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ИССЛЕДОВАНИЕ ПОВЕРХНОСТЕЙ ОТКЛИКА, ОПИСЫВАЮЩИХ МАТЕМАТИЧЕСКУЮ МОДЕЛЬ ВЛИЯНИЯ ТЕМПЕРАТУРЫ И СОДЕРЖАНИЯ ВЕО В КОМПОЗИЦИОННЫХ МАТЕРИАЛАХ НА ПРЕДЕЛЫ ТЕКУЧЕСТИ И ПРОЧНОСТИ

Методом ридж-анализа проведено исследование поверхностей отклика, описывающих математические модели влияния температуры и содержания ВеО на границы прочности и текучести композиционных материалов, используемых, в частности, при производстве авиационной техники. Показано, что на основе математической модели, построенной путем реализации центрального ортогонального композиционного плана (ОЦКП) второго порядка, могут быть найдены субоптимальные значения технологических режимов. Эти режимы обеспечивают получение оптимальных значений границ текучести и прочности композиционного сплава на основе бериллия с учетом ограничений, налагаемых на технологический процесс.

Ключевые слова: ридж-анализ, субоптимальные значения, композиционный материал, оксид бериллия, предел текучести, предел прочности, поверхность отклика.

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THE DETERMINATION OF ELECTROLYTE STABILITY AND CONDITIONS FOR ELECTROCHROMIC WO₃ FILMS DEPOSITION

Для осаждения электрохромных плівок WO₃ запропоновано гальваностатичний режим: $i_c = -0.2 \text{ mA/cm}^2$, 30 хв. Плівки, отримані у таких умовах прозорі, якісні та мають гарну адгезію до основи. Показано, що використовуваний електроліт нестабільний та з часом змінює свої властивості. Для відновлення електроліту запропоновано додавати перекис водню згідно з рецептурою.

Ключові слова: оксид вольфраму, осаження електрохромних плівок, пероксовольфрамова кислота, вікно потенціалів.

1. Introduction

Electrochromic devices are a class of devices that under applied current are able to change their optical properties:

glossiness, color, transparency. The electrochromic devices can usually be in few optical states: uncolored, colored and partially colored. Optical properties of electrochromic devices can be controlled by applying electrical current of different

polarity for different duration. Electrochromic devices can be potentially applied in automobile and building industry (Fig. 1), and also in advertisement industry and design.

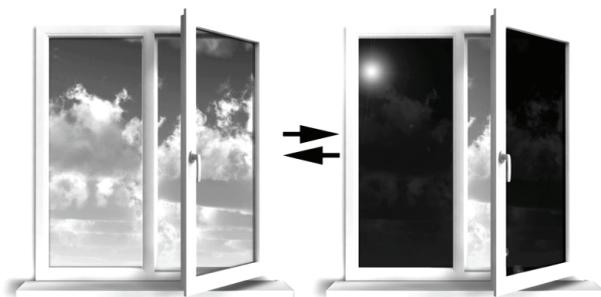


Fig. 1. An example of «smart windows» based on electrochromic glass panes

These devices can also find application in manufacturing of indicators for slow-changing values – room or outdoor temperature, gas prices, currency exchange rates etc. The electrochromic devices that switch between transparent and opaque state can be used in hospital as privacy curtains for examination rooms.

Nevertheless, the main advantages of using electrochromic devices are mentioned in paper [1]:

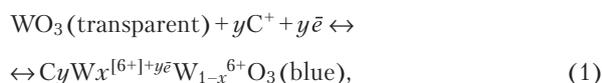
«...the computer modeling of energy consumption has showed, electrochromic windows decrease energy consumption on room conditioning by up to 49 %, and decrease electricity consumption in «prime time» by 16 % and lighting expenses to 51 %».

Also, some electrochromic systems can be used as chemical power sources. This way, by changing the optical state such systems can store electrical energy. When use of electrochromic systems is unnecessary (during night time or non-working hours), the stored energy can be released allowing for additional savings of energy resources.

Thus the research aimed at the development of electrochromic material deposition methods, operation regimes of electrochromic devices, and also research of already existing electrochromic materials are important from perspective of energy efficiency of individual objects and country as a whole.

2. The object of research and its technological audit

Many systems that can potentially be used in creation of electrochromic devices are known [2]. Among such systems, the inorganic electrochromic materials, which are a subject of present research, are well known. The color change of these materials is a result of an electrochemical reaction. The initial state, which is usually transparent, changes to colored as a result of electrochemical reduction (the so-called cathodic materials) [3, 4] or electrochemical oxidation (the so-called anodic materials) [5, 6]. The tungsten trioxide is a well-known cathodic material [7]. The reaction occurring during coloration can be written as follows:



where C – cation: H^+ , Li^+ , Na^+ (depending on electrolyte); $x < 1$.

High coloration efficiency and reversibility of WO_3 are the main advantages of this electrochromic material. WO_3 films are consider to other anodic electrochromic material – $\text{Ni}(\text{OH})_2$. The latter, being oxidized to NiOOH , gives brown color.

Blue WO_3 and brown NiOOH , when added produce color from neutral grey to black, depending on film thickness (Fig. 2), i. e. almost without secondary shades.

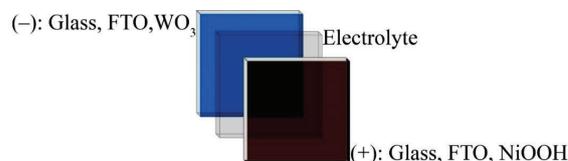


Fig. 2. A schematic of an electrochromic device with two electrochromic layers

Many methods for deposition of WO_3 are known: spray pyrolysis [8], solution hydrolysis [9], vacuum sputtering [10], anodic electrodeposition [11], hydrothermal method [12] cathodic electrodeposition [13], magnetron sputtering [14]. Among all method, the electrodeposition has few advantages: simplicity of automation and control over film parameters, no requirements for complex equipment and powerful power sources. A simplified method for electrodeposition of WO_3 was proposed in paper [12]. The electrolyte composition was as follows: 0.0125 M Na_2WO_4 , H_2O_2 with various ratios between Na_2WO_4 and H_2O_2 . The electrochemical deposition was carried out by applying constant negative potential for a certain time. With such implementation, the current density would vary with time. Thus, in opinion of authors, such method is not suited for a real production process because of difficulties with controlling the thickness and film structure. It should also be noted, that hydrogen peroxide is not stable and decomposes when exposed to light. This can cause changes in electrolyte composition, which would affect the deposition process and properties of prepare WO_3 .

3. The aim and objectives of research

The aim of the research is to find conditions and intricacies of WO_3 film deposition made from peroxotungstic acid-based electrolyte.

In order to achieve the aim, few objectives are formulated:

1. Find the electrodeposition regime, at which transparent WO_3 films with good adhesion to substrate and electrochemical properties can be prepared.
2. Determine the stability of peroxide-based electrolyte.
3. Find the potential window for cyclic voltammetry, in which the WO_3 can be reversibly colored without changes in properties of conductive substrate.

4. Research of existing solutions of the problem

Before starting the experiments the possible distribution of current density along the height of working electrode was analyzed. Because solution used in experiments is acidic its conductivity is rather high. On the other hand, the fluorine-doped tin oxide coated glass (further referred to

as FTO glass) would be used as a substrate. The material possesses high degree of transparency and high conductivity, albeit lower than metallic conductors [15, 16]. Based on that, it is assumed that increasing current density would result in reduced uniformity of current distribution, which would negatively impact uniformity of the film.

For deposition of nickel hydroxide thin films from aqueous solutions using similar technique, a current density of -0.1 mA/cm^2 is used [17]. For deposition of WO_3 from peroxotungstic acid-based electrolytes even higher current densities are used [18, 19]. Thus the initial current density and time were set to minimum according to [17]: -0.1 mA/cm^2 , 10 min. In addition, high cathodic current densities in acidic media can lead to dissolution of conductive layer of FTO glass [20, 21]. However, the WO_3 films prepared at such conditions had low degree of coloration, which authors tied this to their low thickness. Because of that, the current density and deposition time were increased to -0.2 mA/cm^2 and 30 min.

The change of electrolyte's properties was discovered when stored electrolyte was used for film deposition. The change of peroxotungstic acid-based electrolyte's properties with time was never mentioned in literature [13, 18, 19, 22]. Except for [23], where it is said that such electrolytes are rather stable.

In order to identify and analyze the instability of electrolyte, the electrolyte was 'aged' at room temperature and lighting. The change in electrolyte properties was evaluated based on properties of prepared films. Assuming the stability of peroxotungstic acid, the electrolyte was regenerated with hydrogen peroxide solution, which was added after an insoluble precipitated on the walls of the flask.

Few attempts were also made in order to establish the working potential window. Different values of upper and lower potentials were used in experiments, with constant rate of potentiodynamic measurements of 5 mV/s . When searching for lower potential (the more negative), the lower limit at which reduction of conductive coat to metallic tin, with highest degree of coloration was established.

5. Methods of research

All experiments were conducted using analytical grade reagents.

For deposition of WO_3 film following electrolyte solution was used: $0.0125 \text{ M Na}_2\text{WO}_4$, H_2O_2 with ratio of, acidified with HNO_3 to pH 1–2. The films were deposited on to FTO glass ($\Omega = 7.5 \text{ Ohm/cm}^2$, Working area $2 \times 2 \text{ cm}$).

In order to evaluate optical and electrochemical characteristics, the cyclic voltammetry (CVA) with simultaneous recording of coloration-bleaching process was used. The cell depicted in Fig. 3 was used for this purpose.

The reference electrode was Ag/AgCl (KCl sat.) electrode (not shown in Fig. 3). The counter-electrode was made from nickel foil. $0.1 \text{ M H}_2\text{SO}_4$ solution was used as electrolyte in all experiments. The optical characteristic was recorded with ADC E-154 (Russian Federation), electrochemical characteristic were recorded using digital potentiostat-galvanostat Elins P-8 (Russian Federation). Cycling parameters: potential window from -400 to $+500 \text{ mV}$, scan rate 5 mV/S , number of cycles – 5. Coloration degree was used as one of the characteristics that characterizes electrochromic properties. The coloration degree was calculated as a difference between

film transparency in colored and bleached state, averaged by five cycles.

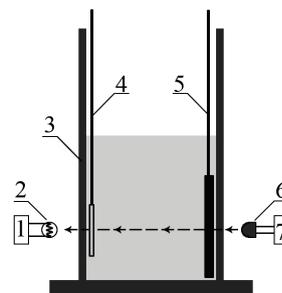


Fig. 3. Cell for electrochemical and optical measurements: 1 – analog-to-digital converter; 2 – photoresistor; 3 – cell made from transparent polymer; 4 – working electrode; 5 – counter-electrode with a gap for light beam; 6 – source of white (5500 K) light; 7 – source of stabilized current

In order to determine the structure of deposited WO_3 films, the XRD patterns were of films were recorded without separating films from FTO substrate. The XRD patterns were recorded using Dron-3 diffractometer (monochromated $\text{Co-K}\alpha$ radiation) (Russian Federation).

6. Research results

It has been discovered that transparent and uniform WO_3 film with sufficient thickness can be deposited at current density of -0.2 mA/cm^2 and deposition time of 30 min that was employed in all experiments. Under these conditions, the hard, transparent WO_3 with good adhesion to FTO glass (Fig. 4, a) could be obtained. However, as expected, the electrolyte instability led to different properties of deposited films. After electrolyte had been aged for 1 week, the freshly deposited films were colored (Fig. 4, b).



Fig. 4. Photographs of films deposited on FTO glass: a – made from freshly-prepared electrolyte; b – made from electrolyte that had been aged for 1 week under light

Upon further ageing the flask containing electrolyte solution would be covered with a white film (Fig. 5), at that point the WO_3 film could not be deposited from such electrolyte. The reason for this likely lies in decomposition of hydrogen peroxide, and as a result the decomposition of peroxotungstic acid. As such, it has been proposed to regenerate the electrolyte by adding H_2O_2 according to initial composition. The next day after addition of hydrogen peroxide, the white film had been completely dissolved.

In order to determine the difference between properties of WO_3 films prepared from fresh and regenerated electrolyte, the electrodeposition curves (Fig. 6) were recorded. It is noticeable that curves do not differ in their shape, but their potentials are quite different. This

is explained by different concentrations of electroactive species in electrolytes.



Fig. 5. Flask with electrolyte for electrochemical deposition of WO_3 (1 month since preparation)

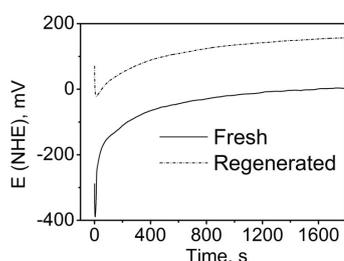


Fig. 6. Potential-time curves of working electrode (FTO glass) in fresh and regenerated electrolyte during deposition

For further comparison of WO_3 films prepared from fresh and regenerated electrolytes, the XRD patterns of WO_3 films on FTO glass were recorded. For comparison, the XRD pattern of FTO glass without film was also recorded (Fig. 7). The XRD patterns with films differ in presence of «noise» and somewhat high peak at 25° , especially the film prepared from fresh electrolyte. The noise on the pattern is determined by the presence of small peaks along the whole spectra.

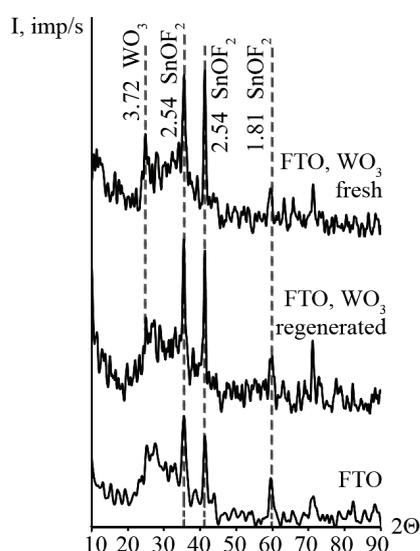


Fig. 7. XRD patterns of pure FTO glass and FTO glass with deposited films

In order to compare the electrochromic and electrochemical properties of WO_3 films prepared from regenerated

and freshly-prepared the cyclic voltammograms along with coloration-bleaching curves were recorded (Fig. 8, 9). In addition, the potential window was chosen according to achieve good coloration without damaging the conductive layer (SnO_2): +500 mV to -400 mV versus normal hydrogen electrode (NHE). During preliminary experiments, it has been established that lowest possible potential value has to be above -800 mV, because at this potential the reduction of SnO_2 to Sn occurs. In order to guarantee that no changes would occur to conductive layer, the lower potential was limited to -400 mV.

As can be seen from Fig. 8, the peak current and degree of coloration are lower from WO_3 film deposited from regenerated electrolyte.

Additionally, the form and position of peaks differ significantly, which indicate structural differences between WO_3 films. The highest coloration degree is observed for WO_3 film (Fig. 9) deposited from fresh electrolyte, which is about 10 %. For WO_3 film deposited from regenerated electrolyte, the coloration degree is about 5 %, which is two times lower.

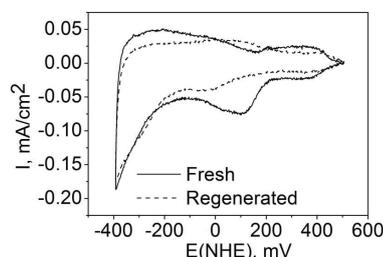


Fig. 8. Cyclic voltammograms (5-th cycle) of films deposited from fresh and regenerated electrolyte

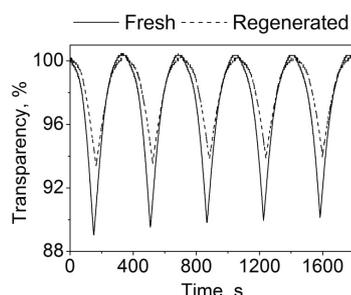


Fig. 9. Coloration-bleaching curves of films deposited from fresh and regenerated electrolyte

As a result of conducted work, the deposition regime for preparation of tungsten trioxide films from peroxotungstic acid has been determined. During experiments it has also been demonstrated, that electrolyte changes its properties over time, which is likely related to decrease of peroxotungstate anion concentration, because of hydrogen peroxide decomposition. Obviously, the peroxotungstate concentration affects the potential value, which was observed upon analysis of potential-time curves of WO_3 deposition (Fig. 6). A sign of such changes in the electrolyte can be the production of first colored tungsten oxide films, and then the deposition of a white film on the walls of the flask with electrolyte

Based on all that has been said, it has been proposed to regenerate electrolyte by adding hydroxide peroxide according to initial composition. However, the films deposited from regenerated electrolyte had lower coloration degree

than those deposited from fresh electrolyte. The difference between films was also observed on cyclic voltammograms. The peak currents of WO₃ deposited from fresh electrolyte had different form and were situated at different potentials. The latter can be a proof of different structure of tungsten trioxide films, which can be related to different electrolyte composition [24]. The X-ray diffraction analysis did not allow to firmly determine the difference between films prepared from fresh and regenerated electrolyte, however, the different structure can be assumed because of different intensity of peak at 25°. It can also be said, that both films (made from fresh and regenerated electrolyte) have low crystallinity and high number of defects, because of the «noise» on both XRD patterns with WO₃, in comparison to pure FTO glass.

7. SWOT analysis of research results

Strengths. The deposition regime, that allows to prepare high quality WO₃ films with good adhesion to FTO glass from peroxotungstic acid-based electrolyte have been found. Additionally, such regime allows to control the film thickness, which in turn allows to control the coloration degree of the electrochromic element, while having no effect on the properties of substrate.

Because of discovered instability of peroxotungstic acid-based electrolyte and proposed method for its regeneration, following strength can be highlighted:

- the volume of deposition bath for electrochemical deposition of WO₃ films can be calculated based on the stability (1 week) of freshly-prepared electrolyte;
- in the case of electrolyte degradation it can be regenerated adding hydrogen peroxide according to the composition.

Weaknesses. Because of the discovered electrolyte instability, it is not feasible to employ large baths for WO₃ deposition. Additionally, the determined current density doesn't allow for deposition of thick WO₃ films for a short time.

Opportunities. The search and implementation of electrochemical method for film deposition allows to significantly reduce the cost of process, increase control over thickness and other parameters of film. This also allows to utilize already existing galvanic equipment for cheapest and available implementation.

Threats. Magnetron and vacuum sputtering can be employed as alternative methods for deposition of electrochromic films, because they allow for deposition of films of specified composition and multi-layer film with variable elemental composition.

8. Conclusions

1. The deposition regime for WO₃ film electrolyte: 0.0125 M Na₂WO₄, H₂O₂ (the ratio between Na₂WO₄ and H₂O₂ is 0.8), pH 1–2: $i = -0.2$ mA/cm², 30 min. Under these conditions the transparent film with good adhesion to substrate are prepared.

2. It has been demonstrated that hydrogen peroxide-base electrolyte (peroxotungstic acid) is unstable over time and can be partially regenerate with H₂O₂. The working period of freshly-prepared electrolyte is approximately one after preparation.

The maximum coloration degree was 10 % for WO₃ deposited from freshly-prepared electrolyte.

3. The cycling potential range [+500 mV; –400 mV (NHE)], at which reversible coloration-bleaching of WO₃ without damage to conductive layer has been established.

It has been proposed that the reason behind lower coloration degree of film deposited from regenerate electrolyte, can lie in structural difference of films prepared from different electrolytes.

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ОПРЕДЕЛЕНИЕ СТАБИЛЬНОСТИ ЭЛЕКТРОЛИТА И УСЛОВИЙ ДЛЯ ОСАЖДЕНИЯ ЭЛЕКТРОХРОМНЫХ ПЛЕНОК WO₃

Для осаждения электрохромных пленок WO₃ предложен гальваностатический режим: $i_c = -0.2$ мА/см², 30 мин. Пленки, полученные в таких условиях, прозрачные, качественные и имеют хорошую адгезию к основе. Показано, что используемый электролит нестабильный и со временем меняет свои свойства. Для восстановления электролита предложено добавлять перекись водорода согласно рецептуре.

Ключевые слова: оксид вольфрама, осаждение электрохромных пленок, пероксодвольфрамовая кислота, окно потенциалов.

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DEVELOPMENT OF A MINERAL BINDING MATERIAL WITH ELEVATED CONTENT OF RED MUD

Розглянуто можливість збільшення обсягів утилізації відходів виробництва глинозему – червоного шламу шляхом використання як техногенної сировини для виготовлення в'язучого матеріалу низько температурного випалу типу романцементу. Показано особливості фазового складу та властивостей в'язучого на основі систем карбонатного компоненту з полімінеральною глиною, пілокварцом і червоним шламом.

Ключові слова: червоний шлам, техногенна сировина для виготовлення в'язучого матеріалу, фазовий склад.

1. Introduction

An increase in the volumes of practical utilization of industrial waste on a multi tonne scale is in line with the comprehensive solution to ecological problems, resource

saving and development of silicate production. Solving this actual problem requires appropriate development of scientific and technical principles for the chemical technology of silicates with determining the laws relative to the influence of the concentration of varieties of technogenic