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SEMI-SOLID GEL ELECTROLYTES FOR ELECTROCHROMIC DEVICES

POLTRDNI GELSKI ELEKTROLITI ZA ELEKTROKROMNE NAPRAVE

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The di-urethanesil organic-inorganic hybrid bis N-triethoxysilyl propylcarbamoil poly(ethylene oxide) 400 (PEOCS) was used for the preparation of electrolytes appropriate for applications in electrochromic devices. The obtained PEOCS-based sol-gel network was able to accommodate the co-solvent γ-butyrolactone up to a molar ratio of PEOCS : γ-butyrolactone = 1 : 20. Lithium bis(trifluoromethanesulfonyl)imide was used as a guest salt. The initial conductivities were of the order 10^{-4} S/cm to 10^{-3} S/cm, but diminished during the course of the condensation reactions. This decrease was less obvious when a larger amount of co-solvent was present. The time-dependent stability of the conductivity was achieved with the addition of 3-chloropropylmethyldimethoxysilane. The best response was achieved for electrochromic devices with the electrolyte PEOCS : γ-butyrolactone : Li^+ salt = 1 : 15 : 0.5, with or without a dialkoxysilane additive.

Keywords: di-uretanesils, ormolytes, organic-inorganic hybrids, EC devices

Di-uretanesilni organsko-anorganski hibrid bis N-trietoksisilil propilkarbamatoil poli(etilen oksid) 400 (PEOCS) smo uporabili za pripravo elektrolitov za elektrokromne naprave. V nastale sol-gel mreže PEOCS smo lahko vključili sotopilo γ-butirolakton celo do molskega razmerja PEOCS : γ-butirolakton = 1 : 20. Litijev bis(trifluorometansulfonil)imid smo uporabili kot litijevo sol. Začetne prevodnosti gelov so se bile v območju od 10^{-4} S/cm do 10^{-3} S/cm, vendar so se nekoliko zmanjšale kot posledica reakcij kondenzacije. To zmanjšanje je bilo manjše v primeru večje vsebnosti so topila v elektrolitu. Časovno stabilnost prevodnosti pa smo dosegli z dodatkom 3-kloropropilmetildimetoksisilana. Najboljše lastnosti smo dosegli z elektrokromnima sklopoma z elektrolitoma PEOCS : γ-butirolakton : Li^+ sol = 1 : 15 : 0,5, brez dodatka dialkoksisilana ali z njim.

Ključne besede: di-uretanesili, ormoliti, organsko-anorganski hibridi, EC-sklopi

1 INTRODUCTION

Conventional battery-type electrochromic (EC) devices consisting of two films with intercalation properties are well established as smart windows, enabling the control of heat-loads and illumination levels inside buildings simply by the application of a potential pulse at the occupant's will[1]. Electrolytes play an important role in electrochromic devices, enabling their functioning and ensuring long exploitation times but, despite numerous investigations, they have remained the weakest part of the whole system. Since liquid electrolytes present long-term sealing problems, various polymeric electrolytes have been tested to date[2], such as proton-conducting electrolytes on the basis of either poly(vinyl alcohol) [3] or poly(vinyl acetate) [4], and lithium salts incorporated into various polymers, such as poly(methyl methacrylate) (PMMA) [5], poly(ethylene oxide) (PEO) [6] and organic-inorganic hybrids[2,7–8]. The latter materials belong to a special class of advanced polymeric materials[9–10] that combine the flexibility of the organic phase like PEO, poly(propylene oxide) (PPO) and poly(propylene glycol) (PPG) with the hardness of the inorganic phase. The latter is introduced as a simple tetraalkoxysilane compound (Class I) or is linked to the organic part via a covalent bond (Class II) [9]. From the materials processing perspective, organic-inorganic hybrids provide the possibility of making a variety of products with multifunctional properties, especially through the use of various trialkoxysilanes (Class II) characterised by hydrolysable reactive trialkoxy groups, which can undergo the sol-gel reactions of hydrolysis (solvolysis) and condensation, leading to the formation of tridimensional networks. Such hybrid electrolytes are called ormolytes (organically modified silicate electrolytes) and are characterised by good transparencies and ionic conductivities of 10^{-6} S/cm to 10^{-4} S/cm, while the mechanical properties surpass those of organic conducting polymers[11–13].

In previous years, we have investigated in our laboratory a di-ureasil organic-inorganic hybrid bis[(N′-(3-triethoxysilylpropyl)ureido]-terminated poly(propylene glycol) 4000 (PPGU, for short), in which the PPG segments and a siloxane backbone are covalently bonded through urea (-NH-C(=O)-NH-) groups, as an electrolyte for proton-conducting membranes in fuel cells[13] and also as a redox electrolyte for dye-sensitised photoelectrochemical cells (DSPEC) [14]. The results have shown a promissing efficiency of 4.1 % for DSPEC, while the conductivity values of membranes were of the order of magnitude of 10^{-4} S/cm to 10^{-3} S/cm at room temperature. Similar di-ureasils, but with PEO chains, have also been studied as ormolytes doped with lithium triflate[15–16], perchlorate[17–18] and bis(trifluoromethanesulfonyl)imide (LiTFSI) [19–21]. The reason for using PEO chains in these ureasil hybrids is their remarkable ability to solvate cations; however, plain salt-PEO mixtures possess rather poor conductivities as a result of the fact that salts increase the tendency of PEO to crystallise and also shift the glass-transition temperature T_g to higher values[22]. On the other hand, organic-inorganic hybrids are often completely amorphous, which improves the ion transport, possess good thermal stability, mechanical resistance and can be easily prepared in the form of thin films. An extensive ATR IR study of ormolytes with lithium triflate[16] have shown that Li^+ ions bond to carbonyl oxygens, leading to the disruption of the PEO/urea and urea/urea hydrogen bonds and to the formation of new and more ordered hydrogen bonded associations. Moreover, at higher Li^+ uploads ($n \leq 20$; $n = OCH_2CH_2/Li^+$), the cation also bonded to the ether oxygen atoms of the PEO chains[16]. The conductivity of the electrolytes with lithium triflate was from 10^{-6} S/cm to 10^{-5} S/cm at room temperature, depending on the amount of salt[15]. However, when lithium perchlorate or LiTFSI was used, the ionic transport became almost independent of the salt concentration and the conductivity increased to an order of magnitude of 10^{-6} S/cm to 10^{-4} S/cm[17,19]. The application of these electrolytes in semi-solid-state EC devices is proposed[20,23–24].

A similar organic-inorganic hybrid on the basis of PEO chains and ethoxysilyl groups, which can be classified as single end-capped urethanesil (urethane -NH-C(=O)-O- bond instead of urea one), was also investigated as an electrolyte with lithium triflate salt[25]. The results showed moderate conductivity values (approximately 10^{-6} S/cm) but the electrochemical window was quite large, the mechanical properties were good and the electrolyte films were highly transparent. The described properties therefore encouraged us to re-examine the properties of urethanesils as possible precursors for the preparation of electrolytes for EC devices (**Figure 1**).

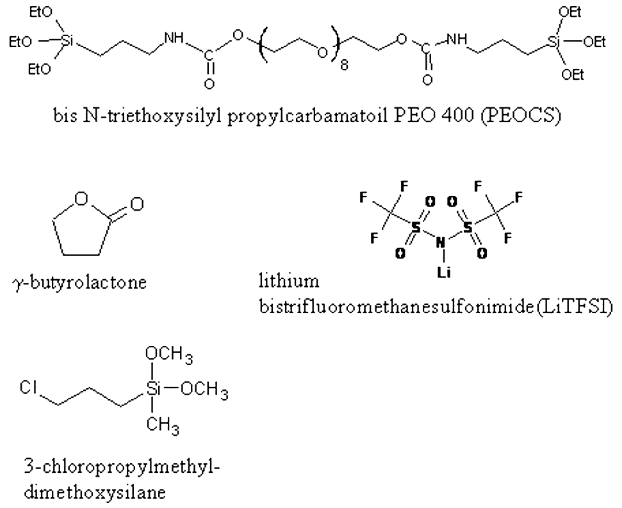

Figure 1: Precursors used for the preparation of the electrolytes for EC devices

Slika 1: Prekurzorji za pripravo elektrolitov za EC-sklope

An analogous di-urethanesil compound, bis end-capped sol-gel precursor bis N-triethoxysilyl propylcarbamoil poly(ethylene oxide) 400 (PEOCS, for short), was synthesised. This compound is characterised by a urethane -NH-C(=O)-O- covalent bond that forms between the isocyanato group of the 3-isocianatopropyl-triethoxysilane and the terminal hydroxyl group of a poly(ethylene glycol) (PEG). Glacial acetic acid ($AcOH_{gl}$) was chosen as the catalyst for the initiation of sol-gel processes, which inevitably leads to the polycondensation of a bis end-capped alkoxysilane PEOCS precursor through a non-hydrolytic solvolysis route, liberating ester molecules[26]. In order to improve the conductivity values, γ-butyrolactone (γ-BL in **Figure 1**) was included in the sol-gel PEOCS network as a co-solvent, because it has already been successfully tested as an additive for lithium ion batteries[27]. The PEOCS hybrid and co-solvent were fully compatible and no segregation of the phases was noted. The final electrolytes were obtained after the dissolution of the LiTFSI (**Figure 1**) salt and were applied in EC devices between electrochromically active poly(3,4-ethylenedioxythiophene) (PEDOT) and V_2O_5 counter-electrode films. The performance of the EC devices was evaluated by *in-situ* UV-visible spectroelectrochemical measurements.

2 EXPERIMENTAL

The PEOCS was prepared by the reaction of 3-isocyanatopropyl-triehoxysilane with an equimolar amount of polyethylene glycol 400 (PEO 400) in tetrahydrofuran (THF). The reaction mixture was stirred together under reflux for 10 h. The THF was evaporated and the final product PEOCS was obtained. The electrolytes were made by mixing PEOCS : γ-BL : LiTFSI in molar ratios of 1 : 1 : 0.5, 1 : 15 : 0.5 and 1 : 20 : 3, with *n* values (where n is the molar ratio of ethyleneoxide moieties per Li^+ ion) of 18, 18 and 3, respectively. The solutions were stirred for several hours until the lithium salt dissolved and then glacial $AcOH_{gl}$ in a molar ratio of PEOCS : $AcOH_{gl}$ = 1 : 6 was added to initiate the sol-gel processes of the alkoxy groups. The fourth electrolyte was prepared with a molar ratio PEOCS : γ-BL : LiTFSI of 1 : 15 : 0.5, but before the addition of LiTFSI and glacial $AcOH_{gl}$, 0.5 mmol of 3-chloropropylmethyldimethoxysilane (CPMDMS in **Figure 1**) was added.

The specific conductivity was measured on an Autolab PGSTAT302N potentiostat-galvanostat with an FRA module in a Teflon cell between two Pt electrodes. The frequency range used for the electrochemical impedance spectroscopy (EIS) was 10^5 to 0.01 Hz. The conductivity (σ/(S/cm)) was calculated according to the equation $\sigma = d/RA$, where R is the measured resistance obtained from the impedance plots, while d and A are the thickness and the area of the sample between the Pt electrodes.

All the types of ormolytes were used for the preparation of the EC devices, with a composition ITO-PET / PEDOT / various electrolytes / V_2O_5 (dip-coated) / FTO glass. The optically active PEDOT films[28] were deposited on sputtered ITO-PET substrates (CPFilms, Inc.; 125 μm, 60 Ω) using a roll-to-roll deposition technique (ISC Fraunhofer). The V_2O_5 films were prepared by the sol-gel route from vanadium (V) oxoisopropoxide[29], deposited by dip-coating on FTO glass (Pilkington) and thermally treated at 150 °C for 1 h. Prior to the EC device assembly, both film electrodes were stabilised in 1-M $LiClO_4$/propylene carbonate (PC) and the assembly was performed with reduced PEDOT and oxidized V_2O_5 films. The devices were designated according to the electrolyte composition, i.e., D(1–1–0.5), D(1–15–0.5), D(1–20–3) and the one with CPMDMS additive D(CPMDMS).

The *in-situ* UV-visible absorbance spectroelectrochemical characterisation of the EC devices was performed using a HP8453 diode array spectrophotometer and an Autolab PGSTAT30 potentiostat-galvanostat. The UV-visible spectra were recorded relative to an empty holder during chronocoulometric (CC; –2 V, 100 s and 2 V, 100 s) measurements every 4 s.

3 RESULTS AND DISCUSSION

Conductivity measurements. Conductivity measurements revealed that pure PEOCS is characterised by a conductivity value of $4 \cdot 10^{-8}$ S/cm, which is far too low for applications in any electrochemical device. The electrolytes for EC devices were therefore made by mixing of organic-inorganic hybrid PEOCS with γ-BL as the co-solvent and then the LiTFSI salt was added. Glacial $AcOH_{gl}$ was used as the catalyst for initiation of the sol-gel processes and the progress of the condensation of the sol-gel network could be evaluated from the conductivity values of the electrolytes, as shown in **Figure 2**. The decrease in conductivity up to the 8th day was most evident for the electrolyte prepared with the molar ratio PEOCS : γ-BL : LiTFSI = 1 : 1 : 0.5 (n = 18), with the lowest content of co-solvent. The value of n was, in this case, close to the values reported as the most optimal for achieving the highest conductivities, i.e., 15–25 depending on the electrolyte composition. When the amount of co-solvent was increased to PEOCS : γ-BL : LiTFSI = 1 : 15 : 0.5 (n = 18), a gradual drop in the conductivity up to the 14th day was still observed, but it was smaller. A simultaneous increase in the content of co-solvent and lithium salt, however, had a beneficial influence on the conductivity value, which did not change significantly with time, but the large amount of lithium salt induced the haziness of the electrolyte. Another approach was, therefore, used to improve the stability of the conductivity response with time. Namely, with the addition of various dialkoxysilanes, which can contribute to condensation reactions in only two directions, it is possible to prevent shrinkage of the sol-gel network. Therefore, 3-chloropropylmethyldimethoxysilane (CPMDMS in **Figure 1**) was added to the electrolyte with a molar ratio of PEOCS : γ-BL : LiTFSI = 1 : 15 : 0.5 and the conductivity did not change with time up to the 18th day (**Figure 2**).

Glass-transition temperature measurements. The T_g value is an important characteristic of ormolytes, since it controls the lower temperature limit of conduction in these materials and should therefore be kept as low as possible. Korwin and Masui[30] found that an increase in Li^+ and tetraethoxysilane content raises the T_g of the incorporated polyether, due to a restriction of the polymer's segmental motion by dipole-dipole and ion-dipole interactions and also by the cohesive contraction of the material. DSC measurements revealed that the T_g value of our PEOCS was –71.0 °C. Interestingly, de Zea Bermudez et al. [25] observed two T_g values, at –110 °C (T_{g1}) and –30 °C (T_{g2}) for undoped urethanepropyltriethoxysilane; however, their uretanesil compound was single end-capped and characterised by 7 repeating ethyleneoxide units. They tentatively associated T_{g2} with the mobility of the short side pendant oligopoly(ethyleneoxide) chains, but the origin of T_{g1} remained unassigned. The addition of a co-solvent to the PEOCS : γ-BL : LiTFSI = 1 : 1 : 0.5 electrolyte increased the T_g value to –39.0 °C, which is usually correlated with a decrease in the flexibility of the host polymer chain segments[19]. However, the concurrent increase in the conductivity values can be ascribed to the different constitution of the electrolyte, due to the presence of a

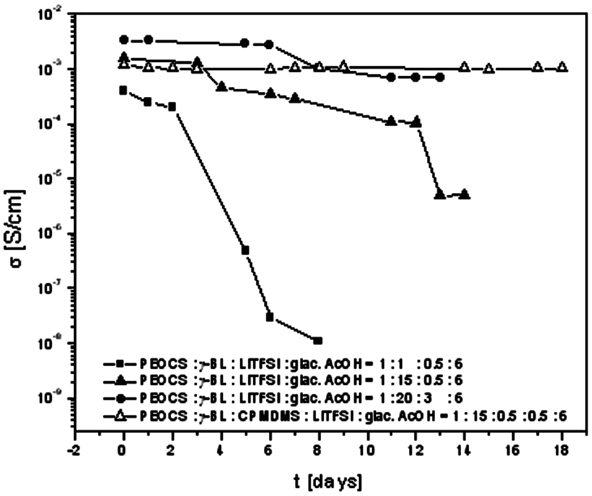

Figure 2: Time-dependent conductivity measurements of various PEOCS-based electrolytes

Slika 2: Časovno odvisne meritve prevodnosti različnih elektrolitov na osnovi PEOCS liquid phase, which enabled ion transport to occur, not only by the segmentional motion of the polymer chains but also by diffusion through the liquid phase. Electrolytes with a higher content of γ-butyrolactone no longer showed T_g values.

Electrochromic devices. The described PEOCS-based electrolytes were also tested in EC devices with an optically active PEDOT layer and a V_2O_5 counter-electrode film. The first electrolyte tested was PEOCS : γ-BL : LiTFSI = 1 : 15 : 0.5 (EC device D(1–15–0.5) in **Figure 3**). As is evident from **Figure 3A**, the transmittance of the device D(1–15–0.5) in the bleached state was low, i.e., below 33 % *T*, and the optical modulation at 634 nm was about 20 %. This is a consequence of the large thickness of the roll-to-roll deposited PEDOT films (800 nm) and, for comparison, the *in-situ* UV-visible measurement of a PEDOT film in a three-electrode electrochemical cell filled with 1-M $LiClO_4$/PC electrolyte is shown (**Figure 3A**), revealing the optical modulation $\Delta T_{634\ \mathrm{nm}} \approx 34$ %. The *in-situ* UV-visible measurements of the EC device D(1–15–0.5) showed that this device coloured in approximately 12 s and bleached in 8 s when exposed to potentials ±2 V vs. a counter electrode (**Figure 3B**).

When equivalent EC devices D(1–1–0.5) and D(1–20–0.5) were made, the recorded optical changes between the coloured and bleached states (Figure 4) were even smaller than in the case of device D(1–15–0.5) (**Figure 3**). The reason for the lower mobility of ions in D(1–1–0.5) in **Figure 4** is probably the smaller content of solvent, while for D(1–20–3), the amount of solvent was large (1 : 20). However, this electrolyte also contained a much larger amount of LiTFSI salt, which negatively influenced the performance of this EC device.

The performance of the EC device D(CPMDMS), which was prepared from electrolyte PEOCS : γ-BL : CPMDMS : LiTFSI = 1 : 15 : 0.5 : 0.5 and which had the most stable conductivity response (**Figure 2**), is shown in **Figure 3** (grey lines). Its optical response is quite similar to that of device D(1–15–0.5), composed of the same electrolyte, but without the addition of CPMDMS. Namely, the change in photopic transmittance (**Table 1**) reached ΔT_{ph} = 26.0 for D(1–15–0.5) and 22.5 for (D(CPMDMS). The switching characteristics also remained similar; colouring was achieved in 12 s, while bleaching became slightly more sluggish. Nevertheless,

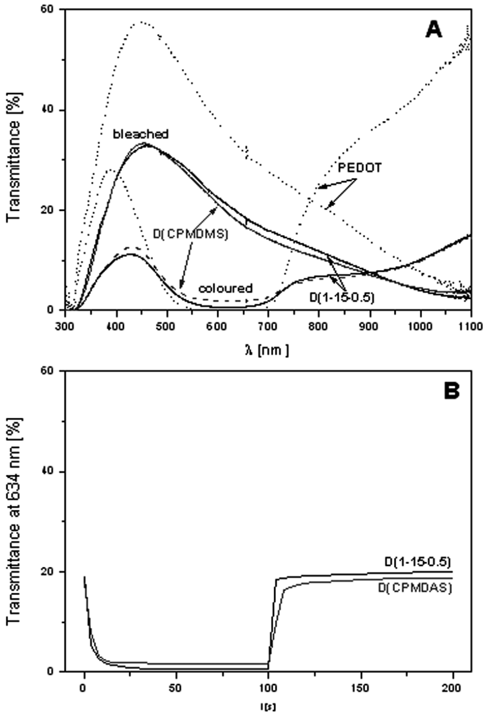

Figure 3: *In-situ* UV-visible spectroelectrochemical measurements of EC devices D(1–15–0.5) and D(CPMDMS): A) spectra obtained during chronocoulometric colouring at –2 V and bleaching at 2 V and B) monochromatic spectral response at 634 nm. A) UV-visible spectra of PEDOT film on ITO-PET measured in electrolyte 1 M $LiClO_4$/PC (coloured at –1 V vs. Ag/AgCl, bleached at 1 V vs. Ag/AgCl) are shown for comparison.

Slika 3: In-situ UV-vidne spektroelektrokemijske meritve EC-sklopov D(1–15–0,5) in D(CPMDMS): A) spektri, dobljeni pri kronokulometričnem obarvanju pri –2 V in razbarvanju pri 2 V in B) monokromatski spektralni odziv pri 634 nm. A) UV-vidni spektri PEDOT plasti na ITO-PET, izmerjeni v elektrolitu 1 M $LiClO_4$/PC (obarvan pri –1 V vs. Ag/AgCl, razbarvan pri 1 V vs. Ag/AgCl) so prikazani za primerjavo.

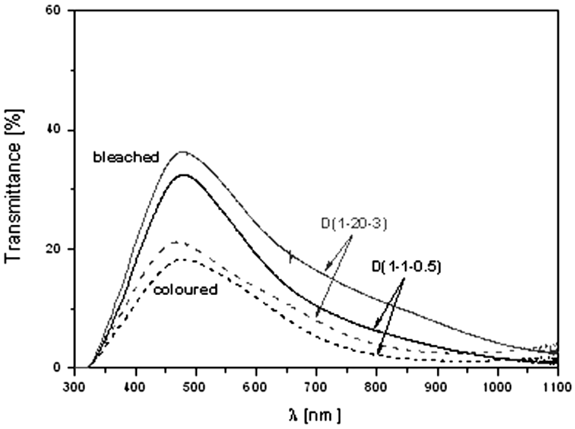

Figure 4: *In-situ* UV-visible spectroelectrochemical measurements of EC devices D(1–1–0.5) and D(1–20–3)

Slika 4: In-situ UV-vidne spektroelektrokemične meritve EC-sklopov D(1–1–0,5) in D(1–20–0,5)

Table 1: Lightness L^* and photopic transmittance T_{ph} of EC devices obtained from UV-visible spectra measured during chronocoulometric charging (–2 V, 100 s; 2 V, 100 s). For comparison, data for PEDOT film are also shown

Tabela 1: Svetlost L^* in fotopična transmisija T_{ph} EC-sklopov, izračunana na osnovi UV-vidnih spektrov, izmerjenih med kronokulometričnim obarvanjem (–2 V, 100 s) in razbarvanjem (2 V, 100 s). Za primerjavo je prikazana tudi svetlost PEDOT-plasti

EC device	L^*(col)	L^*(bl)	T_{ph}(col)	T_{ph}(bl)
PEDOT	13.2	72.5	1.6	44.4
D(1-1-0.5)	44.5	57.2	14.2	25.1
D(1-15-0.5)	11.1	59.2	1.3	27.3
D(1-20-3)	44.9	61.1	14.5	29.4
D(CPMDMS)	21.9	58.0	3.5	26.0

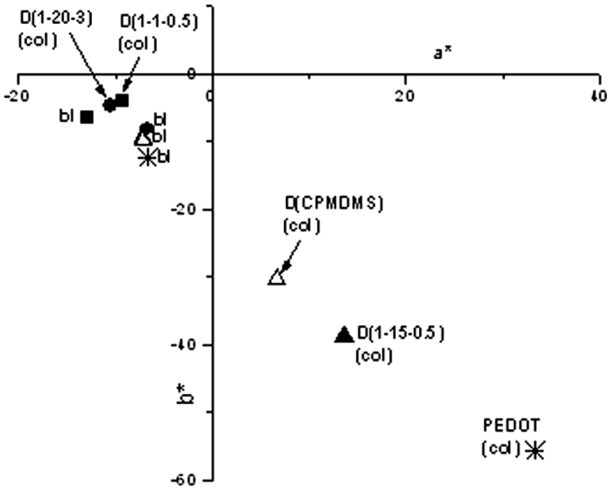

Figure 5: Colour coordinates of EC devices D(1–15–0.5), D(1–1–0.5), D(1–20–3) and D(CPMDMS) calculated in a $L^*a^*b^*$ CIE colour space

Slika 5: Barvne koordinate EC-sklopov D(1–15–0,5), D(1–1–0,5), D(1–20–3) in D(CPMDMS), izračunane v $L^*a^*b^*$ CIE barvnem prostoru

the stability of the conductivity response favours the application of an electrolyte with CPMDMS additive.

Colour coordinates. The colour coordinates that were calculated in the $L^*a^*b^*$ CIE colour space for EC devices and PEDOT film (**Figure 5**) showed that the PEDOT film moves from the region of dark-blue when coloured ($a^* = 33.4$, $b^* = –55.7$) to the region of light-blue when bleached ($a^* = –6.7$, $b^* = –12.3$) and similar behaviour was also characteristic of EC devices D(1–15–0.5) and D(CPMDMS), with the best optical performance. The colour coordinates of the other two EC devices, D(1–1–0.5) and D(1–20–3), could be found between $–6 < a^* < –13$ and $–4 < b^* < –8$ for the coloured and bleached states, indicating their lower colouration compared to the devices D(1–15–0.5) and D(CPMDMS). Similarly, the difference in the lightness L^* (Table 1) of the coloured state is also remarkable, being of the order of 11 to 22 for the PEDOT film and devices D(1–15–0.5) and D(CPMDMS), but much higher (L^* ˜ 44) for the EC devices D(1–1–0.5) and D(1–20–0.5).

4 CONCLUSIONS

It was shown in this work that di-urethanesil-based ormolytes incorporating lithium bis(trifluoromethanesulfonyl)imide salt and co-solvent γ-butyrolactone can be sucessfully applied in EC devices with an optically active poly(3,4-ethylene-dioxythiophene) (PEDOT) film and a V_2O_5 counter electrode. The best EC devices were characterised by optical modulation above 30 % at 634 nm and fast-switching kinetics (colouring and bleaching in less than 12 s). The stability of the conductivity response over the course of an 18-day measurement was achieved by the addition of dialkoxysilane 3-chloropropylmethyldimethoxysilane, which enables condensation reactions only in two directions, thus profoundly influencing the structural properties of the sol-gel network. Two major conclusions can be made on the basis of this work: (i) that the investigated organic-inorganic hybrid bis N-triethoxysilyl propylcarbamatoil poly(ethylene oxide) 400 is able to incorporate quite large amounts of co-solvent in its network and (ii) that dialkoxysilanes successfully stabilize the structure of the formed sol-gel network. Both conclusions open tremendous possibilities for improvements to existing ormolytes used in current EC devices, by the application of other co-solvents, lithium salts and dialkoxysilanes.

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