URETHANOSIL IONIC NANOCOMPOSITE GEL CONDUCTORS WITH AN IONIC LIQUID: REDOX ELECTROLYTES FOR ELECTROCHEMICAL DEVICES

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Abstract

The urethanosil semi-solid type of electrolyte with incorporated redox species (I^-, I_3^-) was found to be appropriate as an intermediate layer between the WO_3 working electrode and the Pt counter-electrode in hybrid electrochromic devices. Urethanosils were prepared by the sol-gel route from single end-capped alkoxysilane precursors, which were synthesized using mono ether terminated oligoethyleneglycols and isocyanatopropyltriethoxysilane. In the sol-gel processing of the redox electrolyte, besides the urethanosil precursor tetraethoxysilane served as a network former, oxalic acid as a gelation promoter, various iodides/ iodine as a source of redox species and triethyleneglycol as a non-volatile solvent. Time-dependent IR ATR measurements were performed to follow solvolysis and condensation of the organically modified silica framework. To take advantage of the high ionic mobility, negligible volatility, low viscosity and large electrochemical window, an ionic liquid ($EtPrIm^+I^-$) was also considered as a co-solvent and simultaneously as a source of the iodide redox moiety.

Key words: sol-gel, redox electrolytes, electrochromic devices

Introduction

We reported recently that sol-gel derived silica-based nanocomposite redox electrolytes having a semi-solid state consistency may be used in dye-sensitized photoelectrochemical cells (DSPEC)[1-4] and hybrid electrochromic (HEC) cells.[5-7] They were based on a bis end-capped triethoxysilane chemically bonded via the urea groups to a long poly(propyleneglycol) chain (ICS-PPG 4000 for short). Redox conductivity was attained by incorporating KI and I_2 in the ethanolic solution of the ICS-PPG 4000 precursor. The precursor solution gelled with the addition of acetic acid (AcOH). The resulting hybrid silica gels contained a complex mixture of I^-/I_3^- species, ethanol and ethylacetate as a reaction product. The latter compound appeared as a consequence of the solvolysis reactions caused by the AcOH gelation promoter. This resulted in non-hydrated gels containing a low silanol content. Although the cells exhibited very good performances, their lifetime was limited to a few months; EtOH evaporated (cells were

not sealed to increase the severity of testing) and KI crystallized in the electrolyte entrapped in the cells. Although the evaporation of EtOH could be prevented by appropriate sealing, resulting in better longevity of the electrochemical cell, we decided rather to avoid evaporation of EtOH, substituting it with a suitable non-volatile solvent. The following criteria were taking into account in choosing the co-solvent: (i) it should dissolve KI and I_2, (ii) it should favour the formation of I_3^- and I^- from the added KI + I_2, (iii) it should be compatible with a carboxylic acid catalyst and sol-gel precursor (iv) it should support diffusion of charged species by increasing the ionic conductivity of the gel electrolyte and (v) the boiling point should be above 250 °C to have a negligible vapour pressure at the operating conditions of a HEC (~80 °C) cell. Sulfolane (bp ~ 280 °C), chosen first, fulfilled most of the mentioned criteria (i-v), and HEC cells composed of ICS-PPG 4000/ KI + I_2/ sulfolane/ AcOH[5] performed more than 3000 repetitive colouring/bleaching cycles before they deteriorated. However, AcOH catalyst and the corresponding reaction products of the solvolysis reactions (i.e. ethylacetate) are both relatively low-boiling point liquids and unsealed HEC cells failed to work after a few months.

Therefore, our aim was to prepare redox electrolytes based on a new type of sol-gel precursor compatible with solid oxalic acid (OxA) and high-boiling point co-solvents. We used triethyleneglycol (TEG) and 1-ethyl-3-propylimidazolium iodide (EtPrIm$^+$I$^-$). The latter compound is an ionic liquid containing alkylsubstituted imidazolium cations and iodides. We chose this type of ionic liquid to avoid the addition of MI salts (M = Li, K, Na). The weak AcOH (pK = 4.27) was substituted with the stronger OxA (pK = 1.23). Since our previous ICS-PPG 4000 sol-gel precursor was not compatible with the chosen co-solvents and OxA catalyst, two new types of sol-gel precursors were synthesized: 2-methoxyethyl-3-(triethoxy-λ^4-silyl)propylcarbamate (ICS-2ME) and 2-(2-methoxyethoxy)ethyl-3-(triethoxy-λ^4-silyl)propylcarbamate (ICS-DEM). Both belong to the class of single-capped urethanosils (carbamatosils) containing –(HN)-(CO)-O-groups linked to the reactive triethoxysilane groups on one side and a short PEO chain on the other. Since single end-capped urethanosils are not easy to gel, tetraethoxysilane (TEOS) was added as a network former. The synthetic routes of the sol-gel precursors and ionic liquid are presented below, as well as the role of the OxA catalyst in performing the solvolysis reactions of the complex precursor mixture.

The as-prepared redox electrolytes were tested in HEC cells. This type of cell represents an alternative to the better known three layered battery-type and liquid EC devices with incorporated luminophores.[8] While the battery-type EC cells have not yet attained popularity as "smart" windows for buildings, the liquid EC devices have already become widely used as rear-view mirrors for cars, preventing glare due to their ability to control electrically the level of reflected light. HEC cells, in contrast to three layered battery-type EC cells, consist of an active electrochromic material (usually TiO_2 with viologen dye attached)[9] deposited on a transparent conducting oxide electrode facing a counter electrode with a deposited, catalytically-active, thin layer of platinum. The space between them is filled with a liquid electrolyte, usually an organic solvent containing I^- /I_3^- or a ferrocene/ferrocenium redox couple. Because only two active layers are needed for the operation of HEC cells; this type of EC cell represents a considerable step forward in simplicity of design with respect to the three layered battery-type EC devices, diminishing the cost of fabrication and the number of possible modes of failure. In this work we used (instead of nanocrystalline TiO_2,[9] sensitised with viologen derivatives, and a liquid electrolyte) a non-hydrated WO_3 film prepared via the peroxo sol-gel route[10] and a urethanosil semi-solid electrolyte. Its advantage in comparison with a liquid electrolyte is that leakage is avoided, but a high ionic conductivity and a good wetting of the active electrode is more difficult to achieve.

Experimental

Synthesis of urethanosil precursors and ionic liquid

The synthesis of single end-capped urethanosil precursors is a straightforward long-lasting (few days) reaction. In all cases we used 3-isocyanatopropyl-triethoxysilane (ICS) in combination with various mono ether terminated oligoethyleneglycols that are commercially available. The synthesis of two urethanosil precursors is described below.

ICS-2ME (3). Into 40 g of tetrahydrofurane (THF) 11.76 g (0.154 mol) of 2-methoxyethanol (2) was dissolved. To this solution 38.24 g (0.154 mol) of ICS (1) was added dropwise. The solution was then heated slightly below the reflux temperature (64 °C) for 48 hours with constant stirring. The solvent was removed by distillation under reduced pressure. 48.1 g of product (**3**) was obtained with a high yield (96%).
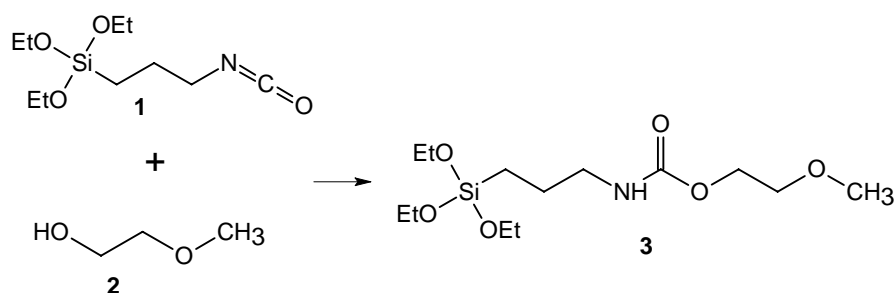
ICS-DEM (5). The same procedure as above was used. Instead of 2-methoxyethanol, 16.35 g (0.136 mol) of diethyleneglycol-monomethylether (**4**) was dissolved in THF and 33.65 g (0.136 mol) of ICS was added to this solution. 47.7 g (95%) of product (**5**) was obtained after isolation.
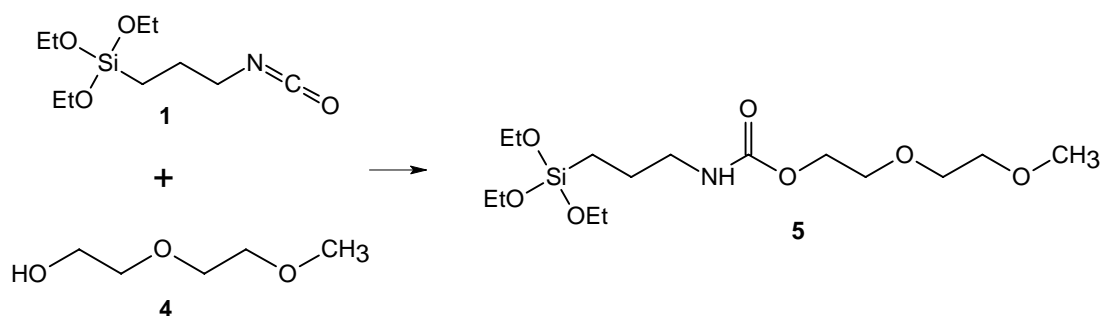
1-ethyl-3-propylimidazolium iodide ionic liquid. Synthesis of 1,3-dialkylimidazolium ionic liquids does not require very much effort. One can start from commercially available 1-methylimidazole for a one-step or from imidazole for a two-step synthesis.

(i) 1-Ethylimidazole was synthesized according to Bonhote.[11] From 50 g (0.734 mol) of imidazole, 55 g (0.81 mol) of sodium ethoxide and 88 g (0.81 mol) of bromoethane, 48.5 g of 1-ethylimidazole was obtained with a 69% yield.

(ii) Under vigorous stirring 88 g (0.52 mol) of propyliodide (*Fluka*) was added dropwise over 1 h to a solution of 41.25 g (0.43 mol) 1-ethylimidazole in 200 mL of 1,1,1-trichloroethane (*Fluka*). The mixture was then refluxed for 3 h. Ionic liquid was decanted from the hot solution into a separatory funnel, washed twice with 100 mL of 1,1,1-trichloroethane and dried under reduced pressure. 100.6 g (88%) of 1-ethyl-3-propyl-imidazolium iodide was obtained.

1-ethyl-1*H*-imidazole   1-ethyl,3-propylimidazolium iodide
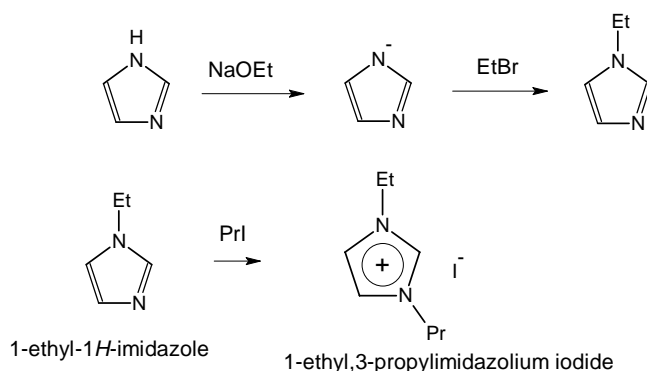
Preparation of a gel electrolyte for hybrid electrochromic device application

The preparation of the precursor solution followed by the construction and characterization of HEC is schematically presented below. To a solution of oxalic acid in TEG (1:1 wt. ratio), the inorganic iodide salt or ionic liquid 1-ethyl-3-propylimidazolium iodide and I_2 were added ($I^-:I_2$ = 10:1 mol. ratio). Both silica precursors (ICS-2ME or ICS-DEM and TEOS, 1:1 wt. ratio) were then admixed to form a sol, which was used for the construction of the HEC.
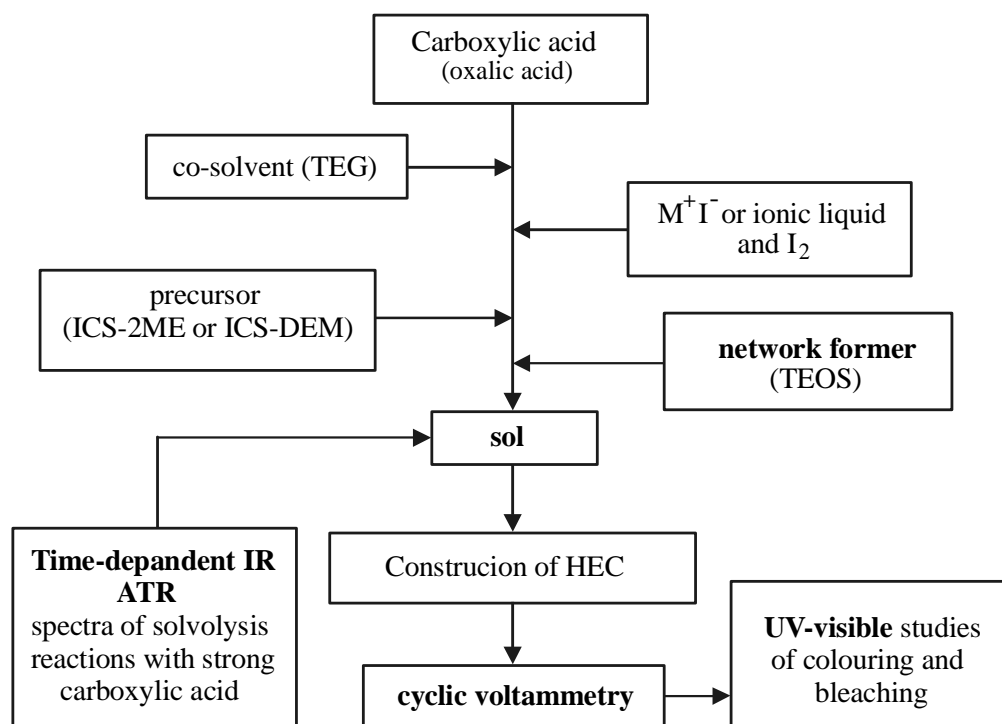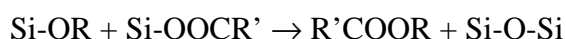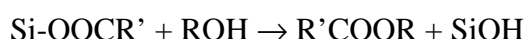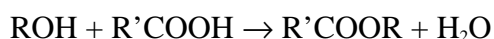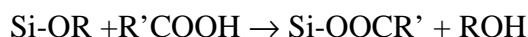
The HEC cells were constructed from nanocrystalline WO_3 films prepared using a peroxo sol-gel route.[10] The HEC cells were assembled in such a way that a drop of the sol (redox electrolyte) was placed on the WO_3 film and immediately covered with a Pt-coated SnO_2:F-glass substrate. No sealing of the HEC cells was used; the electrolyte gelled inside the HEC cell.

Results and discussion

Matrix gelation

Time-dependent in-situ IR ATR measurements of the ICS-DEM/ TEOS/ TEG/ OxA model system (Figure 1) were made to follow the gelation process of the organically modified silica matrix (without the addition of a redox pair) at various time intervals after oxalic acid in TEG was mixed with the silica precursors. IR ATR spectra were recorded from the beginning (t=0, first spectrum in Figure 1) to 140 hours of ageing (last spectrum in Figure 1). The band attributed to the carbonyl stretching mode of OxA at 1741 cm^{-1} shifted to a higher wavenumber and also, a new band appeared at 1311 cm^{-1}. We ascribed them to the oxalic acid ester, which formed due to the solvolysis reactions of siliceous species:

$$Si\text{-}OR + R'COOH \rightarrow Si\text{-}OOCR' + ROH$$

$$ROH + R'COOH \rightarrow R'COOR + H_2O$$

$$Si\text{-}OOCR' + ROH \rightarrow R'COOR + SiOH$$

$$Si\text{-}OR + Si\text{-}OOCR' \rightarrow R'COOR + Si\text{-}O\text{-}Si$$

It is important to stress that the ester band at 1311 cm^{-1} increased over the whole period, indicating that the oxalic acid ester reaction product did not evaporate when the gel dried. This is due to its lower vapour pressure as compared to e.g. acetic acid ester, which gradually evaporated from the gel catalyzed with acetic acid,[12] causing the deterioration of the corresponding electrochemical cell performance after a few months. This is important spectroscopic evidence, showing the advantage of using oxalic acid over acetic acid as catalyst. The only volatile component evolving in the sol-gel transition of the ICS-DEM/ TEOS/ TEG/ OxA system is EtOH, the side solvolysis

reaction product. Its formation and continuous evaporation is evidenced in the IR ATR spectra with characteristic vibrations at 1047 cm^{-1} and 878 cm^{-1}.
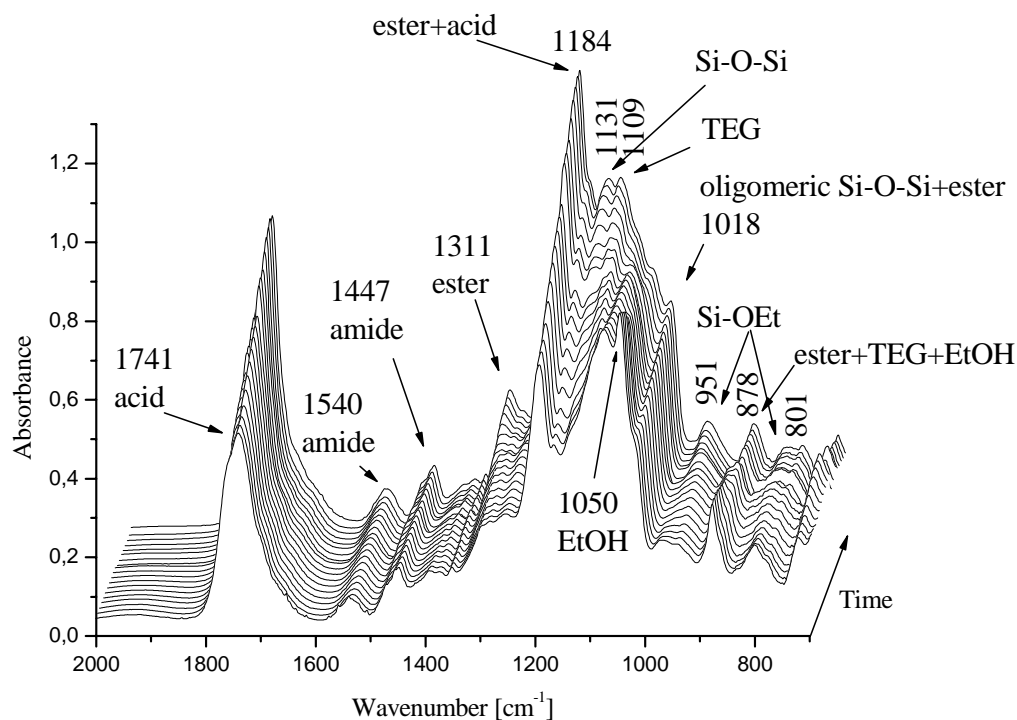

Figure 1. Time-dependent IR ATR spectra of ICS-DEM/ TEOS/ TEG/ OxA model system: gelation study.

The condensation of the silica network is clearly seen from the Si-O-Si stretching band near 1100 cm^{-1}, which gained in intensity. In addition, a new band at 1018 cm^{-1} appeared and increased with time of ageing. We attributed it to the Si-O-Si stretching band of the oligomeric silica species on the basis of a detailed spectroscopic study of some acetic acid catalysed gels,[12] where this band occurred at 1020 cm^{-1}. Obviously, cross-linking took place but did not end up in the fully condensed hybrid silica structure.

Performance of the HEC cell

Before the electrochromic properties of the HEC cell employing ICS-DEM/ TEOS/ TEG/ OxA/ M$^+$I$^-$+I$_2$ redox electrolyte are given, briefly the operating principles of the cell are discussed to show the role of the redox electrolyte. The HEC cell is schematically shown in Figure 2. When a cathodic potential is applied to the WO$_3$ film,

the inserted charge needs compensation to stabilize the W^{5+} oxidation state. That is achieved by the insertion of M^+ ions coming from the electrolyte:

$$WO_3 \text{ (transparent)} + xM^+ + xe^- \leftrightarrow M_xWO_3 \text{ (blue)}$$

As in the battery-type of EC cells the electrolyte serves as a source of compensating positive ions. In this regard both EC cells are similar. Due to the potential gradient in the redox electrolyte I^- ions diffuse through the sol-gel network bringing charge to the Pt counter-electrode, performing the following redox reaction:

$$3I^- \leftrightarrow I_3^- + 2e^-$$
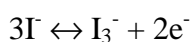
In the HEC cells studied previously[5,6] the redox electrolytes contained KI and I_2 serving as a source of I^- and I_3^- ions, and the intercalating K^+ species. During gelation and the evaporation of EtOH, KI did not remain dissolved in the sols but became finely dispersed in the form of KI microcrystallites having submicrometre dimensions. Due to the redox reaction shown above, a separate counter-electrode having ion-storage characteristics is not needed for HEC cell functioning.

The functioning of the HEC cell with a $WO_3/(I^-/I_3^-)$ redox electrolyte is facilitated due to the appropriately adjusted energy levels of the conduction band (CB) of WO_3 (0.53 V vs. NHE) and redox potential of the I^-/I_3^- couple lying nearly at the same potential (~0.5 V vs. NHE).[13] In DSPEC cells the efficiency of the cell depends largely on the recombination losses of photoejected electrons with oxidized dye molecules or the redox couple which is in contact with the large area TiO_2 film. The I^-/I_3^- couple could in that case act as an electron scavenger, reducing the number of holes (i.e. I_3^- ions) at the photoanode (i.e. TiO_2/ electrolyte interface), and consequently decreasing the number of I_3^- needed at the Pt/ electrolyte interface to accept electrons coming through the external circuit to the Pt counter-electrode. DSPEC cells function well because the CB of TiO_2 is close to 1 V vs. the NHE electrode, preventing high recombination losses. Recombination losses do not represent a drawback for HEC cell operation, because a potential is constantly applied across the cell.

The insertion of M^+ ions was inferred from the in-situ UV-VIS spectroelectrochemical measurements performed on the HEC cell in the course of potential sweeping;[5] the transmittance dropped at cathodic potentials and became restored during the anodic scan. Insertion of K^+ ions and consequent colouration was fast and took place in a few seconds, in contrast to much longer times of colouring / bleaching changes of the battery-type EC cells where the colouring / bleaching kinetics of the cell is governed by the properties of both electrodes. The electrochromic kinetics of HEC cells is therefore limited mostly by the ionic conductivity of the redox electrolyte which does not exceed 10^{-4}-10^{-3} S/cm.

Results obtained for the colouring / bleaching changes of the HEC cell (one example is presented on Figure 3) employing redox electrolytes with the composition ICS-DEM/ TEOS/ TEG/ OxA/ M^+I^- (or ionic liquid) $+I_2$ and ICS-2ME/ TEOS/ TEG/ OxA/ M^+I^- (or ionic liquid) $+I_2$ showed that all HEC exhibited a reversible EC effect up to the 100th cycle, except those where LiI was used as a source of the intercalating species. That exception we related to the affinity of LiI to water.[14] For HEC cells where an ionic liquid was used, the intercalating species were protons, while the colouring of other cells actually relied on the alkali ions and not protons, which could be generated due to the presence of the oxalic acid catalyst.
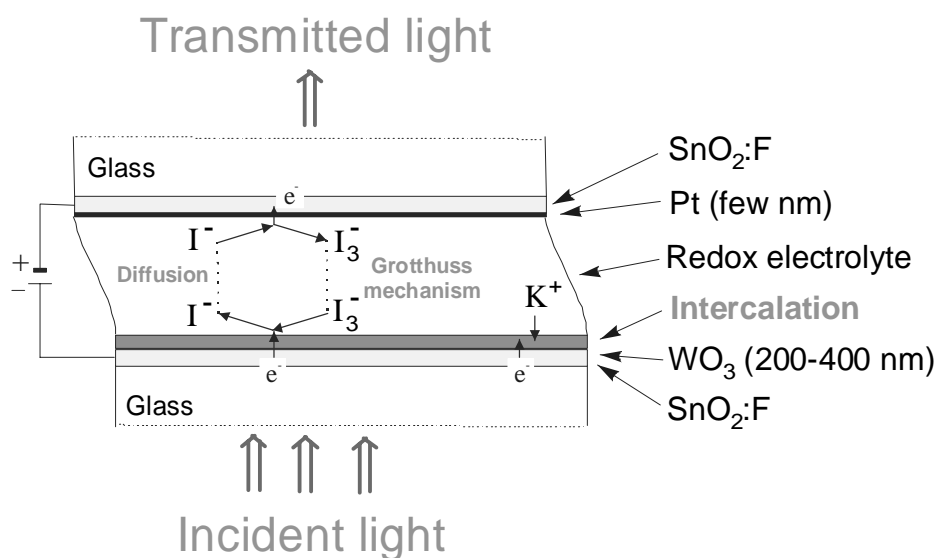

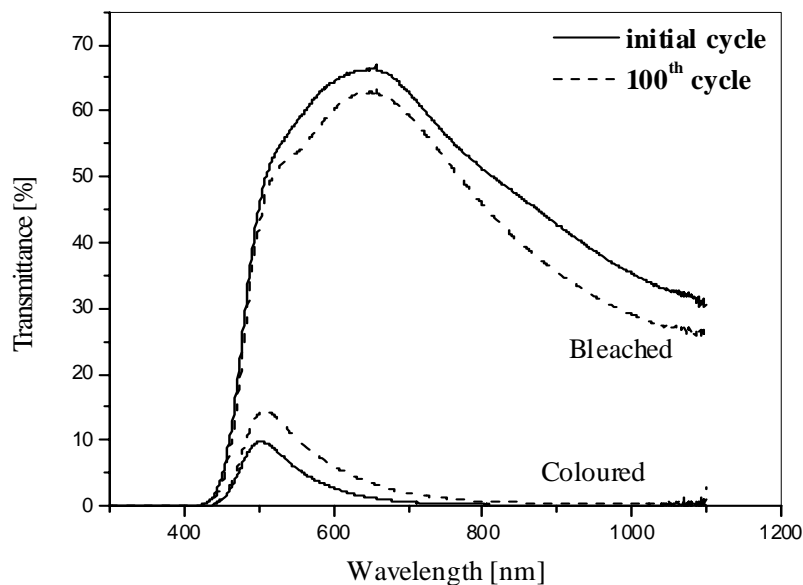**Figure 2.** Schematic representation of a HEC cell.

Figure 3. In-situ UV-VIS spectroelectrochemical measurements of a HEC cell with ICS-DEM/ TEOS/ TEG/ OxA/ NH_4I+I_2 redox electrolyte.

Conclusions

Some novel urethanosil-type precursors were synthesized so as to be compatible with the other components of redox electrolytes: namely, the co-solvents (TEG and $(EtPrIm)^+I^-$ ionic liquid), gelation promoter (OxA), network former (TEOS) and inorganic redox pair (M^+I^-/I_2; $M^+= NH_4^+$, Li^+, Na^+ and K^+), also serving as a source of the intercalating species into a nanocrystalline non-hydrated WO_3 film. The oxalic acid in the system was confirmed (by means of in-situ IR ATR spectroscopy) to be actively involved in the solvolysis reactions of siliceous species, their oligomerization and condensation. Hybrid electrochromic cells were constructed from the redox electrolyte sandwiched between the active WO_3 electrode and a Pt counter-electrode. The electrochromic effect of the cell employing ICS-DEM/ TEOS/ TEG/ OxA/ NH_4I+I_2 redox electrolyte was demonstrated.

Acknowledgements

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Povzetek

Pokazali smo, da so uretanosilni poltrdni elektroliti z vgrajenimi redoks zvrstmi (I^-, I_3^-) ustrezna vmesna plast med WO_3 delovno elektrodo in Pt protielektrodo v hibridnem elektrokromnem sistemu. S pomočjo reakcije med oligoetilenglikoli-monometiletri in 3-izocianatopropiltrietoksisilanom smo pripravili kratke uretanosilne (karbamatosilne) alkoksisilanske prekurzorje s samo enim alkoksisilanskim koncem. S temi prekurzorji smo, s pomočjo oksalne kisline, dobili redoks gel elektrolite. Kot vir redoks zvrsti smo uporabili anorganske (LiI, NaI, KI, NH_4I) in organske jodide ter jod. Kot topilo nam je služil težkohlapni trietilenglikol. Solvolizo in kondenzacijo smo zasledovali s časovno odvisno IR ATR spektroskopijo. Ionska tekočina ($EtPrIm^+I^-$) je bila prvič uporabljena v takem sistemu zaradi njene vsestranske uporabnosti v elektrokemijskih aplikacijah, kjer sta potrebni visoka prevodnost in ionska gibljivost. Ionske tekočine imajo zelo nizke parne tlake, nizko viskoznost in široko elektrokemijsko okno.