

Interphase formation on lithium solid electrolytes—An in situ approach to study interfacial reactions by photoelectron spectroscopy



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ABSTRACT

Interfacial reactions of solid electrolytes play an important role in all-solid-state batteries. The interface resistances—describing charge transfer between electrode and solid electrolyte—and the cycle stability of the battery depend on the chemical and physical properties of the interfaces. As buried interfaces in all-solid-state batteries are difficult to investigate, the knowledge on interfacial reactions and the interfacial kinetics is poor—especially in case of the interface between solid electrolytes and alkali metal. Here, a simple and straightforward technique for the investigation of the formation of an interfacial reaction zone (interphase) at the surface of a solid electrolyte is presented. The key concept is to use the internal argon ion sputter gun in a standard lab-scale photoelectron spectrometer to deposit thin metal films (e.g. lithium) on the sample surface and to study the reaction between metal and solid electrolyte by photoelectron spectroscopy directly after deposition. As an example for the formation of interphases on solid electrolyte materials, lithium is deposited on lithium lanthanum titanate (LLTO), and the reaction is observed by XPS in situ. The obtained spectra show the formation of reduced titanium ions and titanium metal due to the reaction of LLTO with Li—i.e. by lithium insertion. The presented experimental approach can be used for the deposition of virtually any metal on the sample and can be easily adapted to a wide range of applications such as enhancing the electronic conductivity of samples in situ, studies of electronic contact properties in devices, detailed analysis of emission depth distribution functions for thin overlayers or to create internal binding energy standards.

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1. Introduction

In rechargeable lithium ion batteries (LIB), the kinetics of interfaces and interphases between the electrodes and the electrolyte are essential for the proper battery function [1]. The instability of organic electrolytes in contact with the anode material and the resulting formation of the solid electrolyte interphase (SEI) in cells using liquid electrolytes are limiting factors for the cycle life on the one hand, and reactions at the cathode surface may cause additional problems. On the other hand, SEI formation is crucial for the functionality of lithium ion batteries in preventing parasitic effects and suppressing continuous electrolyte decomposition [2]. In essence, the formation of interphases at reactive interfaces can have a strong impact on the function and durability of electrochemical devices in general.

Against this background, ceramic solid electrolytes often appear as chemically more stable. Therefore all-solid-state concepts for lithium-based batteries attract recently new interest—in particular as these promise inherent safety when no flammable or toxic liquids are used. Moreover, metallic lithium with its very high specific capacity may be

employed as negative electrode if the solid electrolyte provides a stable barrier to dendrite growth [3]. Unfortunately, the interface between the electrode and the solid electrolyte is buried and not accessible in situ by microscopic or surface sensitive techniques. Thus, information on interfacial reactions and degradation phenomena in the neighboring phases is mainly restricted to electrochemical characterization—which is phenomenological and chemically unspecific—and to X-ray diffraction—without spatial resolution in the case of wide angle XRD. Recently, in operando transmission electron microscopy has been applied to study solid-state batteries, but this approach is extremely laborious and the interpretation of results from ultra-thin lamellae exposed to high intensity electron beams is always critical [4–6]. Thus, the knowledge on reactions at interfaces between electrodes and solid electrolytes is sparse due to the difficulties mentioned above. This is particularly unsatisfactory in the case of lithium metal anodes in contact with lithium solid electrolytes. Here, the physical and chemical properties and characteristics of the metal/electrolyte contact are of vital importance for the functionality of an all-solid-state battery.

Considering the lithium metal/solid electrolyte contact in detail, we can distinguish three different types of interface formation: In the first case (“thermodynamically stable interface”), the solid electrolyte is not reacting with the lithium metal at all and a sharp *two-dimensional interface* is formed, which is schematically shown in Fig. 1a. This case

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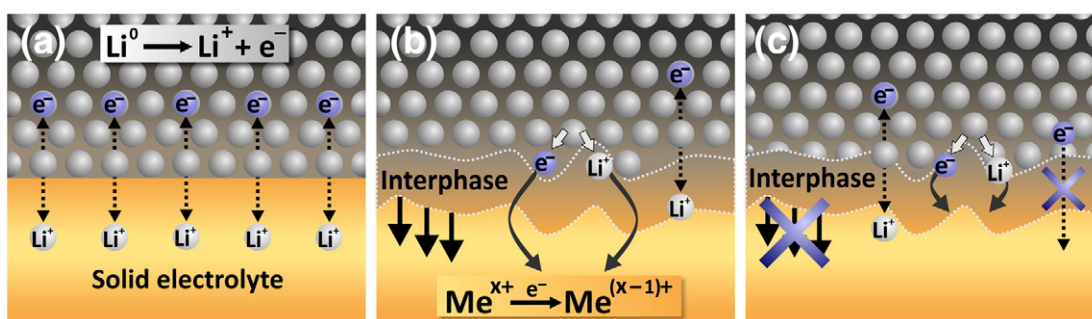


Fig. 1. Types of interfaces between lithium metal and a solid lithium ion conductor. a) Non-reactive and thermodynamically stable interface; b) reactive and mixed conducting interphase (MCI); c) reactive and metastable solid-electrolyte interphase (SEI).

requires that the two phases in contact are in thermodynamic equilibrium *a priori*. In the second case (“thermodynamically unstable interface”), both materials form a *three-dimensional interphase* due to chemical reactions between the solid electrolyte and lithium metal, as shown in Fig. 1b and c. This case is characterized by a thermodynamic driving force for a chemical reaction between the two constituents of the interface. Depending on the transport properties of the formed reaction products, the interphase may steadily grow “into” the solid electrolyte and thereby alter the properties of the whole bulk material. The formation of such a mixed conducting interphase (we propose to call it MCI, or “insertion-type interphase”) [7] will eventually allow electron transport through the electrolyte and finally lead to the self-discharge of the battery (Fig. 1b). It is well known that the electronic conductivity of many metal oxides that are insulating in their highest oxidation states strongly increases upon reduction. Therefore, we can assume that many solid electrolytes comprising multivalent cations are prone to form such an MCI in contact with lithium metal. We would like to add that this case is nothing else than lithium insertion into a solid compound with mixed conduction. It simply represents a bad choice of solid electrolyte. Thermodynamically driven MCI formation can only be avoided by introducing a protecting film as “artificial SEI”—as e.g. demonstrated by Visco [8] et al., Imanishi [9] et al. and Wang [10] et al. in their concept of protected lithium anodes or by Reinacher et al. [11]. Secondly, and in contrast to the case of an MCI as shown in Fig. 1c, a stable interphase may form if the reaction products are electronically non-conductive or if the electronic conductivity is low enough to limit the growth of the interphase to a very thin film (“stable SEI”). This layer is then comparable to the SEI as known from batteries comprising liquid electrolytes. The performance of the battery will then critically depend on the ion conducting properties of the interphase.

Obviously, cycling experiments can only give very indirect and un-specific evidence for the formation of resistive interphases. Frequently, the electrochemical stability of materials in contact with lithium metal is proven or disproven by cyclic voltammetry measurements, again only giving unspecific and often unreliable evidence [12]. Time resolved impedance spectroscopy in a suitable cell arrangement offers more information and helps to quantify the influence of an interphase, but is also not chemically specific [12]. Recently, we already reported preliminary results from the use of X-ray photoelectron spectroscopy, which is a powerful technique for studying surface reactions, in the study of solid electrolyte degradation (in the case of lithium aluminum germanium phosphate (LAGP) and lithium tantalum titanium phosphate (LATTP)) [7]. Instead of contacting two bulk phases, one phase was supplied as thin film in situ to the solid electrolyte while applying XPS as surface analytical technique. A detailed description of the experiment, its perspectives and wide range of applicability was yet not given and will be presented here. Schwöbel et al. recently studied the reaction of lithium phosphorous oxide nitride (“LiPON”) thin films in contact with lithium [13]. Using an advanced UHV cluster tool, they repeatedly deposited thin layers of lithium metal on “LiPON” in a lithium dispenser,

transferred the sample under UHV conditions to the XPS chamber and analyzed the reaction products that had formed on the surface. They found that “LiPON” is not stable in contact with lithium metal and that lithium oxide (Li_2O), lithium phosphide (Li_3P) and lithium nitride (Li_3N) are formed. As “LiPON” is successfully employed in thin-film batteries the authors assumed that a stable interphase is formed (stable SEI formation, see Fig. 1c). A comparable in situ approach studying aluminum films on polymers has been applied by Marcus et al. [14] using a UHV chamber deposition chamber connected to a XP spectrometer. The potential of a more user-friendly and fast technique has yet not been explored.

In the present paper we report on a simple and fast approach for the metallization (lithiation) of materials and their in situ analysis in a standard lab-scale photoelectron spectrometer by ion beam sputtering using the built-in argon sputter gun. As a proof-of-concept we demonstrate the interphase formation of lithium lanthanum titanate (LLTO) solid electrolyte, which is known to react with lithium metal. In the past decades, the chemical stability of perovskite type lithium lanthanum titanate (LLTO [15–18]) was investigated electrochemically [16,19–26] by standard cycling procedures and ex situ using XPS [24]. The experimental setup is not limited to battery materials and allows the sequential deposition of ultra-thin metal films on any kind of sample (bottom-up-approach) thereby facilitating the in situ chemical analysis by XPS during the formation of various interfaces and/or interphases. The main purpose of this article is to give a detailed description of the technique, its strengths and pitfalls, and to present the comprehensive study of LLTO as an example.

2. Experimental

2.1. Material preparation and cell construction

LLTO ($\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$) was prepared by ball milling of stoichiometric mixtures of Li_2CO_3 (Sigma Aldrich), La_2O_3 (chempur) and TiO_2 . La_2O_3 was pre-heated at 1000 °C for 12 h and handled in an Ar-gas filled glove box before synthesis. After first ball milling, the mixture was heated at 900 °C for 4 h, milled again (500 rpm, 3 mm ZrO_2 balls) using a Fritsch Pulverisette 5 and heated at 1150 °C for 12 h in air. The obtained powder was milled with 500 rpm and afterwards pressed isostatically at 4000 bar and sintered for 6 h at 1350 °C in a MoSi_2 oven. Phase purity was checked using X-ray diffraction. Ionic conductivity was measured by AC impedance spectroscopy using a Biologic sp300 impedance analyzer in the range of 7 MHz to 100 mHz with a potential amplitude of 20 mV. For conductivity measurements, two blocking gold electrodes were used.

Two different types of DC conductivity measurements were carried out: One using blocking gold and the other using lithium electrodes, both electrodes were vapor deposited. The electronic partial conductivity was measured via a simple polarization method by applying 1 V. Thermodynamic data were obtained from HSC Chemistry 7.00 (Outotec Research) database. Data for the LLTO phase were not available,

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