of the aging mechanisms of novel cathode-active materials via operando XAS/XES

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In Short

- Quantum-mechanical characterization of (de)lithiated Ni-Co-Mn and Ni-Co-Al oxides for energy storage applications.
- Identification of their degradation products via high-throughput computational screening.
- Analysis of the electronic structure of the cathode materials and their degradation products of the battery cell using density functional theory for comparison with experimental spectroscopic data taken *ex situ* and in *operando* conditions.

The increasing industrial demand for efficient, cost-effective, and non-polluting battery materials motivates fundamental research in the field of chemistry, physics, and materials science to shed light onto the microscopic properties of the transition-metal oxides, such as Ni-Co-Mn (NCM) and Ni-Co-Al (NCA), that are currently regarded with most interest for this type of applications. Deeper understanding is requested on both the electronic structure of the pristine materials as well as their degradation products forming under the delithiation cycles. Clarifying both aspects is the central goal of the project *operaXX*, in collaboration with the experimental partner groups from Berlin and Munich and financed by the Federal Ministry for Education and Research (BMBF) since November 2020.

In the initial phase of this project, our work has been focused on the electronic and spectroscopic characterization of the lithiated binary oxides and their delithiated counterparts [1]. As an example, we have considered LiCoO_2 (see Fig. 1a) and we have analyzed in detail the role of electron-hole correlations in the x-ray absorption spectra (XAS) of this material. Assessing this aspect is essential from a methodological viewpoint. As shown in previous work, depending on the nature of the material, excitonic effects can be sizeable even for core excitations [2,3]. In this case, their explicit inclusion in the calculation through the solution of the Bethe-Salpeter equation (BSE) [4] is essential to correctly reproduce the spectra. In LiCoO_2 , we have demonstrated that these correlation effects are minor. As

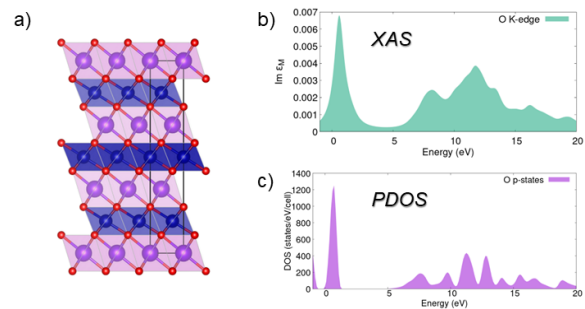


Figure 1: a) Ball-and-stick representation of the LiCoO_2 crystal: the conventional unit cell is marked by a black line; Li atoms are in purple, Co atoms in blue, and O atoms in red; b) X-ray absorption spectrum (XAS) computed from the O K-edge of LiCoO_2 solving the Bethe-Salpeter equation. The spectral onset is set to zero. c) Projected density of states (PDOS) on the unoccupied O p-orbitals, which are the final states of the transitions from the O 1s levels (K-edge). The bottom of the conduction band is set to zero.

shown in Figs. 1b)-c) for the O K-edge spectrum (excitations from O 1s electrons), the x-ray XAS computed from the BSE is in excellent qualitative agreement with the contributions of the unoccupied O p-orbitals to the projected density of states (PDOS). The same behavior is obtained for the Co K-edge and $L_{2,3}$ -edge spectra compared against the contributions to the PDOS of Co p-states and Co s- and d-orbitals, respectively [1]. These results suggest that accessing the target states of the core-level excitation in the PDOS of the material is sufficient to identify the spectral fingerprints for a reliable comparison with the experiments. This findings is very important in view of characterizing NCM and NCA cathodes simulated in supercells containing tens or even hundreds of atoms: the costs of BSE calculations on these systems would be unaffordable.

Equipped with this knowledge, we are now ready to focus on realistic NCA and NCM cathodes and on their degradation products. Both topics are at the heart of this application. To investigate the stability and the electronic properties of the aforementioned materials, it is essential to identify their possible configurations. The terms “NCM” and “NCA” are referred to an entire family of compounds containing the indicated atoms. The relative amount of Ni, Co, and Mn/Al represents the first degree of freedom to address. Moreover, these systems are to be considered not only in their initial configuration but also during and after the delithiation process. This increases further and dramatically the number of possible systems to simulate. A similar problem has to be faced when dealing with the degradation

products. Binary oxides of all transition metal atoms forming NCA and NCM exist in several stoichiometries and polymorphs, which, in principle, should all be taken into account. As a matter of fact, experimental studies offer reliable indications that only cubic crystal phases are formed at specific oxidation states of the material during the delithiation process. Another degree of freedom is given by the magnetization of the materials. It is evident that such a large number and variety of systems demand an automatized framework to be efficiently dealt with.

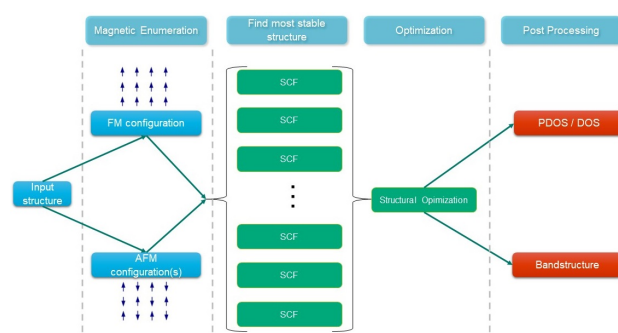


Figure 2: Sketch of the high-throughput workflow.

To this end, we have designed an automatized workflow on top of the AiiDA infrastructure [5] that is able to construct and screen the possible configurations of the degradation products of NCM and NCA (see Fig. 2). The density-functional theory calculations nested in the workflow will be performed with the plane-wave, pseudopotential code Quantum Espresso [6]. As input structures, we will consider the entries available for the relevant compositions on computational databases such as Materials Project [7] and OQMD [8]. The end product of this computational procedure is the delivery of stable structures which can be considered reliable candidates forming during the aging process of the cathodes. Since the experimental characterization of these systems is performed via *operando* XAS, we will compute the PDOS of the identified candidates for degradation products and compared them with the measured spectra.

To investigate the electronic structure of NCA and NCM, we will adopt a slightly different approach. In order to reduce the computational complexity, we will focus initially on simplified compositions that represent an optimal trade-off between the cathode-active systems included in the experimentally tested battery cells and the feasibility of our computations. For NCM, the so-called “811” stoichiometry (80% Ni, 10% Co, and 10% Mn) will be simulated in a crystal cell with space group $R\bar{3}m$ [166]. For NCA, the commercial compound with 80% Ni, 15% Co, and 5% Al will be taken into account. Under these

pre-conditions, we will generate all possible structures and, by comparing their total energies, we will pinpoint the most stable ones for which the PDOS will be computed and compared with the experimental spectral data. Finally, for the accomplishment of the last step of the project, we will simulate the delithiation process in the selected structures. To this end, we will consider snapshots of evolving NCA and NCM cathodes, namely compounds including a decreasing amount of intercalated Li ions.

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More Information

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Project Partners

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