

THIN FILMS FOR ELECTROCHROMIC DEVICES

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Introduction

The electrochromic glazing has the composition of special thin films coated on one of its surfaces. This thin film composition consists of the following layers: transparent layer, electrochromic layer (ion host layer), ion conductor, layer of reversible electrochromic layer (ion donor layer), transparent layer deposited on the glass substrate.

The transparent layers of the electrochromic glazing must have high light transmission for visible range of solar radiation, high electric conductivity and chemical and electrochemical neutrality. These layers are connected with electric voltage.

Electrochromic layer is electrochromically active layer in the whole electrochromic system. In the presence of electric field the electrochromic process is occurred within the layer - the insertion of ions and electrons from the ion donor layer. During this process the change of chemical composition of layer and change of its optical properties does not change the material crystalline lattice structure and for this reason the reversible reaction can be activated by change of electric field of reversible polarity and the material turn into the initial phase.

Ion conductor layer is represented by the central electrolyte in the electrochromic film composition. It must have relatively high conductivity – more than 10^{-12} S.cm⁻¹ at the room temperature. High light transmission of the electrolyte is also requirement. Central electrolyte serves as the source of ions for the active layer. This layer serves for the fluent transport of ions between electrochromic layer (host layer) and layer of reversible electrode (ion donor layer).

Reversible electrochromic layer is a layer that can collect ions. Ions from the electrochromic layer transport in the reversible direction into the ion donor layer in the presence of electric voltage of the reversible polarity [1, 2].

Experimental

Experimental investigation of the electrochromic properties of active layers was carried out. Within the frame of this experiments the electrochromic device was completed from the following layers:

1. ITO - sputtered layer as transparent conductive layer
2. WO₃ – electrochromic layer
3. PMMA-LiClO₄ – gel electrolyte as ion conductor
4. V₂O₅ – reversible electrochromic layer
5. ITO - sputtered layer as transparent conductive layer

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The both transparent ITO layers were prepared by the magnetron sputtering deposition method on glass substrates at the Institute of Scientific Instruments of Academy of Sciences in Brno.

Functional active layers (the electrochromic and reversible layer) were deposited by the dip-coating method [3]. Electrochromic layer WO_3 was prepared as the mixture of distilled de-ionized water with tungsten acid H_2WO_4 . Ammonia water was added for dissolution of the tungsten acid during continuous mixing. This compound was mixed about 30 minutes to the complete solution of the tungsten acid. After the mixture filtration phosphorous acid H_3PO_4 was added for acidification of the solution for pH between 1,4 and 1,5.

The solution prepared in the above mentioned way was left for five days to increase its viscosity. The glass substrate with deposited ITO layer was dipped into the solution for 10 minutes [4]. In this way the convenient adhesion of the solution with the substrate was achieved. The glass sample was drawn from the solution with velocity $1,5 \text{ mm}\cdot\text{s}^{-1}$ and then dried up at temperature of 150°C for two hours. After the drying process another layer was deposited in the same way of the dip-coating method. The sample was dried for six hours at the drying temperature in the end. After the drying process the monolithic and transparent layer without deposition defects has been created on the glass substrate.

Reversible electrochromic layer of V_2O_5 was prepared by mixing of ammonium vanadate NH_4VO_3 with distilled de-ionized water and during steady mixing oxalic acid and lithium hydroxide $LiOH\cdot nH_2O$ were added. Phosphoric acid for acidification of the solution was added and the solution was left several days to increase its viscosity.

Substrate with deposited ITO layer was dipped into the solution and left there for 10 minutes - for the better adhesion with the substrate. The sample was drawn up with the drawing velocity $1,5 \text{ mm}\cdot\text{s}^{-1}$ and then it was dried at the room temperature. Three layers were deposited in this process. After the deposition the glass sample was put into the desiccator at the room temperature for two days. After that the sample was slowly tempered up to the temperature of 90°C and dried for two hours. In the end the temperature was slowly increased up to 120°C and the sample was left at this temperature one hour. The cooling of the sample took place in the stove and it was carried out in a very slow process.

The velocity of the heating and cooling process was very important – if the layer is heated for high temperature very quickly it becomes dark and fissured (defected), if it is rapidly cooled it turns white and lost its transparency. The reversible layer had yellow-brown colour after the deposition, during the drying process the colour was changed from yellow-green to blue-green. This colour the sample kept after the drying. The layer has been transparent and monolithic.

The ion conductor layer for the electrochromic glass was created from the gel PMMA electrolyte with $LiClO_4$. Gel was prepared by mixing of MMA (methyl methacrylate), $LiClO_4$, propylene-carbonate and Super-acrylate [5].

Results and Discussion

Measurement of cyclic voltage changes of the deposited glass samples and the completed electrochromic element was carried out with laboratory measurement equipment of the AUTOLAB with three-electrode measurement system. Samples were contacted by a colloid silver coating to decrease electric resistance between ITO layer and electrode (in measurements). Firstly electro-chemical properties of layers WO_3 and V_2O_5 were measured (before the total electrochromic element completion). Subsidiary reference

electrode was contacted with Lithium particles. Electrolyte was created from the solution of LiClO_4 in propylen-carbonate. Results of these measurements are shown in Figure 1 and 2.

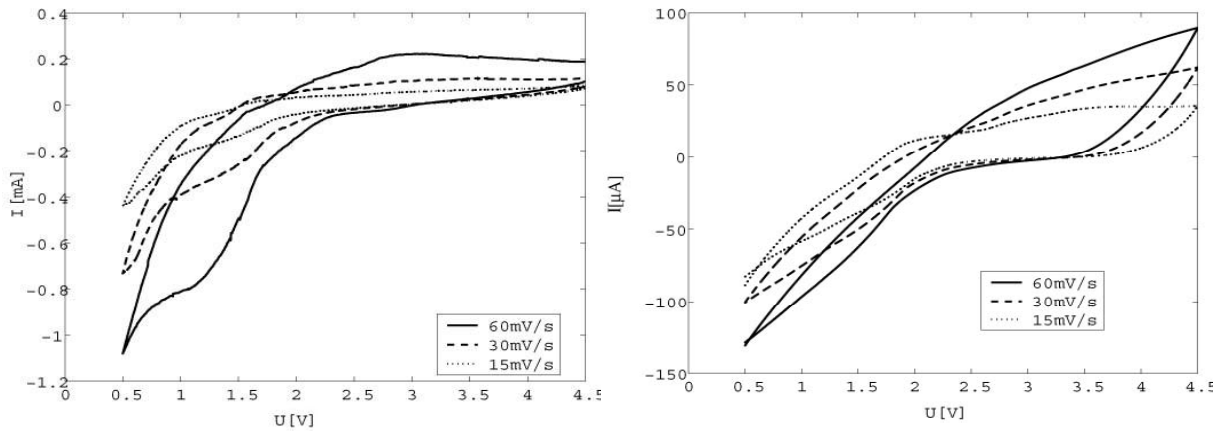


Fig. 1 (left) Cyclic voltametry of WO_3 layer measured in LiClO_4 solution.

Fig. 2 (right) Cyclic voltametry of V_2O_5 layer measured in LiClO_4 solution.

Completed electrochromic sample was completed from layers of WO_3 and V_2O_5 , gel electrolyte with LiClO_4 was used as the ion conductor. After the polymer process the gel was inserted between two glasses with deposited active electrochromic layers. The better adhesion of the gel with active layers was achieved by etching of the gel surfaces with methyl-methacrylate. The whole electrochromic glass sample was compressed in the end. The sample was measured – the monitoring of voltage cyclic changes - see Figure 3.

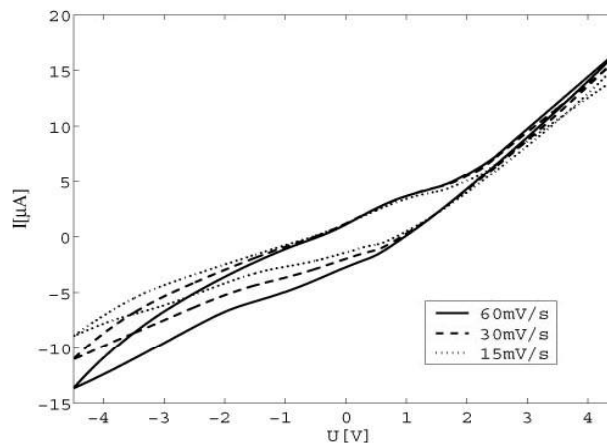


Fig. 3 Cyclic voltametry of completed electrochromic device.

Conclusions

The layer of WO_3 deposited by the dip-coating method has proven electrochromic properties (coloration at voltage of 1 V and lower, bleaching at voltage over 2 V). This process is not totally reversible – during the bleaching process the layer stayed partly coloured. The layer of V_2O_5 (dip-coating deposited) has similar properties as the layer deposited by the magnetron sputtering method. During the completion of the

electrochromic glass sample problems with adhesion of the solution with the substrate and also problems with temperature changes in layers during the deposition and stabilisation were monitored. Completed element is coloured at voltage about -2V and bleaching process (not totally reversible) was measured at voltage of +2.5V.

Acknowledgements

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