



Patterning of lithium lanthanum titanium oxide films by soft lithography as electrolyte for all-solid-state Li-ion batteries

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Abstract

The combination of sol–gel processing and soft-lithographic patterning presents a promising route towards three-dimensional (3D) micro Li-ion electrodes, and may offer a viable approach for the fabrication of all-solid-state 3D Li-ion batteries. The methods are relatively simple and therefore cheap and moreover easy to scale up. In this paper, micro-patterned films of the Li-ion conducting perovskite-type phase with nominal composition $\text{Li}_{0.29}\text{La}_{0.57}\text{TiO}_3$ (LLT) were prepared on silicon, using sol-gel synthesis in combination with micro-molding. After thermal annealing at 700 °C, the phase formation, morphology, chemical composition and LLT film thickness were investigated by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Analysis of X-rays (EDAX) and Atomic Force Microscopy (AFM). The ionic conductivity of the LLT powder prepared during this study, determined by impedance spectroscopy, was $2.68 \cdot 10^{-6}$ S/cm at 25 °C.

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1. Introduction

Portable electronic devices play an important role in our daily life and rechargeable Lithium-ion batteries are widely used as energy power supplies in those devices [1]. However, the conventional rechargeable lithium-ion batteries have their shortcomings in terms of safety, cycle life, and performance [2]. One of the important issues is the use of hazardous and flammable organic liquid electrolytes in Lithium-ion batteries which leads to safety problems such as leakage and risk of explosion [3]. In

addition, the liquid electrolyte reduces the cycle life of the battery due to the formation of a solid electrolyte interface (SEI) between the liquid electrolyte and the electrode material during charging/discharging cycles. This SEI blocks the Lithium-ion current and decreases the battery's performance [4,5].

Another shortcoming is related to the power and energy the battery can supply. If the electrode-electrolyte interface is not large enough, an increase in the energy density would limit the power output of the battery due to the charge transfer limitations. Regarding the safety and life time of the Lithium-ion batteries, they can be greatly enhanced using solid electrolytes [6]. However, increasing the energy density and/or higher power output of the battery will require higher current densities, leading to additional voltage drops. These voltage drops can be prevented by enlarging the electrode-electrolyte interface area which reduces the current density. Thus using solid electrolytes and giving them 3D architectures may enhance the safety and performance of Li-ion batteries [7]. There are several solid-state lithium-ion battery designs with 3D electrolytes, such as honeycomb type, all-solid-state integrated array structure and 3D ordered macro porous

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structure (3DOM) [8–12]. All these have been proposed and reported to increase the interfacial area between the electrode and the electrolyte as well as performance of solid state batteries.

In this study, we demonstrate a low-cost technique to prepare 3D structures in $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ (LLT) electrolyte, which is one of the fastest Lithium ion conductors with a bulk conductivity of $\sigma=10^{-3}$ S/cm at room temperature [13]. Using an elastic PDMS mold, micro-molding was combined with sol–gel chemistry to obtain patterned LLT films. The phase formation and elemental composition as well as the morphology of the LLT patterns were investigated by XRD, AFM and SEM (combined with EDAX measurements). The possibility of obtaining 3D patterned electrolyte thin films with micron scale features offers many interesting opportunities in all-solid-state lithium-ion batteries especially when it is combined with electrode depositions.

2. Experimental details

2.1. Preparation of the precursor solution

The $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ precursor solution was prepared by sol–gel synthesis. Lithium acetate (99.99%, SigmaAldrich) and lanthanum acetate (99.99%, SigmaAldrich) were dissolved in 10 ml of a mixture of 2-propanol (SigmaAldrich) and water (1:1 v/v). 2.5 g of acetic acid (Sigma Aldrich) was added as chelating agent with a molar ratio of 5:1 with respect to total metal ions. Next, stoichiometric amounts of Ti butoxide (99.99%, SigmaAldrich) were added to the solution, such that the molar ratio Li:La:Ti corresponded with 0.35:0.55:1. The mixture was heated up to 30 °C and stirred well for two hours to obtain a clear solution. The obtained precursor solution was stable for several months after preparation.

Before further handling, the precursor solution was separated into two batches. One batch was used for micro-molding experiments and the second batch was slowly evaporated and concentrated at 70 °C until a yellowish transparent gel was obtained. The gel was then dried at 100 °C for 12 h in air to yield a black precursor powder which was ground well and calcined at 700 °C for 5 h in air atmosphere to obtain LLT powder.

2.2. Micromolding experiments

The molds were fabricated from commercial poly(dimethyl siloxane), PDMS (Sylgard 184, Dow Corning). The polymer and a curing agent were mixed according to the manufacturer's instructions, and the still liquid polymer was poured onto a relief-patterned, silane-coated master prepared by photolithography. The elastomer was cured at 65 °C for 4 h, then peeled gently from the master. The silicon (Si) substrates were cleaned by immersing in an ethanol/acetone mixture (1:1 v/v). A drop of LLT precursor solution was placed onto the substrate heated to 30 °C with a pipette, *i.e.* drop casting. The precursor solution showed sufficient wettability on the Si the substrate to yield a homogeneous liquid film, required for the micromolding process. Next, the PDMS mold was pressed onto it with a defined pressure of typically 1–1.5 bar (Fig. 1). Immediately afterwards, the

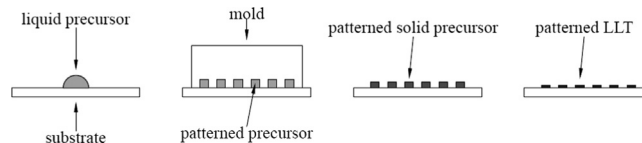


Fig. 1. Micromolding and drying of LLT precursor films. First the precursor is dropped on the substrate, next a mold is placed patterning the precursor. Later, the mold is removed and the sample is heated to 700 °C, yielding patterned LLT.

sample was heated to 80 °C within 10 min, and kept at this temperature for at least 1 h to let sufficient solvent diffuse into the PDMS, thus solidifying the patterned film. After this time the mold was peeled off the film and the sample was kept at 80 °C for another hour, before finally heating it to 220 °C with a rate of 10 °C/min. Films dried in this manner were stable for several weeks. After the patterning and drying, the sample was heated to 700 °C in air for pyrolysis and kept there for 1 h to fully crystallize into metal oxide ceramic phase. In this way thin LLT films with line and pit patterns were fabricated.

2.3. Characterization

Thermo-Gravimetric combined with Differential Thermal Analysis (TG/DTA) of the precursor solution dried at 100 °C was conducted by using Mettler Toledo TGA/SDTA 851. Al_2O_3 crucibles of 70 μl capacity were used when heating from 25 to 1000 °C with a heating rate of 5 °C/min in flowing air atmosphere (50 ml/min). The crystal structure of the patterned thin films was investigated by X-ray powder diffraction with a Bruker Endeavor D4 diffractometer, using $\text{CuK}\alpha$ radiation at room temperature. θ – 2θ scans were taken in the 2θ range from 5° to 90° with a step size of 0.01° and counting time of 1 sec/step. The morphology of the patterned films was investigated by SEM (Quanta 3D FEG instrument, FEI Company) and AFM (Solver P47, NT-MDT, in non-contact mode with NT-MDT NSC11 cantilever). Ionic conductivity measurements of polycrystalline powders were performed on pellets with 12 mm diameter and 1 mm thickness, coated with gold on both sides. The measurements were performed at room temperature in air, using a potentiostat with a frequency response analyzer (Ivium Stat) in combination with IviumSoft Electrochemistry Software, operating at 100 mV constant potential within the frequency range from 1 MHz to 5 Hz. The impedance spectra were resolved with IviumSoft using an equivalent circuit ($R_{\text{tot}}Q_{\text{tot}}(Q_{\text{el}})$) where R is the resistance, Q the constant phase element, and the subscripts “tot” and “el” refer the total and electrode, respectively.

3. Results

3.1. Thermogravimetric analysis of the precursor decomposition

Fig. 2 shows the TG-DTA curves obtained from the dried precursor powder annealed in air with a heating rate of 5 °C/min, in the temperature range from 25 to 1000 °C. The first major weight loss of 36% is observed between 230 and 430 °C, which is associated with a minor exothermic peak at 280 °C

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