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## Surface and bulk properties of Li-ion electrodes – A surface science approach



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### ABSTRACT

Lithium-Ion batteries are important devices for present and future energy storage, offering high energy density and durability. Positive electrode (cathode) materials are predominantly transition metal oxides containing lithium, such as layered oxides or oxides with spinel structure. The electronic/ionic structure of these materials in the bulk as well as at the phase boundary of the solid-electrolyte interface is a key for their properties, such as electrode potential, degradation and reactivity.

This contribution gives examples of surface science investigations on battery materials, addressing especially electronic structure of layered-oxide cathode materials and cathode-electrolyte interface formation. In a surface science approach, well-defined surfaces/interfaces are prepared by thin film deposition techniques and analyzed with surface sensitive analytical methods such as photoelectron spectroscopy (XPS, UPS) and X-ray absorption spectroscopy (XAS) before and after polarization in liquid electrolyte or contact with electrolyte components. Surface science offers the possibility to analyze the electronic and chemical structure of surfaces and interfaces, allowing conclusions on the electronic and ionic structure of the bulk, on reactivity with other phases, and on electrochemical interface formation.

After an introduction into the methodology and fundamental phenomena, the contribution focuses on the role of the electronic structure and electric double layer for electrode degradation and surface layer formation. Charge transfer (electrons and ions) and defect formation is discussed on basis of energy level diagrams extracted from experimental data.

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### 1. Introduction

Due to their high energy density and durability Li-ion batteries are widely used in consumer electronics. The widespread use in other, emerging applications such as electromobility and stationary energy storage requires still significant development efforts to meet the requirements with respect to energy density and durability.

In this context, the fundamental understanding of cathode materials and cathode-electrolyte interfaces is essential [1,2]. Defect formation in cathode materials as well as chemical and electrochemical reactions at their interfaces result in degradation and poor performance. In order to increase the energy density of the batteries, cathode materials with more positive potential and higher capacity are being developed, increasing the thermodynamic driving force for reactions especially at the

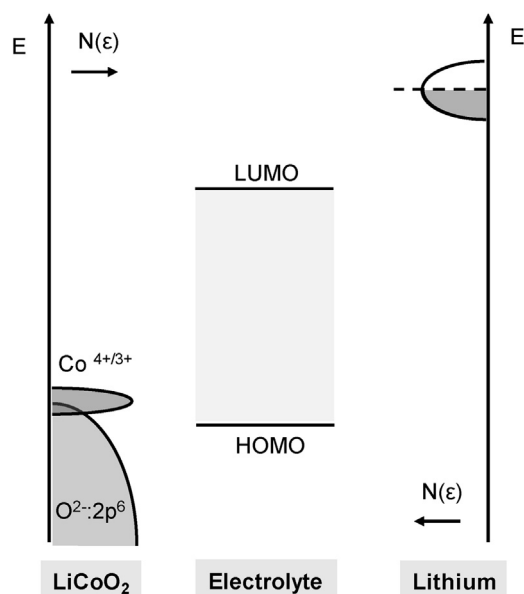
cathode-electrolyte interfaces. This imposes an increased need for fundamental understanding of interface processes and development of protective surface coatings.

Cathode materials and electrode-electrolyte interfaces have been analyzed in the past by various techniques such as electron spectroscopy, optical spectroscopy, or electron microscopy (see e.g. [3–5]). Photoemission (UPS, SXPS) has the unique advantage in that it gives access to the energy level structure of the material and their interfaces, which is intrinsically related to electrode potential, stability and electrochemical interface formation [2,6].

The electronic structure of cathode materials is an intrinsic key property for electrode potential, practical capacity, and degradation [2,6,7]. A central issue is the interaction between transition metal (TM) and oxygen (O) states, i.e. their hybridization, which govern charge compensation without and with involvement of oxygen anions (anion oxidation), eventually resulting in degradation by oxygen loss. Based on the electronic structure of transition metal oxides, general concepts have been proposed [6], in particular the concept of the intrinsic voltage limit, linking O-anion oxidation to the relative position of TM-3d related redox states and O-2p states [6] (see Fig. 1 for more details). While such concepts have

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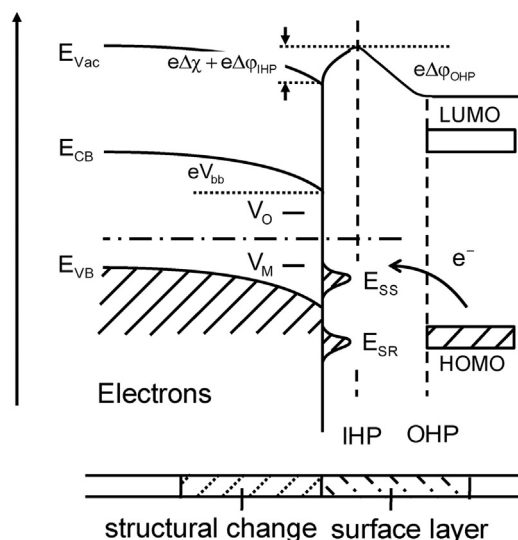
**Fig. 1.** Electronic structure of  $\text{LiCoO}_2$  cathode material together with electronic structure of lithium and electrolyte, forming a generalized electron energy level diagram of an electrochemical cell (adapted from Ref. [9]). The intrinsic voltage limit of the cathode material is reached when the Fermi level crosses into the  $\text{O}2p$  states. For positions of the electrode Fermi level outside the HOMO-LUMO gap electrochemical reactions are expected. For more explanation, see text.

proven immensely useful for the understanding of cathode properties, experimental data are still missing for most cathode materials, and the dependence of electronic structure on the lithiation state is often not considered (rigid band vs. non rigid band behavior). More recently, direct analysis of the electronic structure of common layered oxide cathode materials as function of lithium content has demonstrated pronounced changes upon delithiation [2,8], highlighting the significance of electronic structure modifications for the stability of cathode materials as well as the need for the characterization of electronic structure.

The electronic structure of electrode-electrolyte interfaces is of interest with respect to reduction or oxidation reactions at surfaces and interfaces. Electrochemical oxidation of the electrolyte is only expected when the Fermi level of the cathode is located below the highest occupied molecular orbital (HOMO) of the electrolyte, resulting in a hole transfer from electrode to electrolyte, and reduction only when the Fermi level of the anode is located above the lowest unoccupied molecular orbital (LUMO) [6,7] (see Fig. 1 for illustration). The energy difference between the HOMO of the electrolyte and its LUMO is commonly referred to as its intrinsic stability window [6].

While the generic concept as presented above is widely applied for the design of electrode-electrolyte interfaces, it does not consider a range of effects such as chemical interaction between electrode and electrolyte, i.e. chemisorption, or the presence of an electrochemical double layer (see Fig. 2 for illustration). Such effects can have significant influence on the decomposition of the electrolyte [1,2,5], and indeed electrolyte oxidation and surface layer formation is observed already at comparably low potentials (see [10–12]). Despite significant research efforts in the past, however, the fundamental understanding of electrolyte oxidation and surface layer formation remains still limited.

The formation of surface layers at electrode-electrolyte interfaces is coupled to particle exchange (electrons and ions) between electrode and electrolyte, as well as to decomposition reactions occurring at the interface. Initial reactions take place on the pristine electrode surface, further reactivity is then closely related to



**Fig. 2.** Schematic electron energy level diagram of cathode-electrolyte interface. The double layer has its origin in the Li-ion electrochemical equilibrium across the interface, but it is also influenced by local phenomena such as adsorption. The reactions lead to structural changes in the electrode surface and surface layer formation, with modification of the double layer potential distribution involving space charge ( $eV_{bb}$ ) and electrostatic double layers ( $e\Delta\chi$ ,  $e\Delta\phi$ ).

the properties of the surface layers. Whereas ion equilibrium, ion transfer and related potential effects have been discussed in some detail (see e.g. [13,14]), possibly coupled electronic effects have been less considered. Electroneutral chemical reactions only proceed if charged species of opposite sign are transferred across the interface. As (functional) electrode-electrolyte interfaces are easily permeable for Li-ions, the transfer of negatively charged species, i.e. electrons, is probably the limiting process.

Surface science methodology has been successfully applied for decades to understand the electronic structure of semiconductors and metals [15], solid-solid semiconductor interfaces [16–18], as well as the surfaces/interfaces of semiconductor- and metal electrodes [19,20]. The investigation of intercalation electrodes and their surfaces/interfaces is a comparably new field, and involves both extensive electronic and ionic effects.

After an introduction into the methodology and fundamental phenomena, the contribution focuses on the role of the electronic structure and electric double layer for electrode degradation and surface layer formation. Charge transfer (electrons and ions) and defect formation will be discussed on basis of energy level diagrams extracted from recent or unpublished experimental data. Special attention is given to the interrelation between core level emissions and valence band signature.

## 2. Surface science investigations on battery materials

A modern surface science approach offers a variety of experimental methods to probe the electronic structure of battery materials and their interfaces. Whether there are single components, model systems or assembled full cells to be investigated, an elaborated experimental infrastructure and a careful preparation are mandatory. However, while the ionic nature of intercalation materials and the electronically insulating properties of electrolytes are challenging, it is nevertheless feasible to address their electrochemical behavior on an elementary level of charge transfer processes and chemical bonds only accessible by photoelectron spectroscopy and related methods. This section provides an overview of the different experimental techniques for preparation, analysis and *in situ* characterization.

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