HYBRID ELECTROCHROMIC CELLS EMPLOYING I_3^-/I^- REDOX PAIR IMMOBILIZED IN SOL-GEL ORGANIC-INORGANIC OR PMMA POLYMER ELECTROLYTE

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Introduction

An electrochromic material is able to change its optical properties when a voltage is applied across it. The optical properties should be reversible; it means that the original state should be recoverable if the polarity of the voltage is changed. These properties make electrochromic materials of considerable interest for optical devices of several different types, such as elements for information display, light shutters, smart windows, variable-reflectance and variable-emittance thermal radiators [1].

The aim of this study is the comparison of the hybrid electrochromic devices (HEC) cells incorporating sol-gel and polymeric I_3^-/I^- redox electrolyte [2]. The advantages of HEC cells (Fig.1) compared to the usual battery type EC cells is that the counter electrode with intercalaction properties can be replaced with a thin Pt layer on SnO_2:F glass. The redox pair was introduced in electrolytes with the dissolution of I_2 and one of the iodide salts like LiI and KI, their dissolution beeing dependent on the properties of the electrolyte matrix. Transformation of iodide and triiodide species according to reaction $I_3^- + 2e^- \leftrightarrow 3I^-$ may occur on Pt and WO_3 electrodes, while the optical modulation of HEC cells remains to be determined by active electrochromic WO_3 film and intercalation/deintercalation of certain cations (H^+, Li^+, K^+).

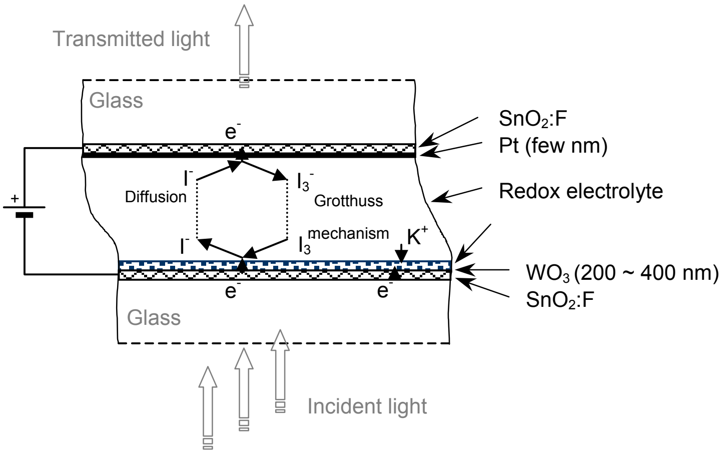

Fig. 1 *Schematic representation of an HEC cell.*

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Experimental

Optically active WO_3 films covering SnO_2:F glass substrates were nanocrystaline with the grain size 30 nm and were prepared by using peroxo-synthesis route and thermally treated at 450 °C for 30 minutes. A drop of the redox electrolyte was placed on WO_3 film and immediately covered and pressed with platinised SnO_2:F glass substrate serves as counter electrode (Fig. 2). The sol-gel electrolyte was prepared from unhydrolyzed organic-inorganic precursor ICS-PPG that was synthesized from 3-isocyanatopropyltriethoxy silane (ICS) and poly(propyleneglycol)-bis-(2-amino-propyl)ether (PPG) with molar weight 4000. After the dissolution of $Li+I_2$ or $KI+I_2$ acetic acid was added as catalyst for the gelation of ICS-PPG precursor. Co-solvent sulpholane was chosen because of its high boiling point in order to prevent its evaporation from the HEC cell. The polymeric PMMA electrolyte was prepared as a mixture of methyl methacrylate (MMA) monomer, polymeric PMMA resin containing 1% of dibenzoylperoxide served as polymerisation initiator (Superacryl®, Spofa-Dental, Czech Republic) and optional component [3]. Optional component was presented by LiI and I_2 dissolved in propylene carbonate. To compare the electrochemical properties of active layer with different pre-treatment we have prepared two samples of HEC cell with WO_3 pre-heated. The electrochemically active layer WO_3 film in which HEC with ICS-PPG 4000 sol-gel electrolyte contained LiI and KI salts was thermally treated at 450 °C for 30 minutes and then re-heated at 300 °C for 10 minutes before assembling. The HEC cells contained PMMA electrolyte were stored in a desiccator for one day in order to avoid creating of air bubbles. Appearing of these bubbles is portably connected with shrinking of polymer electrolyte due to the polymerisation.

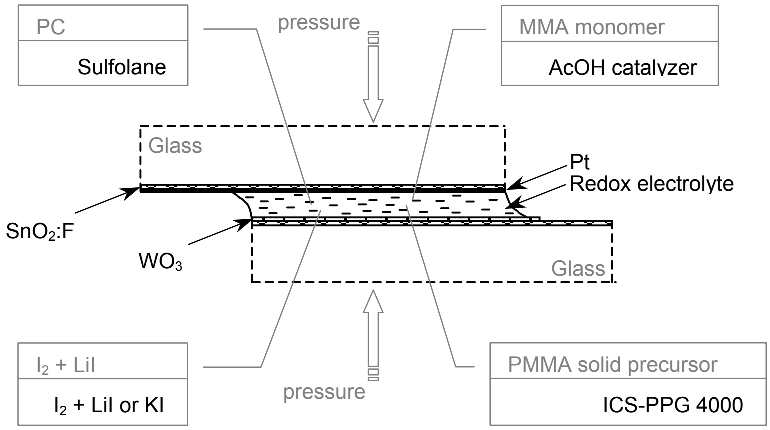

Fig. 2 *Preparation of an HEC cell with different basic substances of the redox electrolyte.*

In-situ UV-visible spetroelectrochemical measurements of the HEC cells were made using the HP 8453 (Hewlett Packard, USA) diode array spectrophotometer in combination with an Eco Autolab (Eco Chemie, The Nederlands). Potentiostat module PGSTAT 12 was used to perform cyclic voltammetry and cronocoulometry measurements. The cyclovoltammetric (CV) curves were obtained by the scan rate of 20 $mV.s^{-1}$ and were scanned from 0 V to -2 V, reversed to 2 V and then finished at 0 V. The kinetics of the coloration and bleaching was obtained by applying a cronocoulometric (CC) technique by performing the intercalation of K^+ ions at -1,5 V for 100 s and deintercalation at 2 V (100 s). Reported potentials correspond to the potential applied to the WO_3 film (working electrode) with respect to the platinised SnO_2:F glass substrate (counter electrode).

Results and Discussion

Cyclovoltammetric curves of the HEC cells are shown in Fig. 3, together with the monochromatic transmittance response measured at λ = 634 nm. The CV was measured at a scan rate 20 $mV.s^{-1}$ and starting potential at an initial potential IP = 0 V. At approximately 0.5 V in cathodic direction (Fig. 3B) the current density started to increase significantly and simultaneously the HEC cells began to color (Fig. 3A). The device made from ICS-PPG 4000 sol-gel electrolyte and K^+ ions coloured the most up to -1.5 V while the devices with ICS-PPG 4000 and Li^+ ions coloured up to -1.3 V. No significant changes in order to intensity of coloration/bleaching during the cycling up to 191st cycle were observed. The most interesting finding was that the pre-heating of WO_3 layer influenced the extend of bleaching. Higher transmittance values were obtained for pre-heated WO_3.

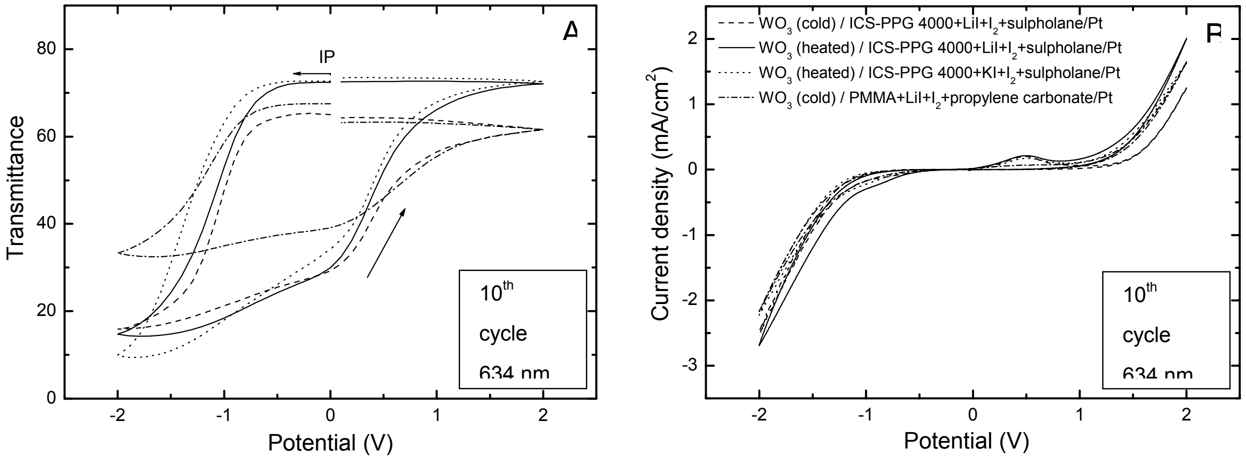

Fig. 3 *In-situ UV-visible spectrochemical measurements of the various HEC cells: A) Transmittance changes, B) CV curves; Cyclic voltammetry was performed between -2 V and 2 V with the scan rate of 20* $mV.s^{-1}$*.* WO_3 *(heated) -* WO_3 *prepared at 450 °C then re-heated prior the cell preparation;* WO_3 *(cold) -* WO_3 *prepared at 450 °C and not re-heated prior the cell preparation.*

The colouring/bleaching changes of the HEC cell with the redox electrolyte are shown in Figure 4. We measured the UV-visible spectra of the HEC devices and we observed the biggest optical change at wavelengths above 600 nm (Fig. 4A, B). The best response was obtained for both devices with pre-heated WO_3, mostly on the area of higher transmittance in the colored state (Fig. 4A). If we look at kinetics during chronocoulometry (Fig. 4C), we can say, that the devices colored in approximately 30 s. The slowest response was found for device with ICS-PPG 4000 and K^+ ions. Bleaching was faster for devices with cold

WO_3, while for devices with pre-heated WO_3. The bleaching of devices with WO_3 pre-heated was more slow but more reversible. The lines of charges (Fig. 4D) suggest that I_3^-/I^- reaction does not occur only at the Pt-side of the device, but also on WO_3 side. Due to the presence of redox I_3^-/I^- pairs and possible reaction at both sides of the self-erasing effect, meaning that we disconnect the device in colored state it bleaches. Self erasing is the fastest for devices with PMMA and the one with ICS-PPG 4000 and K^+ ions.

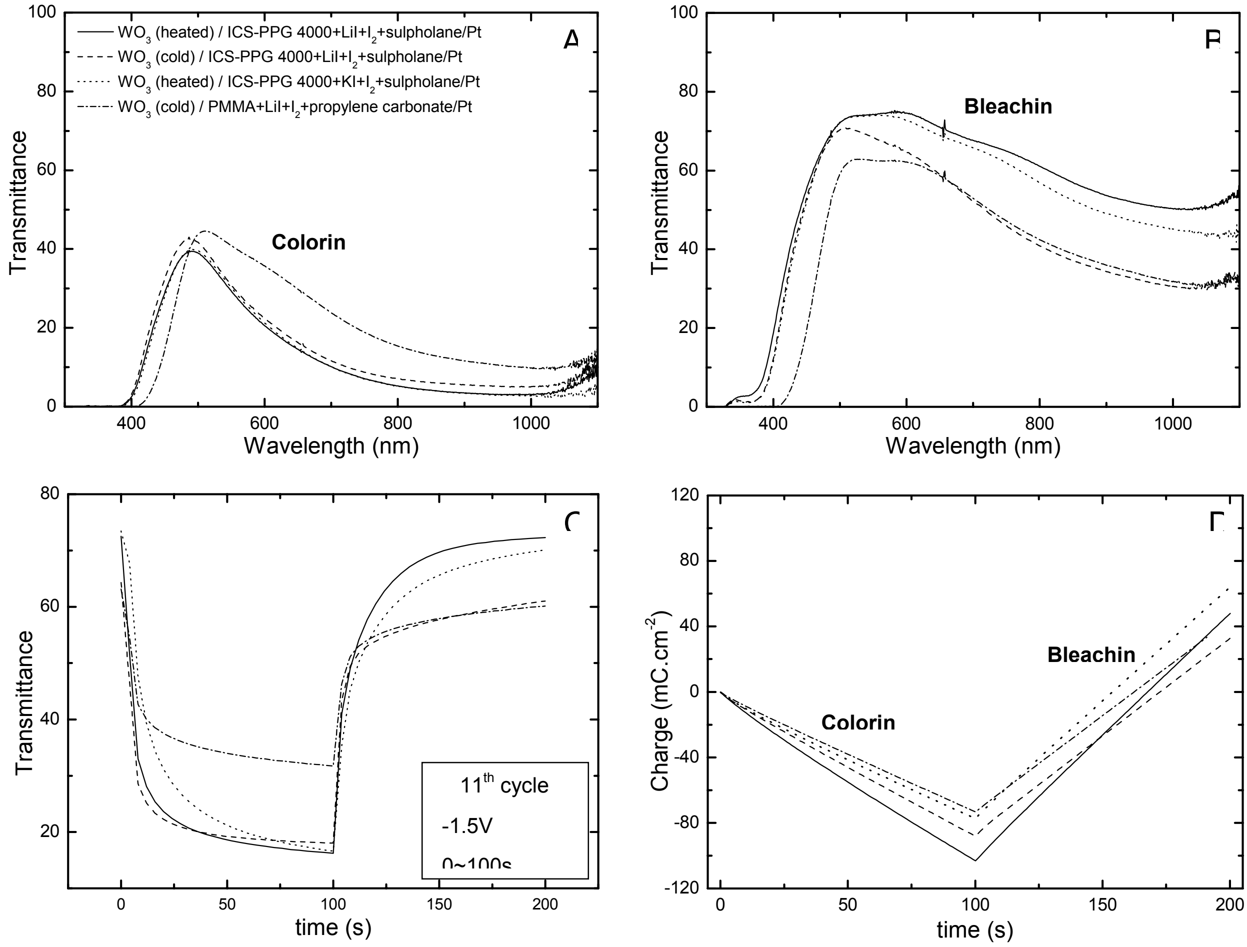

__Fig. 4__ In-situ UV-visible spectrochemical measurements of various HEC cells during colouring/bleaching: A) spectra during coloring, B) spectra during bleaching, C) monochromatic transmittance at 634 nm and D) chronoculometring curves.

Conclusions

We have compared the behaviour of hybrid electrochromic (HEC) devices with incorporated I_3^-/I^- redox pairs in two different kinds of polymer matrix; organic (based on PMMA) and organic-anorganic (based on ICS-PPG 4000).

We can assume that the deepest coloration was achieved for ICS-PPG 4000 with K^+ ions device. The coloration was slightly lower for ICS-PPG 4000 devices incorporating Li^+ ions. The transmittance once after bleaching was about 10 % higher for devices with pre-heated

WO_3 than for devices with cold WO_3. On the other hand, pre-heating of WO_3 slowered the kinetics of coloring. The pre-heating propably influences the OH modes on the surface (like in the case of TiO_2) and though influences the extent of bleaching and the bleaching kinetics.

Acknowledgements

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References

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