

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 has 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 2.53×10^{-4} 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.

Keywords: SPE, poly(ϵ -caprolactone), LiClO₄, ionic conductivity, thermal analysis, electrochromic devices.

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 ($2000 \text{ g}\cdot\text{mol}^{-1}$) [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.

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 $530 \text{ g}\cdot\text{mol}^{-1}$) 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. Samples 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 electrolytes were identified using the notation d-PCL(530)_n 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 ($530\text{g}\cdot\text{mol}^{-1}$) 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)_nLiClO₄

A volume of 1.762ml of ethanol, an appropriate mass of LiClO_4 and 0.204ml 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 30min, 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 $5^\circ\text{C}\cdot\text{min}^{-1}$ 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 $10^\circ\text{C}\cdot\text{min}^{-1}$ 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 65kHz and 500mHz 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 25µm 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, 1mm thick, Aldrich, 99.9% purity) on a stainless steel current collector. A thin-film sample of d-PCL(530)_nLiClO₄ 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 $20 \text{ cm}^3 \cdot \text{min}^{-1}$ and an oxygen flow of $0.4 \text{ cm}^3 \cdot \text{min}^{-1}$. 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)_nLiClO₄/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 24h 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.

3. Results and discussion

3.1. Thermal behaviour of electrolytes

The results of DSC analysis of the organic-inorganic xerogel-based electrolyte system are presented in Figure 1. From these curves it is evident that materials with compositions with $n \geq 3.5$ are completely amorphous. At very salt-rich compositions of electrolyte, with $n \leq 2.2$, the presence of a diffuse endothermic peak at about 80°C may be associated with various possible causes. In other SPE systems salt-polymer complexes have been detected by fusion peaks, however this range of temperature is too low for this type of event. The TGA curves of these high salt content samples shows a loss of mass between about 50 and 100°C and therefore our assignment is to the loss of fortuitous water from the salt dispersed in the polymer matrix. No other electrolyte sample shows residual water evolution over this range of temperature and therefore the process is only significant at the very high salt content compositions formed with the hygroscopic LiClO_4 guest.

As the concentration of the guest ionic species increases in the electrolyte composition, at decreasing values of n , the exothermic process associated with thermal degradation of the electrolyte becomes more evident and the onset temperature of degradation reaches a minimum at the electrolyte with composition of $n = 4.4$.

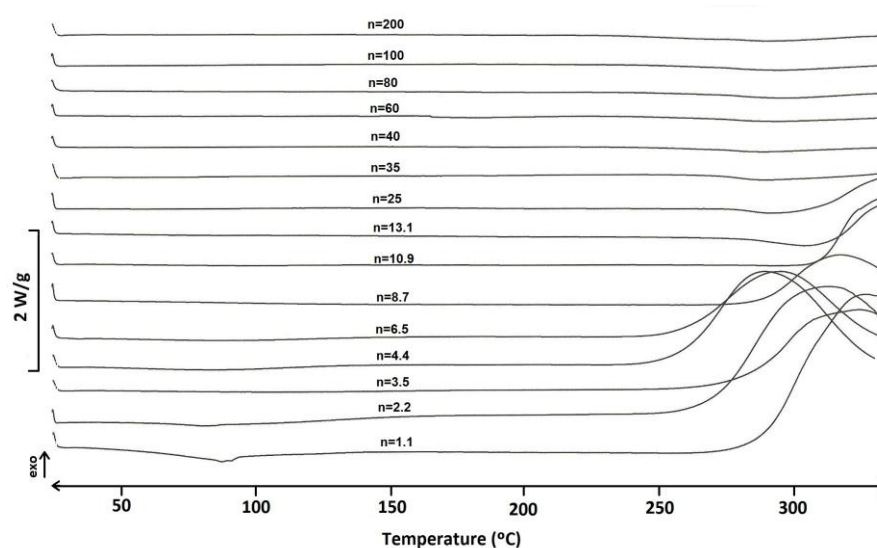


Figure 1. DSC curves of selected d-PCL(530)_nLiClO₄ di-urethane.

The onset temperature of thermal decomposition was evaluated by thermogravimetric analysis using extrapolation of the baseline and tangent of the curve of thermal events to identify the initiation of sample weight loss (Figure 2). These studies confirm that weight loss associated with thermal degradation of samples occurred at temperatures in excess of 240°C, for all compositions.

The un-doped host matrix shows an onset of thermal degradation at temperatures greater than 375°C. Addition of LiClO_4 evidently causes a decrease in thermal stability, a conclusion consistent with that reported by other authors in studies of various other systems based on the same [11] or other diureasils with the same guest salt [13].

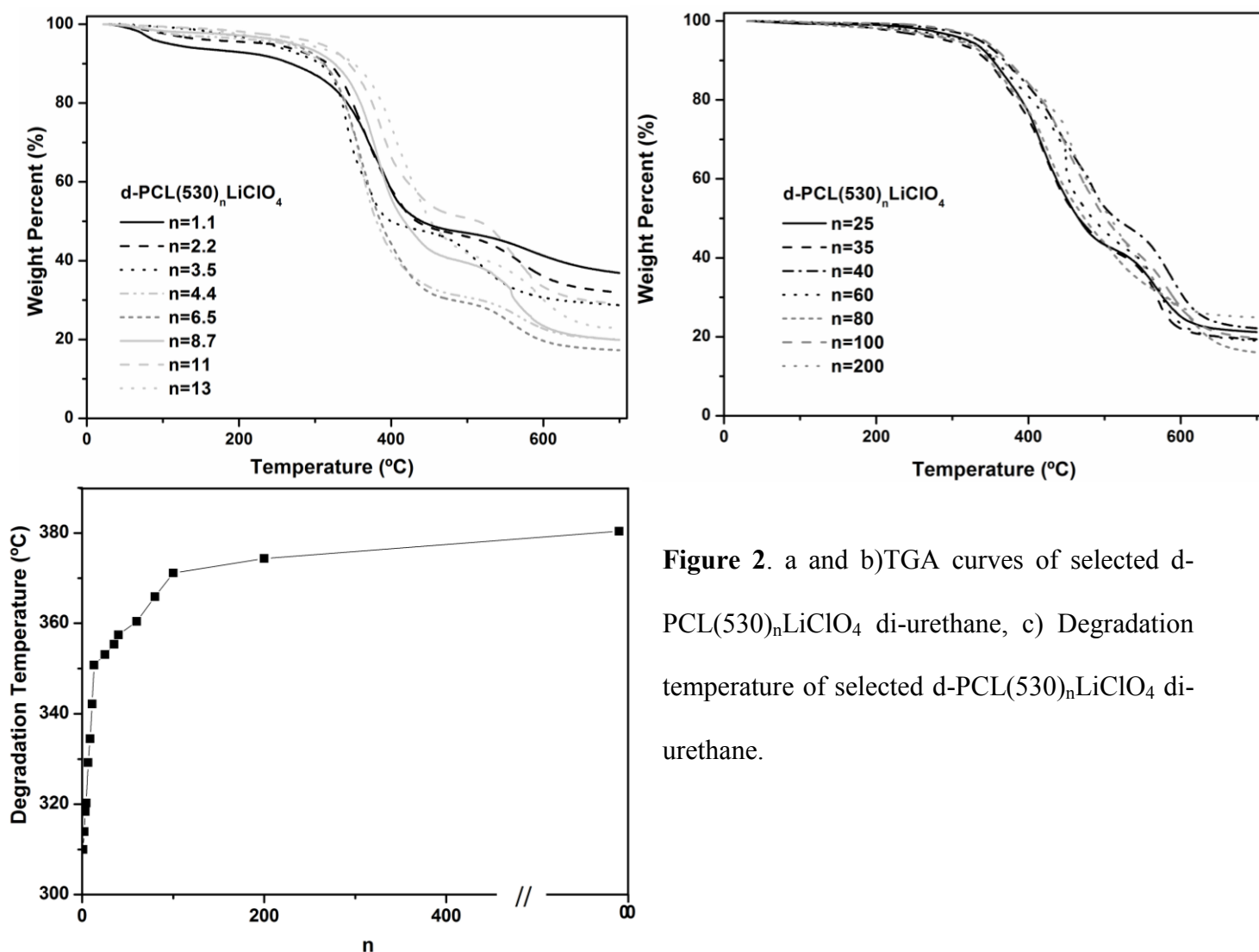


Figure 2. a and b) TGA curves of selected $\text{d-PCL}(530)_n\text{LiClO}_4$ di-urethane, c) Degradation temperature of selected $\text{d-PCL}(530)_n\text{LiClO}_4$ di-urethane.

Clearly the choice of the guest salt has a significant influence on various aspects of SPE performance. The addition of lithium perchlorate is generally associated with an improvement in

ionic conductivity, however the presence of the perchlorate anion brings a penalty in terms of thermal stability. The pronounced exothermic peak attributed to degradation of the electrolyte has an onset substantially higher than the temperature range of operation of optical displays. Nevertheless, less hazardous anions are available and it is certainly worth exploring electrolyte formulations with LiBF_4 , LiAsF_6 , LiPF_6 and $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ [14] as guest species in this host matrix. Ionic mobility in an electrolyte is largely determined by the relaxation modes of the polymer host. Lower values of T_g indicate that the local chain segment motion of the host polymer in the electrolyte system is less constrained by intermolecular interactions. The T_g s of various compositions of $\text{d-PCL}(530)_n\text{LiClO}_4$ electrolytes are represented in Table 1, where it may be clearly seen that values of T_g are shifted to higher temperatures when the salt content is increased. The onset of T_g was observed to increase slowly with concentration up to $n=2.2$, where a sudden change in behaviour was observed. This change is accompanied by a reduction in optical transparency and an increase in the mechanical rigidity of the electrolyte film.

Table 1- Glass transitions temperatures of electrolyte selected samples.

Sample	n=1.1	n=2.2	n=3.5	n=4.4	n=6.5	n=8.7	n=10.9	n=13.1
T_g (°C)	-18.35	-46.02	-46.14	-46.36	-46.72	-46.81	-48.01	-49.06

3.2. Ionic Conductivity

The ionic conductivities of selected hybrid electrolyte compositions over the temperature range from 25 to 100 °C, and as a function of salt content, are illustrated in Figure 3. These hybrids show a non-linear variation of $\log(\text{ionic conductivity})$ with temperature over a range of salt compositions with n from 1.1 to 200. This behaviour contrasts with that reported for semi-crystalline materials based on the PEO host matrix that generally show two linear segments with a change of gradient close to the melting temperature of PEO spherulites. The non-linear variation observed with the di-

urethane system studied has been frequently reported for systems with predominantly amorphous character, and this behaviour is expected from the information obtained by DSC characterization. The variation of the conductivity of solid polymer electrolytes with composition, illustrated in the conductivity isotherms included in Figure 4, shows the presence of a local conductivity maximum at $n = 4.4$.

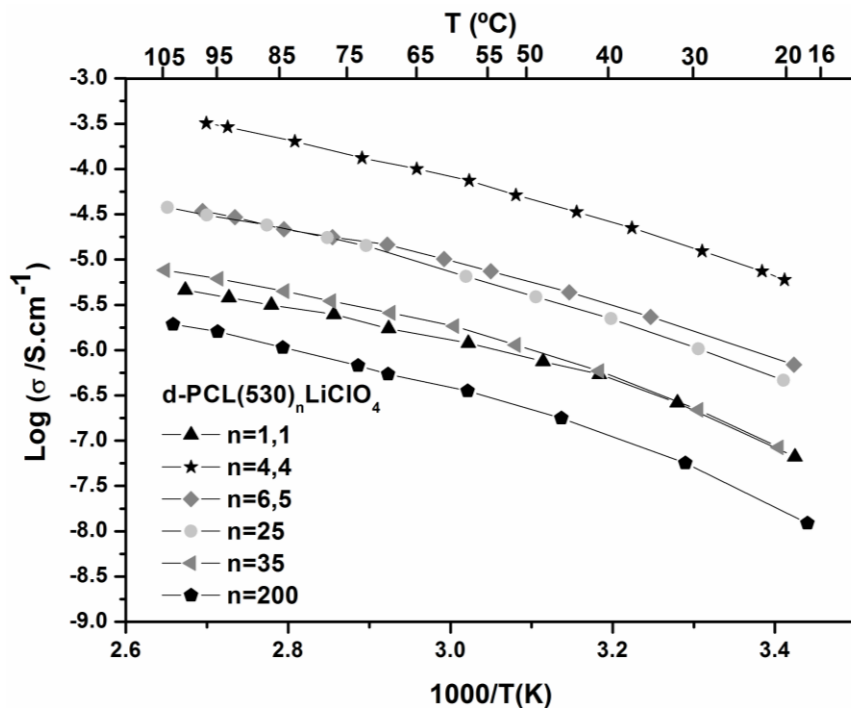


Figure 3. Arrhenius conductivity plots of selected d-PCL(530)_nLiClO₄ di-urethanes.

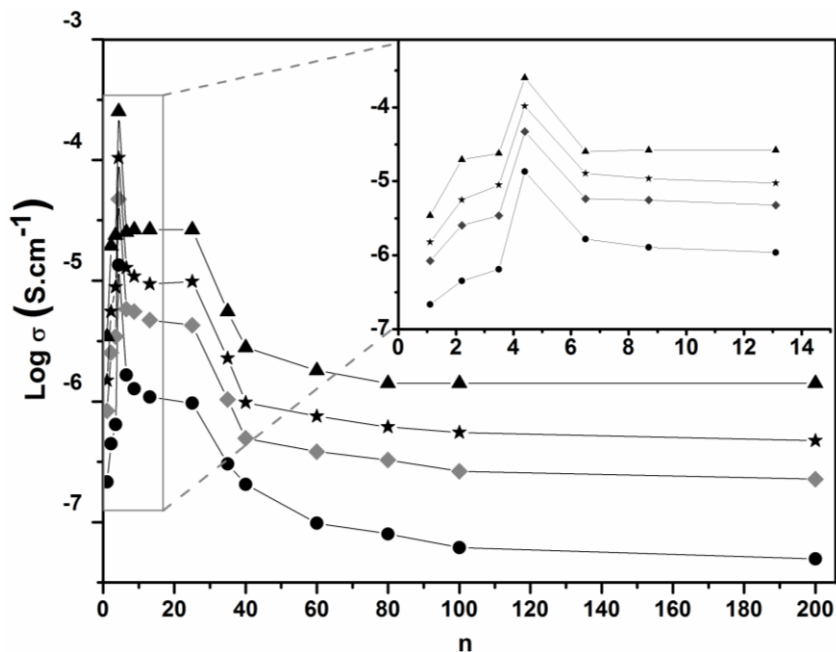


Figure 4. Conductivity isotherms of the d-PCL(530)_nLiClO₄ di-urethanes.

At about 25°C, this electrolyte composition presents a conductivity of $9.64 \times 10^{-6} \text{ S.cm}^{-1}$, and at 90°C $2.53 \times 10^{-4} \text{ S.cm}^{-1}$, values significantly higher than those reported by Nunes et al. [11] for d-PCL(530)_{0.5} LiCF₃SO₃, Teixeira et al [15] for the d-PCL(530)₃₄Mg(CF₃SO₃)₂ system or for PEO_nLiClO₄ [15] but lower than that of systems based on U(2000) doped with the LiClO₄ guest salt [13]. This result was expected, as the PEO-based electrolytes are generally poor conductors at ambient temperature due to the presence of crystalline material. The conductivity isotherms derived from these results are included in Figure 4 and confirm that this electrolyte system behaves in a similar manner to that reported for other ormolytes systems [11, 17, 18]. As the mechanism of ionic transport is directly dependant on the flexibility of the polymer chain, components that increase free volume are expected to have a beneficial influence on conductivity. A further increase in salt content, beyond the salt composition associated with the electrolyte with the lowest T_g, results in an increase in the energy required for chain rotation and a decrease in the segment mobility. Restrictions in the motion of the polymer chain segments, which are responsible for ion transport, explain the sudden decrease in conductivity, again a fairly common observation in solvent-free polymer electrolyte systems.

From this discussion it is clear that the nature of the guest salt not only influences the thermal stability of the electrolyte but also largely determines the total ionic conductivity. In general, lithium salts with polyatomic anions with good charge dispersion dissolve and are well-dissociated, even in the low dielectric medium formed by the polymeric host. Good solubility and dissociation are necessary to provide a sufficient number of charge carriers to support ionic conductivity. Bulky anions with good charge dispersion, such as Li(CF₃SO₂)₂N [14], also cause an increase in free-volume and disrupt the host polymer chain segment organization with a beneficial lowering of T_g and an increase in segment mobility. Increased polymer segment mobility results in a corresponding increase in ionic conductivity. The combination of the host matrix described in this study with

appropriate guest salts may therefore provide significant improvements in ionic conductivity and also reduce the optical response time in practical EC devices.

3.3. Electrochemical Stability

The electrochemical stability range of the samples was determined by microelectrode cyclic voltammetry over the potential range -1.0V to 7.0V. The overall stability of electrolytes was excellent, with no electrochemical oxidation occurring at potentials lower than 4.0V versus Li/Li⁺ (figure 5), a practical operating range considered to be more than adequate for application in electrochemical devices. At potentials close to 4 V the current increases as decomposition of the electrolyte begins. The products formed on the microelectrode surface are removed on the return sweep and eventually lithium is deposited at a potential of about -0.5V.

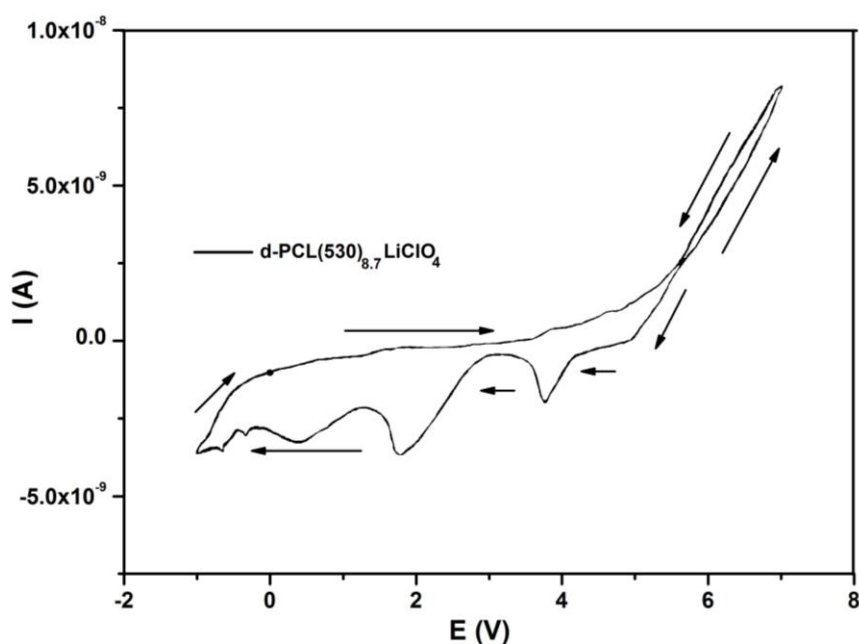


Figure 5. Cyclic voltammogram of the d-PCL(530)_{8.7}LiClO₄ obtained with a 25 μm gold microelectrode as working electrode and lithium counter and reference electrodes (sweep rate = 100 mVs^{-1}).

3.4. Electrochromic device

The four-layer glass/IZO/WO₃/SPE/IZO/glass asymmetric configuration, used to evaluate the performance of the SPE layer as a multi-functional component, was chosen in order to simplify the processes taking place during the application of the writing and bleaching potentials. In this assembly the source of lithium ions for insertion into the active WO₃ layer is the electrolyte layer itself. In spite of the absence of a lithium-supplying counter electrode, an adequate optical response is obtained in the prototype EC test device. An important advantage associated with this test device configuration is that the four-layer assembly is sufficiently transparent to permit the change in the spectra of the WO₃ layer to be recorded without interference from a counter electrode process. Naturally a more practical arrangement for an operational display would include a counter electrode with a complementary optical response [19] (transparent in the lithium-inserted state and colored in the lithium-stripped state) that would increase the visual change between written and bleached states.

The optical behaviour of the display was reproducible and superior to that observed with comparable devices incorporating conventional liquid electrolytes, particularly with respect to the stability of the electrochromic material. We observed that the initial value of the luminous transmittance of devices based on polymer electrolytes was also slightly higher than that of comparable devices assembled using LiClO₄-based non-aqueous liquid electrolytes. This may be due to the significant reduction of the electrolyte layer thickness made possible through the use of the polymeric component. Leakage performance, memory effect and resistance to deterioration of device performance due to ingress of humidity were also notably improved.

The evaluation of devices based on the d-PCL(530)_nLiClO₄ di-urethane electrolyte confirmed that the active layer of the assembled device changed from almost transparent to a blue color, associated with WO₃ reduction and simultaneous Li⁺ insertion, as a result of the application of a positive voltage. Inversion of the applied voltage resulted in WO₃ oxidation and the return of the active

layer color to its initial state. The coloring voltage used in the electrochromic prototypes was 1.5 V for a period of 30 s. This hybrid electrolyte was found to show adequate optical transparency, and to support operation of a prototype device with good stability and good optical memory.

The results presented in Figures 6 report the optical transmittance in the wavelength range from 300-870 nm for the device based on d-PCL(530)_{4,4}LiClO₄, the most conducting electrolyte sample. In the transparent state, more than 60 % of visible light is transmitted and this demonstrates that the electrolyte films are highly transparent in nature. On application of a potential of -1.5 V, the transmittance of the device was reduced to 25.80 %, for d-PCL(530)_{6,5}LiClO₄, thus showing a variation of 35.89 %. During the negative half-cycle of the device, as a result of the application of -1.5 V potential, Li⁺ ions are intercalated into the electrode material and this is colored due to reduction of W⁶⁺ to W⁵⁺. During the positive half-cycle, when a voltage of +1.5 V is applied, Li⁺ is deintercalated from the electrode and the electrode returns to the original transparent state due to oxidation of W⁵⁺ ions to W⁶⁺ [20]. Table 2 summarizes the average transmittance (in the visible part of the spectrum) and the optical density exhibited by the prototype devices.

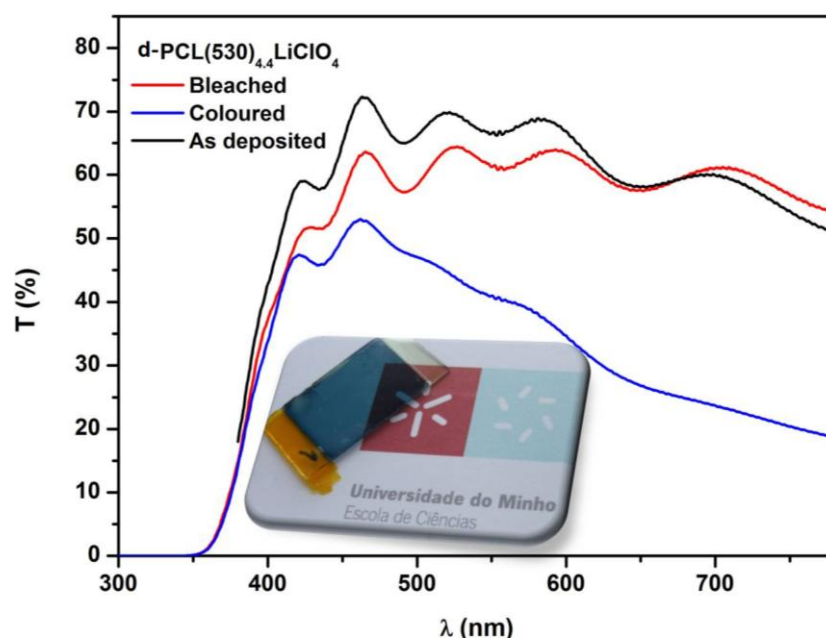


Figure 6. Optical transmittance (left axis) as a function of wavelength in the 300-870 nm region for

the glass/IZO/WO₃/d-PCL(530)_{4.4}LiClO₄/In₂O₃:ZnO/glass ECDs, in the as-deposited (black line), bleached (red line) and colored (blue line) states in the 1st cycle. Photographs of the ECDs in the colored states are shown as inset on the graphs.

The electrolyte compositions selected for the assembly of devices were those with the highest ionic conductivity, and the results obtained were similar for all the compositions studied. Ion insertion or extraction processes during coloring/bleaching may also compromise the long-term stability of the EC materials. Device degradation rates were found to increase as a result of an increase in the rate of the ion transfer processes. This degradation is caused by departing too far from an ideal thermodynamic intercalation process [21].

The lifetime of the prototype EC device may of course also be limited by the nature of the four-layer assembly used to characterize the performance of the SPE component. With no lithium-supplying counter electrode in the test assembly, for the reasons given at the beginning of this section, the number of operational cycles may be effectively limited by the availability of lithium ions at the electrode/electrolyte interface. The choice of a suitable counter electrode is therefore a priority for further development of practical EC devices.

The exploratory results reported in this study are encouraging, however it is obviously necessary to improve both the mechanical and conductivity behaviour of the SPE component layer. The sol-gel approach to the preparation of hybrid organic-inorganic materials offers unique advantages. Mild reaction conditions can permit access to high-purity host matrices with precisely "tailored" physical properties that provide appropriate electrochemical behaviour in the final material [3,22]. Electrolyte, sealant and separator functions may therefore be combined in the same component of the device by careful choice of precursors and appropriate control of preparative conditions. Clearly further optimization is required in order to exploit the full potential of these materials as multifunctional layers in practical devices.

Table 2- Summary of the average transmittance (in the visible part of the spectrum) and the optical density exhibited by the prototype devices.

Sample	T Coloured state (%)	T Bleached state (%)	T As deposited (%)	Optical density
d-PCL(530) _{4,4} LiClO ₄	34.55%	57.07%	60.28%	0.22
d-PCL(530) _{6,5} LiClO ₄	25.80%	50.84%	61.69%	0.29
d-PCL(530) _{8,7} LiClO ₄	34.71%	58.62%	61.38%	0.23

4. Conclusions

Organic–inorganic xerogels based on di-urethane cross-linked PCL/siloxane hybrid networks were prepared by the sol-gel process. These electrolytes were produced as thin, transparent and self-supporting films with excellent mechanical stability over the range of operating temperatures normally envisaged for electrochromic devices. Some further improvement in conductivity may be expected as a result of optimization of the nature and concentration of guest salt and the chain segment length of the host matrix.

Prototype EC devices assembled with these electrolytes presented promising results and confirmed the applicability of this class of materials in commercial devices.

5. Acknowledgements

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