

Application of hybrid materials in solid-state electrochromic devices

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Abstract

Sol-gel derived cross-linked PEO/siloxane xerogels (designated as di-ureasils) were prepared using lithium trifluoromethanesulfonyl imide (LiTFSI) as a guest salt. In this paper we describe the assembly of a prototype solid-state electrochromic device (ECD) based on a four-layer sandwich structure, with the following configuration: glass/IZO/WO₃/polymer electrolyte/IZO/glass. The electrochromic switching performance of these devices was characterized as a function of salt concentration. The average transmittance in the visible region of the spectrum was above 69% for all the bleached samples characterized. After coloration the structures assembled with d-U(900)_nLiTFSI presented an average transmittance in the visible wavelength region above 22% and an optical density above 0.49.

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1. Introduction

Certain materials show the capacity to undergo reversible coloration through the introduction and removal of ionic guest species. These electrochromic materials have been attracting significant attention, partly due to academic interest in their properties but also because of the potential commercial impact of their technological applications. Examples of successful electrochromic devices already exist in rear-view mirrors for vehicles that automatically dim to avoid dazzle or smart windows that adjust the properties of the active layer to control incident sunlight transmission [1-3]. It is likely that further development will result in an increase in the number of these devices in domains with even greater commercial importance such as smart time-lapse, temperature-fluctuation labels [4] or reactive sun-roofs. A critical component in electrochromic devices is the ion-conducting electrolyte. Lithium-based electrolytes have been proposed for application in devices due to the long-term stability for solid-state smart window application and because the diffusion coefficient of the lithium ion in WO_3 is higher than that of other metallic cations [5].

Organic-inorganic hybrid electrolytes are innovative materials with electrochemical and mechanical behaviour suitable for a wide range of practical applications. The main synthetic route for the formation of these advanced systems is the sol-gel method [6]. In the last few years, the use of hybrid materials has been increasingly adopted for the production of low cost polymer networks with potentially-attractive features for optical devices [7]. The preparative strategies developed can be readily modified to produce thin-film electrolyte sections with appropriate chemical, electrochemical and mechanical properties.

In this paper we describe the fabrication and evaluation of a prototype solid-state electrochromic device based on a four-layer sandwich structure with the following configuration: glass/IZO/WO₃/d-U(900)_nLiTFSI/IZO/glass.

2. Experimental

2.1. Materials

Lithium bis(trifluoromethanesulfonyl)imide was dried under vacuum at 190°C for 7 days and then stored in a dry argon-filled glovebox with a water content lower than 10 ppm. The O,O'-bis(2-aminopropyl) polyethylene glycol (commercially available as Jeffamine ED-900®, Fluka, average molecular weight 900 gmol⁻¹) was dried under vacuum at 25 °C for several days prior to use. The bridging agent, 3-isocyanatepropyltriethoxysilane (ICPTES, Aldrich 95 %), was used as received. Ethanol (CH₃CH₂OH, Merck, 99.8%) and tetrahydrofuran (THF, Merck, 99.9%) were dried over molecular sieves. High purity distilled water (Millipore) was used in all experiments.

2.2. Samples preparation

The synthesis of Li⁺-doped di-ureasils has been described in detail elsewhere [8, 9]. The framework of these xerogels, represented by U(900), contains oxyethylene segments with about 15 repeat units bonded at each end to a siliceous backbone through urea bridges. In accordance with the conventional nomenclature, electrolyte composition was expressed as d-U(900)_nLiTFSI where n represents the molar ratio of oxyethylene moieties to Li⁺ ions. The procedure used for d-U(900)_nLiTFSI involved grafting a diamine containing approximately 15 oxyethylene repeat units onto the ICPTES precursor, to yield the di-urea bridged hybrid precursor (Scheme 1). This material was subsequently

hydrolyzed and condensed in the sol-gel stage of the synthesis to induce the growth of the siloxane framework.

Step 1 - Synthesis of the di-ureasil precursor, d-UPTES(900): 2.0 g of Jeffamine ED-900® was dissolved in 10 ml of THF with stirring. A volume of 1.097 mL of ICPTES was added to this solution in a fume cupboard (molar proportion 1 Jeffamine ED-900®: 2 ICPTES). The flask was then sealed and the solution stirred for about 12 h at moderate temperature ($\approx 40^\circ\text{C}$). A urea cross-linked organic-inorganic material, designated as di-ureapropyltriethoxysilane (d-UPTES(900)), was obtained under these conditions.

Step 2 - Synthesis of the di-ureasil xerogels, d-U(900)_nLiTFSI: A volume of 1.038 mL of CH₃CH₂OH, an appropriate mass of LiTFSI and 0.120 mL of water were added to the d-UPTES(900) solution prepared in the previous step (molar proportion 1 ICPTES: 4 CH₃CH₂OH: 1.5 H₂O). The mixture was stirred at room temperature in a sealed flask for approximately 30 min and then decanted into a Teflon® mould, covered with perforated membrane of Parafilm® and stored in a fume cupboard for 24 h. After this period the mould was transferred to an oven at 50°C and the sample was aged for a period of 3 weeks. A final period of 1 week at 80°C completed the process.

Transparent Conductive Oxide: Indium zinc oxide (IZO) films were deposited on glass substrates by r.f. (13.56 MHz) magnetron sputtering using a ceramic oxide target of ZnO/In₂O₃ (5cm diameter, from Super Conductor Material, Inc., purity of 99.99%). The sputtering was carried out at room temperature, with a partial pressure of oxygen of 2.5×10^{-3} Pa with a constant deposition pressure of 0.15 Pa. The distance between the substrate and the target was 10 cm and the rf power was held constant at 100 W. Details concerning the film preparation as well as the physical properties can be found in ref [10].

Electrochromic film: the tungsten oxide films (WO_3) were prepared by thermal evaporation using WO_3 pellets (SCM, 99.99% purity). The deposition pressure was 1.6×10^{-3} Pa.

2.3. Electrochromic cell assembly, Substrate A / d-U(900)_nLiTFSI/ Substrate B

Electrolyte compositions were prepared by direct application of a small volume of the d-U(900)_nLiTFSI electrolyte to the surface of a glass plate onto which a IZO/ WO_3 coating had been previously deposited. The gel was dried in a vacuum oven for a period of 7 days. The thicknesses used for the electrolyte, IZO and WO_3 component layers were 100, 170 and 400 nm respectively. A second IZO-coated glass plate was placed on top of the dry electrolyte layer and the two plates were pressed together to spread the electrolyte in a thin film between the electrochromic surfaces. The entire assembly procedure described was carried out under a laboratory atmosphere. The prototype solid-state electrochromic device structure is represented schematically in Figure 1.

3. Results and Discussion

3.1 - Electrochemical behaviour of the d-U(900)_nLiTFSI electrolytes

Research in the domain of solid polymer electrolytes has been growing rapidly since it was accepted that solid state ionic conductors could substitute liquid electrolytes in electrochemical devices. Apart from presenting ionic conductivities suitable for use in electrochemical devices such as solid-state smart windows, polymer electrolytes also eliminates problems concerning evaporation or leakage of the solvent. For successful applications in electrochemical applications, polymer electrolytes should present conductivities better than 10^{-5} S/cm in the temperature range from -20°C to 60°C , have good

mechanical, thermal stability and a wide electrochemical stability window [11]. For application in electrochromic devices, polymer electrolytes should present high transparency to intensify the chromatic contrast of the device.

The SPE system presented in this paper was characterized by ionic conductivity measurements, cyclic voltammetry at a gold microelectrode and thermal analysis and demonstrated to be adequate for application on electrochromic devices [12]. The conductivity behaviour of all polymer electrolytes based on d-U(900) and LiTFSI was found to show a non-linear variation of log conductivity with $1/T$ in the range between 25 and 100°C. The most conducting composition of this system is d-U(900)₁₅LiTFSI which reaches $7.6 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 95°C. At room temperature the composition with the highest conductivity is d-U(900)₂₅LiTFSI ($2.9 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$). The results of thermal analysis of the d-U(900)_nLiTFSI electrolytes confirm that the samples with n ranging from 200 to 5 are completely amorphous and the lowest decomposition temperature observed with the d-U(900)_nLiTFSI system was registered for the $n = 40$ composition (358°C).

Electrochemical stability with a wide potential range is necessary for electrochemical devices such as primary and secondary batteries and electrochromic displays. The electrochemical stability of the electrolyte was determined by microelectrode cyclic voltammetry over the potential range -2.0 to 7.0 V. The potential limit for the electrolyte system was determined as the potential at which a rapid rise in current was observed and where the current continued to increase as the potential was swept in the same direction.

The overall stability of the electrolytes is good with no electrochemical oxidation occurring at potentials less than 5 V versus Li/Li⁺. This result confirms the applicability of this electrolyte composition also presents a broad stability window (5V Li/Li⁺), which confirm the applicability of this SPE system to electrochromic devices.

3.2 – *Electrochromic structure device*

The difference in the transmittance between the colored (written) state and the fully bleached (unwritten) state indicates the light modulation capability of electrochromic devices. A SPE component in an optical device must meet various pre-requisites. One of these is that the film must exhibit high transmission. If this condition is not fulfilled the electrolyte will reduce the colour contrast of the optical device [13].

The scheme in Figure 1 shows the prototype device assembly of the electrochemical display characterized in preliminary experiments. The evaluation of devices based on d-U(900)_nLiTFSI di-ureasils 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 (Figure 2). Inversion of the applied voltage resulted in WO₃ oxidation and the device should returned to its initial state. The coloring voltage used in the electrochromic prototypes were 1.5 V during 30 seconds. With future studies we expect this hybrid electrolyte to have adequate optical density, good stability and good optical memory. Figure 3 shows the optical transmittance in the wavelength range 400-800 nm for the preliminary electrochromic devices (ECDs) based on d-U(900)_nLiTFSI di-ureasils, which represent the compositions with best optical performance transparency and excellent mechanical properties. These samples also correspond to electrolyte compositions with highest ionic conductivity [12]. Electrolytes have been one of the most challenging components in the development of reliable solid-state electrochemical devices. The electrolyte serves as an ion store that exchanges charged species over the electrode-electrolyte interface during the electrochemical process, thus maintaining the overall electroneutrality of the system.

Table I summarizes the average transmittance (in the visible part of the spectrum) and optical density exhibited by the electrochromic devices.

The average transmittance in the visible region of the spectrum was above 69% for all the bleached samples analyzed. After coloration the structures assembled with d-U(900)₅LiTFSI and d-U(900)₄₀LiTFSI ormolytes, presented a good color contrast (above 24%) and an optical density above 0.49, providing a good performance in coloring/bleaching process (Figure 4). These results are very satisfactory, especially when compared to those obtained with the incorporation of d-U(900)_nLiClO₄ electrolytes [7]. The reasons for the variation of optical density with electrolyte composition observed in Figure 4 are not yet clear and require further study. The results are consistent with mechanical interfacial effects or the supply of ions due to higher ionic conductivity, both aspects of electrolyte performance that vary significantly with composition.

The encouraging results observed in this exploratory study confirm the advantages that derive from the use of di-ureasil matrices in ECDs. Clearly further optimization of the procedures (like for example the use of a counter electrode based on NiO as well as an appropriate sealant should be used to avoid the degradation of the polymer) is required and improvements in device response time and optical transmittance under open circuit voltages may be expected.

4. Conclusions

In this work novel di-ureasil d-U(900) composites incorporating LiTFSI guest salt were investigated and used as multi-functional components in prototype electrochromic devices. All the devices incorporating d-U(900)_nLiTFSI electrolytes presented good stability and storage properties under open circuit.

The encouraging results obtained with electrochromic smart windows based on diureasil matrices doped with LiTFSI, provide motivation for future optimization studies and improvements in device response time, optical transmittance and memory effect under open circuit voltages may be expected.

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References

- [1] C. G. Granqvist, *Solid State Ionics*, 53-56 (1992) 479.
- [2] C. G. Granqvist, *Solar Energy Materials & Solar Cells*, 60 (2000) 201.
- [3] E. Syrrakou, S. Papaefthimiou and P. Yianoulis, *Solar Energy Materials & Solar Cells*, 85 (2005) 205
- [4] P. Wang; Q. Dai; S M. Zakeeruddin; M. Forsyth; D. R. MacFarlane; M. Graetzel, *J. American Chemical Society* 126 (2004) 13590.
- [5] E. Masetti, D. Dini, F. Decker, *Solar Energy Materials and Solar Cells* 39 (1995) 301.
- [6] C.J. Brinker, Scherer GW (1990) *Sol-gel Science: The Physics and Chemistry of Sol-Gel Processing*. Academic Press, San Diego CA.

- [7] P. C. Barbosa, M. M. Silva, M. J. Smith, A. Gonçalves, E. Fortunato, *Electrochimica Acta* 52 (2007) 2938-2943.
- [8] S.M. Gomes Correia, V. de Zea Bermudez, M.M. Silva, S. Barros, R.A. Sá Ferreira, L.D. Carlos, A.P. Passos de Almeida, M.J. Smith, *Electrochimica Acta* 47 (2002) 2421.
- [9] S.C. Nunes, V. de Zea Bermudez, D. Ostrovskii, L.D. Carlos, *Journal of Molecular Structure* 702 (2004) 39.
- [10] E. Fortunato, A. Pimentel, A. Gonçalves, A. Marques, R. Martins, *Thin Solid Films* 502 (2006) 104.
- [11] W. H. Meyer, *Adv. Mater.* 6 (1998) 439.
- [12] P. C. Barbosa, L. C. Rodrigues, M. M.Silva, M. J. Smith, *J. Power Sources* 180 (2008) 607.
- [13] M-H. Cui, Jun-Shi Guo, H-Q., Xie, Z-H. Wu, S-C. Qiu, *Journal of Applied Polymer Science* 65 (1997) 1739.

Figure Captions

Scheme 1. Synthesis of the d-U(900)_nLiTFSI ormolytes.

Figure 1. Schematic illustration of the electrochromic structure device.

Figure 2. Electrochromic device in colored state for selected compositions: a) d-U(900)₅LiTFSI, b) d-U(900)₁₀LiTFSI, c) d-U(900)₃₀LiTFSI, d) d-U(900)₄₀LiTFSI.

Figure 3. Optical transmittance as a function of wavelength for the electrochromic device in colored state using (a) d-U(900)₅LiTFSI; (b) d-U(900)₁₀LiTFSI; (c) d-U(900)₁₅LiTFSI; (d) d-U(900)₃₀LiTFSI; e) d-U(900)₄₀LiTFSI.

Figure 4. Optical density at 620nm of selected electrolytes compositions.

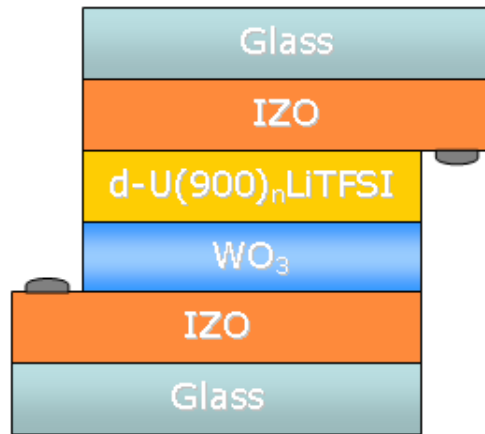


Figure 1

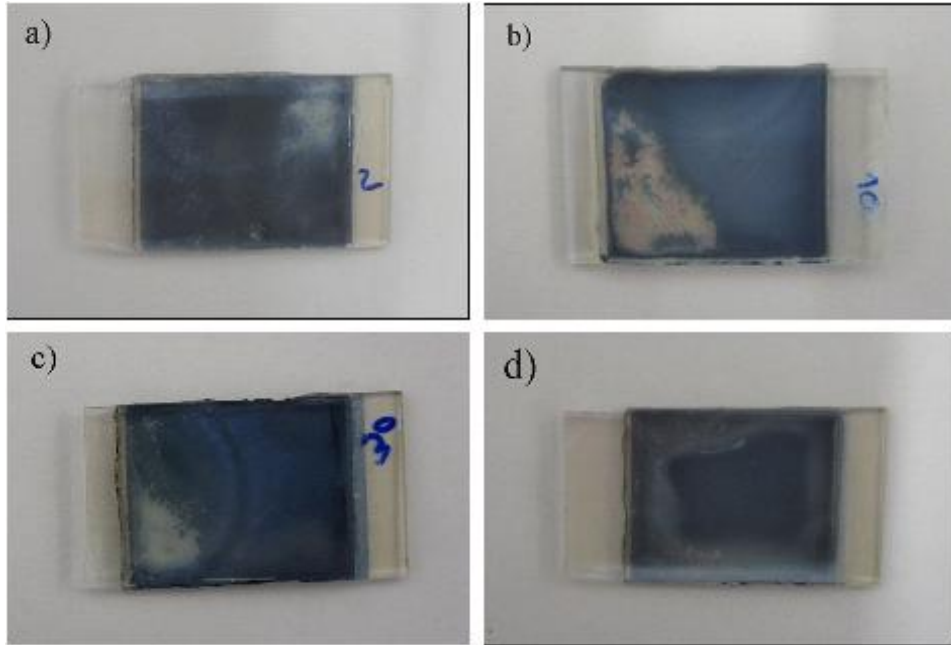


Figure 2

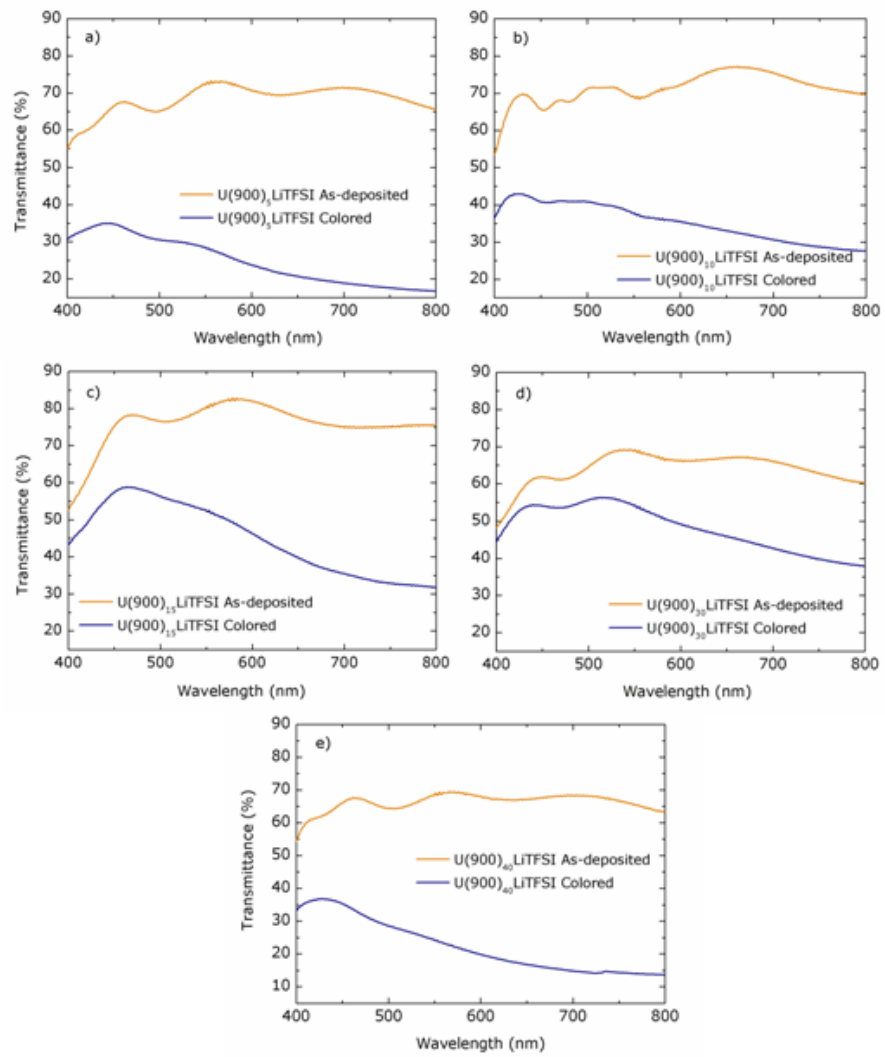


Figure 3

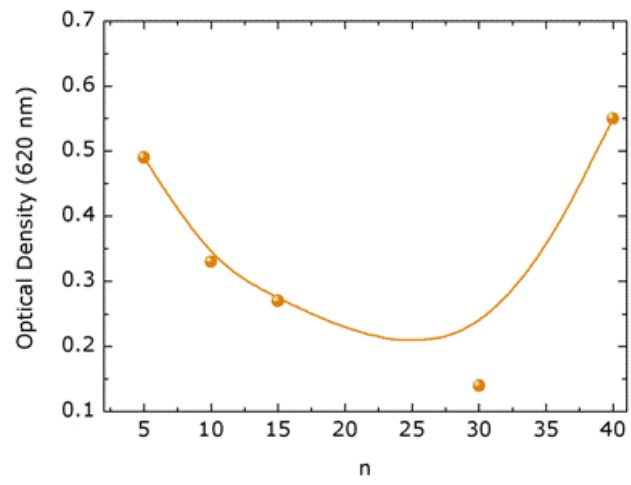


Figure 4

Table 1

Average transmittance and optical density exhibited by electrochromic devices using d-U(900)_nLiTFSI.

| Sample | Transmittance in bleached state (%) | Transmittance in colored state (%) | Optical density (620 nm) |
|-----------------------------|-------------------------------------|------------------------------------|--------------------------|
| U(900) ₅ LiTFSI | 68 | 25 | 0.49 |
| U(900) ₁₀ LiTFSI | 71 | 35 | 0.33 |
| U(900) ₁₅ LiTFSI | 76 | 45 | 0.27 |
| U(900) ₃₀ LiTFSI | 64 | 48 | 0.14 |
| U(900) ₄₀ LiTFSI | 66 | 22 | 0.55 |