

ELECTRODEPOSITION OF THIN LAYERS FOR ELECTROCHROMIC DEVICE

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Abstract: Two different thin layers, tungsten oxide (WO_3) and titanium dioxide (TiO_2), were separately deposited electrochemically on ITO glasses and then treated by heat. In the first part of the work, optical and electrical properties of electrodeposited WO_3 were observed in dependence on deposition time and thermal treatment. As an ion-conductive layer, there were used two different electrolytes, one containing lithium ions and other one containing sodium ions. The second part of the work is focused on preparing of TiO_2 and its using as an active electrochromic layer. Different deposition times were observed, as well as heat treatment of electrodeposited layers.

Keywords: Electrochromism, electrodeposition, WO_3 , TiO_2

1. INTRODUCTION

Electrochromic materials can be divided into three groups: inorganic cathodic compounds, inorganic anodic compounds and organic and polymeric compounds. These materials must be prepared as thin layers on an electrically conducting substrate. Glass sheets covered by Indium Tin Oxide (ITO) or Fluorine-doped Tin Oxide (FTO) layer are usually the material of first choice. This work is concentrated on electrochromic oxides.

Tungsten oxide (WO_3) is the most common material used in commercial so called “smart windows”. All layers (conductive, active, ion-conductive and ion-storage layers) are usually prepared by vacuum method, e.g. ion sputtering, evaporation. Electrodeposition seems to be also applicable and perspective method, thus this method was used for preparing thin layer of WO_3 . This material has outstanding properties for using in electrochromic device. Its impressive ability of incorporation ions and darkening to almost non-transparent level make it very valuable in optic industry. However, there are some disadvantages connected with it: the first disadvantage is its tinting to blue color, which can be found inappropriate in some situations; the second disadvantage is high price of tungsten. Therefore, there is a place for looking for new materials that could have comparable electrochromic options without its disadvantages. In this work, titanium dioxide (TiO_2) will be prepared as a thin active layer for electrochromic device and compared with WO_3 .

2. EXPERIMENTAL

A solvent for electrodeposition of WO_3 layers was prepared by dissolving tungsten powder in a mixture of 30% hydrogen peroxide and distilled water. The dissolving was carrying out in the fridge in order to subdue the exothermic reaction. After 24 hours of stirring, the solvent was filtered and acetic acid was added in it. Then, it was refluxed by using heat 55 °C for 6 hours in order to decompose the rest of hydrogen peroxide and to acetylate peroxy-tungsten acid. After this, ethanol was added in the solvent in ratio 1:1 to increase adhesivity. Prepared solution must be stored in cold (<10 °C) and can be used for deposition within 10 days.

Thin layer of WO_3 was electrodeposited onto ITO conductive layer on glass sheet. It was used potential $U_{\text{DEP}} = -0,45 \text{ V}$ versus $\text{Ag}/\text{AgCl}/\text{KCl}$ reference electrode. Platinum electrode was used as a counter electrode. In order to find out the dependence of electrochromic properties on deposition time, the layers were deposited for five different times t_{DEP} (5 to 15 minutes). The current was measured by ampere-metric method and varied between $-2,3 \text{ V}$ and -3 V , figure 1. Some samples were treated by heat (60 to $200 \text{ }^\circ\text{C}$) for 1 hour.

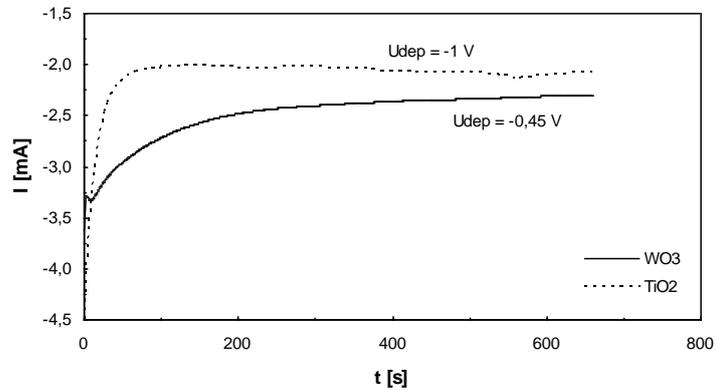


Figure 1: Dependence of current on deposition time for different layers and using different potentials

A solvent for deposition of TiO_2 layers was prepared by dissolving $\text{C}_4\text{K}_2\text{O}_9\text{Ti}$ and KNO_3 in deionized water. The pH value was approximately 4,5. Layers were deposited by using cathodic reduction method on glass sheet coated with ITO. Platinum was used as a counter electrode and potential was measured versus saturated calomel electrode (SCE). By using EQCM method, it was found, that the best potential for deposition is about -1 V , figure 2. There were chosen four different times of deposition t_{DEP} (5 to 11 minutes). The electric current varied between -2 V and $-2,2 \text{ V}$, figure 1. In purpose to improve chemical stability and mechanical properties, some of obtained samples were treated by heat (80 to $320 \text{ }^\circ\text{C}$) for 1 hour.

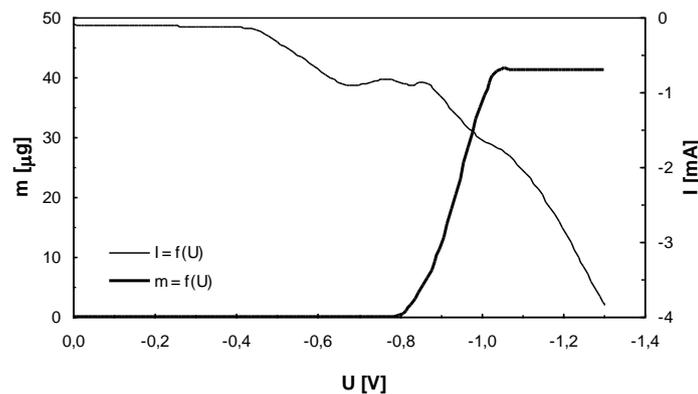


Figure 2: TiO_2 thin layer electrodeposition on EQCM platinum crystal

Electrochromic device was simulated by using liquid electrolyte (LiClO_4 or NaClO_4 dissolved in propylene carbonate) as an ion-conductor, platinum electrode as a counter electrode and electrodeposited thin layer (WO_3 or TiO_2) as an active electrochromic layer. The potential was set versus Cd/Cd^{2+} (WO_3) or SCE (TiO_2) reference electrode.

3. RESULTS

Electrodeposited thin layers of WO_3 were compact and fluent with no cracks or blurs. Longer deposited layers were thicker (15 minutes = 526 nm) and darker than layers deposited shorter time (5 minutes = 203 nm). In the figure 3, voltammogram shows that applying the same potential it was obtained higher electric current at layers deposited longer time (e.g. 15 minutes) than layers deposited shorter time (e.g. 5 minutes). Higher current represents more drifting lithium ions in electrolyte and incorporating into the layer. Although, the reversibility is poorer as the deposition time is increasing.

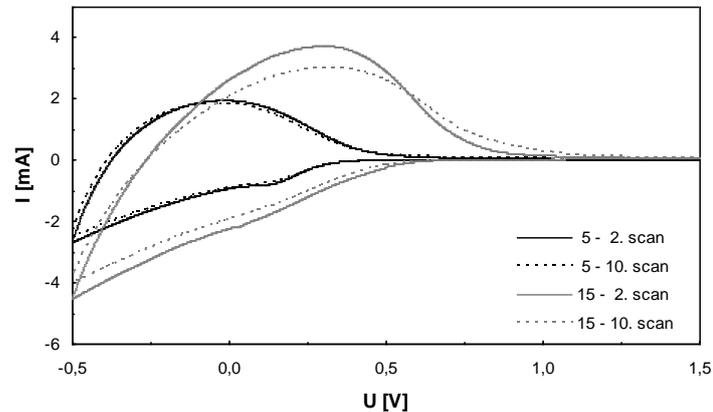


Figure 3: Cyclic voltammogram of WO_3 layers in 0,5 M LiClO_4 electrolyte deposited with different deposition time

By using spectrophotometric method, the transparency was observed during voltammetry. Higher amount of lithium ions incorporating into the crystalline structure of WO_3 deposited longer time occurs lower transparency of the layer, as it is shown in figure 4. The sample deposited for 15 minutes was even able to get colored to 15 % transparency. On the other hand, the sample deposited just for 5 minutes was able to reach 50 % transparency, but in bleached state the glass was transparent as well as an ordinary glass without any coating – it was more than 90 % transparent.

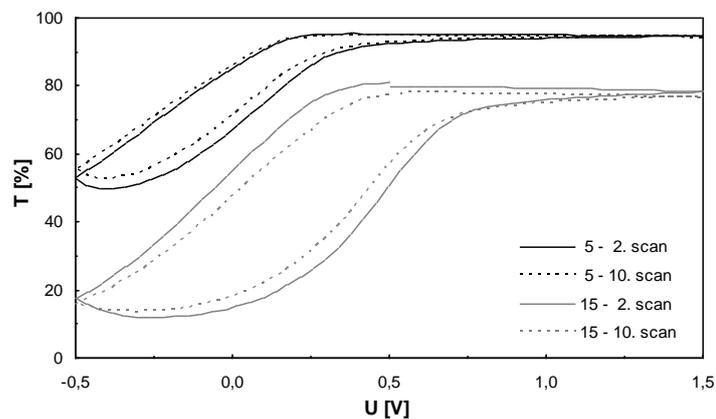


Figure 4: Dependence of the WO_3 layered glass transparency on potential in 0,5 M LiClO_4 electrolyte

Transparency dependence on wave length of WO_3 layered glass is shown in figure 5. The samples in colored state are more transparent in range 400 to 500 nm than other spectrum. This can be explained by the color shade of the sample after incorporation of lithium ions into the layer.

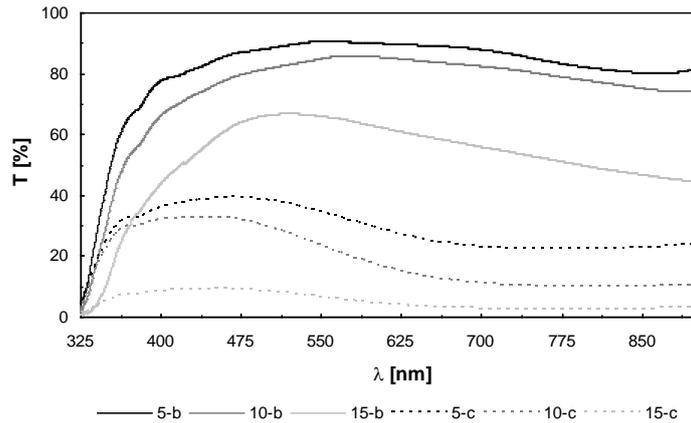


Figure 5: WO₃ layered glass transparency dependence on wave length in bleached (lines) and colored (dots) states

On the figure 6, there is shown the impact of the heat treatment on WO₃ properties. The layers treated by temperature 60 °C have worse ability to incorporate lithium ions into their structure, but on the other hand, they prove better performance in bleached state – they become more transparent after changing the polarity of potential. Higher temperature (e.g. 120, 200 °C) significantly aggravates the properties of the layer and this layer is not applicable for using in electrochromic device.

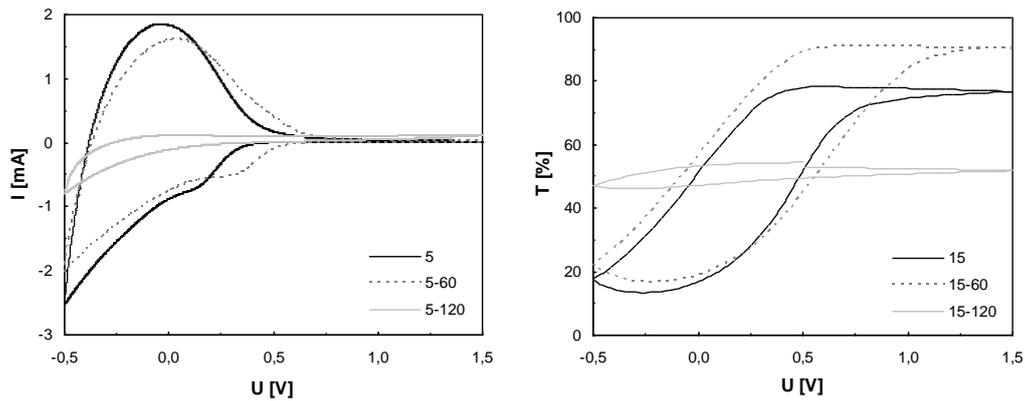


Figure 6: Impact of the heat treatment on WO₃ thin layer and its electrochromic properties

Electrodeposited WO₃ thin layer performs very good electrochromic properties also in using with sodium ions. In long term cycling, WO₃ shows better performance in LiClO₄ electrolyte, incorporating of sodium ions into the layer is less reversible than lithium ion incorporation, figure 7.

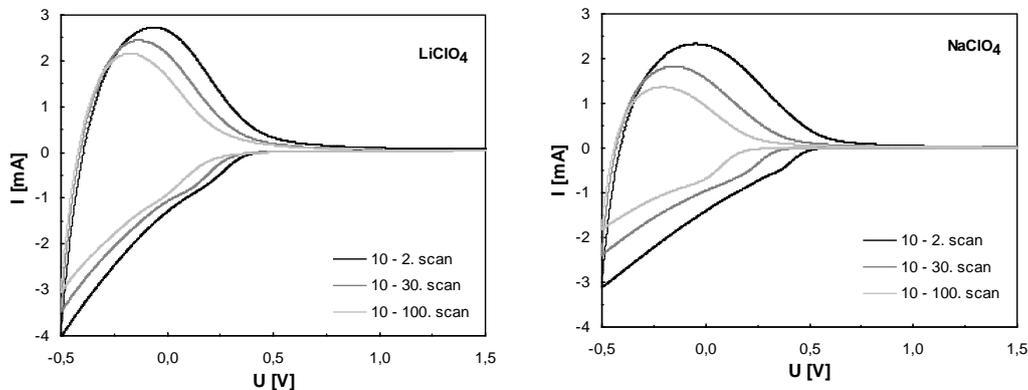


Figure 7: Comparison of using WO₃ in 0,5 M LiClO₄ and 0,5 M NaClO₄ electrolyte

Thin layers of TiO₂ were electrodeposited for four different deposition times: 5, 7, 9 and 11 minutes. The best electric properties were shown by the sample with TiO₂ layer deposited for 7 minutes. Deposited sample had light yellowish color. In figure 8, there is comparison between TiO₂, WO₃ and conductive ITO layer. Higher potential has to be applied for incorporation lithium ions into TiO₂ layer than into WO₃ layer. In TiO₂, the process of incorporation ions into the layer takes longer time and it is less efficient than in case of WO₃. Despite of this, TiO₂ layer can be used as an active layer in electrochromic device. Incorporation process seemed pretty reversible. In colored state, TiO₂ becomes dark brown.

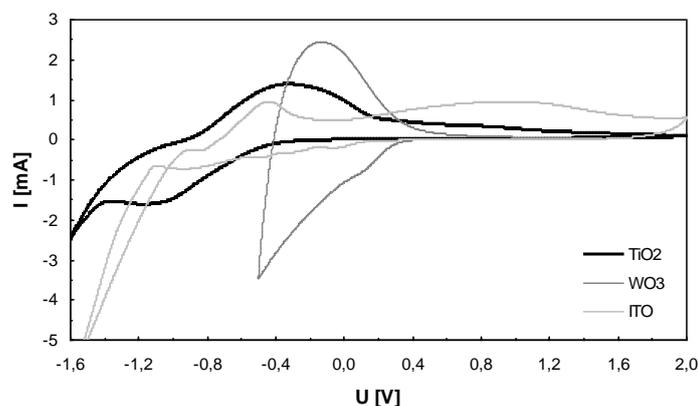


Figure 8: Cyclic voltammetry of TiO₂, WO₃ and ITO layers in 0,5 M LiClO₄

It was found that heat treatment has negative impact deposited TiO₂ layer. None of treated layers had as good properties as layer which had been dried at room temperature.

4. CONCLUSIONS

Electrodeposited WO₃ thin layers proved very good electrochromic performance. The sample with WO₃ deposited for 15 minutes under -0,45 V was able to tint to almost 15 % transparency and reversibly bleach to 80 %. The stability was performed by 100 cycles; the reversibility appeared to be steady. Drying of samples by 60 °C improved their optical properties in bleached state, although the optical properties in colored state get worse. Implying higher temperature significantly aggravated overall properties.

By using EQCM method, it was found that it is possible to prepare thin layer of TiO₂ by cathodic reduction. There were found fair electrochromic properties at sample deposited for 7 minutes at -1 V. Heating process did not improve its properties.

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