Preparation, Electronic Structure and Optical Properties of the Electrochromic Thin Films[*]

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Abstract. A new multilayer electrochromic device has been constructed according to the following pattern: $glass_1$/ITO/WO_3/gel electrolyte/BP/ITO/$glass_2$, where ITO is a transparent conducting film made of indium and tin oxide and with the surface resistance equal 8–$10\,\Omega/cm^2$. The electrochromic devices obtained in the research are characterized by great (considerable) transmittance variation between coloration and bleaching state (25–40% at applied voltage of 1.5 to $3\,V$), and also high coloration efficiency (above $100\,cm^2/C$). Self-consistent energy bands, dielectric permittivity and optical parameters are calculated using a full-potential linear muffin-tin orbital method. The numerical solution of the Debye-Smoluchowski equations is developed for simulating recombination probability of Li^+ ions in amorphous electrolyte.

Keywords: electrochromic device, band structure, optical properties.

1 Introduction

Electrochromic devices have many application possibilities in display devices, optical shutters, smart windows and mirrors because of the many advantages of open circuit properties, low power consumption and high coloration efficiency, etc.

The electrochromic multilayer device is characterized by its ability to sustain reversible and persistent changes of the optical properties when voltage is applied to it. The basic function of the electrochromic (EC) device is to exhibit repeated coloration/bleaching cycles with back and forth sweep of small voltages.

The multilayer electrochromic device has a sandwich structure (consists of many layers). Numerous studies [1–6] have been conducted on the electrochromic device in the following form: glass/ITO/WO_3/electrolyte/BP/ITO/glass, where ITO is a transparent conducting layer made of indium tin oxide film. The electrolyte function is very important: it should be a good conductor for small voltages, and a good isolator, when there is no voltage applied.

Searching for the optimal properties of the electrolyte, and thus – of the electrochromic device, resulted in using different electrolytes, varying in their composition and the preparation methods, even in the case of devices consisting of the same layers, i.e., PEO+$LiClO_4$+PC+EC [1], PEO+PC+$LiClO_4$ [2], PMMA+PC+EC+$LiClO_4$ [3], PMMA+PC+EC+$LiClO_4$+THF [4], PVC+PC+EC +$LiClO_4$+THF [5, 6], where: PEO – poly(ethylene oxide), PC – propylene carbonate, EC – ethylene carbonate, PMMA – polimethylmetacrylate, THF – tetrahydrofuran, PVC – poly(vinylchloride).

In the presented work, the following multilayer electrochromic device was constructed: $glass_1$/ITO/WO_3/electrolyte/BP/ITO/$glass_2$. A new electrolyte was prepared for the device, and the influence of the thin films preparation methods on the final electro-optical properties of the obtained multilayer devices was established.

2 Experimental

The device to be used for electrolytic deposition of (WO_3) thin films and the prussian blue films was built of the following elements: generator, allowing performance at the galvanostatic conditions, with the possibility of changing applied current voltage and density; suitable measurement instruments (ammeter and voltmeter); and an electrolyte plate with a coat controlled by an external thermostatic device, allowing performance at constant temperature. The process of electrodeposition was performed at the temperature of $25°C$. During the films deposition, the following elements were placed inside the electrolyte plate: glass

plate with an ITO layer and additional electric input in the form of a silver way, an opposite electrode consisting of a platinum net of the same external measures as the plate with the layer ($5 \times 5\,cm^2$); and a reference electrode, which was a saturated calomel electrode (SCE). There was an additional electrical input in the form of a silver belt, placed on the top of the ITO-coat substrate. (Conductive silver belts were applied on the top of the ITO-coat substrate). The sheet resistance of ITO-coated glass substrates was measured by the four-point probe method and was 8–$10\,\Omega/cm^2$.

The electrodeposition was performed from the solution of sodium tungstate two hydrate ($Na_2WO_4 \cdot 2H_2O$), at the concentration density of 0.25, 0.4 and $0.5\,mol/dm^3$ and the pH equal 7.0. After dissolving sodium tungstate in redistilled water, pH of the solution was at the range of 8.9–9.8. In order to obtain a proper pH value, a certain amount of oxalic acid was being added, under the control of a pH-meter. During the electrodeposition, different current densities: 50, 100, 150, $200\,\mu A/cm^2$ were applied. The time of deposition varied from 10 to 90 minutes. Practically, it resulted in a charge per surface unit of $20\,mC/cm^2$ to $800\,mC/cm^2$, and the controlled potential against the saturated calomel electrode (SCE) during the electrodeposition varied between $-1.08\,V$ and $-1.59\,V$. The deposited films underwent thermal treatment of heating at the temperature of $300°C$, $400°C$, and $450°C$, in the air atmosphere, during 1 to 3 hours. Under the conditions of the temperature changes, it is possible to obtain different layer structures (crystal or mixed, it means, partly crystal, and partly amorphous). To obtain a double layer, we first crystallized a WO_3 film by annealing in air at a temperature of $450°C$ for $1\,h$ and subsequently we electrodeposited on it another WO_3 film and annealing in air at a temperature of $300°C$ for $1\,h$. Films was of the double layer structure; crystalline and amorphous/crystalline [7, 8].

Optical properties of the obtained layers were studied through the measures of transmission in the range of 1.0 to $4.0\,eV$ (relation $T = f(E)$ on the spectrophotometer HACH DR-4000/U.

The device to be used for electrolytic deposition of (WO_3) thin films and the prussian blue films was built of the following elements: generator, allowing performance at the galvanostatic conditions, with the possibility of changing applied current voltage and density; suitable measurement instruments (ammeter

and voltmeter); and an electrolyte plate. The solution adequate for the deposition was made by mixing a solution of hexacyanoferrate (III) potassium – $K_3[Fe(CN)_6]$ of $0.01 \, mol/dm^3$ concentration with a solution of ferric (III) chloride – $FeCl_3$ of $0.01 \, mol/dm^3$ concentration, in the proportion (ratio) of 1:1. The solution contained $5 \, mM$ of $FeCl_3$ and $5 \, mM$ of $K_3[Fe(CN)_6]$. The thickness of the PB was controlled by counting the passed charge, witch is proportional to the amount of PB deposited. The charge capacity for the deposition was controlled at $5.0 \, mC/cm^2$ to $20.0 \, mC/cm^2$. The conditions of the electrodeposition were as follows: current density was 5, 7.5, 10, $15 \, \mu A/cm^2$, the charge density between $5 \, mC/cm^2$ and $20 \, mC/cm^2$, electrodeposition potential, measured in the reference to the saturated calomel electrode, was at the range of $+0.71 \, V$ to $+0.85 \, V$, depending on the surface resistance of the ITO layer and current density.

The electrolyte which contained a matrix consisting of two polymers (contest: 38% EC, 38% γ-BL, 8% $LiCF_3SO_3$, 10% PMMA, 6% PEO, THF) presented the best properties. Its high conductivity ($\sigma = 4.8 \, mS \cdot cm^{-1}$) ability to easy deposition onto the layers, stability (resistance) in time, and a high transmittance value of radiation in the visible region makes it very useful in the electrochromic devices.

The assembly of the seven-layer electrochromic device was performed according to the presented pattern (Fig. 1): glass/ITO/WO_3/electrolyte/BP/ITO/glass, where ITO was an indium – tin oxide film, WO_3 – electrochemically deposited tungsten oxide film, and BP – electrochemically deposited prussian blue film. Before assembling the multilayer electrochromic device, the WO_3 electrode was pre-charged with protons.

A constant current density of $0.10 \, mA/cm^2$ was used in cathodizing the tungsten oxide electrode for $5 \, min$ into the tungsten oxide thin film to create tungsten bronze, H_XWO_3. The tungsten bronze was then rinsed with distilled water and dried in air atmosphere. In the multilayer electrochromic device thin layer WO_3 with H_XWO_3 was the working electrode and BP was counter-electrode. The polymer electrolyte was flow-coated on both electrode and laminated 2 days. Procedure resulted in an averaged thickness of $150 \, \mu m$ for the copolymer electrolyte as measured by a micrometer across the samples.
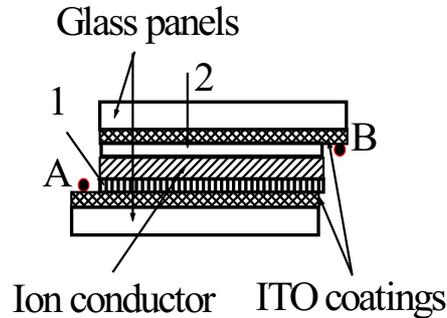
Fig. 1. Schematic representation of the assembling of the electrochromic device. Electrochromic layer (1) is WO_3, counter electrode (2) is Prussian blue film, A and B – silver-way.

3 Theorie

The band structure of the $LiWO_3$ was calculated using ab-initio fully self-consistent density functional method within the local density approximation. Basic functions and matrix elements were constructed using a full-potential linear muffin-tin orbital method (FP-LMTO). Technical details of this method are presented in work [9]. The exchange and correlation potential was parameterized according to local density approximation [10].

The equilibrium structure for the $LiWO_3$ is calculated by examining the behavior of the total energy as a function of lattice constant a_0. The equilibrium lattice constant for perfect perovskite phase of $LiWO_3$, is found from the total-energy minimization $a_0^{theor} = 3.81$ Å. This is in good agreement with experimental value $a_0^{exp} = 3.71$ Å. The tetrahedron integration of this work was performed using a $(6, 6, 6)$ special k-points mesh. The zero-temperature energy-dispersion curves of the perfect perovskite phase for $LiWO_3$ are shown in Fig. 2.

As we can see from Fig. 2 the compound $LiWO_3$ is characterized by the presence of energy gap between the upper filled valence band and partly filled conduction band. Fermi level is located approximately in the lower part of the conduction band. This result is in satisfactory agreement with the theoretical data [11]. The band gap, now located in the occupied part of the spectrum, is increased to 1.1 eV.
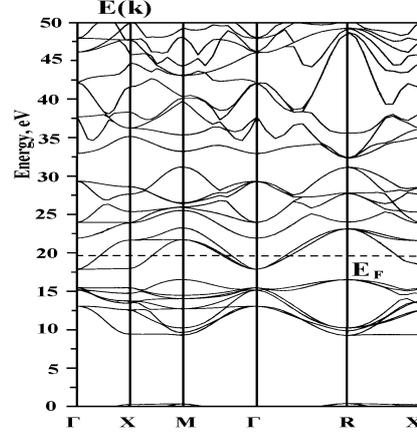
Fig. 2. Band structures for LiWO$_3$.

The macroscopic imaginary part dielectric function in the random-phase approximation [12] is expressed by the form:

$$\varepsilon_2(\bar{q}, \omega) = \varepsilon^{intra}(\bar{q}, \omega)$$

$$+ \frac{8\pi}{q^2\Omega} \sum_{n \neq l, \bar{k}} \frac{\left[f_l(\bar{k} - \bar{q}) - f_n(\bar{k})\right] \left|\langle n, \bar{k}|e^{i\bar{q}r}|l, \bar{k} - \bar{q}\rangle\right|^2}{E_{l,\bar{k}-\bar{q}} - E_{n,\bar{k}} + \hbar\omega}, \quad (1)$$

where the first term represents the intraband contribution and is expressed as Drude formula [13]. The second term in (1) contains the transitions from occupied states in valence bands to unoccupied states in conduction bands. $E_{n,\bar{k}}$ and $|n, \bar{k}\rangle$ are the energy eigenvalues of Hamiltonian and the corresponding wave functions, $f_n(\bar{k})$ is the Fermi-Dirac distribution function.

The frequency-depended dielectric functions of LiWO$_3$ were calculated using (1) and Kramers-Kronig relations. Fig. 3 show the results of these calculations in the optical limit ($\bar{q} \to 0$). As can seen from Fig. 3, the onset of the absorption edge in ε_2 occurs at $3.4\,\text{eV}$ which corresponds to the transitions from occupied states in the upper part of valence band (M) to unoccupied states in conduction bands nearly of the Fermi level.

The optical properties of LiWO$_3$ have been calculated using imaginary part of the permittivity. Fig. 4 display the experimental transmittance spectrum of the system: glass1/ITO/WO$_3$/gel electrolyte/BP/ITO/glass$_2$ and calculated parameter

of absorption for LiWO$_3$. The absorption function for LiWO$_3$ calculated from interband and intraband transitions, has a peak around an energy of electromagnetic radiation $5.3\,\text{eV}$.
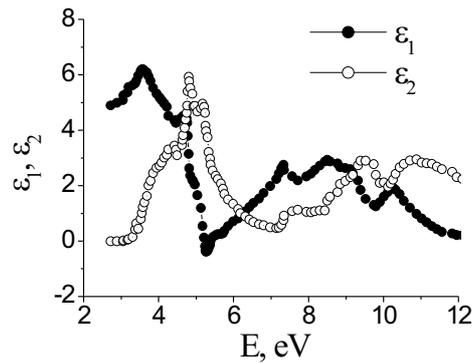
Fig. 3. Imaginary (2) and real (1) part of permittivity of LiWO$_3$.
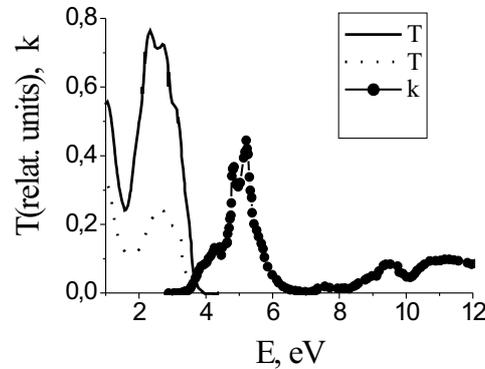
Fig. 4. Experimental transmittance spectrum of the system: glass$_1$/ITO/WO$_3$/gel electrolyte/BP/ITO/glass$_2$. (Solid line – bleached, dot line – colored). Calculated parameter of absorption (k) of LiWO$_3$.

We formulated model of the Li$^+$ diffusion process for hydrocarbon amorphous electrolyte. The theory based on the hopping diffusion model. The diffusion coefficient and jump length for the Li$^+$ ions are calculated. $D^{theor} =$

$0.72 \cdot 10^{-2}\,\mathrm{m^2/s}$. We have developed a method of diffusion-controlled reactions [14] for simulating of Li^+ recombination process.

The numerical solutions [15] of the Debye-Smoluchowski equation

$$\frac{\partial n(\bar{r}, t)}{\partial t} = \nabla \left[D^{theor} \left[\nabla n(\bar{r}, t) + \frac{n(\bar{r}, t)}{kT} \nabla V(\bar{r}) \right] \right], \qquad (2)$$

where

$$V(\bar{r}) = -\frac{e^2}{\varepsilon r} \qquad (3)$$

is developed for calculating recombination times of Li^+ ions in electrolyte. Fig. 5 shows of the Li^+ recombination probability as a function of time.
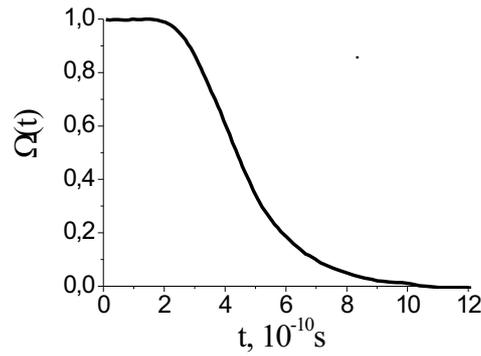
Fig. 5. Survival probability of Li^+ ions as a function of time.

4 Conclusions

Application of tungsten oxide of double layer structure (crystalline and amorphous/crystalline) in our experiments turned to be a very good solution, and also resulted in obtaining very good properties of the electrochromic devices constructed in our research.

We have reported ab-initio, self-consistent calculations (using the local approximation to density functional theory) for the electronic structure of cubic $LiWO_3$. Fermi level is located in the conduction band. Calculated band structure

LiWO$_3$ gives a metal state which is in agreement with other theoretical date. The calculated spectrum of the imaginary part dielectric permittivity and absorption function for LiWO$_3$ show that the onset of the absorption edge occurs at 3.4 eV.

The theoretical recombination times have been evaluated using the numerical solutions of the Debye-Smoluchowski equation.

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