

Surface science investigations of electrode-electrolyte interfaces in Li-ion batteries



TECHNISCHE
UNIVERSITÄT
DARMSTADT

René Hausbrand, Gennady Cherkashinin, André Schwöbel, Wolfram Jaegermann



This talk: electronic structure and reactivity of interfaces

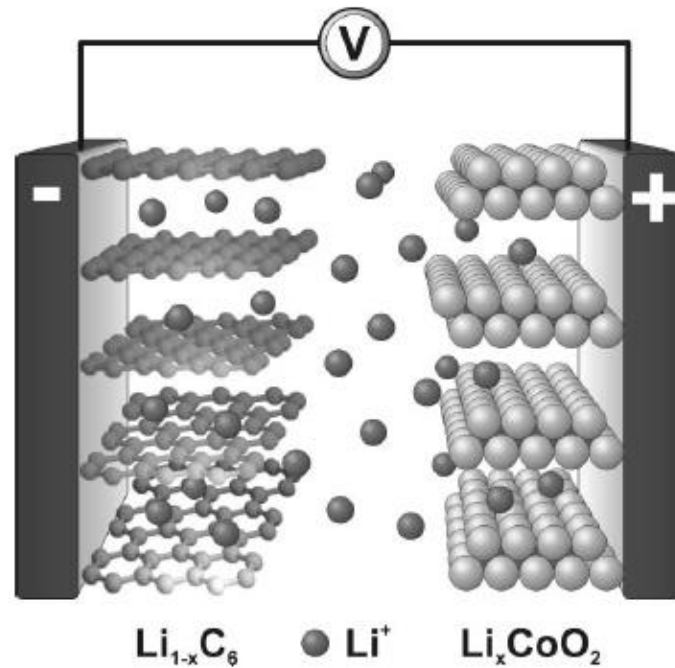
A3

Poster: electronic structure of cathode materials (G. Cherkashinin)



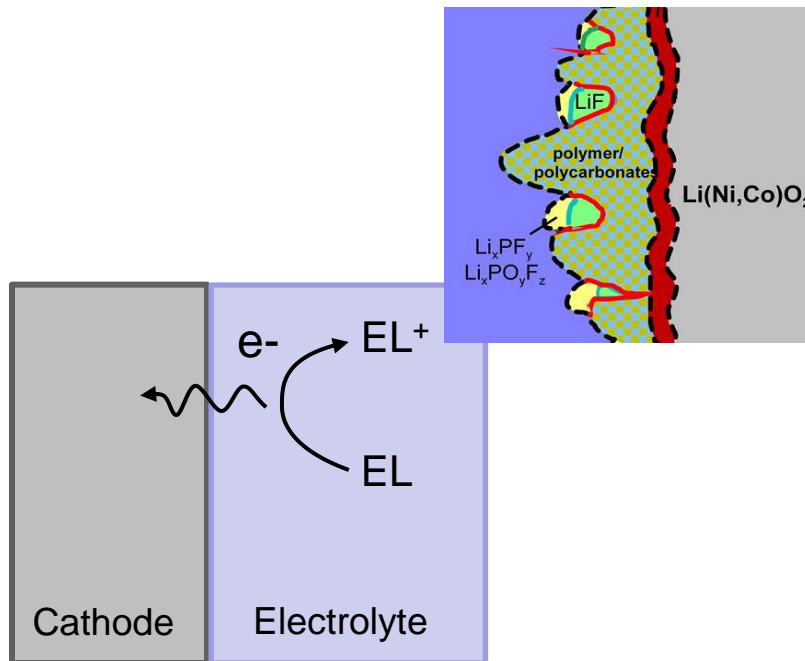
- Introduction
 - Electron energy level alignment, electron transfer
 - Surface science approach
- Electron transfer and reactivity of electrode-electrolyte interfaces
 - DEC on LiCoO_2
 - LiPON on LiCoO_2
 - Li on LiPON
- Conclusion
- Acknowledgements

Li-ion cell, ion transfer

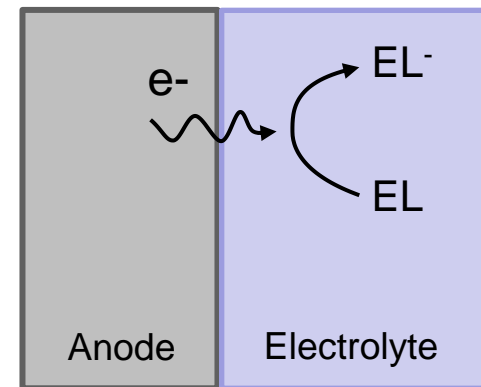


Insertion electrodes =>
exchange of ions at electrode-electrolyte interface, ionic electrode

Parasitic electron transfer



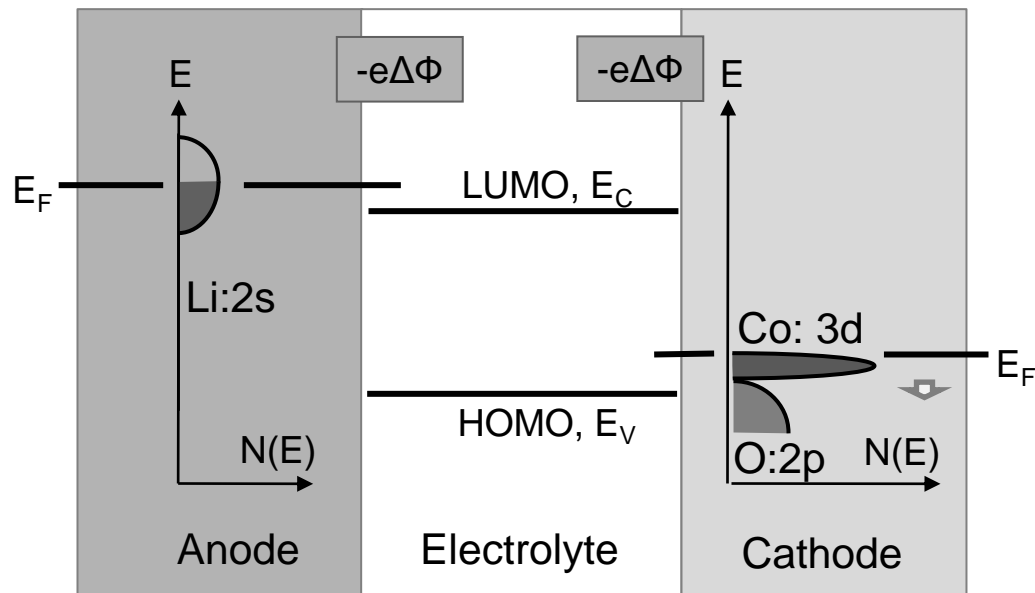
Electrolyte oxidation
(Cathode reduction)



Electrolyte reduction
(Anode oxidation)

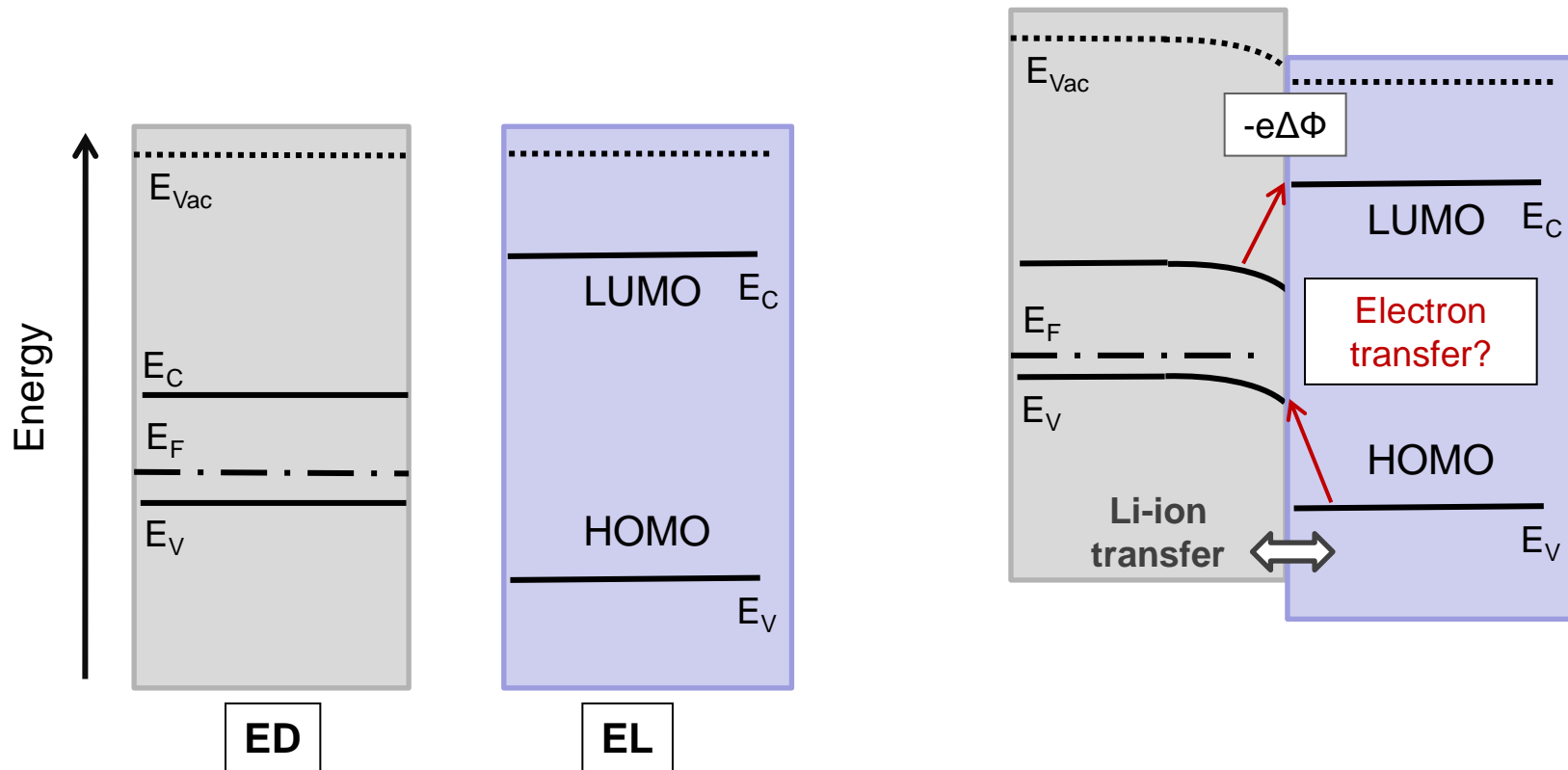
Electron transfer leads to SEI (solid-electrolyte interface/interphase) formation and related degradation mechanisms

Electronic energy level diagram



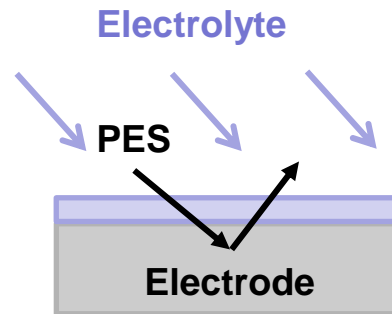
Energy level alignment and electric potential gradients electron transfer

Electron transfer and reactive interfaces



Electron transfer means a chemical reaction between ED and EL => reactive interface

Surface science approach



**Stepwise adsorption or deposition
with intermediate analysis (PES)**

Known approach for electronic materials (SCs), novel for ionic materials

R. Hausbrand et al, Progress in Solid State Chemistry (2014)

Photoemission

Information from photoemission

XPS:

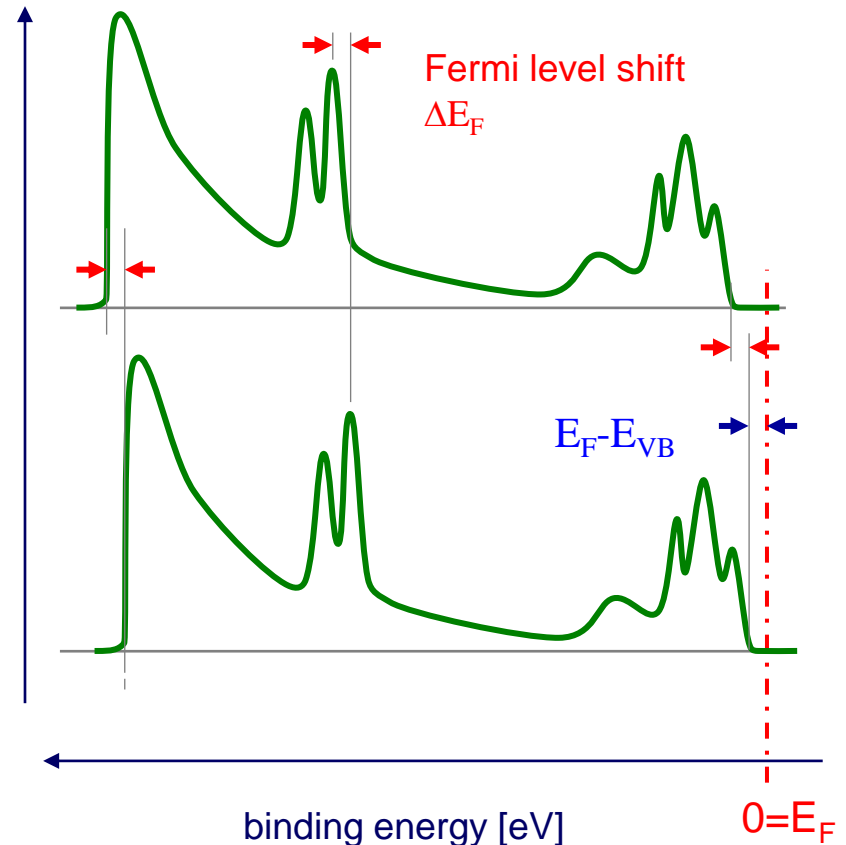
core levels, oxidation states, composition

UPS (SPES):

valence bands, work function

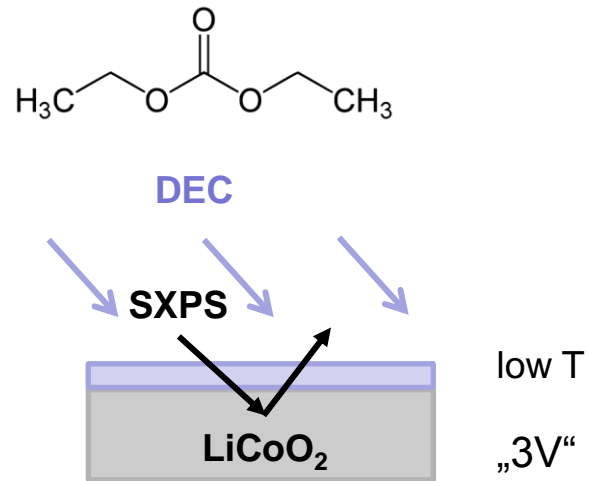
Combination of core levels, valence band and work function:

Fermi level changes, band bending
Surface potential changes



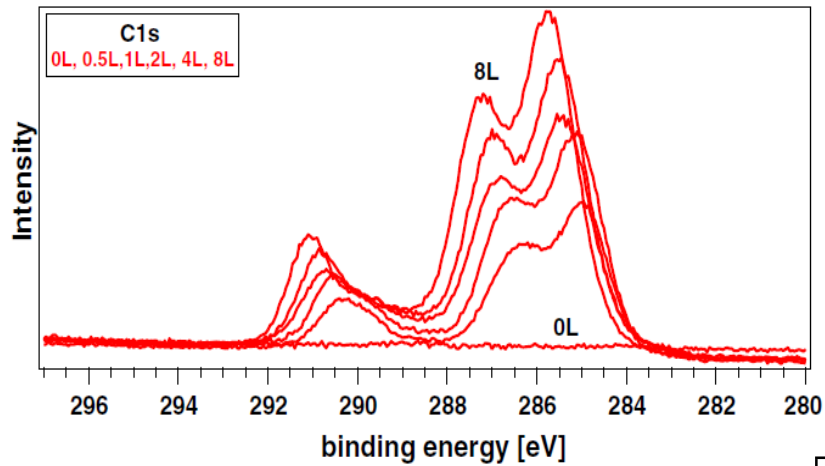
$$\Delta\Phi = \Delta E_F - \Delta\chi$$

DEC adsorption on LiCoO_2

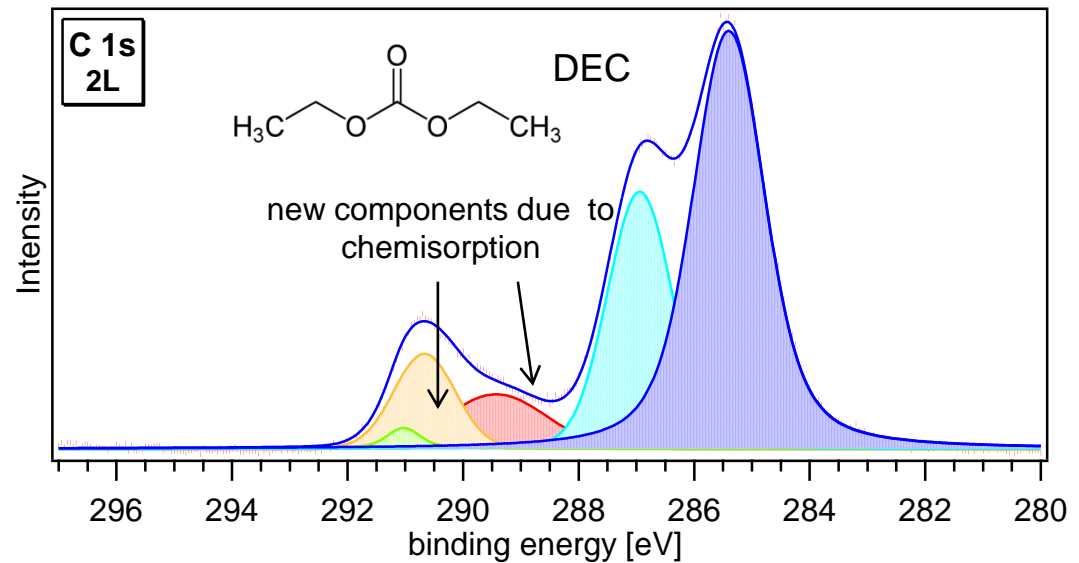


Stepwise adsorption with intermediate
analysis (PES)

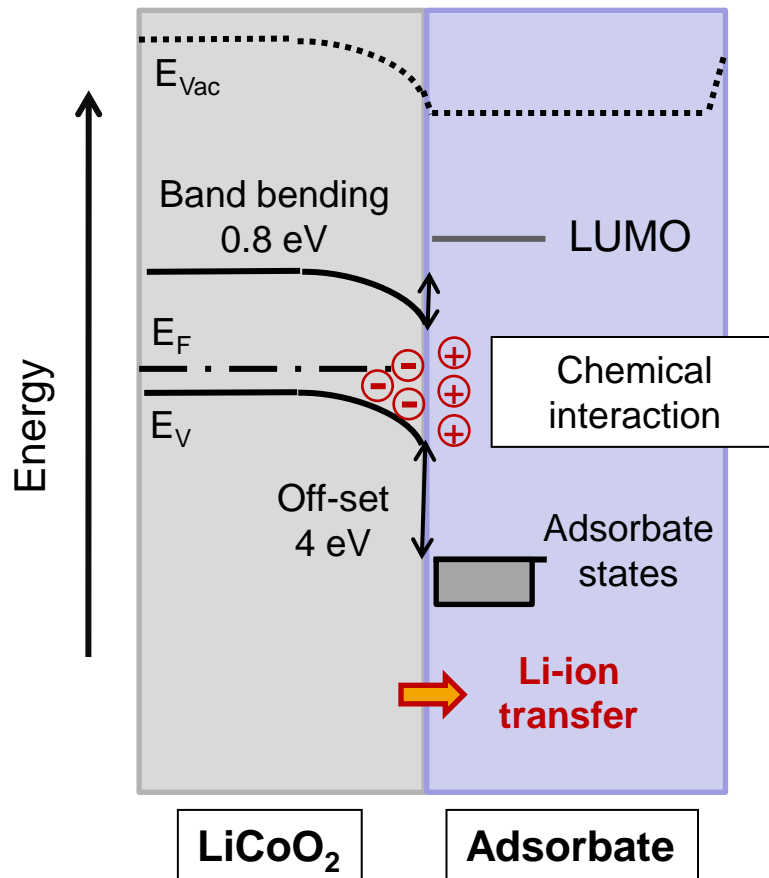
DEC adsorbate features



D. Becker et al, Solid State Ionics (2013)

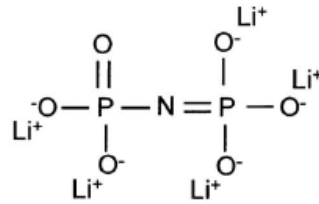
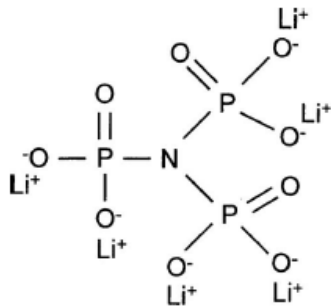


DEC on LiCoO_2 : Energy level diagram

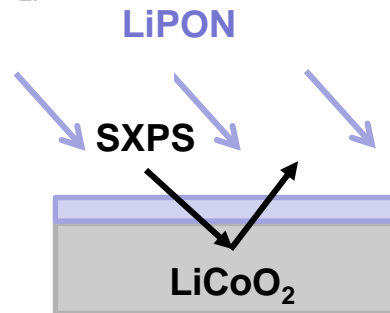


- adsorption of DEC leads to chemical interaction
- but no DEC oxidation expected due to very large HOMO-valence band offset
- formation of electric potential gradient (band bending), driven by Li-ion transfer

Surface science interface investigation

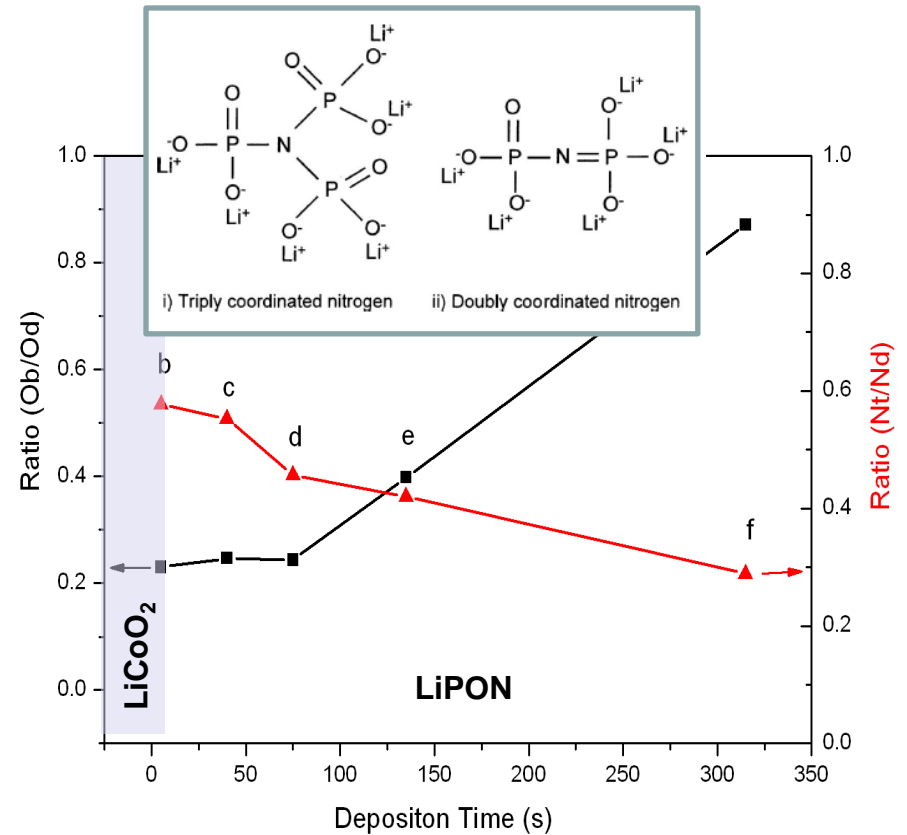
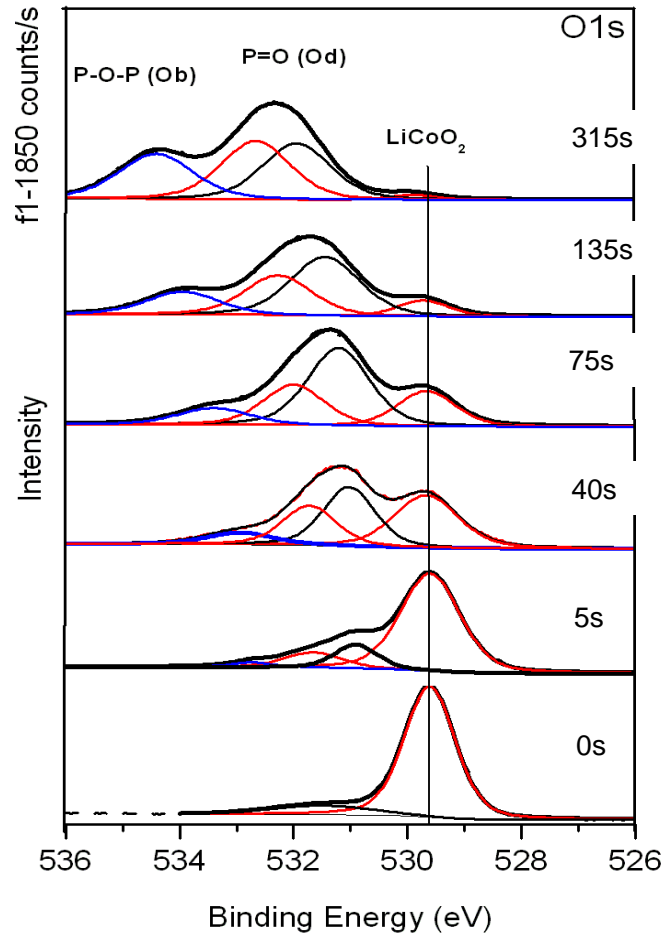


LiPON: highly stable solid state electrolyte



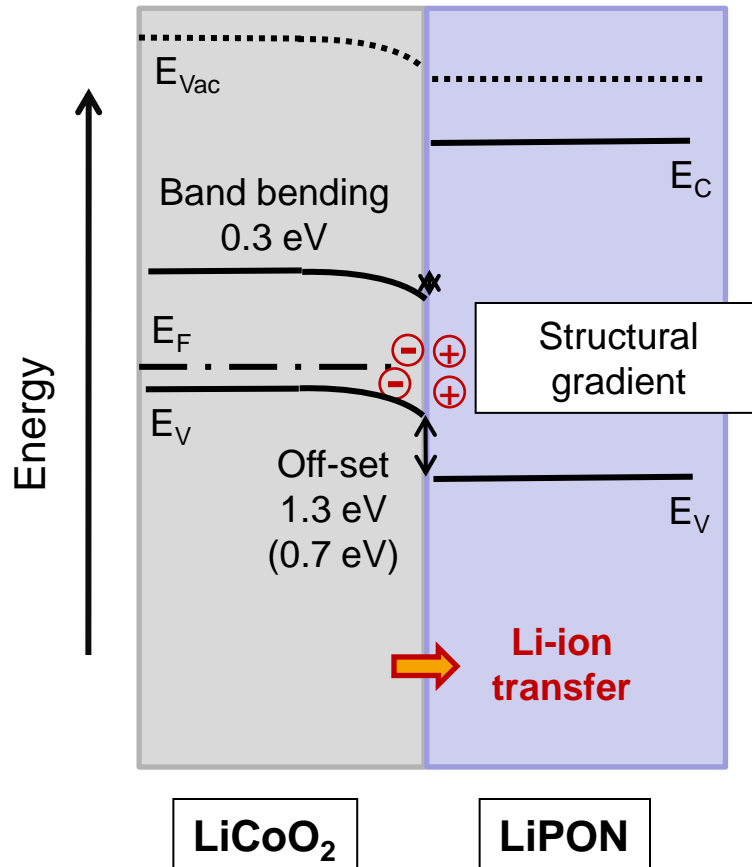
Stepwise deposition with intermediate analysis (PES)

LIPON at the interface



S. Jacke et al., Ionics (2010)

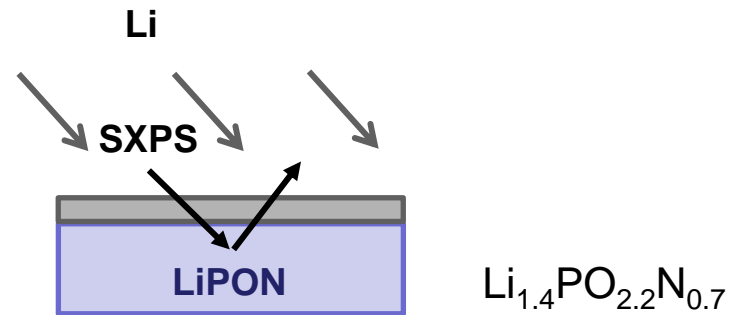
LiPON on LiCoO₂: Energy level diagram



- Interface formation leads to structural gradient in the LiPON
- but only to minor changes in the LiCoO₂
- no electrolyte oxidation by electron transfer expected due to large valence band energy offset
- presence of small electric potential gradient (band bending)

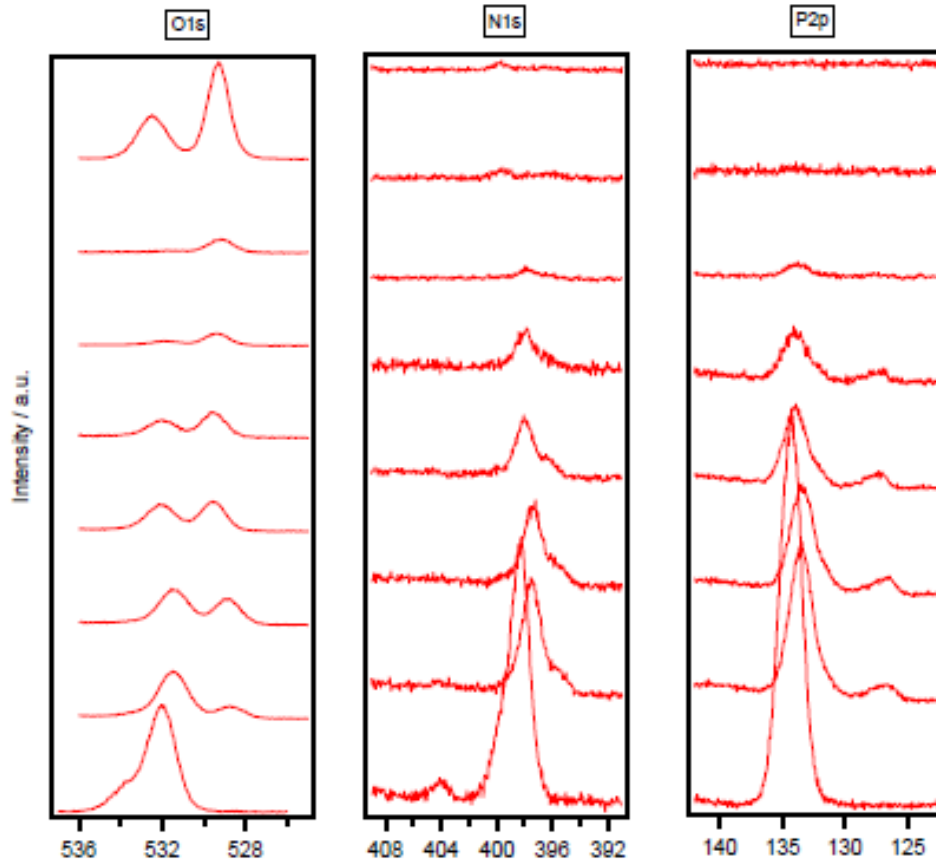
Song et al. Electrochemical and Solid State Letters (2011)

Li deposition on LiPON

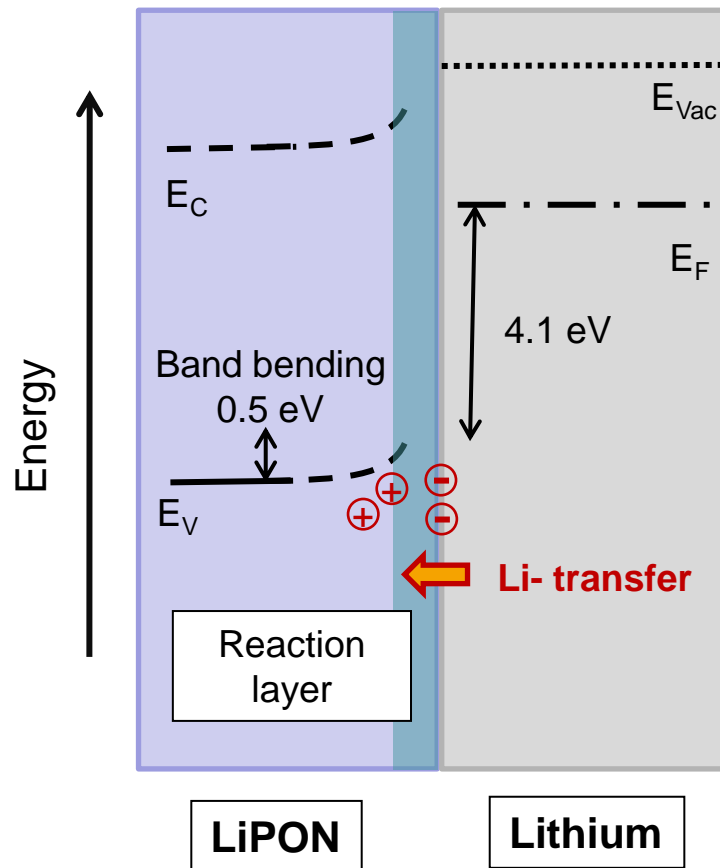


Stepwise deposition with intermediate
analysis (PES)

Evolution of LiPON spectra



Li on LiPON: Energy level diagram



- Contact of metallic lithium to LiPON ($\text{Li}_{1.4}\text{PO}_{2.2}\text{N}_{0.7}$) leads to formation of reaction layer containing units of the type Li_3PO_4 , Li_3P , Li_2O and Li_3N .
- no pronounced reaction is observed in case of orthophosphate-type layers, however
- band bending is observed in the LiPON
- $\text{LiCoO}_2|\text{LiPON}|\text{Li}$ cell voltage ca. 2.8 V

Conclusion

- All electrode-electrolyte interfaces investigated by our surface science approach show a modified structure for the electrolyte phase at the interface; changes in the electrode material remain minor
- For the interface Li-LiPON interface formation proceeds under electron transfer (reactive interface formation), while this is not recognized for the interfaces with LiCoO_2
- Surface science approach allows significant insights into reactivity and charge carrier (electrons and ions) transfer properties of electrode-electrolyte interfaces.

Acknowledgements

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- Battery group AG Jaegermann



Thank you!