

Ab-initio simulation of Li migration in $\text{Li}_x(\text{Co,Ni})\text{O}_2$ ($0 < x < 1$) – LIPO/LIPON based cathode-electrolyte interface systems

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Technological goal

Understand mechanisms and processes behind degradation and fatigue phenomena during electrochemical cycling

Hypothesis

Long-term “cyclability”, initial capacity and current density may mainly be limited by Li ion diffusion in the cathode material and by resistance at the interface between cathode and solid electrolyte

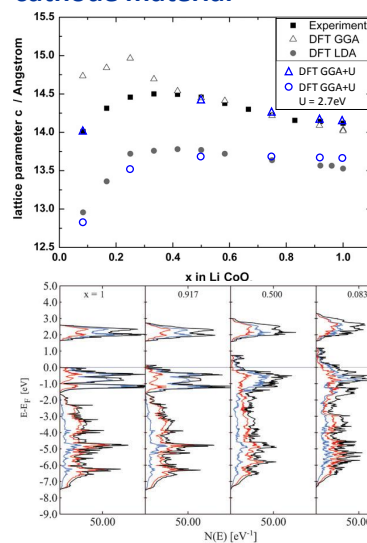
Research program

Crystal and electronic structure of cathode material upon intercalation and de-intercalation of Li atoms^{1,2}

Calculate Li diffusion in cathode material

Calculate Li diffusion through cathode-electrolyte interface

Crystal structure and electronic structure of the cathode material^{1,2}



Lattice parameter c during intercalation for different exchange correlation functionals and experiment. Increase of c due to electrostatic repulsion of O layers less screened by missing Li. Decrease of c due to charge decrease at O atoms lowering the repulsion of O layers. Li intercalation layers are responsible for these effects.

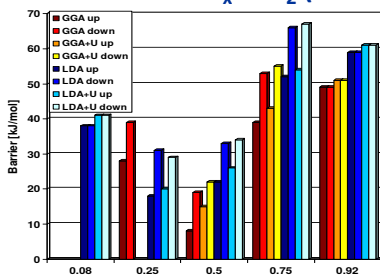
Electronic density of states during de-intercalation (LDA+U)

-1.5 to 0 eV: Co 3d t_{2g} symmetry

-8 to -1.5 eV: O 2p

During de-intercalation electrons are removed from Co (oxidation), Co-O bond length decreases, covalence increases. Re-orientation of charge distribution not captured by rigid band model.

Li diffusion in Li_xCoO_2 ($0 < x < 1$)

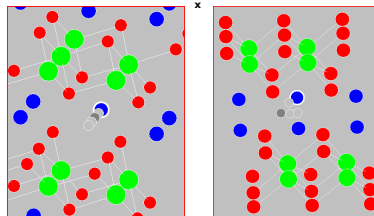


Migration barriers in kJ/mol for different extent of intercalation x and exchange correlations

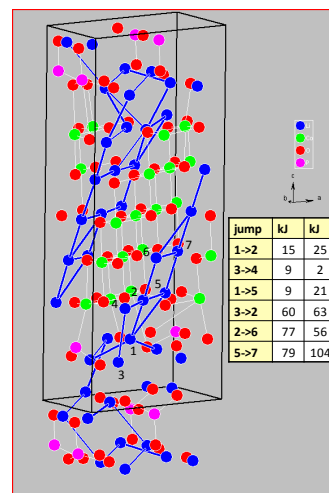
“Up” and “down” indicate the barrier height with respect to initial and final state. Barriers decrease during de-intercalation. Little difference due to Hubbard U term, but about 10 kJ/mol higher barriers for LDA. Barriers are calculated lower than in Ref. 3.

Migration paths

Depending on the extent of Li intercalation different migration paths are observed. For high Li intercalation paths are linear whereas for lower extent the paths become curved, being responsible for lower energy barriers.



Li diffusion through Li_xCoO_2 - LIPO interface



LiCoO_2 - LIPO interface building and optimization

Partial γ surface scan and optimization by GGA

Li migration barriers through the interface region to LIPO

Tendency: reduced barriers directly at the interface and interface enhanced barriers in the cathode

Computational aspects

- Ab initio calculations by MedeA-VASP
- Interfaces constructed by the interface building tools of MedeA
- Minimum energy paths and transition states by the climbing image nudged elastic band method as implemented in the MedeA-TSS (Transition State Search) module

References:

- Changes in the crystal and electronic structure of LiCoO_2 and LiNiO_2 upon Li intercalation and de-intercalation, S. Laubach, S. Laubach, P. C. Schmidt, D. Enslin, S. Schmid, W. Jaegermann, A. Thißen, K. Nikolowski, H. Ehrenberg, Phys. Chem. Chem. Phys. **11**, 3278-3289 (2009)
- Structure, electronic structure and defect formation energies of $\text{Li}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_2$ as a function of x ($0 < x < 1$) and y ($y = 0, 0.5, 1$), S. Laubach, S. Laubach, P. C. Schmidt, M. Gröting, K. Albe, W. Jaegermann, W. Wolf, Z. Phys. Chem. **223**, 1327-1340 (2009)
- Lithium diffusion in layered Li_xCoO_2 , A. Van der Ven, G. Ceder, Electrochemical and Solid-State Letters **3**, 301-304 (2000)