Optical and kinetic properties of cathodically deposited amorphous tungsten oxide films


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Abstract
Optical properties and the coloration–decoloration kinetics of electrochromic films of amorphous tungsten oxide (a-WO₃), produced by cathodic deposition from a sodium tungstate based aqueous peroxide electrolyte, have been investigated. As films color in 1 N H₂SO₄, sequential appearance of bands with maxima at ~1 eV, 1.6 eV, 2 eV, and 2.4 eV is observed in their optical absorption and electro sorption spectra, is the same as in the case of reduction of nanosized hydrated-WO₃ colloids with a gradual decrease in their size to that of 12-tungsten polyanions with Keggin structure, indicating the presence of such polytungstates in cathodically deposited a-WO₃, too. When polytungstate is reduced by one electron, an absorption band with a maximum at ~1.6 eV appears in the optical spectrum of the film. This band corresponds to the optical excitation of charge transfer of the W⁵⁺ → W⁶⁺ type between two adjacent tungsten atoms. The reduction of polytungstate by a second electron with potential shift towards more negative values is accompanied by the appearance of an analogous band with a maximum at ~2 eV. The reduction of such polytungstates involves participation of the bulk of injected electrons, indicating their dominate role in the nanostructure of the films investigated. The effective co-diffusion coefficient of electrons and protons in cathodically deposited a-WO₃ exhibits a potential dependence with a maximum at 0.1 V against a silver-chloride electrode, where its value is ~10⁻⁸ cm²/s. It has been shown that the decrease in this coefficient at potential values of over 0.1 V is caused by a decrease in electron mobility.
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1. Introduction

Amorphous tungsten oxide (a-WO₃) films find application in electrochromic devices [1–3]. The coloration and decoloration processes in the near infrared and visible regions of optical spectrum are effected by double ion-electron injection and extraction [1–4]. The coloration of an a-WO₃ electrode in the course of current flow is caused by the capture of electrons injected into the film onto the unoccupied d-orbitals of W⁶⁺ centers with their reduction to W⁵⁺ centers (with the change of the tungsten oxidation state from +6 to +5), which are just a-WO₃ color centers. The charge of these electrons in the bulk of the film is compensated by mobile monovalent cations, such as H⁺, Li⁺ or Na⁺, which enter the film from the electrolyte and are located near the oxygen atoms that form bridge and terminal bonds such as W–O–W and W=O [5,6]. The extraction of injected electrons from colored film on the reversal of an a-WO₃ electrode current flow results in the decoloration of the a-WO₃ electrode.

One of the simplest and most economical methods for the deposition of a-WO₃ layers with good reproducibility of electrochromic characteristics on transparent current-conducting substrates is cathodic deposition [1,7–14], whose mechanism is reported in Ref. [7]. Deposition is
usually performed from an electrolyte containing soluble polyoxometalates and peroxometalates [15–17]. Deposition of an oxide on the cathode from an acidified tungsten-containing peroxide electrolyte is reported in [18–20]. The method for the preparation of starting electrolyte is described in [21], and depending on deposition conditions, the cathode deposit may be X-ray amorphous [7,10,22] or nanocrystalline [9]. Under galvanostatic deposition conditions, a linear dependence of film thickness on deposition time holds, but the film retains the smooth homogeneous surface only up to a thickness of no more than one micron [7,22]. It was shown by the method of Fourier transforms of extended X-ray absorption fine structure that such films are characterized by four different distances between tungsten and oxygen atoms, which range between 1.5 Å and 2.4 Å [23]. The smallest distances in this range correspond to double bonds such as W=O and the largest ones to bonds of tungsten to water molecules; these molecules complement the coordination of tungsten to octahedral coordination, which is characteristic of them.

This paper presents results of investigation of the variation of spectral absorption distribution and co-diffusion rate of injected electrons and protons in cathodically deposited a-WO3 at different potential values. The experimental data obtained speak in favor of nanocluster structure of electrodeposited a-WO3 films with 12-tungsten polyanions with Keggin structure predominating in them.

2. Experimental

a-WO3 films were produced by cathodic electrodeposition from a Na2WO4-based aqueous electrolyte (0.2 M) with addition of 30% hydrogen peroxide (0.13 M) and H2SO4 (up to pH = 1). Deposition was performed in a transparent electrolytic cell with a platinum counter electrode at a constant cathode current density of 1 mA/cm² and a temperature of 23–25 °C. a-WO3 films were deposited on a transparent conducting SnO2 film, spray deposited on a glass substrate, and on the polished surface of sheet tungsten. The design of the electrolytic cell allowed us to perform interferometric control of deposition: by recording interferograms simultaneously for two He–Ne laser beams with different angles of incidence on the electrode surface. Computer-aided analysis of these interferograms by the technique described in [21] enabled separate determination of current values of the thickness and refractive index of the growing a-WO3 layer. According to the results of investigations by XRD, TEM and TG-DTA, which were given earlier in [22], the deposited films are X-ray amorphous and strongly hydrated because they contain a large number of coordinately linked (up to 15 wt%) and free water molecules. The specific density of such films is less than 50% of the density of crystalline WO3, which agrees with the low value of their refractive index, 1.6–1.7 (at n = 2.5 for crystalline WO3).

The measurements of optical and electrochemical characteristics of the electrodes made were carried out in a transparent electrolytic cell, filled with 1 N H2SO4, with a platinum counter electrode and silver-chloride reference electrode, with respect to which all potential (E) values are given. The measurements were made on a PC-controlled unit, which comprised an EP-21 potentiostat and an MDR-12 (LOMO) monochromator. The potential values and working-electrode current magnitudes were measured with V7-23 digital voltmeters with 0.2 s measurement time and an error of 0.01% of the upper measurement limit. The same voltmeter was used for periodical measurements of luminous flux level at the monochromator output (in the case of measuring transmission spectra, with an interval of 1 nm), but because of noise and photomultiplier zero drift the error of such measurements at the photosresponse maximum was ~0.1%. In order to avoid the influence of SnO2 sheet resistance on the kinetics of the coloration and decoloration process, the curves of current and light absorption against time were measured on samples of films deposited on a polished sheet tungsten surface. Periodical measurements of experimental points of these curves were made using two fast-acting analog-to-digital converters F7077/1. The error of the measurements of the curve of electrode current and normalized optical reflection from the electrode against time was ~1% of their initial values.

As in Ref. [7], the efficiency of reversible coloration of deposited films, ΔD/ΔQ (ratio of change in their optical density, ΔD, to the value of charge injected into the film, ΔQ) at the wavelength of λ = 650 nm was 50 cm²/C. The electrosorption spectra of films deposited on tungsten were measured on a setup similar to those for measuring electroreflectance spectra of semiconductors [24]. The electrode potential was set with superposition of an alternating signal of 0.1 V amplitude at 20 Hz frequency on its constant component (Eg). The alternating component of current from a photomultiplier, which was proportional to the change in the intensity of monochromatic light reflected by a-WO3 electrode, was recorded using phase detection. The value of the constant component of this current was maintained at the same level by means of an electronic circuit controlling the photomultiplier supply voltage. In this case, the change in the intensity of reflected monochromatic light because of reversible coloration of a-WO3 electrode was 2–3 orders of magnitude larger than that caused by change in reflection coefficient at the WO3/electrolyte and WO3/W interfaces. Therefore, we regarded experimental plots of the alternating component of photomultiplier current against λ in this work as electrosorption spectra of a-WO3.

The knowledge of transport kinetics parameters in electrochromic films is of great importance in understanding the behavior of these films during insertion/extraction processes. The charge of injected electrons (with a concentration of the order of 10¹² cm⁻³) in the colored layer of a-WO3 is compensated by the charge of mobile protons. Because of the large percentage of water molecules in the structure of cathodically deposited film, the proton transport in it is over hydrogen bonds of these molecules (as OH⁻). At such high concentrations of charge carriers
of different polarity, the diffusion mechanism of their co-

movement in the bulk of a-WO$_3$ is most probable. Under 

non-stationary conditions, the difference in electron and 

proton mobility must give rise, by analogy with concen-

trated solutions of liquid electrolytes, to a diffusion poten-

tial, which equals the velocities of these species. In this 

case, the value of the effective co-diffusion coefficient ($D_{\text{eff}}$) 

doingce of electrons and protons in the bulk of such film is deter-

mined mainly by the velocity of the less mobile species, 

which is usually taken to be a proton.

When there is no potential barrier to protons at the film/

electrolyte interface, rapid, almost instantaneous, establish-

ment of charge carrier concentration at the film surface, 

which is equilibrium one for the given $E$ value, may be 

assumed. Then coloration may be regarded as a diffusion 

process of co-propagation of protons and electrons into a 

film of finite thickness $d$ from a constant source on the sur-

face with concentration $N_0$. The general solution of diffusion 

equations for the (proton) flow across the WO$_3$/electrolyte 

interface is in this case [25]

$$i(t) = \left(\frac{2eN_0 D_{\text{eff}}}{d}\right)^{\infty}_{n=0} \exp\left\{-\left[(2n+1)^2 \pi^2 D_{\text{eff}}t/(4d^2)\right]\right\},$$

(1)

where $e$ is the electron charge, and $t$ is the coloration time. 

This solution is of the same form for decoloration. Series 

(1) converges rapidly, its convergence being the better the 
greater $t$, and at $t \geq t_D = 0.25d^2/D$ ($t_D$ = characteristic dif-

fusion time) one can confine oneself to the first term of the 

sum with an error of no more than 1%. Then, with the 

exception of the initial coloration stage, at $t \geq t_D$

$$\ln |i(t)| = \ln\left(\frac{2eN_0 D_{\text{eff}}}{d}\right) - \pi^2 D_{\text{eff}}t/(4d^2),$$

(2)

That is the plot of $i(t)$ in the $\ln|i(t)| - t$ coordinates yields a 

straight line with the slope $\pi^2 D_{\text{eff}}/(4d^2)$, which intersects 

the ordinate axis at the value of $\ln\left(\frac{2eN_0 D_{\text{eff}}}{d}\right)$. The values of $D_{\text{eff}}$ given in the paper were determined from the slope in 

these coordinates of experimental plots of $i(t)$, which we re-

corded in the course of coloration and decoloration of an 
a-WO$_3$ electrode under the action of rectangular potential 
pulses of different amplitude. The slope of the linear 

$\ln|i(t)| - t$ plots was determined by visually drawing straight 

lines through experimental $i(t)$ points. The points of the 

initial stage of the coloration (decoloration) process, where 

$t < t_D$, were excluded from these points. The points of the 

final stage of this process, where the current magnitude 

was comparable to the measurement error, were also 

disregarded.

3. Results

3.1. Dependence of coloration spectra on potential

Fig. 1 shows experimental plots of current density $i(E)$ 

and optical transmission variation $T(E)$ against potential 

for a cathodically deposited a-WO$_3$ film at different $\lambda$ val-

ues. These plots, which were obtained in film coloration–

decoloration cycle by varying the potential value between 

$E = 0.5$ V and $-0.5$ V, demonstrate the reversibility of the 

film coloration process in the near infrared and visible 

regions. In the fundamental absorption region of a-WO$_3$ 

(at a wavelength of $\lambda = 330$ nm), the film coloration was 

accompanied by a gradual increase in $T$, which was compa-

rable to its decrease at $\lambda \approx 1$ $\mu$m (Fig. 1). The increase in $T$ 

in this region of optical spectrum is caused by the fact that 

the coloration of a-WO$_3$ is accompanied by a reversible shift.

![Fig. 1. Plot of $i(E)$ and variation of the optical transmission of an a-WO$_3$ film 0.28 $\mu$m in thickness in coloration–decoloration cycle with potential shift between $E = 0.5$ V and $-0.5$ V at a sweep rate of 10 mV/s.](image)
of its fundamental absorption edge towards shorter wavelengths [22].

The potential dependence of electronic charge injected into film, \( Q(E) \), optical film density \( D(E) = \log(1/T) \), and the efficiency of the film coloration and decoloration process as the ratio \( dD/dQ \) was determined from the plots of \( i(E) \) and \( T(E) \) shown in Fig. 1. Plots of \( dD/dQ \) against \( E \), which were obtained for a number of fixed \( \lambda \) values in the spectral range 500–1200 nm, are shown in Fig. 2. They show what contribution to the optical absorption by the film is made at these \( \lambda \) values by \( W^{5+} \) centers formed from \( W^{6+} \) centers with different reduction potential. The greatest contribution to coloration falls at its initial stage, in which \( W^{5+} \) centers with optical absorption peak in the range 1100–1200 nm are formed, and the value of \( dD/dQ \) reached \( \sim 270 \, \text{cm}^2/\text{C} \). When the light wavelength decreases, the maximum of the plot of \( dD/dQ \) against potential comes to be shifted towards lower \( E \) values, i.e., \( W^{5+} \) centers with absorption in the shorter-wavelength region of the spectrum are formed from \( W^{6+} \) centers with lower reduction potential.

Reversal of potential sweep results in film decoloration owing to the change of the charge state from \( W^{5+} \) centers to \( W^{6+} \). As the potential shifted from \(-0.5\) V to its initial value of \( 0.5 \) V, the film decoloration efficiency \( dD/dQ \) gradually increased, the closeness of the \( E \) values to which the maxima of coloration and decoloration efficiency correspond being retained for each \( \lambda \) value (Fig. 2). It follows that the potentials at which the \( W^{6+} \) and \( W^{5+} \) centers change their charge state are close together.

Fig. 3 (a) (curves 1–3) shows the spectral distribution of optical density for absorption, \( \Delta D(h\omega) \), which appears in the course of coloration of an a-WO\(_3\) film 1 \( \mu \)m in thickness at potential values between \( E = 0.4 \) V (for which \( D = 0 \)) and \( E = 0 \) V, \(-0.2 \) V and \(-0.4 \) V, respectively. In the initial stage of coloration, when the potential varies between \( E = 0.4 \) V and \( E = 0 \) V, an intense absorption band with a maximum at \( h\omega \approx 1 \, \text{eV} \) appears in the optical spectrum of the film. But as \( E \) varies from 0 V to \(-0.4 \) V the \( D \) value trends towards saturation in the region of this band’s maximum, and the absorption in the shorter-wavelength region of the spectrum continues to increase through the reduction of other \( W^{5+} \) centers with higher position of their unoccupied d-orbital on the energy scale. The contribution of these \( W^{5+} \) centers to the absorption by the cathodically deposited film in the potential ranges 0 to \(-0.2 \) V and \(-0.2 \) to \(-0.4 \) V is shown by the difference absorption spectra II and III in Fig. 3 (a), which were obtained by subtracting spectrum 1 from spectrum 2 and spectrum 2 from spectrum 3. These difference spectra exhibit sequential appearance of two more absorption bands with maxima at \( h\omega \approx 1.6 \, \text{eV} \) and \( 2 \, \text{eV} \). In the voltammetric curve for the coloration process (Fig. 3(b)), three consecutive cathode current buildup portions correspond to the three above optical absorption bands. In the region \( h\omega > 3 \, \text{eV} \), the quantity \( \Delta D \) in Fig. 3(a) transfers to the region of negative values; this corresponds to the ‘bleaching’ effect of cathodically deposited
oxide through a gradual shift of its fundamental absorption edge towards higher quantum energies by $\Delta \hbar \omega \approx 0.42$ eV [22].

3.2. Electrosorption spectra

Fig. 4 shows electrosorption spectra of a cathodically deposited a-WO$_3$ film 0.26 μm in thickness at constant-component values of potential of $E_S = 0.3$ V and 0 V. These spectra exhibit the same absorption bands as the coloration spectra in Fig. 3, with maxima at 1.2–1.3 eV, 1.6 eV, and 2 eV. The smaller half-width of these bands in electrosorption spectra allows a doublet structure of the band at 1.2–1.3 eV and an additional band with a maximum at 2.4 eV to be revealed. The variation of $E_S$ from 0.3 V to 0 V is accompanied by an increase in electrosorption intensity owing to an increase in the number of electrons and protons which periodically enter the film and leave it. This increase in electrosorption intensity is, however, not the same in different spectral regions in Fig. 4 and falls mainly at the region $\hbar \omega \geq 1.5$ eV; this is typical of the coloration spectra shown in Fig. 3. At $\hbar \omega \geq 3.1$ eV, the electrosorption spectrum in Fig. 4 changes its sign and becomes actually an ‘electrotransmission’ spectrum, which is caused by a periodical reversible change (with a frequency of 20 Hz) of the position of the fundamental-absorption edge of a-WO$_3$.

The structure of electrosorption spectra becomes better defined with decreasing a-WO$_3$ layer thickness. Fig. 5 shows electrosorption spectra which were obtained for a thin (~0.08 μm thick) cathodically deposited oxide layer at $E_S = 0.3$ V, 0 V, and −0.3 V. The position of the maxima in these spectra (at $\hbar \omega = 1.2–1.3$ eV, 1.6 eV, 2 eV and 2.4 eV) is practically independent of the a-WO$_3$ electrode potential. The shift of $E_S$ towards more negative values leads to a redistribution of absorption intensity at these maxima, which is the same as in Figs. 3 and 4. In order to demonstrate this redistribution, the electrosorption at the maximum at $\hbar \omega = 1.2–1.3$ eV in the spectra shown in Fig. 5 was reduced to the same level. The thin lines in Fig. 5 show the possibility to distinguish in these spectra individual absorption bands, approximated by Gaussian distribution. The accuracy of this approximation is lower for the marginal spectral regions since the doublet structure of the absorption band with a maximum at 1.2–1.3 eV was not, e.g., taken into account in it.

3.3. Kinetics of electrochromic effect in a-WO$_3$

The plots of $\ln |i(t)|$, measured using periodic analog-to-digital conversion, which were obtained at a tungsten electrode with a layer of cathodically deposited a-WO$_3$ at several coloration potential values, are shown in Fig. 6 in $\ln |i(t)|$–$t$ coordinates. At $t > t_D = \sim 0.5$ s, these dependences are linear, which is corroborated by the diffusion mechanism of the cooperative motion of protons and electrons in the film on the side of the a-WO$_3$/electrolyte interface. The $D_{eff}$ values that were determined from the slope of the straight lines drawn (by eye) by experimental points in Fig. 6 are shown in Fig. 7 (circles). The independent estimation of $D_{eff}$ from $t_D$, which is $\sim 3 \times 10^{-9}$ cm$^2$/s, also corresponds to the arrangement of these points along the ordinate axis in Fig. 7 at $E \leq 0.25$ V.

The remaining points (squares) correspond to the $D_{eff}$ values that were obtained for this electrode from the time dependence of anode current during partial decoloration of a-WO$_3$ layer at potential values that were 0.1 V higher than the precoloration potential. In such measurements, the experimental points of $\ln |i|–t$ plots fall better on straight lines with the same slope as in coloration because in this case the deviation of experimental points from the
Fig. 6. Plots of \( \ln|i| \) vs. \( t \) coordinates for an a-WO\(_3\) film 0.64 \( \mu \)m thick in a cycle of its coloration at different potential values and subsequent decoloration at 0.4 V potential. For each coloring potential value at \( t > 0.5 \) s, the trend of the experimental points is close to rectilinear one; this is shown here by straight lines drawn through them by eye.

lines drawn is minimized due to the dependence of \( D_{\text{eff}} \) on \( E \). The plot of \( D_{\text{eff}} \) against \( E \) shown in Fig. 7 has a maximum at \( E \approx 0.1 \) V, where the value of effective diffusion coefficient is \((9.5 \pm 0.3) \times 10^{-9} \) cm\(^2\)/s.

The decoloration of the film at \( E > 0.3 \) V proceeds faster than coloration (Fig. 6) since the concentration of W\(^{5+}\) centers that is equilibrium concentration for this potential cannot set up at its surface any more. In this case, even complete disappearance of color cannot compensate for the potential difference applied to the WO\(_3\)/electrolyte interface. The uncompensated part of this potential difference creates an electric field, which penetrates into the bulk of semiconductive a-WO\(_3\) and accelerates the escape of protons into the electrolyte [4].

4. Discussion

The absorption bands with maxima at \( \hbar \omega \approx 1.6 \) eV and 2 eV in Fig. 3(a) and the bands found in electrosorption spectra (Figs. 4 and 5) are a characteristic sign of reduction of polytungstate anions with Keggin structure [26–29]. This suggests that such anions are present in cathodically deposited a-WO\(_3\) too. These anions are characterized by a reversible behavior at electrodes and closeness of \( E_{1/2} \) values for cathodic reduction waves and anodic oxidation waves of reduced forms [30]. Their salts, such as the salt H\(_3\)PW\(_{12}\)O\(_{40}\)·29H\(_2\)O, which possessed electrochromism [31], contain between some anions voids with a large number of free water molecules [26,32]. After reduction of such polyanions in solution, their optical spectra are much the same [26] and exhibit the same bands as in Fig. 5. Reduction at the cathode by one electron leads to the appearance of an intense band with a maximum at 1.6–1.7 eV, and two less intense bands with maxima at 1.0–1.1 eV and 2.4–2.5 eV appear in their optical absorption spectrum [28–30]. When a second electron is introduced into the anion, another more intense band with a maximum at 1.9–2.0 eV appears in its absorption spectrum instead of the band with a maximum at 1.6–1.7 eV, and the position of the maximum of the longer-wavelength and less intense band falls now at the region 1.2–1.3 eV. As in the case of a-WO\(_3\), these absorption bands correspond to charge transfer such as W\(^{5+} \rightarrow W^{6+}\) [26,29,30,32].

During film coloration the value of cathode current is proportional to the rate of filling of W\(^{6+}\) centers with injected electrons at a given \( E \) value. Its higher values in the negative-potential range in Fig. 1 correspond to the fact that the bulk of these electrons in the cathodically deposited film is spent on the reduction of polyanions with Keggin structure and on the formation of type II and III color centers (Fig. 3b). This indicates predominance of such complex anions in the structure of cathodically deposited a-WO\(_3\). In addition to them, there is a quantity of larger associates in the film, the reduction of which at the initial stage of coloration (at positive \( E \) values) is accompanied by the appearance in the optical spectrum of an intense absorption band with a maximum at 1100–1200 nm. Such associates may be probably regarded as nanoclusters, which are characterized by a shift of absorption band towards shorter wavelength, in the case of reduction, with decrease in their size [33,34]. An analogous dependence of the position of the absorption peak on the size of nanoclusters during its decrease to that of 12-tungsten polyanions with Keggin structure was revealed in [27] in the case of reduction of hydrated-WO\(_3\) colloids, too. The presence of nanoclusters of different size in the structure of cathodically deposited films makes it also possible to compare the initial reduction potentials of their W\(^{6+}\) centers. The lowest value of this potential is peculiar to polytungstates having a Keggin structure, which predominate in cathodically deposited a-WO\(_3\).
The plot of $D_{\text{eff}}$ against $E$ shown in Fig. 7 has a maximum at $E \approx 0.1\,\text{V}$. A similar plot of $D_{\text{eff}}(E)$ was obtained earlier from impedance measurements for vacuum-evaporated a-WO$_3$ films (in the case of coloring them in propylene carbonate with 1 M LiClO$_4$) [5]. The initial increase in $D_{\text{eff}}$ is attributed by the authors of [5] to the change from the movement of Li$^+$ ions inside individual clusters to their faster movement over the surface of clusters, where the terminal W$^{6+}$=O bonds are localized. Hydrated WO$_3$ films obtained by the sol-gel method are characterized at all $E$ values by continuous increase in $D_{\text{eff}}$ with their coloration with Li$^+$ [35], which is caused, in the opinion of the present authors, by an increase in electronic conductivity. This agrees with the fact that in the course of coloration of such films, their electronic conductivity increases by a factor of over $10^6$ [36].

In amorphous semiconductor materials, to which a-WO$_3$ belongs, electronic conduction is effected by hops of electrons between centers of localization. Such centers of electron localization in cathodically deposited a-WO$_3$ films are apparently nanoclusters with possibility of changing the charge state of their W centers at the given $E$ value. At the initial stage of coloration, in the range $E > 0\,\text{V}$, where 12-tungsten polyanions with Keggin structure are not yet reduced, such centers of localization can be only nanoclusters of larger size. In the presence of a large quantity of 12-tungstates, pores and free water molecules, the electronic conductivity of the film may be low owing to ‘hops’ between such nanoclusters. Therefore, the increase in $D_{\text{eff}}$ at the initial stage of coloration of a cathodically deposited film in 0.5 M H$_2$SO$_4$ (Fig. 7) may be caused by an increase in its electronic conductivity.

The fact that the initial increase in $D_{\text{eff}}$ can be attributed to the increase in electronic conductivity is corroborated by the variation of kinetic dependences of the coloration–decoloration process of cathodically deposited films with increasing pH of the starting electrolyte. In a film deposited from an electrolyte with pH = 2, a sharp deceleration of the coloration–decoloration process at the maximum absorption by W$^{5+}$ centers near 1000 nm is observed at $E \geq -0.1\,\text{V}$, whereas the electric field accelerated separation and withdrawal of the bulk of charge carriers take place here within $t \approx 0.1\,\text{s}$ (Fig. 8). The charge of electrons injected into centers of localization at $E \approx -0.1\,\text{V}$ is $\sim 5\%$ of the maximum value of $Q$ in the film at $E = -0.5\,\text{V}$. This large change (by several orders of magnitude) in the mobility of charge carriers in the film between $E = -0.1\,\text{V}$ and $-0.2\,\text{V}$ is unlikely to be due to a change in the path of proton transport by the mechanism proposed in [5]. Increase in distances between large nanoclusters in such an oxide seems to reduce the probability of electron hop between them and hinders the participation of electrons captured by them in transport phenomena at $E > -0.1\,\text{V}$ because with decrease in the acidity of the starting electrolyte to pH = 3, a deposit is formed on the cathode in the form of a conglomerate of small particles, which are loosely bound to one another and can be readily removed from the substrate. This deposit is practically not colored any more.

5. Conclusions

Electrochromic films of amorphous WO$_3$, obtained by cathodic deposition have a nanocluster structure with predominance in it of 12-tungsten polyanions with Keggin structure. In the course of coloration of such films at different potentials, W$^{5+}$ color centers with different optical characteristics, depending on the size of nanocluster and the number of injected electrons localized on its tungsten atoms, are formed in them. When the size of nanoclusters decreases to that of 12-tungstates with Keggin structure, their initial reduction potential decreases by $\sim 0.3\,\text{V}$, and the absorption by the W$^{5+}$ centers formed in them becomes shifted towards shorter wavelength. In this case, the optical characteristics and their potential dependence of W$^{5+}$ centers in 12-tungstates with Keggin structure are identical to those of polyanions of the same structure in solution after reduction of them by one and two electrons. It has been shown that the cooperative propagation of injected
electrons and protons from the film surface to the substrate during the coloration of such a film takes place by a diffusion mechanism, and that the plot of the effective diffusion coefficient of these mobile charge carriers against potential has a maximum at $E_{0.1} V (\text{against Ag/AgCl})$, where $D_{\text{eff}}/C_{0.9} \cdot 10^{8} \text{cm}^{2}/\text{s}$. The lower $D_{\text{eff}}$ values at the initial stage of a-WO$_3$ coloration at $E > 0.1 \text{V}$ are regarded as a result of electron mobility being lower than the mobility of protons as H$_3$O$^+$ in this strongly hydrated oxide.

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