



A surface science approach to cathode/electrolyte interfaces in Li-ion batteries: Contact properties, charge transfer and reactions



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ABSTRACT

Reactions and charge transfer at cathode/electrolyte interfaces affect the performance and the stability of Li-ion cells. Corrosion of active electrode material and decomposition of electrolyte are intimately coupled to charge transfer reactions at the electrode/electrolyte interfaces, which in turn depend on energy barriers for electrons and ions. Principally, energy barriers arise from energy level alignment at the interface and space charge layers near the interface, caused by changes of inner electric (Galvani) potential due to interfacial dipoles and concentration profiles of electronic and ionic charge carriers.

In this contribution, we introduce our surface science oriented approach using photoemission (XPS, UPS) to investigate cathode/electrolyte interfaces in Li-ion batteries. After an overview of the processes at cathode/electrolyte interfaces as well as currently employed analysis methods, we present the fundamentals of contact potential formation and energy level alignment (electrons and ions) at interfaces and their analysis with photoemission. Subsequently, we demonstrate how interface analysis can be employed in Li-ion battery research, yielding new and valuable insights, and discuss future benefits.

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1. Introduction

It is widely recognized that interfaces inside Li-ion batteries play a crucial role for their performance and degradation [1]. In fact, the rational design of interfaces (and interphases, respectively, both intra-electrode as well as intra-cell) appear a key issue for the design of future batteries [2]. Real working electrodes are generally composite structures of active material, binder (e.g. PVDF) and

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carbon (electronic conductor). Each material is in contact with one or more other materials as well as with the electrolyte, resulting in manifold interfaces. Among them, the interface between active material and electrolyte (in the following simply termed *electrode/electrolyte interface*) bears special importance due to transfer of lithium ions.

Storage and operation of Li-ion battery electrodes results in electrode surface film formation, playing an important role for cell properties and performance [3]. Such surface films arise from the reactions at the electrode/electrolyte interface (side reactions), and significantly influence the lithium ion transfer. While the surface film on the carbon anode has been intensively investigated (solid electrolyte interphase, SEI), the surface film on cathode materials has been given less attention. More recently, the relevance of cathode surface film formation for battery degradation was recognized, initiating efforts to understand film formation and cathode/electrolyte interface properties in more detail (see e.g. Refs. [4–7]).

The cathode surface film is different from the carbon anode surface film in that cathode material participates actively in its formation and only very thin films are formed. Side reactions specifically occurring at the cathode/electrolyte interface depend, next to type of electrode and electrolyte, on state of charge and operating conditions. Interfacial side reactions lead to surface deterioration of the electrode and decomposition of the electrolyte, resulting in surface layers on the electrode. For cathode materials, the surface layer is composed of different layers and is laterally inhomogeneous [4]. Cathode surface deterioration results in an inorganic surface layer, while electrolyte decomposition results in a layer consisting of organic and inorganic compounds. For cathode materials in alkyl carbonate based electrolytes, manifold initial and subsequent reaction mechanisms are discussed, such as decomposition of electrolyte species by nucleophilic attack, oxidation of solvent molecules, solvent polymerization, disproportionation of electrode material, direct reduction of electrode transition metal ions and transition metal dissolution (see e.g. Refs. [4,8–10]). Important key concepts for initial reactions are the oxidation of electrolyte species due to high electrode potentials [11], electrode-surface induced decomposition of electrolyte species [8], and the formation of reduced electrode-surface transition metal ions, either due to reduction by the electrolyte [9] or due to disproportionation [8,10]. Notably, fluoric acid (HF) and water, if present, significantly promote electrode surface deterioration and influence surface film formation [4,8]. Thin protective coatings (e.g. ZrO_2 , Al_2O_3 , LiPON, LiF) may be employed to counteract interfacial reactions and increase the stability of the cathode (see e.g. Refs. [12–14]).

A number of analysis techniques have been employed to analyse surfaces of cathodes, such as X-ray Photoelectron Spectroscopy (XPS) [4,6,10,15], X-ray Absorption Spectroscopy (XAS) [16], and Infrared Spectroscopy (IR) [8,17], sometimes in-situ [16,17]. Generally, these techniques have been used to evaluate the principal chemical structure of surface films (or parts thereof) of soaked and operated cathodes via fingerprinting. The use of XAS focused on the analysis of surface deterioration, while FT-IR was mainly used to identify electrolyte decomposition compounds. XPS was employed both to identify surface deterioration of the cathode material as well as to analyse compounds originating from electrolyte decomposition.

Despite the numerous efforts to illuminate the structure of, and processes at, cathode/electrolyte interfaces, there is no clear and experimentally-based picture on the electronic (and ionic) structure and elemental charge transfer processes. Surface science methodology offers the possibility to investigate surface reactivity and interface formation in the light of electronic structure, but has only been used on exception to investigate insertion compounds or

battery-related materials. Typical experiments are comprised of adsorption (or condensation) of a phase onto a well-defined substrate under vacuum conditions, accompanied by analysis of methods with high surface sensitivity, such as photoemission spectroscopy (PES), analysis based on XAS, or high resolution electron energy loss spectroscopy (HREELS). Most interesting for the investigation of insertion electrodes are surface science analysis based experiments performed in-situ on working cells [18].

PES probes the electronic structure (electron energy level structure) of occupied states and is a major analysis technique in surface science. It is sensitive to electrical fields perpendicular to the surface, allows evaluation of the work function and can be highly surface sensitive. PES comprises XPS, Ultra-violet Photoelectron Spectroscopy (UPS) and synchrotron based techniques. XAS is sensitive to the electronic structure of unoccupied states as well as to local structure (near edge x-ray absorption fine structure (NEXAFS) and extended x-ray absorption fine structure (EXAFS), respectively), while HREELS (like IR) measures the vibrational structure [19]. Surface science techniques, applied on well defined model surfaces, have been used to obtain detailed insights in the elementary processes of many surface related processes, e.g. in electrochemistry [20–22], photoelectrochemistry [23,24] and corrosion (see e.g. Refs. [25,26]).

In this contribution, we introduce our ultra-high vacuum (UHV)-based surface science oriented approach to investigate the formation of, and charge transfer at, cathode–electrolyte interfaces in lithium ion batteries, and discuss three cases in the light of inner electric potential gradient and energy level alignment. Our approach consists of step by step interface formation by subsequent condensation of electrolyte phase on thin film model electrodes and intermediate analysis by photoemission (XPS, UPS). Such experiments on model systems allow the identification of fundamental processes and will be expanded in the future to practical interfaces in lithium ion batteries. In this way we aim to support the development of high voltage batteries, and of next generation battery concepts (all-solid state batteries, metal-air batteries).

More specifically, we discuss the interface formation of a layered cathode material (lithium cobalt oxide, $LiCoO_2$, LCO) with an aprotic solvent (diethyl carbonate, DEC) [27,28], a protic solvent (water) [29] and a solid state electrolyte (phosphorous oxynitride, LiPON) [30,31]. LCO is a commonly used cathode material, featuring good energy density, power density and cycle life, and with a comparably simple chemistry it is a prototype layered oxide. LCO thin films can be prepared in high quality by magnetron sputtering [32]. During electrochemical de-intercalation of lithium in lithium hexafluorophosphate electrolyte ($LiPF_6$), the formation of lithium fluoride, phosphate and fluorophosphate, next to carbonaceous species, was previously observed with XPS [15]. DEC is a common solvent in lithium ion electrolytes, water a common contaminant in such electrolytes and LiPON a common solid electrolyte used in thin film batteries.

2. Ionic interfaces and the surface science approach

2.1. Ionic interfaces – theoretical considerations

Ionic phases are the key components of electrochemical systems. The theory of ionic solids has been given considerable attention, see e.g. Mott [33] and Wagner [34], or, more recently, Maier [35–38] and Weppner [39]. Using defect chemistry, mobile ionic species can be treated as a dilute species, with energy levels according to their location in the lattice and a chemical potential according to population [38,40], resulting in a conceptual similarity to valence electrons and – holes in semiconductors. In the presence of external defects, one energy level is typically strongly

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