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Enhancing Silicon Performance via LiPON Coating: A Prospective Anode for Lithium Ion Batteries

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ABSTRACT

Thin film bilayers of silicon and LiPON are synthesized via rf magnetron sputtering, whereas the thickness of both layers is in the nanometer range, i.e. between 50 and 400 nm. Electron microscopy on the samples confirms a well-defined layer structure and a high interface quality of the layer stacks. Cyclic lithiation/delithiation of the bilayers via chronopotentiometry, moreover, reveals an astonishing capacity retention and high coulombic efficiency when compared to pure silicon films. This strong improvement in electrochemical performance is attributed to a stabilization of the silicon electrode by the nano-sized LiPON coating. Moreover, it is found that the rate of improvement depends on the thickness ratio between LiPON and silicon. Hence, samples with different thickness of LiPON and silicon, respectively, are investigated to get detailed insight into the electrochemical long term stability of the bilayer samples. Based on these investigations, an electro-mechanical model is suggested that describes in detail the microscopic degradation mechanism of LiPON coated silicon electrodes.

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1. Introduction

Lithium ion batteries have been attracting a huge attention during last decades. However, there is still some significant need for improvement, e.g. regarding lifetime, safety, and energy density. Therefore, many researchers have been working to increase the energy density of lithium ion batteries by utilizing electrode materials of increased storage capacity. In case of the anode, several different materials have been in focus, whereas silicon is one of the most prominent ones. In particular, silicon anodes provide a very high theoretical capacity up to $4200 \, \mathrm{mAh \, g^{-1}}$, which is more than 10 times higher than those of conventional graphite electrodes $(372 \, \mathrm{mAh \, g^{-1}})$ [1].

However, if utilizing silicon as an anode for lithium ion batteries, some major issues have to be faced, which so far have prevented the use of silicon in technical batteries. One of these issues is the large volume change of silicon during its cyclic lithiation/delithiation, which denotes up to 400% [1]. This leads to high mechanical stress inside the silicon electrode and thus to the formation of crack networks, which finally cause a severe loss in battery capacity. Another important issue is the strong formation of solid electrolyte interface (SEI) layer on top of the silicon surface,

which is due to electrolyte decomposition during electrochemical cycling at low potentials. This process is accompanied by an irreversible consumption of lithium and hence by a strong capacity fade and decrease in coulombic efficiency.

In literature there are many reports that suggest different ways to overcome the silicon instability and its capacity fade. Some works focus on measuring and modelling the mechanical stress inside of the silicon in order to get better insight of stress conditions during lithiation/delithiation [2,3]. Other authors suggest the use of silicon nanoparticles, nanowires or patterned nanostructures to compensate large volume changes and avoid stress accumulation and contact loss [1,4–6]. Also there is the suggestion to deposit appropriate particles on the surface of silicon powders, in order to stabilize the silicon and limit the amount of SEI formation [7,8]. Another quite interesting suggestion is the synthesis of composite electrodes, consisting of silicon and other active or inactive components [9,10]. There are also approaches to use current collector materials of stronger adhesion to silicon, in order to better withstand the delamination of silicon during its cyclic lithiation/delithiation [11].

Although some of these approaches are quite promising, there has still been no breakthrough to use silicon-based electrodes in technical lithium ion batteries. Therefore, in this work, we utilize an alternative approach to increase the cycling stability and efficiency of silicon anodes: We cover silicon with a thin ion-conductive layer, i.e. a thin film solid state electrolyte. Such thin

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film electrolytes have been widely employed in thin film battery applications, and they have also already been utilized in some cases to stabilize e.g. $LiCoO_2$ cathodes [12], metallic lithium anodes [13]. In this paper we particularly use amorphous lithium phosphorous oxynitride (LiPON) layers as protective coating and study the influence of these LiPON coatings on the mechanical and electrochemical properties of silicon electrodes.

LiPON is chosen since it can be prepared as well-defined mechanically stable thin films, providing a high ionic conductivity at room temperature of about $10^{-6}\,S\,cm^{-2}$ [14,15]. Moreover, it is supposed to be mostly stable within the voltage range of silicon lithiation/delithiation, so it is also well suited to be used in technical battery applications.

However, despite these quite promising electrochemical properties of LiPON, only minor is known about the behavior of LiPON if coated on top of a silicon anode. Li et al. [16] reported about a significantly decreased SEI formation, if placing a thin LiPON layer on top of a silicon electrode, which has to be noted as an important and promising result. However, beside these electrochemical findings about decreased SEI formation, the question of a mechanical stabilization of silicon by LiPON is another essential issue, since the mechanical stability of the electrode system crucially determines its degradation during cycling. This point has already been pointed out by Lin et al. [17] in case of conversion electrodes, but to the best of our knowledge, basically nothing is known in literature about the mechanical behavior of silicon coated by LiPON, especially if considering long term cycling.

Therefore, in this paper we investigate the performance improvement of silicon electrodes coated by LiPON, with particular emphasis on the effect of mechanical stress and the influence of the layer thickness. Hence, especially in the second part of this work, we focus on the mechanical behavior of silicon-LiPON electrodes during electrochemical cycling, in order to understand e.g. the crack growth process and failure mechanism of the electrodes.

For this purpose, we made use of thin film model electrodes, i.e. we used silicon films of well-defined thickness, surface area, and surface morphology and deposited LiPON layers of different thickness on top of these silicon films. Afterwards, these silicon/LiPON bilayers were investigated from an electrochemical and a structural point of view. Within these investigations it is found that both, the coulombic efficiency and the cycling stability of the silicon can significantly be improved by LiPON coating. In other words, a protective LiPON coating mechanically stabilizes the silicon electrode and thus slows down e.g. the process of crack formation and growth.

2. Experimental

2.1. Thin film preparation

Thin films of titanium, silicon, and LiPON have been deposited by balanced magnetron sputtering. In all cases, targets of 4 inch in diameter were used, and the target to substrate distance was adjusted to about 6 to 7 cm. In particular, dc magnetron sputtering was utilized to deposit thin layers of titanium with a thickness of 25 nm, serving as a current collector, whereas quartz glass was used as a substrate. Afterwards, silicon layers with a thickness between 50 and 200 nm were deposited on top of the titanium by rf sputtering, using a rf power of $1\,W\,cm^{-2}$ and argon as process gas at a pressure of $5\,10^{-3}\,mbar$.

In some cases, an additional LiPON layer with a thickness between 50 and 400 nm was deposited on top of the silicon film. The LiPON deposition was carried out by reactive rf magnetron sputtering, using a sintered Li_3PO_4 target and pure nitrogen as process gas. During deposition of LiPON, the nitrogen pressure was adjusted to $2.1\,10^{-2}\,mbar$ and the rf power was set to $1.4\,W\,cm^{-2}$. For target preparation, commercially available lithium phosphate powder (abcr, 98%) was uniaxial cold pressed at a pressure of 4 MPa and afterwards heat treated at $900\,°C$ for 3 hours under ambient atmosphere.

2.2. Electrochemical characterization

In order to investigate the electrochemical lithiation/delithiation of the thin film samples, galvanostatic cycling was carried out inside a liquid electrolyte (1 M $LiClO_4$ in EC:DMC, 1:1 mass ratio). Here, a three electrode setup was applied, using metallic lithium wires as counter and reference electrodes. The measurement cells were assembled inside an argon filled glovebox, which guarantied oxygen and humidity concentrations below 0.1 ppm. Afterwards, chronoamperometry and chronopotentiometry were performed, using a VSP-300 galvanostat/potentiostat (BioLogic Science Instruments), whereas the voltage range during the chronopotentiometry was chosen between 50 mV and 3 V vs. Li/Li^+ reference.

In order to verify the electrical properties of the LiPON layers, impedance spectroscopy measurements were performed, using an all-solid state setup. For this purpose, LiPON was deposited between a bottom platinum electrode and a copper top one. Afterwards, the impedance of this layer stack was measured between 30 and $70\,°C$ in a frequency range between 1 MHz and 100 Hz, while the amplitude of the ac voltage during impedance spectroscopy was set to 50 mV.

2.3. Characterization of morphology and stoichiometry

To investigate the microstructure of our samples, transmission electron microscopy (TEM) was carried out, using a Libra 200 FE transmission electron microscope (Zeiss). TEM samples were prepared by conventional grinding, dimpling, and ion beam milling, describe elsewhere [18].

The surface morphology of the films was investigated by scanning electron microscopy (SEM), using a Nova Nano SEM 230 (FEI). The thickness of the samples was determined by a Dektak XT stylus surface profilometer (Bruker). Here, scans were performed with a depth resolution of 5 Å.

The chemical composition of the LiPON layers and was determined via inductively coupled plasma optical emission spectroscopy (ICP-OES). For these purpose, LiPON films were solved in HCL solution prior to the ICP-OES measurement.

3. Results

3.1. Characterization of LiPON layers

The stoichiometry of the LiPON layers was verified via ICP-AES. Here, a ratio between lithium and phosphor of 2.3:1 was found, whereas in case of the Li_3PO_4 target, this ratio was determined to 2.9:1. Hence, compared to the target, a slightly decreased lithium concentration might be present in our LiPON films, which could be related to a higher scattering probability of light lithium atoms, when passing from the target to the substrate.

To investigate whether this decreased lithium concentration influences the electric properties of our LiPON, a 200 nm thin LiPON layer was deposited between two metal electrodes (Fig. 1-a). Afterwards, temperature-dependent impedance spectroscopy was carried out to measure the ac conductivity of the sample. An example of such impedance spectrum, measured at $30\,°C$, is shown in Fig. 1-a.

As clearly observed, the impedance data show a high frequency semicircle, representing the electrical bulk properties of the LiPON,