



Electrochemical lithiation of thin silicon based layers potentiostatically deposited from ionic liquid



Codruta Aurelia Vlaic^a, Svetlozar Ivanov^{a,*}, Ralf Peipmann^a, Anja Eisenhardt^b, Marcel Himmerlich^b, Stefan Krischok^b, Andreas Bund^a

^aElectrochemistry and Electroplating Group, Technische Universität Ilmenau, Gustav-Kirchhoff-Str. 6, 98693 Ilmenau, Germany

^bInstitute of Physics and Institute of Micro- and Nanotechnologies, Technische Universität Ilmenau, PF 100565, 98684 Ilmenau, Germany

ARTICLE INFO

Article history:

Received 3 December 2014

Received in revised form 29 March 2015

Accepted 31 March 2015

Available online 3 April 2015

Keywords:

silicon electrodeposition

ionic liquid

Li ion battery

quartz crystal microbalance

X-ray photoelectron spectroscopy

ABSTRACT

Thin silicon layers containing about 20% carbon and 20% oxygen were deposited on copper substrates by potentiostatic electroreduction from a 1 M SiCl₄ 1-butyl-1-methyl-pyrrolidinium bis (trifluoromethyl) sulfonylimide [BMP][TFSI] electrolyte. The electrodeposition process was investigated by means of voltammetric techniques, coupled with in-situ microgravimetry (quartz crystal microbalance, QCM). The electrochemical and QCM data suggest a possible contribution of a partial Si⁴⁺ to Si²⁺ reduction and/or a restructuring of the metallic substrate. Considerable impact of side reactions parallel to the deposition process was indicated by QCM measurements performed under potentiostatic and potentiodynamic conditions. The deposition of silicon-based films was confirmed by energy dispersive X-ray analysis (EDX). Analysis of the chemical composition of the deposit and its elemental distribution were achieved by depth profiling X-ray photoelectron spectroscopy (XPS). The electrodeposited silicon containing layers showed stable lithiation and delithiation with capacity values of about 1200 mAhg⁻¹ and 80% capacity retention after 300 cycles in standard EC/DMC electrolytes. In ionic liquid (IL) the material displayed lower capacity of ca. 500 mAhg⁻¹, which can be attributed to the higher viscosity of this electrolyte and deposition of IL decomposition products during lithiation.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

There is a great expectation worldwide that lithium ion batteries (LIBs) will power the hybrid and electric vehicles of the future. Accordingly, commercially available LIBs require reduction in cost, enhanced safety and especially, much higher energy and power densities [1,2]. Consequently, one major aspect of LIB research is focused on finding novel electrode materials with enhanced energy and power densities.

The development of thin-film and microbatteries based on Li ion technology established a further main direction for the progress of the electrochemical energy storage. Microbatteries are necessary for a wide range of applications, comprising small medical devices, sensors, microelectronics and micro-electromechanical-systems (MEMS) [3–8]. The research work in these fields is motivated by the possibility to miniaturize electrochemical power sources with specific geometries, which can be integrated into electronic and

medical devices for special application [3,4]. Due to their narrow geometry, a space and shape optimization of the battery is required. Therefore, deposition of stable and thin layers is a constructive approach for attaining simultaneously the required geometry and high energy density. *Thin film all-solid* (micro) battery technology is usually based on a consecutive deposition of micrometer sized layers of a cathode material, a solid electrolyte (e.g. lithium-phosphorous oxynitride-LIPON) and an anode material (e.g. lithium or silicon tin oxynitride anode). The active materials and the solid electrolytes are usually deposited by means of magnetron sputtering or other vacuum techniques. Even though during the recent years there is a significant progress in this field, still the major disadvantages of *all-solid-state* thin film batteries are the low rate capabilities and the sluggish Li-ion transport in the solid electrolyte [3].

One useful alternative approach for boosting the performance of microbattery systems is a novel 3D microbattery technology [3,5–8]. Beside their specific geometry, 3D microbatteries have further advantages related to electrolyte development. Instead of a solid electrolyte, a hybrid polymer electrolyte (HPE) consisting of a polymer soaked with a conventional carbonate based Li ion

* Corresponding author. Tel.: +49 3677 69 2842; fax: +49 3677 69 3104.

E-mail address: svetlozar-dimitrov.ivanov@tu-ilmenau.de (S. Ivanov).

electrolyte can be used [3]. Thus, the ionic conductivity and ion mobility of the electrolyte and therefore the battery performance can be substantially enhanced.

Along with the conventional carbonate electrolytes incorporated in polymers, ionic liquids have their special application in the HPE development as well [9]. Advantages are their electrochemical stability, low vapor pressure and non-flammability [10], offering additional safety and reliability of the battery. Based on the above-mentioned breakthrough in the field of microbattery technology, it can be concluded that fundamental studies on cyclability of thin film materials in conventional and ionic liquid based electrolytes are necessary. Before their eventual implementation into microbatteries with specific geometry and architecture basic characterization of the novel materials at standard electrochemical conditions, where the maximum of their performance can be extracted is essential. The obtained results can be further used as a benchmark for (micro) battery development at technological and engineering levels.

Silicon, an extensively studied material suitable for thin film deposition has a theoretical capacity of 4200 mAhg^{-1} , more than ten times higher compared to the capacity of the currently used graphite [11]. Its main disadvantage is the huge volume expansion ($>300\%$) upon alloying with lithium, inducing disintegration of the electrode material, loss of electrical contact, poor reversibility and a rapid capacity fade [12]. Different approaches including nanostructuring [12,13], use of silicon in amorphous form [14–16] as well as forming composites with carbon [11] or other materials [11,17] resulted in improved performance of the electrode. The nanostructured silicon anodes accommodate mechanical stress more efficiently, display diminished crack formation and decreased structural instability. Furthermore, nanodimensional materials, organized in the form of thin films or dispersed nanopowders, provide shorter diffusion lengths and additional surface storage sites for lithium [11].

Electrodeposition is one promising alternative to vacuum physical deposition techniques, due to its technical simplicity, the chance for low cost processing and its attractiveness for further technological scale-up [18]. Similarly to physical vapor deposition, the Si electrodeposition process yields a thin layer [19], preferable for thin film and microbattery applications. Furthermore, the electrodeposition is a versatile technique, allowing control of the morphology by adjusting the experimental conditions and obtaining deposits on different substrate geometries. Concerning this advantage electrodeposition of Si as a stage for 3D microbattery technology was recently achieved from propylene carbonate based electrolyte [5]. Additionally, silicon electrodeposition is potentially important not only for LIB applications but also for the deposition of materials in photovoltaic cells [20], electrical, electronic [21], and optical devices [22] as well as for corrosion-resistant coatings [23]. Due to the negative standard electrode potential of Si (approx. -1.7 V vs. NHE [24]) and the high reactivity of its precursors (e.g. halides) only some non-aqueous electrolytes can be used to electrodeposit Si. These include a variety of organic electrolytes [5,18,20,25–35] and inorganic molten salts [36]. The room temperature electrolytes are based on propylene carbonate [5,18,28,29], acetonitrile [30], dichloromethane [25] and ionic liquids [19,22,31–35]. The electrolytes containing volatile solvents display certain drawbacks, including high vapor pressure, flammability and need a supporting electrolyte, which is often incorporated into the deposited film [27]. Molten salts require high temperatures and are extremely reactive. It is worth noting that ionic liquids combine the advantages of having a large potential window, do not require supporting electrolyte and can be handled safely (low volatility and flammability). Furthermore, in the recent years ionic liquids have been tested as electrolytes in LIBs [16,37–39]. However, the high viscosity, considerable price

and in many cases insufficient cathodic passivation, still limit their application as commercial electrolytes for electrodeposition and for implementation in LIBs.

The main goal of this work is to explore the electrodeposition of thin Si layers on copper substrates from SiCl_4 containing [BMP][TFSI] with the central intention to shed more light on the deposited layer composition and structure. This is achieved by the correlation of experimental data obtained through electrochemical, microgravimetric and spectroscopic methods of investigation.

The interest in the performance of the deposited Si layers as Li alloying materials is related to their possible direct implementation in thin film and 3D microbatteries. It was correspondingly shown that Si thin films deposited on TiO_2 nanotube template arrays via magnetron sputtering [39] and plasma enhanced physical vapor deposition (PECVD) [40] have a good perspective to be implemented as advanced anodes for microbatteries. This paper reports on electrochemical deposition of Si containing layer as a prerequisite for TiO_2 nanotube modification by means of Si electroreduction, which will be addressed in our further work.

Targeting practical application of the obtained Si coatings in LIBs the Si/Cu electrodes are investigated as anodes in standard and in environmentally benign, non-flammable ionic liquid electrolytes with improved safety.

2. Experimental

2.1. Reagents and chemicals

Ethylene carbonate (EC), dimethyl carbonate (DMC), SiCl_4 , LiTFSI and LiPF_6 were purchased from Alfa Aesar. The reagents were used as received without further purification. The ionic liquid [BMP][TFSI] was obtained from IoLiTec (Heilbronn, Germany). It was dried at 50°C under argon atmosphere and vacuum until a value of 15 ppm H_2O was reached. The H_2O content in the electrolyte solutions was monitored by Karl - Fischer titration, using a Metrohm 831 KF Coulometer.

2.2. Silicon electrodeposition

Silicon electrodeposition was carried out in a home-made PTFE electrochemical cell designed for quartz crystal microbalance (QCM) measurements (see section 2.4). The three-electrode system consisted of a Cu plate as working electrode (0.23 cm^2 geometric area) and two Pt wires as counter and quasi-reference electrodes (QRE), respectively. The Pt electrodes were thoroughly cleaned with HNO_3 prior to use. Before silicon electrodeposition, the Cu electrodes were freshly polished and sonicated in ethanol for 10 minutes. The cell assembly and electrochemical measurements were performed at room temperature (20°C) in a glove-box (MBRAUN UNILab LMF auto) maintaining H_2O and O_2 levels below 0.1 ppm. The potentiostatic deposition of silicon was performed at -2 V vs. Pt QRE for 2 hours from 1 M SiCl_4 in [BMP][TFSI]. Immediately after the deposition, the samples were thoroughly rinsed with DMC.

2.3. Chemical and structural characterization

The surface morphology of electrodeposited Si samples was investigated using an ultrahigh resolution scanning electron microscope (FE-SEM, Hitachi S-4800) equipped with EDX analysis.

The chemical composition of the electrodeposited films was investigated by X-ray photoelectron spectroscopy (XPS) depth profiling using a Specs SAGE system (base pressure $<1 \times 10^{-8}$ mbar) equipped with a Phoibos 150 electron analyzer including a 1D delay line detector. $\text{AlK}\alpha$ radiation was generated by a XR 50 M X-ray source in combination with a Focus 500 monochromator. For

Download English Version:

<https://daneshyari.com/en/article/184261>

Download Persian Version:

<https://daneshyari.com/article/184261>

[Daneshyari.com](https://daneshyari.com)