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Short communication

Electrochemical synthesis of lithium nanotubes from an ionic liquid

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ABSTRACT

In this paper we present the first results on the template-assisted synthesis of lithium nanotubes from the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ($[Py_{1,4}]$ TFSA). Lithium was electrochemically deposited from a 0.5 mol kg^{-1} LiTFSA in $[Py_{1,4}]$ TFSA solution inside the pores of a copper-sputtered polycarbonate membrane. Afterwards the membrane was dissolved with THF and the samples were investigated by scanning electron microscopy (SEM). The results show the formation of partly free standing lithium nanotubes which form nanowires with increasing deposition time.

1. Introduction

In recent years there has been a rising interest in the development of high capacity energy storage systems. Nowadays, special attention is paid to rechargeable lithium-ion batteries which are suitable for application in full electric vehicles [1,2].

Metallic lithium has long been known as the most attractive anode material for these batteries due to its advantageous electrochemical properties. It has a high theoretical specific capacity of 3862 Ah g^{-1} and together with the low density (0.52 kg L^{-1}) it can provide a theoretical charge density of 2047 Ah L^{-1} [3]. However, up to now safety issues of employing metallic lithium anodes have not been fully clarified due to the formation of dendritic lithium which can lead to short circuiting. Furthermore, the dendrite growth causes capacity fading during cycling. Recently, we showed the feasibility of the electrosynthesis of macroporous lithium in the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ($[Py_{1,4}]$ TFSA) using polystyrene opal structures [4,5]. The wide electrochemical window of $[Py_{1,4}]$ TFSA enabled the electrodeposition of Li which is not possible from aqueous electrolytes as among of all metals Li has the lowest reduction potential. The macroporous structure of the obtained deposits allows the dendrite free deposition/stripping of lithium. Arrays of nano-wires/tubes would also be quite interesting, from a fundamental point of view.

In this communication we report on the template-assisted electrosynthesis of lithium nano-tubes/wires in the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ($[Py_{1,4}]$ TFSA) using track etched polycarbonate (PC) membranes. After chemical dissolution of the membrane, partly free-standing lithium nanotubes and nanowires were obtained. In a recent paper [6] we briefly mentioned that it is possible – in principle – to electrodeposit lithium as nanowires from the ionic liquid $[Py_{1,4}]$ TFSA containing LiTFSA as a source of lithium.

2. Experimental

The synthesis of Li nanotubes was done by a template-assisted electrochemical deposition route in the ionic liquid $[Py_{1,4}]$ TFSA (Io–Li–Tec) of the highest available purity. Commercially available ion track-etched polycarbonate membranes (IT4IP, Belgium) with a pore diameter of 200 nm, a thickness of 20 µm and a pore density of 10^9 cm^{-2} were employed. One side of the membrane was sputtered with a copper layer of 200 nm thickness to get a conductive substrate for the electrochemical experiments.

The ionic liquid was dried for 48 h at 60 °C under vacuum to reach a water content of about 7 ppm. Lithium bis(trifluoromethylsulfonyl) amide (LiTFSA, 99.95%, Aldrich) was used as a source of lithium, and it was dried for 24 h under vacuum prior to use. Afterwards, the corresponding quantity of lithium salt was added to the $[Py_{1,4}]$ TFSA to get a 0.5 mol kg^{-1} LiTFSA solution.

The electrochemical cell was made of a Teflon cylinder pressed onto the membrane with a Teflon covered Viton O-ring in between to prevent the electrolyte from leaking. A Pt-ring (99.999%) and a Pt-wire (99.999%) were used as counter and quasi-reference electrodes, respectively.

All experiments were carried out under inert gas conditions in an Argon filled glovebox (OMNI-LAB from Vacuum Atmospheres) with

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oxygen and water contents below 1 ppm. After electrodeposition, the membrane was dissolved in tetrahydrofuran (THF). The samples were investigated by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX, Carl Zeiss DSM 982 Gemini) and photoelectron spectroscopy (XPS).

3. Results and discussion

The electrochemical behaviour of the neat $[Py_{1,4}]$TFSA was investigated using cyclic voltammetry on a copper sputtered PC membrane. As shown in the cyclic voltammogram of Fig. 1a, the cathodic breakdown of $[Py_{1,4}]^+$ starts at a potential of about −2.6 V vs. Pt, and the sputtered copper film anodically dissolves at about 0.05 V. The anodic dissolution of copper in the employed ionic liquid was previously investigated, see [7].

Fig. 1b shows a cyclic voltammogram recorded on a Cu-sputtered PC membrane in the ionic liquid $[Py_{1,4}]$TFSA containing 0.5 mol kg^{-1} LiTFSA. The cyclic voltammogram shows the typical electrochemical behaviour of lithium with an obvious redox process as a result of Li deposition/stripping. Additionally, a shift occurs in the baseline of the forward scan that gives an indication for upd and alloying processes. The bulk deposition of lithium begins at −3.2 V and takes place together with partial decomposition of the ionic liquid. From the comparison of the two CVs in Fig. 1(a and b) it can be concluded that the addition of lithium salt to the ionic liquid leads to a certain increase in the electrochemical stability of the solution in the cathodic regime under these conditions. The enlargement of the electrochemical window of ionic liquids during electrodeposition of alkali metals has been reported [8,9].

The potentiostatic deposition of lithium inside the pores of the membrane was done at a potential close to the beginning of the bulk deposition in order to control the deposition rate of lithium inside of the pores. From the current–time curve (Fig. 1c) recorded over a time of 45 min at a potential of −3.55 V it can be postulated that there are different deposition steps. In the first 15 min the current slightly decreases. During the next 15 min the curve shows a slight increase in the current subsequently followed by a strong increase in the current until 45 min total deposition time when the current reaches a maximum value. In the first deposition experiment we applied a constant potential of −3.55 V versus Pt quasi reference electrode for 15 min. Afterwards, the membrane was dissolved with tetrahydrofuran (THF) and the deposit was investigated by SEM. The SEM images of Fig. 2 show quite regular and partly free-standing lithium nanotubes. Lithium shows a constant growth inside of the pores along the walls leading to the formation of tubes instead of wires. One explanation could be that the deposition takes place together with the cathodic breakdown of the TFSA anion of the ionic liquid and also the partial decomposition of $[Py_{1,4}]^+$. The EDX analysis shows the presence of a certain amount of fluorine, oxygen and nitrogen on the samples caused by the decomposition of the TFSA anion from the ionic liquid. The XPS results (Supporting material) of a Li nanotubes sample obtained at −3.55 V for 15 min show also the presence of oxygen, nitrogen, carbon and fluorine. Howlett et al. [10] reported that the surface film formed on lithium deposited on copper contains the reduction products of the $TFSA^-$ and also there were hints on the presence of reduced species from $[Py_{1,4}]^+$. Additionally, the formation of lithium nanotubes supports our observations from Ref. [5] where we have found that the lithium grows around the polystyrene spheres and creates an inverse opal structure after dissolution of the polystyrene spheres. With increasing time the nanotubes are continuously filled with lithium and form nanowires. After a deposition time of 30 min some of the nanotubes are already filled (Fig. 3).

The maximum current density of 3.3 mA cm^{-2} was reached after 45 min. At this point the deposition was stopped and SEM images of the deposit were acquired, Fig. 4. The pictures show a dense and compact deposit of mostly lithium nanowires. From these images it can be clearly seen that the lithium first grows along the walls inside the pore as nanotubes and by increasing the deposition time the deposition laterally propagates at the inner walls inside the pores forming wires instead of tubes. The nanowires are well distributed over the whole deposition area.

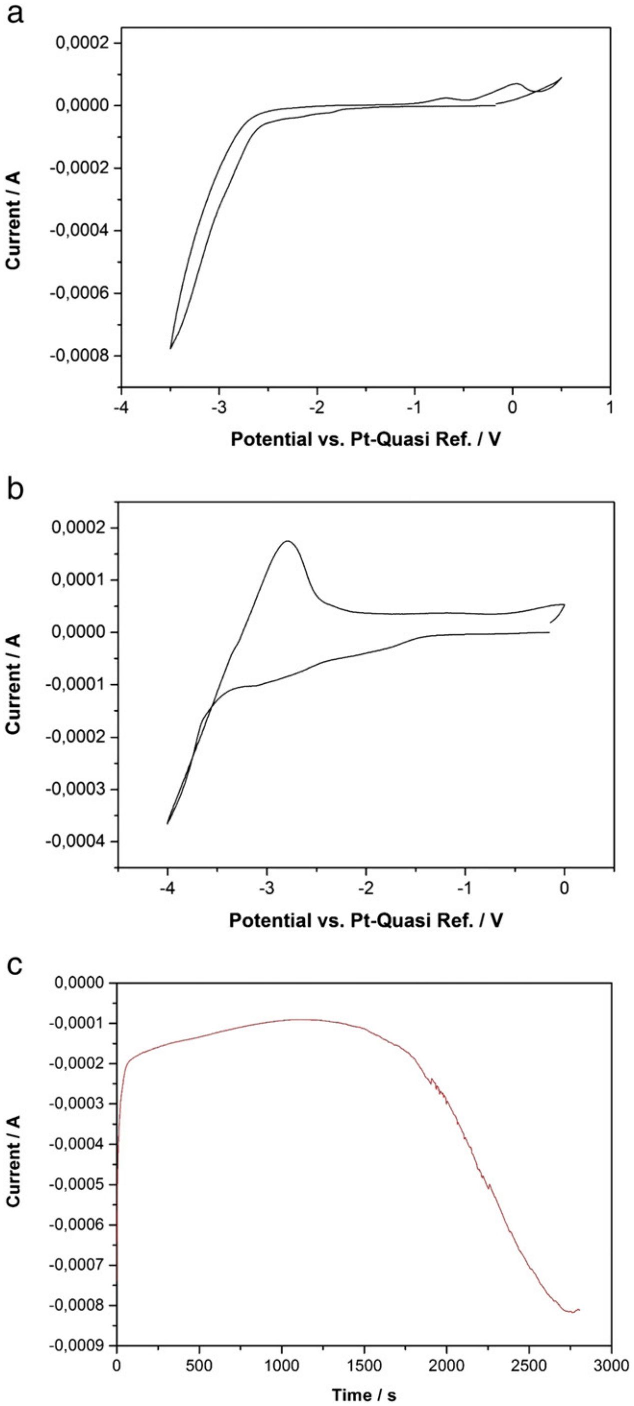

Fig. 1. a) CV of neat $[Py_{1,4}]$ TFSA on a copper-sputtered (200 nm) PC membrane. Scan rate: 10 mV s^{-1}. b) CV of 0.5 mol kg^{-1} LiTFSA in $[Py_{1,4}]$ TFSA recorded on a copper-sputtered (200 nm) PC membrane. Scan rate: 10 mV s^{-1}. c) Potentiostatic current–time curve at −3.55 V over 45 min in 0.5 mol kg^{-1} LiTFSA/$[Py_{1,4}]$ TFSA recorded on a copper-sputtered (200 nm) PC membrane.

A similar behaviour of growth was observed in the case of the deposition of germanium and silicon inside of such a membrane. The use of a membrane with a small pore diameter such as 100 nm leads to the deposition of nanowires. However, if the deposition was done