Process related effects upon formation of composite electrolyte interfaces: Nitridation and reduction of NASICON-type electrolytes by deposition of LiPON
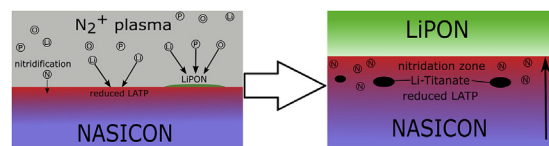
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HIGHLIGHTS

- LiPON protective coating on NaSICON substrate.
- Nitridification of NaSICON solid electrolyte by nitrogen plasma.
- Formation of reaction phase at the NaSICON-LiPON interface.
- Partial reduction of NaSICON solid electrolyte during deposition of LiPON.

GRAPHICAL ABSTRACT

ABSTRACT

Commercial NASICON-type electrolyte plates are coated with a thin film of LiPON to obtain a composite electrolyte system with high conductivity at room temperature that can be used in contact with metallic Lithium. The formation of the interface between the NASICON substrate and the LiPON coating is studied using an in-situ X-ray photoemission spectroscopy (XPS) surface science approach. The process of LiPON deposition induces changes in the surface chemical structure of the NASICON substrates as observed by XPS, including the partial reduction of Ti and the incorporation of N into the NASICON. The practical impact of the interface formation is studied by impedance spectroscopy, revealing a substantial increase of resistance for LiPON coated samples.

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1. Introduction

The growing demand for innovative mobile electronic devices, electromobility and local stationary energy storage requires electrochemical storage devices with high energy density and/or superior endurance. Since 1990 the main technology for mobile energy storage is more or less constant: Li-Ion batteries consisting mainly of transition metal oxide cathodes, organic liquid electrolytes and carbon anodes [1]. Currently research is focused on optimising this technology as well as on finding new, superior types of batteries [2,3]. Among the latter, all solid state batteries have attracted a lot of attention over the past years [2]: This type of batteries promises much higher energy densities than current technology [4] due to reduction of inactive mass and the incorporation of metallic lithium as anode material instead of carbon [3]. Apart from the energy density, all solid state cells are deemed also safer: when inorganic electrolytes are used, the risk of fire is minimised [7].

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On the way to all solid state cells, the crucial part of research is the replacement of the liquid electrolyte by solid materials [8,9], especially inorganic solid electrolytes [2,7]. Suitable materials have to meet different requirements, such as Li-ion conductivity $>10^{-3}$ S cm^{-1} at working temperature and stability in contact with the electrode materials, above all metallic lithium [2,10]. Although promising room temperature conductivities in the range of 10^{-3} or even 10^{-2} S cm^{-1} have been obtained, there is still no overall suitable solid electrolyte available. Electrolyte materials offering high ionic conductivities at room temperature are sulphide-based materials or oxide-based compounds with perovskite, garnet or NASICON structure. Unfortunately, each of these material classes suffers either instability in contact with metallic lithium such as sulphides [11], perovskites [12,13], and NASICON structured materials [20], or reactions with the atmosphere such as sulphides [14] and garnets [15]. The instability of perovskites and NASICON structured materials has its origin in the presence of Ti^{4+} [12,13] in the material, which is reduced upon contact of the materials with lithium to Ti^{3+} under formation of a reaction layer with no passivating function due to its electronic conductivity. For the reaction with atmosphere, humidity is the most crucial aspect: lithium and sulphur in garnet solid electrolytes both react with water, resulting in lithium loss and the formation of toxic H$_2$S [14], with adverse consequences for the conductivity.

A strategy to obtain electrolyte systems with improved properties is to combine existing solid electrolytes into composite electrolytes, or to coat existing solid electrolyte plates with a thin film consisting of another electrolyte which has a passivation/protection function, respectively. In this regard, coating NASICON structure material with a thin protection layer of LiPON [16,17] is attractive to make the compound stable in contact with lithium. NASICON structured materials are non-stoichiometric materials with a framework of MO$_6$ octahedra and (Si,P)O$_4$ tetrahedra, enclosing a 3D network of interconnected pathways in which the positions are partially occupied by Li-ions [18]; specifically, NASICON-type materials such as Li$_{1+x}$Al$_x$Ti$_{2-x}$ (PO$_4$)$_3$ offer high room temperature conductivities in the range of 10^{-3} S cm^{-1} and are stable against atmosphere [15,19,20]. LiPON is a nitrogen-substituted phosphate glass with a Li-ion conductivity of around 10^{-6} S cm^{-1} (RT) that has been used successfully as electrolyte in thin film batteries together with metallic lithium anodes [21,22]. Such batteries demonstrate good performance and are highly stable, which can be attributed to the favourable properties of the interlayer forming between LiPON and lithium, i.e. good Li-ion conductivity and low electronic conductivity, as recently indicated by work of Schwöbel et al. [23] and [24]. The good properties of a NASICON material coated with LiPON have already been demonstrated when used together with a Li anode [16]. Also, investigations have been performed to reduce the interface resistance between NASICON and LiPON by incorporating a thin Ti layer [25]. However, the crucial part of this electrolyte combination, the interface, has not been studied in detail yet.

In this paper, we investigate the properties of LiPON coated NASICON-type electrolyte materials with a focus on the NASICON-LiPON interface formation. As substrates, two different commercially available electrolyte plates were used, for the LiPON deposition a sputter process was employed. The interface between these materials has not been subject of intensive studies in the past, and was investigated here by means of step-by-step deposition and analysis by photoelectron spectroscopy (XPS). Such a surface science approach allows the analysis of chemical and electronic structure of buried interfaces with surface sensitive analysis techniques [26], and was previously already successfully applied to the analysis of other Li-ion battery interfaces [26,27]. To study the macroscopic influence of the effects observed by XPS, impedance measurements were carried out on the composite electrolytes and interface resistances were characterised. Such an approach can give way to tailoring the properties of future composite electrolytes to task specific demands.

2. Experimental

2.1. LATP and LATGP substrates

For the investigations, we used two types of solid electrolyte materials as substrates that are commercially available from Ohara Inc. In the form of 150 μm thick plates: One electrolyte (LATP) is a partially sintered material consisting of Li-Al-Ti-Si-P-O NASICON particles [28,29]. The other electrolyte (LATGP) is a polished glass ceramic of the Li-Al-Ge-Ti-Si-P-O system [29,30]. The crystalline phase, accounting for the high room temperature conductivity, is of the NASICON structure type [31]. The plates were used as obtained from the supplier, i.e. without any surface treatment prior to analysis, LiPON deposition or other treatments.

2.2. LiPON deposition

In order to investigate the formation of the NASICON - LiPON interfaces, LiPON was deposited stepwise in sub-nm thickness onto the pristine (as delivered) electrolyte plates as substrates with XPS analysis after each step. These interface experiments were performed in an integrated UHV-system (base pressure $<10^{-8}$ mbar), which consists among others of a home-built sputtering chamber for LiPON deposition and the XPS analysis unit. Furthermore, LiPON was deposited in one step as a coating with a thickness of approximately 200 nm to investigate the interface resistance by electrochemical impedance spectroscopy (EIS).

For both interface experiments and impedance analysis, LiPON was deposited by a reactive rf magnetron sputter process with a power of 50 W from a crystalline 2″ Li$_3$PO$_4$ target (Lesker, 99.95%) in nitrogen plasma without substrate heating (N$_2$ flow 10 SCCM; process pressure $3 \cdot 10^{-3}$ mbar). The deposition rate was approximately 3 nm/min on an inert substrate. To ensure a clean process, the target was presputtered for 20 min before each deposition while the substrate was located behind a shutter, ensuring that the sample surface was not affected by plasma or sputtering process during this time. With this LiPON deposition process, we obtain LiPON layers free of carbon with a composition of Li$_{1.16}$PO$_{2.26}$N$_{0.84}$ and a room temperature conductivity of $1.5 \cdot 10^{-6}$ S cm^{-1} [23].

2.3. Nitrogen plasma treatment

Next to LiPON deposition, i.e. in a separate experiment, pristine NASICON-electrolyte plates were subjected to plasma treatment to investigate the influence of nitrogen plasma and incorporation of nitrogen on surface chemical structure and impedance. The plasma treatment was carried out in a separate chamber not connected to the integrated UHV system. The samples were exposed to rf nitrogen plasma for 3 h at a power of 50 W (pressure 0.5 mbar), and afterwards analysed by XPS and EIS. These samples were investigated by XPS to identify reactions taking place solely because of the reactive nitrogen plasma, without LiPON deposition. Additionally impedance measurements were performed with these samples after the photoelectron spectroscopy.

2.4. Photoelectron spectroscopy (XPS)

XPS analysis was performed by a laboratory analysis unit (VersaProbe from Physical Electronics), using a monochromatic Al-Kα source and an incidence angle of 45°. The analyser was operated in