HYBRID ELECTROCHROMIC DEVICES COMPRISING A NANOCOMPOSITE SEMI-SOLID STATE SOL-GEL REDOX ELECTROLYTE WITH TRIETHYLENE GLYCOL OR SULFOLANE CO-SOLVENTS

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Electrochromic devices attracted interest as “smart” windows for building applications. They consist of electroactive layer (usually WO_3) facing counter-electrode layer having ion-storage capacity, while the space between them is filled with ionically conductive electrolyte (Li^+ or H^+) (battery –type EC devices). EC devices exhibit long-term memory effect due to the electronically non-conductive electrolyte. Other types of EC devices exist where Li^+ or H^+ ionic conductor is replaced with polymeric gel electrolyte containing redox species mainly used in electrochromic rear-mirrors for cars (solution type). Recently, we developed hybrid EC device consisted of active WO_3 layer in contact with redox electrolyte containing I^-/I_3^- redox species. No counter-electrode was needed for the functioning of HEC cell. The colouring-bleaching changes are fast and the HEC exhibits self-erasing properties because of the electrically conductive I^-/I_3^- redox electrolyte.

One of the main issues of HEC cells employing liquid or semi solid-state electrolytes is their long-term stability. Reaction products and other volatile components evaporate from the electrolyte if the cell is not properly sealed. Gel dries and shrinks causing the delamination of the cell, what finally leads to the cell failure. In our previous studies we used gels where sol-gel precursors were dissolved in EtOH and catalysed with AcOH. HEC of this type showed fast response (**Fig. 1**) but in a course of time the volatile components were evaporated and the cell stopped to work.

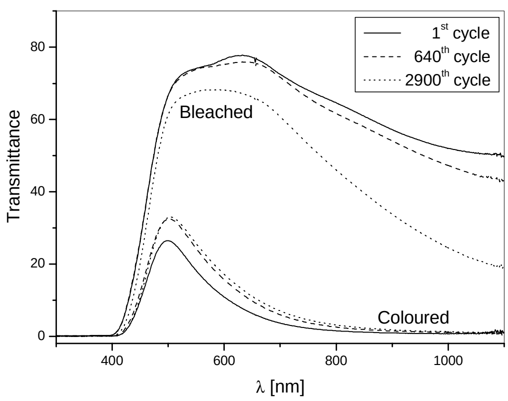

Fig 1: *UV-visible spectra of device type (i)*

In this work we focused on making redox electrolytes containing co-solvents having high boiling points (>200°C), ability to dissolve KI and I_2 (source of I^-/I_3^-) and solid carboxylic acids. We used salicylic and oxalic acids.

Two types of redox electrolytes were made. In type (i) bis end-capped triethoxysilane chemically bonded to the long (n= 67) PPG chain via the urea groups (ureasils) was used (Fig.2a) and catalysed with salicylic acid. Sulfolane served as a co-solvent (Fig.2b). Type (ii) electrolyte was made from single capped alkoxysilane precursor (ICS-2ME) where Si was bonded via the carbamato groups to short polyethylene glycol chains (Fig 2c). Triethylene glycol was used in this case as a co-solvent and catalysis performed with oxalic acid. TEOS was added to cross-link the type (ii) gel where also NH_4I and I_2 was used as a source of I^-/I_3^- ions instead of KI and I_2 as in type (i).

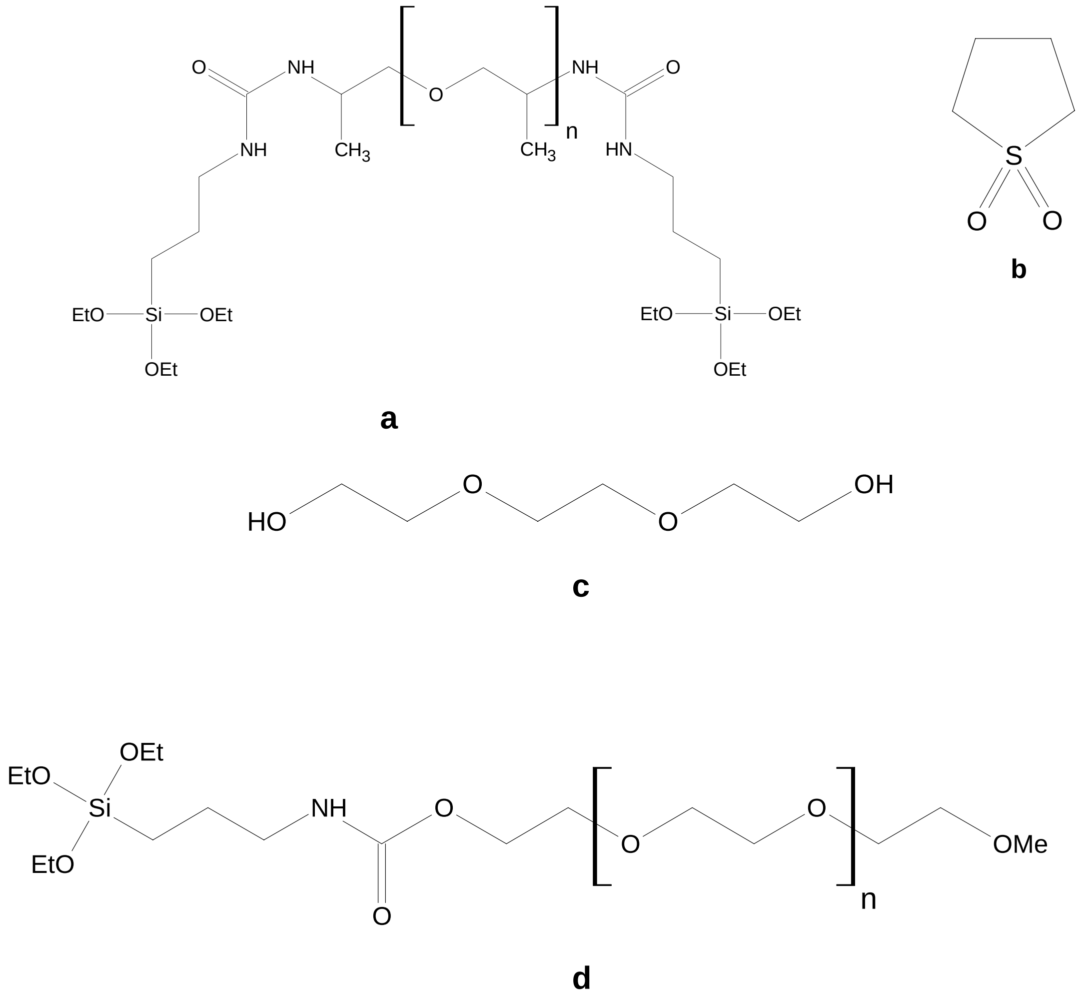

Fig. 2 *Structures of (**a**) bis-end capped ICS-PPG, co-solvents: (**b**) sulfolane, (**c**) triethyleneglycol and (**d**) single-capped polyethyleneglycol precursors:*

We made comparative studies of the electrochromic properties of type (i) and (ii) HEC devices showed fast electrochromic response and deep colouring due to the thick (~300-400 nm) WO_3 crystalline active electrochromic layer in contact with the electrolytes. Stability was checked by performing repetitive electrochromic cycling; type (i) showed persistent electrochromism up to 3000 cycles while the type (ii) exhibited nearly unchanged colouring-bleaching changes up to 5000 cycles.

ATR IR spectroscopic studies of both electrolytes revealed the importance of using strong carboxylic acids (i.e. in type (i) salicylic and type (ii) oxalic acid) for attaining direct condensation of triethoxysilane capped groups to silica via the solvolysis reactions. That was proved by the appearance of the corresponding ester bands and EtOH as a reaction product of the solvolysis and condensation reactions of the corresponding sol-gel precursors catalysed with carboxylic acids.

Stability of the cells was studied using in-situ IR reflection-absorption spectroscopy. Results of the IR spectra analysis showed that the S-O stretching modes of the sulfolane split and shifted indicating the interactions of the mobile ions with the co-solvent. The influence of the crystallinity of the WO_3 films on the HEC performance is discussed; non-hydrated WO_3 films are compulsory for the functioning of the HEC while amorphous – hydrated films failed to act as electrochromic films in this type of electrochromic devices.