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Interface reactions between LiPON and lithium studied by in-situ X-ray photoemission

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ABSTRACT

Lithium phosphorus oxynitride (LiPON) is an amorphous solid lithium ion conductor commonly used in all solid state thin film batteries (TFBs) with $LiCoO_2$ as cathode- and lithium as anode-material. TFBs exceed conventional Li ion batteries with respect to lifetime and safety but may suffer from high ion transfer resistances and interface reactions between the electrodes and the electrolyte. In this contribution we study interface layer formation between LiPON and metallic lithium using an in-situ X-ray photoemission spectroscopy (XPS) surface science approach.

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1. Introduction

Miniaturization of electronic devices and the development of microelectromechanical systems (MEMS) have led to the need of miniaturized batteries [1]. Microdevices should be able to operate autonomously without an external power supply for a long period of time and without any leakage of harmful or flammable liquids [2]. This is especially important for powered medical implants in the human body which might become more important in the future [2]. Batteries based on liquid electrolytes cannot be made much smaller than classical coin cells [3], which are far too large for an application in MEMS with dimensions in the micrometer regime, and always pose the risk of electrolyte leakage. Ideally suited for these low power applications are thin film batteries (TFBs) with solid electrolytes, which can be produced with small footprints as needed for microdevice applications. Furthermore, TFBs are manufactured using thin film deposition techniques which are compatible with integrated circuits [4].

The solid electrolyte which is most frequently used in TFBs is LiPON which has been discovered in 1992 by Bates and coworkers [5]. LiPON is an amorphous alkali phosphate glass, which is usually prepared by sputtering a crystalline Li_3PO_4 target in nitrogen atmosphere. During the sputtering process nitrogen is incorporated into the film by forming phosphorus–nitrogen bonds. The nitrogen incorporation enhances the lithium ion conductivity to values of approximately $1 \cdot 10^{-6}$ S/cm [5], nevertheless the physical mechanism of the ion conductivity enhancement is still not fully clear [6]. Several varying compositions of LiPON have been reported in literature [7–9] showing that thin film amorphous alkali phosphate glasses are existing in a wide composition range.

In a lithium ion battery such as a TFB lithium ions are shuttled between the cathode and the anode and pass the electrode/electrolyte-interfaces. Hence interfaces and reaction layers at the interface play a crucial role for the performance of the battery [10]. Any continuous side reaction occurring at one of the interfaces will lower the lifetime of the battery [11] due to loss of active lithium and barrier layer formation. Nevertheless there is still a lack of knowledge about the exact nature of reaction layers and formation mechanisms between the solid electrode and the solid electrolyte. Research on the interface between the electrode and the electrolyte has been performed using analytical methods such as transmission electron microscopy [1,10], by theoretical calculations [12] or by impedance spectroscopy [13]. To our knowledge no studies on interface properties have been performed using XPS. XPS is a powerful analytical method well suited for the analysis of reaction layers, but is not straightforward to use due to its surface sensitivity and the buried nature of the interface. Therefore we have used a surface science approach to analyze the interface with XPS by exposing our LiPON film stepwise to lithium in ultrahigh vacuum (UHV). At each exposure XPS measurements are conducted. Due to the increasing thickness of the lithium film the substrate emissions are damped. Additionally new chemical species directly at the interface might be formed and detected by XPS. The exposure of intercalation electrodes to lithium in UHV and the analysis by XPS is common in surface science [14,15] but no similar experiments with solid electrolytes are reported in literature. Recently Jacke et al. [16] studied the interface between the cathode material $LiCoO_2$ and LiPON using a similar approach. Additionally Song et al. [17] constructed an energy band alignment of the

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interface $LiCoO_2$ and LiPON from in-situ XPS measurements. In this contribution we study the LiPON electrolyte/lithium anode interface using in-situ XPS. Yu et al. [13] concluded from impedance measurements that the interface between LiPON and Li is stable and no hints for reaction layers have been found.

2. Experimental

All experiments have been performed in the DAISY-BAT (Darmstadt's Integrated System for Battery Research) which is shown schematically in Fig. 1. DAISY-BAT is an integrated UHV cluster tool consisting of several dedicated deposition chambers for battery materials and a Physical Electronic VersaProbe XPS/UPS analysis unit, offering the possibility to prepare layer stacks and perform photoemission analysis without any contaminations from the atmosphere. The base pressure of the system is approximately $1 \cdot 10^{-9}$ mbar. A LiPON film was prepared on a $Si/SiO_2/TiO_2/Pt$ wafer (GMEK) in a self-constructed radiofrequency magnetron sputtering chamber using a crystalline 2″ Li_3PO_4 target (Lesker, 99.95%) in pure nitrogen atmosphere ($p = 8 \cdot 10^{-3}$ mbar). The power density was set to 2.25 W/cm^2. The ionic conductivity of our LiPON is approximately $1 \cdot 10^{-6}$ S/cm, which fits well to literature [5]. The functionality was also confirmed by building complete TFBs using $LiCoO_2$ as cathode- and metallic copper as anode-material giving a well defined voltage plateau at approximately 3.9 eV in the charge/discharge curve. After the preparation of the LiPON film photoemission spectra of the O1s, N1s, P2p, Li1s core level and the valence band region were taken using monochromated Al K_α radiation ($h\nu = 1486.6$ eV). A pass energy of 23.50 eV was used. Hereafter lithium was evaporated stepwise onto the LiPON using a lithium dispenser (SAES Getters) and intermediate PES analysis was performed. The lithium evaporation was conducted in an UHV chamber with a base pressure of $3 \cdot 10^{-10}$ mbar by applying a current of 7.5 A for a defined period of time.

3. Results

In the first part of this section we will focus on the spectral features of the as prepared LiPON film shown at the bottom of Fig. 3 (as synthesized). Afterwards the evolution of the emission lines with increasing Li coverage is discussed and new reaction products are identified. In the final part we will discuss exemplary chemical reactions.

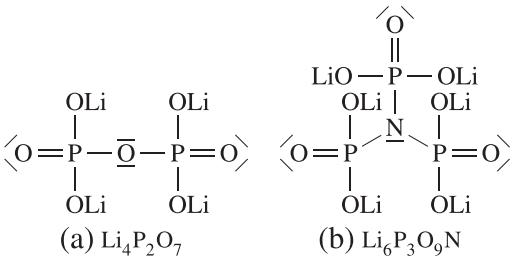

Fig. 2. Chemical structure used for giving possible reaction routes. Such and similar structures are expected to be present in LiPON [24,6,25,19].

Fits of the O1s, N1s and P2p emission of the pristine LiPON are shown at the bottom of Fig. 4. The O1s emission line before exposure is clearly asymmetric with a shoulder at higher binding energies which is attributed to P–O–P bonds (bridging oxygen, O_b). The peak at lower binding energies is attributed to P–O–Li and P═O bonds (non-bridging oxygen, O_{nb}) which are not readily distinguishable due to the resonant bonding in the phosphate tetrahedra [18]. The binding energy difference between O_b and O_{nb} was found to be 1.64 eV with a ratio of $O_b/O_{nb} = 0.22$ by fitting the O1s peak using Voigt profiles which can be seen in Fig. 4.

The N1s peak of the pristine surface, Fig. 3, shows a small component at approximately 404 eV, which is attributed to nitrogen species bond in NO_2^- groups [19,16]. The main N1s emission between 396 eV and 400 eV shows contributions from two different nitrogen species. The emission resulting in a shoulder at higher binding energies is attributed to triply bound nitrogen (N_T). The main emission at lower binding energies is attributed to doubly bond nitrogen P–N–P (N_D) [20]. The binding energy difference between N_D and N_T was fitted to 1.27 eV with a ratio $N_T/N_D = 0.32$ as shown in Fig. 4. A similar binding energy difference of 1.4 eV has been reported by Wang [19].

The P2p signal is symmetric and has been fitted using a single Voigt profile (Fig. 4). No attempt was made fitting the P2p signal using more

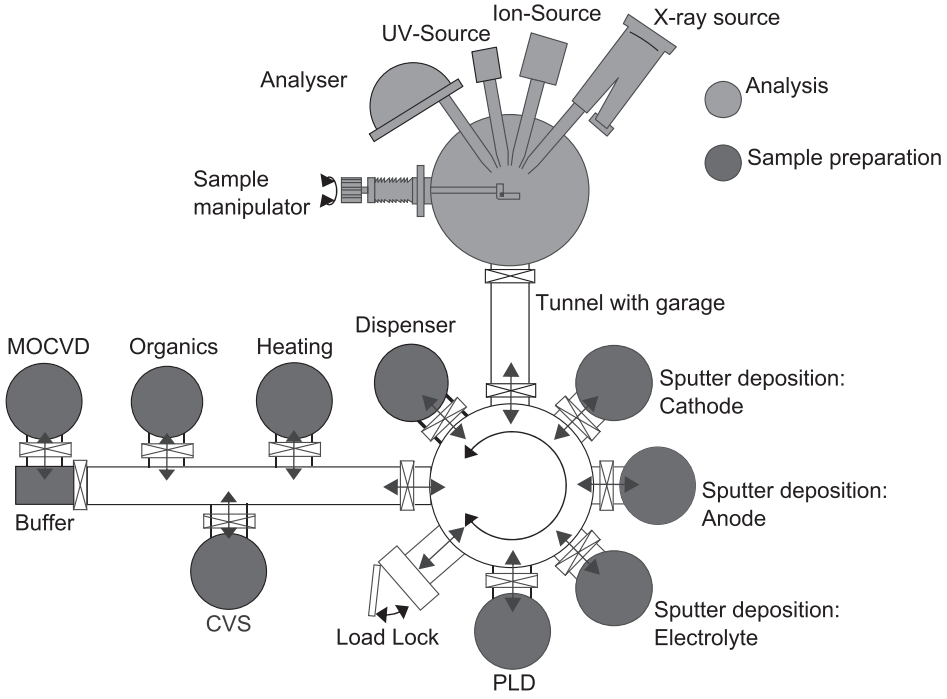

Fig. 1. Scheme of the DAISY-BAT showing the different deposition chambers which are connected via an UHV transfer system to the XPS/UPS analysis unit.

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