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A concept for direct deposition of thin film batteries on flexible polymer substrate



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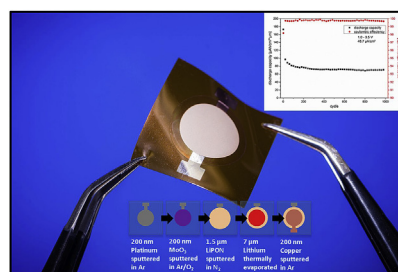
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HIGHLIGHTS

- Transfer of MoO₃-based LIB system from a rigid onto flexible polymer substrate.
- LIB with well-defined layers and homogenous interfaces.
- Good cycle stability of more than 550 full cycles.
- Excellent rate performance with low capacity fading.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, the preparation and characteristics of all-solid-state thin film batteries (TFB) are described. In contrast to the state-of-the-art TFB preparation processes, only room temperature processes are used. The cathode is based on amorphous molybdenum(VI) oxide (MoO₃), for the electrolyte lithium phosphorus oxynitride (LiPON) is employed and lithium metal acts as anode active material. The cycling stability and rate performance were examined and are discussed. The material set shows a very high cycling stability and excellent rate capability. Performing 550 full cycles at a current density of 202.5 μA cm⁻² (10C) a discharge capacity fade of around 15% could be observed. Furthermore, at higher current densities of 2 μA cm⁻² (145C) about one third of the initial discharge capacity remained. Using the proposed technology a shift from inorganic rigid substrates, such as glass to flexible polymer substrates is enabled. The performance of the MoO₃/LiPON/Li TFBs on glass and flexible polyimide substrates were tested and are discussed within this paper.

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1. Introduction

Small, miniaturized energy storage devices currently receive much attention in different markets. One important application is the Internet-of-Things (IoT) [1–4], where small, reliable, self-powered systems enable new functions for private and professional users. Another important application is consumer

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electronics, which is currently influenced strongly by the persisting trend for wearable electronics [5–7]. One critical component in the development of fully flexible devices is the battery. Hereby, lithium ion batteries [8,9] provide an excellent solution, because of their extremely high energy densities compared to other battery systems. Only drawback of commonly used lithium ion batteries is the needed rigid or stiff housing to hold the functional battery layers in place and also to prevent leakage of the liquid electrolyte [10,11].

A promising approach to overcome these limitations is the deployment of solid state electrolytes. Therefore, solid state electrolytes offer several advantages compared to their liquid counterparts. First of all, they offer high safety due to the absence of leakage issues. Furthermore, solid electrolytes, like LiPON [12,13] or garnet-type ceramic oxides like $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) [14,15] are stable against metallic lithium, which exhibits the opportunity of an increased voltage window. Since the ionic conductivity of typical solid electrolyte materials at room temperature ($\sigma_{\text{ionic}} \approx 10^{-6} \text{ S cm}^{-1}$) [16] is significantly lower compared to liquid ones ($\sigma_{\text{ionic}} \approx 10^{-2} \text{ S cm}^{-1}$) [17], thin electrolyte layers ($<5 \mu\text{m}$) are needed to achieve a sufficiently low resistance. One possibility is the use of sputtered electrolyte layers in combination with PVD deposited electrodes in a thin film battery layout. A significant number of reports on TFBs have been presented in the literature and were also commercially introduced [18–20].

Most TFBs use a lithium cobalt oxide (LCO) thin film as cathode active material due to its attractively high voltage versus lithium and excellent stability [21–23]. However, as-deposited layers of LCO are amorphous and suffer from a low diffusion rate. To improve the diffusion of lithium ions through the LCO layer, the electrodes are typically annealed after deposition to increase the crystallinity. However, the temperatures used make the utilization of thermally stable substrates, but rigid such as silicon wafers, aluminate or metal foils inevitable. Deposition on polymer substrates is not possible with this approach due to the degradation of polymers at high temperatures.

One method to enable the use of a polymer substrate is to first deposit the cathode layer on a thermally stable substrate. Afterwards the annealed and crystalline layer is transferred onto a polymer film [24]. Nevertheless, this procedure still requires high temperatures and subsequently to the high energies heavy expenses.

In this paper we present a different process, which is based on the exclusive use of amorphous materials and room temperature processes. The proposed sputter deposited TFB consists of a molybdenum oxide [25–32] cathode, a LiPON electrolyte and a lithium metal anode. First, the battery cell design is verified on a glass substrate. Then the thin film battery is deposited directly on a flexible polymer substrate. The respective battery systems are analyzed in regard to their chemical composition and their morphology. Furthermore electrochemical parameters are determined by means of galvanostatic cycling experiments. Based on these results the feasibility of direct deposition of TFB on flexible polymer substrate is evaluated and will be discussed in detail.

2. Experimental procedure

2.1. Preparation of Li thin-film battery cell

MoO_3 -based lithium ion batteries (LIBs) were fabricated on glass substrate with a thickness of $160 \mu\text{m}$ as well as on flexible polyimide foil with a thickness of $75 \mu\text{m}$. Current collectors, cathode material and the LiPON electrolyte were deposited by conventional planar RF sputtering method (custom made sputter deposition by MBraun) using 4" sputter targets within an argon-filled glovebox. The sputter process was performed upside down, having the

material source on the bottom and the respective substrates at the top of the sputter chamber. That way consistent distances between the sputter target and the substrates could be ensured, which made the different thicknesses of the substrates negligible. The lithium anode was prepared by thermal flash evaporation. The deposition of all films was carried out in a vacuum of below $4 \cdot 10^{-1} \text{ Pa}$ and room temperature, while the single layers were patterned via shadow masks. It should be briefly mentioned, that although the process is declared as room temperature process, the actual temperature within the sputter chamber could raise to about $100 \text{ }^\circ\text{C}$ due to the heat loss of the sputter process. Nevertheless the single layers did not undergo any further heat treatment. Thickness of the deposited materials was regulated by controlling the sputter time and by use of the thickness monitor of a quartz oscillator. Furthermore, the thickness was calculated from geometric parameters and the weighed applied mass as well as verified using Focused Ion Beam–Scanning Electron Microscopy (FIB–SEM) images, additionally.

The first layer on the respective substrates was platinum as the cathode current collector using a platinum sputter target (K. J. Lesker). With a thickness of 200 nm a circle pad with a defined effective electrode area of 0.79 cm^2 was deposited. On top of the Pt a MoO_3 cathode film with a thickness of 200 nm was prepared. For the fabrication of the cathode film a molybdenum target (K. J. Lesker) was utilized. Therefore, a constant gas flow of 30 sccm argon and 10 sccm oxygen was established resulting in a deposition pressure of $3 \cdot 10^{-1} \text{ Pa}$ at a RF power of 200 W . No further heat treatment of the MoO_3 film was performed to retain the amorphous nature of the cathode layer. Afterwards the solid-state electrolyte was deposited onto the MoO_3 . Based on a Li_3PO_4 target (Plasma-materials, Inc.), a RF power of 120 W , a sputter pressure of $2 \cdot 10^{-1} \text{ Pa}$ and a gas flow of 100 sccm dry nitrogen, a $1.5 \mu\text{m}$ thick $\text{Li}_{3.3}\text{PO}_{3.8}\text{N}_{0.22}$ (LiPON) electrolyte layer was obtained. Next, a metallic lithium anode was applied on the electrolyte. Hence, Li metal was thermally evaporated from a tungsten evaporation boat with a deposition rate of 30 \AA s^{-1} at a deposition pressure of $3 \cdot 10^{-3} \text{ Pa}$ and an ultimate thickness of $7 \mu\text{m}$. Finally, via RF sputtering the battery cell was equipped with a 200 nm copper current collector at the anodic side. The scheme of the preparation process is presented in Fig. 1a.

2.2. Measurements

The cathode material was analyzed by means of X-ray photoelectron spectroscopy (XPS) to determine the stoichiometry of the MoO_3 film. The XPS investigations were performed using a Thermo K-Alpha K1102 system. Using monochromatic Al $K\alpha$ radiation (1486.6 eV) at a typical base pressure of $2 \cdot 10^{-7} \text{ Pa}$, the spectra were recorded in constant analyzer energy mode (CAE) and a take off angle of 0° with pass energies of 40 eV for high resolution measurements.

The non-crystallinity of the cathode film was checked by X-ray powder diffraction (XRD). The Siemens D5000 diffractometer was operated in Bragg-Brentano geometry with a step width of $0.02^\circ 2\theta$ and variable divergence slits. Data was collected in a range of $10^\circ 2\theta$ to $60^\circ 2\theta$ using Cu $K\alpha$ radiation.

Microstructural and morphological studies of the battery components and their respective interfaces were investigated via focused ion beam/scanning electron microscopy (FIB–SEM). The cross section image was taken using a FEI Helios NanoLab™ 600 DualBeam™ apparatus, while the samples were prepared by implemented FIB technique. To protect the TFBs from exposure to ambient atmosphere (air, humidity), they were transferred inertly into the microscope via airlock, to prevent any morphological changes.

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