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

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This talk: electronic structure and reactivity of interfaces

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

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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 means a chemical reaction between ED and EL => reactive interface
Surface science approach

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

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

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

$\text{LiPON}$

S. Jacke et al., Ionics (2010)
LiPON on LiCoO$_2$: Energy level diagram

- Interface formation leads to structural gradient in the LiPON
- but only to minor changes in the LiCoO$_2$
- no electrolyte oxidation by electron transfer expected due to large valence band energy offset
- presence of small electric potential gradient (band bending)

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Li deposition on LiPON

Stepwise deposition with intermediate analysis (PES)
Evolution of LiPON spectra
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 $\text{Li}_3\text{PO}_4$, $\text{Li}_3\text{P}$, $\text{Li}_2\text{O}$ and $\text{Li}_3\text{N}$.

- 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
- Surface science approach allows significant insights into reactivity and charge carrier (electrons and ions) transfer properties of electrode-electrolyte interfaces.
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Thank you!