Localized Gap States in LiCoO₂ and their Influence on the Transport Properties in Li ion Batteries

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The electronic structure of Co₂O₃, CoO₂ and LiCoO₂ is analyzed in a comparative study employing synchrotron radiation. We study the Co₂p and O₁s core levels, the X-ray absorption spectra at the Co₂p and the O₁s absorption edges, as well as the valence band and conduction band states of Co₂O₃, CoO₂, and LiCoO₂ by resonant photoelectron spectroscopy. Experiments are performed at the ASAM end station at the U49/2 beam line at Bessy, Berlin. We use thin film samples prepared on metallic substrates from Co-nitrate solutions and compare them to electrochemically titrated LiCoO₂ samples.

In the Co₂p core level data we find that the characteristic satellite features can be used to identify the existence of Co³⁺ and distinguish them from Co⁴⁺ emissions.

The Co₂p and O₂p partial density of states (pDOS) in the valence band (VB) is derived from the valence band spectra which we recorded at resonant excitation at both, the Co₂p and at the O₁s thresholds. We find that the width of the Co₂p derived pDOS is very remarkable as it extends up to -20eV below the Fermi energy. In addition, there appear rather sharp features close to the Fermi energy which have both, O₂p and Co³d character.

The XAS data are used to derive the conduction band (CB) partial density of states. We again find sharp features next to the Fermi energy which arise from unoccupied O₂p states. They appear separated from the Co³d contributions which appear at higher energies. Again these sharp features are split from broad CB states attributed to covalent O₂p/Co³d states.

To explain our data, we start with the covalent interaction between O₂p and Co³d which form the broad features in the CB and VB pDOS. The sharp spectroscopic features around the Fermi energy are assigned to charge transfer Co³d⁷L and Co³d⁸L² states. We attribute these localized states as to the charge carriers which cause the discharge current in Li ion batteries. In addition, we follow the changes upon varying the Li content i.e. the ratio of Co³⁺ / Co⁴⁺. When the Co³⁺ content is small we find a semiconducting behavior with a gap between the localized VB states and the localized CB states of around 1.5eV. With increasing Co³⁺ content, however, that gap is closed mainly by an increase of the O₂p derived localized states which now move towards and even below the Fermi energy. We discuss these findings in the context of studies in the literature reporting on the conductivity and the magnetic properties of Li doped cobaltates.