



Poly (ϵ -caprolactone)/siloxane biohybrids with application in “smart windows”

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ABSTRACT

In view of the potential technological impact of solid polymer electrolytes (SPEs) in the domain of solid-state electrochemistry, particularly in the production of advanced batteries, sensors and electrochromic and photoelectrochemical devices, the sub-class of SPE materials has attracted considerable interest during the last two decades. Li⁺-doped ormolyte systems obtained using the sol–gel method have been investigated in the last few years. In this study we have used conductivity measurements, cyclic voltammetry at a gold microelectrode and thermal analysis to characterize an electrolyte system based on a lithium perchlorate (LiClO₄)-doped di-urethane cross-linked poly(ϵ -caprolactone)(PCL)/siloxane hybrid matrix. The PCL/siloxane host hybrid matrix represents an attractive alternative, as it is expected to have lower environmental impact than electrolytes currently used in commercial devices. The biocompatible, biodegradable and air-permeable properties of the PCL matrix have led to extensive application of this material in the manufacture of suture cord, artificial skin, re-sorbable prosthetic devices and as a container for drug delivery. The amorphous hybrid materials characterized in this study combine acceptable levels of ionic conductivity (9.58×10^{-6} and $2.53 \times 10^{-4} \text{ S cm}^{-1}$ at 25 and 90 °C, respectively) with low environmental impact.

The authors of a previous publication, have concluded that organic–inorganic systems based on poly(ϵ -caprolactone) may be used as dual-function electrolyte/adhesive component in prototype solid-state electrochromic devices. This component provides significant advantages in optical performance, cycle lifetime and durability of the electrochromic devices relative to conventional liquid electrolytes.

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1. Introduction

During the last two decades polymeric electrolytes have attracted considerable interest within the domain of solid-state electrochemistry and are expected to contribute to the improvement of advanced batteries, sensors and electrochromic and photoelectrochemical devices [1,2].

The most studied solid-state polymer electrolyte (SPE) systems are based on poly(ethylene oxide), PEO, and are prepared by the dissolution of various guest ionic salts in the polymeric host matrix [2–9].

Lithium ion-doped ormolyte systems, prepared using the sol–gel method, have given rise to a new sub-class of SPE materials that has also attracted interest during the last two decades [3,4]. This synthetic procedure provides a convenient means of preparing improved polymer/siloxane electrolytes and permits access to amorphous materials with good mechanical resistance and excellent thermal and chemical stability. These key properties

are provided by the silica backbone combined with the flexibility and solvating properties of the oxyethylene chain segments. Thin solid organic/inorganic hybrid films produced by the sol–gel method may be prepared with higher amounts of guest salt than in first-generation electrolyte systems. Many electrolyte systems prepared through the sol–gel procedure have been investigated in recent years [3,4].

In the present study hybrid structures based on polycaprolactone (PCL) chains have been developed to prepare material for electrochemical and/or optical applications. This class of material has not been extensively studied for these applications but has nevertheless been used for medical and surgical purposes that take advantage of the biocompatibility, biodegradability and high gas permeability presented by the high molecular weight molecule (2000 g mol^{-1}) [5,10].

A previous study [11], with the di-urethane cross-linked PCL/siloxane hybrid matrix, has demonstrated that organic–inorganic hybrid systems may be used as dual-function electrolyte/adhesive components in prototype solid-state electrochromic devices. These materials provide significant advantages in optical performance, cycle lifetime and the durability of electrochromic devices relative to comparable devices using conventional liquid electrolytes.

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The measurements used to characterize the electrolyte system based on a lithium perchlorate (LiClO_4)-doped di-urethane cross-linked PCL/siloxane hybrid matrix confirm that acceptable levels of ionic conductivity are supported with low environmental impact.

2. Experimental

2.1. Materials

Lithium perchlorate (LiClO_4 , Aldrich), α , ω -hydroxyl poly(ϵ -caprolactone)(530) (Aldrich, average molecular weight 530 g mol^{-1}) and 3-isocyanatepropyltriethoxysilane (ICPTES, Aldrich) were used as received. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, Riedel de Haën) and tetrahydrofuran (THF, Aldrich) were dried with molecular sieves. High purity distilled water (H_2O) was used in all experiments.

2.2. Sample preparation

Samples of LiClO_4 -doped di-urethane cross-linked PCL/siloxane materials were prepared according to an optimized two-step method previously described in detail [12]. The ormolytes were identified using the notation d-PCL(530) $_n\text{LiClO}_4$, where the electrolyte composition is expressed as n indicating the number of $\text{C}(=\text{O})(\text{CH}_2)_5\text{O}$ PCL repeat units per Li^+ ion. Samples with composition $200 \geq n \geq 1.1$ were prepared.

Step 1. Synthesis of the di-urethane precursor

2.0 g of polycaprolactone diol (530 g mol^{-1}) were dissolved in 10 mL of THF with stirring. A volume of 1.863 mL of ICPTES was added to this solution in a fume cupboard. The reaction flask was sealed and the solution stirred for about 48 h at approximately $70\text{--}80^\circ\text{C}$. A urethane bridged organic/inorganic hybrid material, designated as d-PCL(530)/siloxane precursor, was obtained under these conditions.

Step 2. Synthesis of the di-urethane xerogels, d-PCL(530) $_n\text{LiClO}_4$

A volume of 1.762 mL of ethanol, an appropriate mass of LiClO_4 and 0.204 mL of water were added to the d-PCL(530)/siloxane precursor solution prepared in the previous step (molar proportion 1 ICPTES:4 $\text{CH}_3\text{CH}_2\text{OH}$:1.5 H_2O). The mixture was stirred in a sealed flask for approximately 30 min, cast into a Teflon mould, covered with Parafilm and left in a fume cupboard for 24 h. The mould was subsequently transferred to an oven at 50°C and the sample was aged for a period of 4 weeks.

2.3. Measurements

2.3.1. DSC and TGA measurements

Hybrid electrolyte sections were removed from cast films and subjected to DSC analysis under a flowing argon atmosphere at temperatures between 25 and 300°C and at a heating rate of 5°C min^{-1} using a Mettler DSC 821e. All samples were presented for analysis in $40 \mu\text{L}$ aluminium cans with perforated lids to permit the release and removal of the decomposition products. Samples for thermogravimetric studies were prepared in a similar manner, transferred to open platinum crucibles and analyzed using a Rheometric Scientific TG 1000 thermobalance operating under a flowing argon atmosphere. A heating rate of $10^\circ\text{C min}^{-1}$ was used to analyze all the hybrid samples.

2.3.2. Impedance spectroscopy

Total ionic conductivities of hybrid samples were determined using a constant volume support equipped with gold blocking electrodes and located within a Buchi TO 50 oven. The sample temperature was evaluated by means of a type K thermocouple

placed close to the electrolyte film and impedance measurements were carried out at frequencies between 65 kHz and 500 mHz using an Autolab PGSTAT-12 (Eco Chemie), over a temperature range from 20 to 100°C . Measurements of conductivity were effected during heating cycles. The reproducibility of recorded conductivities was confirmed by comparing the results obtained for a sample subjected to two heating–cooling–heating cycles. The excellent reproducibility of the results obtained using this procedure demonstrated the correct operation of the support and the mechanical stability of the samples.

2.3.3. Electrochemical stability

Evaluation of the electrochemical stability window of hybrid compositions was carried out within a dry argon-filled glovebox using a two-electrode cell configuration. The preparation of a $25 \mu\text{m}$ diameter gold microelectrode surface by the conventional polishing routine was completed outside the glove box. The microelectrode was then washed with THF, dried with a hot-air blower and transferred to the interior of the glove box. Cell assembly was initiated by locating a freshly cleaned lithium disk counter electrode (10 mm diameter, 1 mm thick, Aldrich, 99.9% purity) on a stainless steel current collector. A thin-film sample of d-PCL(530) $_n\text{LiClO}_4$ was centered over the counter electrode and the cell assembly completed by locating and supporting the microelectrode in the centre of the electrolyte disk. The assembly was held together firmly with a clamp and electrical contacts were made to the Autolab PGSTAT-12 potentiostat used to record voltammograms at a scan rate of 100 mV s^{-1} . All measurements were conducted at room temperature within a Faraday cage located inside the dry argon-filled glovebox.

2.3.4. Assembly and characterization of the ECDs

Indium zinc oxide (IZO) films were deposited on glass substrates by r.f. (13.56 MHz) magnetron sputtering using a ceramic oxide target $\text{In}_2\text{O}_3:\text{ZnO}$ (92:8 wt%; 5 cm diameter, Super Conductor Materials, Suffern, NY, U.S.A., purity of 99.99%). Sputtering was carried out at room temperature, with an argon flow of $20 \text{ cm}^3 \text{ min}^{-1}$ and an oxygen flow of $0.4 \text{ cm}^3 \text{ min}^{-1}$. During sputtering the total deposition pressure (argon and oxygen) was held constant at 0.15 Pa. The distance between the substrate and the target was 10 cm and the r.f. power was maintained at 100 W. WO_3 (Super Conductor Materials, purity of 99.99%) films with thickness of about 300 nm were deposited on the transparent conductive oxide IZO-coated glass substrates by r.f. magnetron sputtering (Pfeiffer Classic 500). Sputtering was carried out at room temperature, under an argon and oxygen atmosphere with a constant deposition pressure of 2.6 Pa. The distance between the substrate and the target was 10 cm and the r.f. power was maintained at 200 W. The thicknesses of the WO_3 and IZO layers in the WO_3/IZO -coated glass plate were about 400 nm and 170 nm, respectively.

All-solid-state ECDs were constructed using a four-layer glass/IZO/ WO_3 /d-PCL(530) $_n\text{LiClO}_4$ /IZO/glass sandwich configuration. Device assembly with the EC layer was carried out by direct application of a small volume of the ormolyte sol to the surface of the WO_3/IZO -coated glass plate. After a period of about 24 h the IZO-coated glass plate was placed on top of the resulting ormolyte layer and the two gel-coated plates were pressed together so that the two coated faces bonded together inside the assembled system. In this manner a thin electrolyte layer with a surface area of approximately 2 cm^2 was formed. A strip of contact area was left uncoated on each side of the glass slide in order to make electrical contacts to the external circuit. The entire assembly procedure described in this section was carried out under atmospheric conditions.

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