



Polymer electrolytes for electrochromic devices through solvent casting and sol-gel routes



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ABSTRACT

Ionically conductive membranes of gelatin and d-PCL(530)/siloxane doped with cyano-based ionic liquids (ILs) were prepared through solvent casting and sol-gel methods, respectively. The membranes were characterized in terms of ionic conductivity, thermal behavior, morphology, and structure. All samples, except the d-PCL(530)/siloxane matrix, exhibited a predominantly amorphous morphology. The samples prepared through solvent casting and sol-gel displayed a minimum thermal stability of 170 and 230 °C, respectively. The ionic conductivity varied according with the type, quantity, and length of the alkyl chain of the cation of the ILs. The sample with the highest ionic conductivity was gelatin_{0.5}[C₂mim][N(CN)₂] with $2.40 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C and $1.68 \times 10^{-2} \text{ S cm}^{-1}$ at 95 °C. The good results of ionic conductivity encouraged the assembly and characterization of prototypes of electrochromic devices (ECDs). The best results were obtained with glass/ITO/WO₃/gelatin₁[C₂mim][SCN]/CeO₂-TiO₂/ITO/glass configuration that showed a fast color switching time (~15 s) and a good open circuit memory (~4 h). The ECD changed its color from pale blue to transparent, and its charge density decreased from -17.53 to -2.71 mC cm^{-2} during 640 color/bleaching cycles.

1. Introduction

Electrochromism is the capability of a material to reversibly alter its optical properties due to a redox reaction. This color alternation is induced by application of low current potentials [1]. Electrochromic windows, anti-glare mirrors, helmet visors, goggles, electrochromic displays, and sensors are examples of electrochromic devices (ECDs) envisaged applications [2,3]. Some of these have already reached commercialization, e.g., NTERA is manufacturing iPod EC displays, while Gentex and Donnelly are fabricating auto dimming rear mirrors [4–6].

High performance ECDs should depict high electrochromic efficiency, short response time, good stability, high optical contrast, and good optical memory [1]. Typically, an ECD is composed of a glass substrate (GS), a transparent conducting oxide (TCO), an electrochromic coating (EC), an ion conductor (IC), and an ion storage coating, also referred as counter electrode (CE). Often TCO is indium tin oxide (ITO) and EC is tungsten oxide (WO₃) [3]. The IC is an electrolyte and it can be either liquid, gel, or solid. Its function is to avoid electronic charge

flow but allow mutual ion exchange [7,8]. Though the electrolyte can be either liquid, gel, or solid, but the solid-state design is the preferred one for ECDs. Liquid electrolytes are associated with leakage risks, high flammability, low stability, and show problems on the large scale [1,9]. On the other side, polymer electrolytes (PEs) can act as separators and binders; exhibit reduced reactivity; operate in a wider temperature range; have better mechanical strength and enhanced protection and stability; and their easy processing allows to fine-tune PEs membranes thickness and area [1].

The current research demand for biodegradable, low cost, and highly efficient materials drew attentions to biopolymers. In this work we synthesized and characterized solid polymer electrolytes (SPEs) based on gelatin or poly(*ε*-caprolactone) (PCL(530), where 530 is the average molecular weight of the polymer in g mol^{-1}). Gelatin is a protein produced by partial hydrolysis of collagen, which can be found in animal skin, bone, and connective tissue. Gelatin amino acid composition is characterized by a repeating sequence of Glycine-X-Y triplet, where X and Y are frequently proline and hydroxyproline, respectively [10,11]. PCL(530) is a linear, aliphatic thermoplastic,

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biocompatible, permeable, hydrophobic, non-toxic for living organisms, and biodegradable poly(ester) [3]. Gelatin-based SPEs were prepared through solvent casting method, while d-PCL(530)/siloxane ormolytes (organically modified silicate electrolytes) were obtained through sol-gel. The sol-gel method is a synthetic chemical process that provides a facile and versatile route for the preparation of highly pure materials.

In order to improve ECD stability and reduce switching time, ionic liquids (ILs) were included in the SPEs composition. Additionally, the aim was that SPE simultaneously fulfills the requirements of ionic conductivity above 10^{-4} S cm $^{-1}$, electrochemical windows above 1.0 V, low volatility, and environmental stability [12].

Many ILs present characteristics that make them very interesting from an industrial point of view, namely almost null volatility at room temperature [13], nonflammability [14], and high thermal stability [15]. The interchangeability between thousands of possible cations and anions can be used to tune the properties of ILs [16]. Most common ILs are composed of an organic cation and an inorganic or organic anion [17]. Pure 1-alkyl-3-methylimidazolium ILs with cyano-based anions ([SCN] $^{-}$, [N(CN) $_2$] $^{-}$ or [C(CN) $_3$] $^{-}$) display, at 25 °C, very high ionic conductivities around 2.0×10^{-2} S cm $^{-1}$ and electrochemical windows of about 3.0 V [18–21].

The gelatin- and d-PCL(530)/siloxane-based SPEs studied here were doped with four cyano-based ILs: 1-ethyl-3-methylimidazolium thiocyanate ([C $_2$ mim][SCN]), 1-ethyl-3-methylimidazolium dicyanamide ([C $_2$ mim][N(CN) $_2$]), 1-ethyl-3-methylimidazolium tricyanomethanide ([C $_2$ mim][C(CN) $_3$]), and 1-butyl-3-methylimidazolium thiocyanate ([C $_4$ mim][SCN]). In this work we report the ionic conductivity, thermal behavior, structure, and morphology of gelatin- and d-PCL(530)/siloxane-ILs-SPEs. Finally, the samples were tested in small electrochromic windows and the best results were obtained with glass/ITO/WO $_3$ /gelatin $_1$ [C $_2$ mim][SCN]/CeO $_2$ -TiO $_2$ /ITO/glass configuration, which was characterized by electrochemical and spectroscopic methods.

2. Material and methods

2.1. Materials

Commercial colourless gelatin (Vahine®), glycerol (Himedia, 99.5%), α,ω -hydroxypoly(ϵ -caprolactone) (PCL (530)) (Aldrich, average molecular weight 530 g mol $^{-1}$), and 3-isocyanatepropyltriethoxysilane (ICPTES, Aldrich, 95%) were used as received. Tetrahydrofuran (THF, Aldrich) and ethanol (CH $_3$ CH $_2$ OH, Riedel de Haën) were stored over molecular sieves. Milli-Q water was used in all experiments.

[C $_2$ mim][C(CN) $_3$], [C $_2$ mim][N(CN) $_2$], [C $_2$ mim][SCN], and [C $_4$ mim][SCN] were acquired from IoliTec with a stated purity higher than 98%. All ILs were dried under vacuum and moderate temperature for at least 48 h. 1 H NMR and 13 C NMR were performed for all samples and confirmed the supplier indication.

2.2. Solvent casting

Commercial colourless gelatin (1.0 g) was dispersed in water (15 mL) and stirred for a few minutes at 50 °C for complete dissolution. The IL (0.25–2.0 g) and glycerol (0.625 g), as plasticizer, were added to this solution. The solution was poured on a Petri dish and left to dry for 8 h at 25 °C, then overnight at 40 °C, followed by 4 h at 60 °C and then cooled down to 25 °C. The resulting transparent flexible membranes showed an average thickness of 0.296 ± 0.001 mm. The notation gelatin $_x$ [IL], where x corresponds to the quotient between the mass of the polymer and the mass of the IL, was used.

2.3. Sol-gel

The d-PCL(530)/siloxane-based hybrid electrolytes were prepared

through a procedure described in detail elsewhere [22]. In the first step a urethane cross-link was formed between the hydroxyl (-OH) end groups of PCL(530) (0.80 g, 1.51 mmol) and the isocyanate (-N=C=O) groups of ICPTES (745 μ L, 3.01 mmol), in THF at 70–80 °C, to yield the non-hydrolysed hybrid precursor. In the second step, ethanol (705 μ L, 12.07 mmol) and water (82 μ L, 4.55 mmol) were added to this solution to promote the characteristic sol-gel reactions of hydrolysis and condensation. [C $_2$ mim][SCN] (0.019–0.946 g, 0.11–5.59 mmol) was then incorporated in different quantities. The ormolyte sample, produced as a xerogel film, was aged for 1 month in an oven at 50 °C, followed by a final drying under vacuum at 90 °C for 3 days. The membranes thickness varied between 0.447 and 0.565 ± 0.001 mm. These materials were identified by the notation d-PCL(530)/siloxane $_n$ [C $_2$ mim][SCN], where n corresponds to the number of C(=O)(CH $_2$) $_5$ =O PCL repeat units per [C $_2$ mim] $^+$ ion.

2.4. SPEs characterization

2.4.1. Ionic conductivity

The bulk ionic conductivity was obtained using the complex plane impedance technique (Autolab PGSTAT-12; Eco Chemie) over a frequency range of 65 kHz to 500 mHz and a temperature range from room temperature (–20 °C) to 100 °C. The samples were sandwiched between two gold electrodes (10 mm diameter ion-blocking gold electrode, Goodfellow, > 99.95%) with gold electrode/polymer electrolyte/gold electrode configuration, secured in a suitable constant volume support under an argon atmosphere.

2.4.2. Thermal analysis

Differential scanning calorimetry (DSC) measurements were carried out using a Mettler DSC 821e. 40 μ L aluminum cans with perforated lids were sealed with each sample inside a glove box filled with dry argon. Gelatin-based SPEs were analyzed in the temperature range –60–200 °C, at a heating rate of 5 °C min $^{-1}$. d-PCL(530)/siloxane-based SPEs were analyzed from –60 to 15 °C, at a heating rate of 10 °C min $^{-1}$, and from 25 to 350 °C, at a heating rate of 5 °C min $^{-1}$. All measurements were carried out under a 30 mL min $^{-1}$ flowing argon atmosphere.

Thermogravimetric analysis (TGA) were performed with a Shimadzu TGA-50 equipment between 30 and 900 °C, at a heating rate of 10 °C min $^{-1}$ and under a nitrogen atmosphere with a 60 mL min $^{-1}$ rate flow. Before each analysis and aiming to eliminate the traces of absorbed moisture all samples were subject to a first run from 30 to 105 °C, at a heating rate of 20 °C min $^{-1}$, followed by a second isothermal run at 105 °C during 10 min.

2.4.3. Structural and morphological measurements

X-ray diffraction (XRD) measurements were carried out at room temperature with an X-ray Rigaku Utma 4 diffractometer, power of 50 kV/50 mA, Cu K α irradiation, speed of 2° min $^{-1}$, and an angle range (2 θ) from 10° to 60°.

Scanning electron microscopy (SEM) images were obtained at 10 kV with a LEO 440 microscope. Energy-dispersive X-ray spectroscopy (EDS) of the d-PCL(530)/siloxane $_n$ [C $_2$ mim][SCN] ormolytes were performed with an EDX Link Analytical with a resolution of 133 eV.

Atomic Force Microscopy (AFM) images were taken with a Bruker AFM System (Dimension icon with scan Asyst). In all AFM analyses the intermittent-contact mode was employed by using silicon AFM probes with a force constant of 48 N m $^{-1}$ and a resonance frequency of 190 kHz.

2.5. ECD prototype

2.5.1. ECD construction

CeO $_2$ -TiO $_2$ and WO $_3$ films were deposited by dip-coating on conducting ITO glass substrates (Delta Technologies, sheet resistance

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