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Electrodeposition of thin poly(propylene glycol) acrylate electrolytes on 3D-nanopillar electrodes

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ABSTRACT

Solid polymer electrolytes consisting of poly(propylene glycol) diacrylate and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were deposited onto Cu_2O-coated 3D Cu nano-pillars through cathodic electropolymerization. Electropolymerization, using constant and pulsed current techniques, was used to produce polymer coatings directly onto 3D substrates with thicknesses down to nano-scale dimensions. SEM confirmed that pulsed current deposition is comparatively beneficial for producing uniform and conformal electrolyte coatings along the nano-pillar structure. ATR/FTIR studies of the electropolymerized electrolytes showed that the degree of polymerization in the electrolyte can be increased by a heating treatment after synthesis. XPS analysis confirmed the presence of co-deposited LiTFSI salt in the polymer layer during electropolymerization. The ionic conductivity of the obtained electrolytes was characterized by EIS and is in the order of 10^{-6} S cm^{-1} at room temperature. This work demonstrates that the electrolyte coated on the nano-pillar electrodes may serve as a template for further deposition of electrode materials for the assembly of 3D-microbattery whole-cells.

1. Introduction

Three-dimensional microbatteries (3DMBs) are considered promising energy storage candidates for powering small-scale electronic devices, such as micro-sensors, micro-electromechanical systems and medical implants [1]. These miniature devices, with volumes of 1-10 mm^3, demand both high power and energy densities: the energy per unit area delivery requirements are about 1 J mm^{-2} over a day, equivalent to a power consumption of around 10 μW [1–6]. This, in turn, stimulates new ideas for developing novel Li-ion battery designs with enlarged 3D surfaces within a small footprint area. An obvious gain in areal capacity from about 0.1 mAh cm^{-2} to 1-10 mAh cm^{-2} could be achieved by developing 3D electrodes for microbattery applications [2,4–6]. Various 3D battery configurations have been proposed both theoretically and experimentally [1–3], not only for the fabrication of 3DMBs, but also applicable for Li-ion batteries with conventional dimensions.

Perhaps one of the most feasible approaches towards constructing a solid-state Li-ion 3DMB whole-cell is through sequential deposition of different solid-state battery components, for example a 3D nano-structured current collector with an electrode material coating arranged in the form of plates, tubes or pillars, a solid electrolyte acting as both an ionic conductor and physical separator, and a second electrode deposited on top of the electrolyte [4–6]. In order to minimize the electrolyte volume and to promote good interfacial contacts, it is critical to produce a robust and conformal electrolyte with thickness down to micro- and nano-scales. Furthermore, the electrolyte needs to be pinhole-free and mechanically stable to avoid short-circuits during 3DMB cell assembly [1–6].

Among the different possible electrolyte systems, safe and non-toxic solid polymer electrolytes (SPEs) have been suggested as a replacement to more conventional liquid/gel electrolytes for 3DMB applications [4]. However, the conformal deposition of ionically conductive polymer materials directly onto 3D architectures with large surface areas constitutes a significant challenge. A few LiTFSI/polyether systems produced through UV-induced radical polymerization from acrylate-capped polyether oligomers have recently been reported as potential 3DMB electrolytes [7,8], but these were found difficult to apply to 3D substrates with very complex surface geometry. In order to form conformal and ultrathin polymer electrolytes (down to ~10 nm [1]), electropolymerization and/or electrografting (i.e., covalent linkage to solid surfaces) have been considered effective approaches for self-limiting growth of the deposited polymer [9]. When compared with conventional polymer deposition methods through solution casting and UV-initiated polymerization, electropolymerization should be able to achieve improved adhesion at the electrode/electrolyte interfaces by forming a compact polymer layer

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on the electrode surfaces. Surface modifications of a broad variety of substrates–including metals, metal oxides, different types of carbon and semiconductors–have been thoroughly investigated using electropolymerization of vinyl monomers in aprotic solvents (e.g., acetonitrile and dimethylformamide), such as acrylonitrile [10–12] and various (meth)acrylate derivatives [13–15]. Electropolymerization in aqueous solution has also been reported [16–18]. However, only a few electropolymerized polymer electrolyte systems have so far been reported for microbattery applications [19–23].

This study aims at exploring an electropolymerized SPE, exemplified by deposition on a 3D nano-pillar architecture. Recent studies using electrodeposition approaches to develop different 3D architectures (e.g., aperodic foam and nanopillar) with electropolymerized polymer electrolyte layers have been summarized by our group [6]. Here, we perform in-depth studies of this electrolyte synthesis strategy and detailed characterizations of the electropolymerized electrolytes derived from poly(propylene glycol) diacrylate. Moreover, as compared to constant current deposition, we demonstrate the beneficial use of pulsed current to form conformal coatings along 3D surfaces. This technique promotes the formation of uniform and completely covering electrolyte layers on long nanopillars with sophisticated 3D geometries. Furthermore, co-deposition of lithium-conductive salt in the electrolyte is achieved during electropolymerization, which simplifies the conventional post-doping of salt. A comparative study on the influence of heat-treatment on the electrolytes is also discussed.

A polymer electrolyte system based on poly(propylene glycol) diacrylate (PPGDA) and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) salt has been investigated. The acrylate end-groups in the monomer used here are expected to be electropolymerized onto the metal oxide substrate surface through the formation of carboxylate-metal oxide bonds and undergo propagation to form a cross-linked polymer network [24]. LiTFSI was used as ionically conductive salt in the polymer matrix during the electropolymerization synthesis. The electrodeposition of 3D Cu-nanopillar substrates was achieved by a template-facilitated electrodeposition method [6]. The Cu substrate undergoes spontaneous oxidation forming a 15 nm Cu_2O film, thereby producing a complete 3D anode suitable for Li-ion batteries [6,25–27]. Controlled current chronopotentiometry was utilized to fabricate the electrolyte directly onto the 3D Cu_2O-coated Cu-nanopillars. Alternatively, pulsed current was implemented to synthesize a conformal and uniform electrolyte layer with controlled thickness on 3D electrodes. The electrochemical characteristics of PPGDA/LiTFSI on 3D Cu_2O-coated Cu nano-pillars were studied by cyclic voltammetry and chronopotentiometry. Redox probe analysis was also applied on polymer-coated planar and 3D Cu substrates to examine the presence of pinholes in the electrolytes. The ionic conductivity of the electrolyte was investigated using electrochemical impedance spectroscopy (EIS), and the morphology of the polymer deposits on 3D substrates was analyzed by scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS) was utilized to characterize the chemical composition of the coated 3D substrates, especially the content and distribution of polymer and LiTFSI across the surfaces. Furthermore, the degree of polymerization in the electropolymeried electrolytes on 3D Cu foils was measured by attenuated total reflectance/Fourier transform infrared spectroscopy (ATR-FTIR). The influence of heating the electrolyte after electropolymerization will also be discussed.

2. Experimental

2.1. Materials

All solvents used in the experiments were dried to remove residual water. Ethanol (Solveco, 99.5%) was left over 3 Å molecular sieves for at least one week before use, poly(propylene glycol) diacrylate (Aldrich, Mn ca. 900) (stored in refrigerator) was used as received. LiTFSI (Purolyte) was dried at 120 °C for 12 h in a vacuum oven. Ionic conductivity measurements were carried out on a glassy carbon disk electrode (CH-Instrument, diameter of 3 mm) using Gallium-Indium eutectic (GaIn; Aldrich, 99.99%) as a soft contacting electrode.

The electrodeposition of 3D Cu nano-pillars was performed on planar Cu substrate (Whatman, thickness of 0.55 mm) for most of the measurements. In ATR/FTIR analysis, planar Cu foil (Goodfellow, thickness of 0.02 mm) was used alternatively as the substrate for the electrodeposition of nano-pillars in order to facilitate the characterization. 3D Cu nano-pillar substrates were prepared in-house using the same electrodeposition procedures on both Cu substrates by pulsed galvanostatic deposition from a $CuSO_4$ solution into a porous polycarbonate membrane with 1 μm pore width (Whatman, Cyclopore). A thin layer of Cu_2O was subsequentially formed on the Cu nanopillars via a comproportionation reaction in the Cu^{2+} containing solution [6]. This electrodeposition synthesis yielded 4-8 μm long pillars with an interpillar distance of 1-2 μm.

2.2. Synthesis of polymer electrolytes by electropolymerization

Prior to synthesis, the electrochemical characteristics of PPGDA/LiTFSI in ethanol were analyzed by cyclic voltammetry. A 3-electrode setup was used, consisting of an Ag pseudo-reference electrode, a Pt wire counter electrode and a glassy carbon working electrode. The electrochemical properties were studied between 0 V and -3 V at a scan rate of 20 mV s^{-1}.

A homogenous electrolyte solution of PPGDA/LiTFSI with known [PO]:[Li^+] molar ratio (20:1) was used throughout the studies. The electropolymerized electrolytes were produced from a monomer solution of PPGDA and LiTFSI in ethanol. The solvent was chosen to facilitate the doping of Li-ion salt into the polymer matrix during polymerization and could be conveniently removed before further testing.

Prior to electropolymerization, the 3D substrates were cleaned with 1 M NaOH, ethanol and then dried in vacuum. All experiments were carried out in a setup based on a modified Swagelok™ configuration with gas inlet and outlet valves to ensure a dry argon atmosphere. A constant current of -75 μA cm^{-2} (per footprint area), i.e., approximately -15 μA cm^{-2} (per electrochemical surface area) was used to deposit PPGDA/LiTFSI on 3D Cu_2O-coated Cu nanopillars. The electrochemical surface area of each sample was estimated from (footprint area) × (surface area gain factor). The surface area grain factor was determined by SEM as approximately 5.

Alternatively, pulsed current chronopotentiometry using -75 μA cm^{-2} (per footprint area) pulses of 0.1 s followed by 1 s rest periods were applied over 2500 cycles. After synthesis, residual monomers and salt were removed by thoroughly rinsing the sample and drying it in vacuum.

2.3. Polymer electrolyte characterization

The surface morphology of the electrolyte deposited onto the 3D substrates was examined by a ZEISS LEO 1550 SEM. Some of the micrographs were taken from a tilted sample in order to better observe the profile of the electrolyte layer on the 3D electrodes. The electrolyte layer thicknesses were estimated by comparing the diameters of a single nanopillar before and after electropolymerization. For the calculation of the ionic conductivity, the thickness of the polymer coated on a glassy carbon disk electrode was roughly estimated from the cross-sectional view.

Karl-Fischer titration was performed using a 756 KF Coulometer (Metrohm) to determine the water content in the PPGDA/LiTFSI