



## Original articles

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## Cylindrical model of electrochromic colouration of hydrated vanadium pentoxide thin films with point contacts

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### Abstract

This article analyses experiments on the kinetics of the internal electrochromism of thin (micron) films of hydrated vanadium pentoxide xerogel with point contacts. It describes a cylindrical model of electrochromic colouration, which was used to evaluate the concentration of the colour centres in the initial film and after additional hydrogenation of this film by plasma-immersion ion implantation.

When we compared the calculated values of the concentration of colour centres with the equilibrium concentration of protons in the xerogel, we saw that the mobility of the protons migrating from the depth of the film to the cathode region, which are involved in the electrochemical reaction, was not a determinant of the electrochromism kinetics.

The rate of electrochromic colouration could be increased by the formation of layered film structures based on hydrated vanadium pentoxide, which have increased overall electron conductivity and, as a consequence, low faradaic resistance of the electrochromic cathodic reaction.

**Keywords:** Electrochromism, Hydrated vanadium pentoxide, Plasma-immersion ion implantation, Ion current kinetics

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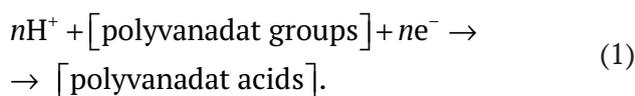


## 1. Introduction

Electrochromism is a reversible change in the optical properties of a material (light transmission and colour) under the influence of an electric field, as a result of the injection/extraction of hydrogen or alkali metal ions [1]. In most cases, the effect takes place in the presence of an external electrolyte, which acts as one of the electrodes (anode) and injects ions into the electrochromic material. This type of electrochromism is used in electrochromic indicators and gas sensors [1–3].

Previously we have discovered and described [4, 5] internal electrochromism (IEC) without contact with the electrolyte in thin films of hydrated vanadium pentoxide (HVP) xerogel  $V_2O_5 \cdot nH_2O$ . When a step voltage pulse is applied between two point electrodes touching the surface of the film, a coloured (red) spot is formed around the cathode (an example is given in coloured figure 3 [6]). The spot usually remains coloured for many hours, but disappears a few minutes after a back (inverse) voltage is applied. Internal electrochromism has a threshold character, i.e., it does not occur below a certain voltage level. The more the electrochromic cell voltage exceeds the threshold level, the stronger the effect becomes: the cathode spot has a deeper red colour, a larger area, and grows faster. In a fully dried HVP sample (water removed), which corresponds to the  $V_2O_5$  structure, internal electrochromism was practically absent [4–6].

There is also no electrochromism in hydrogen vanadium bronzes, where the maximum oxidation state of vanadium is 4. On the other hand, a number of higher poly-vanadium acids (the oxidation state of vanadium is 5) are red in acid solutions. In this regard, we hypothesised [5] that the cause of electrochromism in HVP is the migration of protons to the cathode region, followed by the formation of higher poly-vanadium acid fragments, as colour centres of the type:



Defects containing fragment ions of, for example, hexavanadate  $V_6O_{17}^{-4}$ , which form molecules (clusters) of hexavanadic acid ( $H_4V_6O_{17}$ )

under reaction (1), can act as poly-vanadate groups.

X-ray studies of HVP show [7] that the material has a quasi-one-dimensional layered structure, where crossed fibres, predominantly oriented along the substrate, are connected by water molecules. If we compare the ion and electron components of the conductivity of HVP, we can see that this material exhibits mixed ion-electron charge transfer [8–10]. The electron conductivity of HVP has a pronounced activation character with very low mobility [9] and depends on the content of  $V^{4+}$  ions, which are found in the defects and impurities. The ion component of conductivity, in turn, depends on the water content in HVP, it decreases sharply with a decrease in the water concentration [9]. The migration of protons through ordered hydrogen-bonded water molecules is thought to be the mechanism of ion conductivity. However, there are suggestions [10] that protons can also exhibit a hopping migration through the vanadium-oxygen ( $V_2O_5$ ) HVP layers.

In this article, we analysed our experiments [6, 11] on the kinetics of internal electrochromism and on the passing current in a thin-film HVP structure with point contacts upon additional (homogeneous and inhomogeneous) hydrogenation of the xerogel by plasma-immersion ion implantation (PIII). Using a cylindrical model of electrochromic colouration of the film, we estimated the concentration of electrochromism colour centres in HVP.

## 2. Experimental

The HVP films were synthesised by the liquid-phase sol-gel method [1–3, 5]. In our experiments, vanadium pentoxide gel with a thickness of  $h \sim 1 \mu\text{m}$  was applied onto a glass substrate. Then, the samples were dried for a day at room temperature, so that their composition with partially removed water, according to the results of X-ray analysis, corresponded to the  $V_2O_5 \cdot 1.8H_2O$  phase [6].

The samples were hydrogenated (doped with hydrogen) in a hydrogen plasma by PIII [6]. The PIII unit (Fig. 1) consists of a chamber with a sample holder inside, a vacuum system, a plasma generator, a high-voltage pulse system, and a gas supply system. A plasma source with a heated

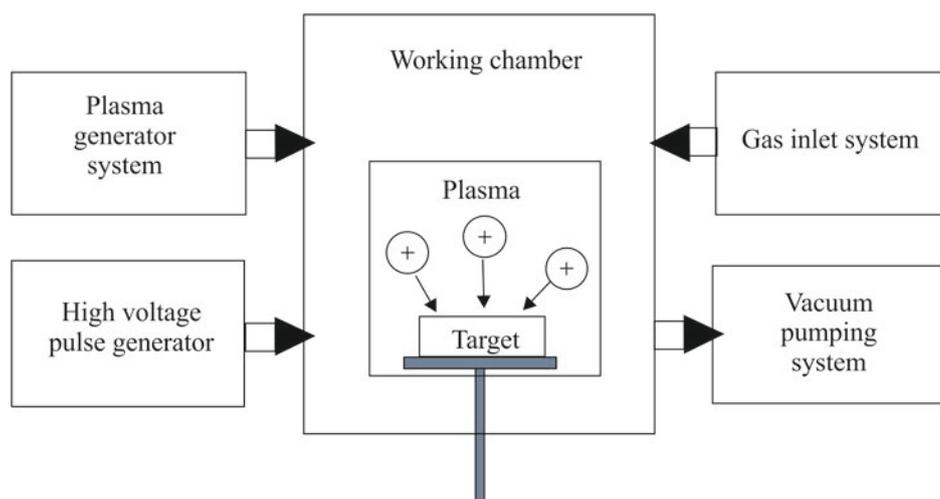


Fig. 1. The PIII unit layout

cathode was attached to one of the flanges of the chamber to produce an electric arc in the chamber. A vacuum system based on the NVR-16D fore-vacuum pump and the 01 AB-1500-004 turbomolecular pump allowed the pressure in the chamber to be reduced to  $10^{-4}$  Pa. Voltage pulses were applied to the sample holder through the HVS-10-10 solid-state switch. Gas was injected into the chamber using a gas supply system of two FC-260 regulators.

Ions were implanted from plasma (at 4 Pa), when negative high-voltage pulses (2 kV) with a frequency of 1.7 kHz were applied to the sample for 5  $\mu$ s. The current pulse amplitude was 50 mA and the total treatment time was 30 min. The implantation dose was approximately  $\sim 3.5 \cdot 10^{17}$  cm $^{-2}$ . During hydrogenation, part of the sample could be covered by a rectangular mask to avoid protons entering that area. The area of the film implanted with hydrogen changed colour from grey-green to dark green. The colour change was due to a partial modification of HVP under the PIII treatment. As determined by nuclear magnetic resonance, it caused the increase in the concentration of V $^{+4}$  [6].

We recorded the growth rate of the cathode spot area (Fig. 2) and the kinetics of the current (Fig. 3) between the clamping point contacts with radii of  $r_0 \sim 0.1$  mm and distance  $d = 3$  mm at voltage  $U_0 = 30$  V in three variants of experiments: (I) – the original HVP film, (II) – the film where the cathode region is the original HVP and the anode region is the hydrogenated HVP, and (III) – the fully hydrogenated film. Note that the area

of the electrochromic colouration over time was determined using the images made by a digital camera with a 1 s sweep length; the current was recorded using a Keithley 2400 source measure unit.

At the beginning of the electrochromic colouration process, a red spot was formed very quickly (in a few seconds) around the cathode (see coloured Fig. 3 in [6]). The spot was perfectly round with a radius of  $\sim 0.4$ – $0.5$  mm. Then it slowly increased, reaching its final size ( $\sim 2$  mm) 5–6 minutes after the voltage was turned on. The colouration rate and the depth of red differed significantly between the experimental variants. Internal electrochromism was most pronounced in the mixed variant (II): it had the maximum

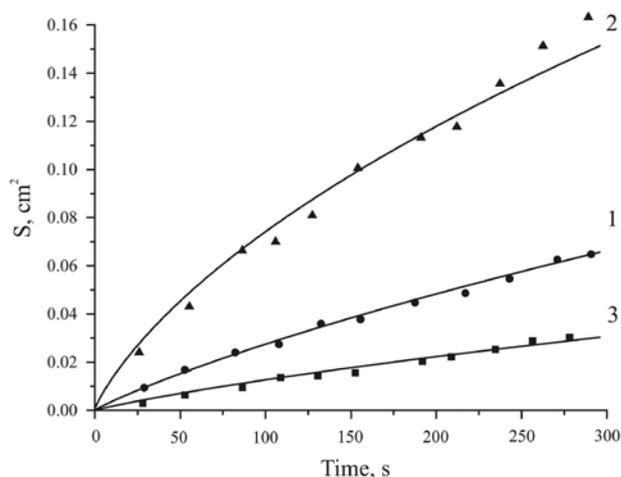
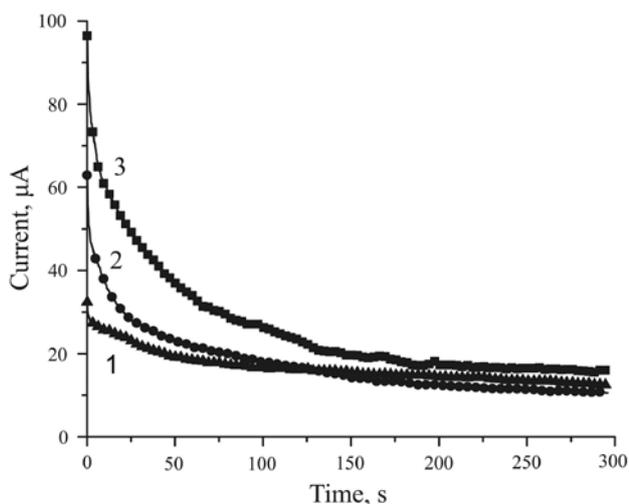


Fig. 2. The growth of the electrochromic spot area over time. 1 – initial film (experiment I), 2 – mixed film (experiment II), and 3 – fully hydrogenated film (experiment III)



**Fig. 3.** Kinetics of the current passing through the HVP films: 1 – initial film (experiment I), 2 – mixed sample (experiment II), and 3 – fully hydrogenated film (experiment III)

growth rate of the spot area (Fig. 2, curve 2), the colour of the spot was bright red. The effect was weaker in the original film (Fig. 2, curve 1) and even less pronounced in the fully hydrogenated film (Fig. 2, curve 3).

The currents recorded (Fig. 3) in all variants of the experiments (I–III) first increased sharply (in a few  $\mu\text{s}$ ) to a maximum. Then they almost exponentially decreased to their stationary values. The largest current peak was recorded in the fully hydrogenated film (Fig. 3, curve 3), and the smallest one was registered in the original film (Fig. 3, curve 1).

### 3. The model of electrochromic colouration

The total recorded current  $I(t)$  (Fig. 3) in HVP, as in a material with mixed electron-ion conductivity, consists of a purely electron current passing through the film, which we regard as constant, and of an ion current  $I_p(t)$  changing over time. The ion current involves additional electrons from the external circuit in charge transfer. These electrons are involved in the IEC electrochemical reaction (1), in the charging of the double layer at the interface of the electrodes, and, possibly, in the process of partial adsorption of hydrogen at the cathode. Since the last two processes can be neglected for a point contact with a very small area ( $\sim 0.03 \text{ mm}^2$ ), the ion current is determined exclusively by the electrochemical

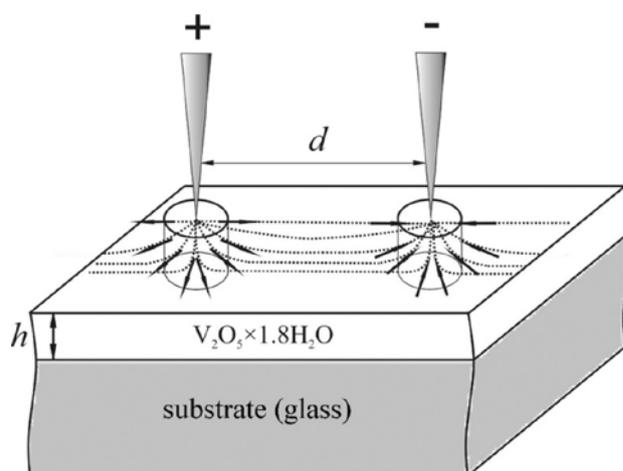
reaction (1). This reaction gradually slows down, and with bigger time values (actually more than 300 s) the electrochromic colouration (Fig. 2) stops. Then we can assume that the purely electronic component  $I(t)$  should be equal to the stationary current  $I(t \rightarrow \infty) \equiv I_{st}$ , when the ionic current disappears, that is,  $I_p(t) = I(t) - I_{st}$ . In turn, at any given point of time the area of the coloured spot  $S(t)$  must be proportional to the proton charge  $Q(t)$  involved in the IEC reaction, and its growth rate must be proportional to the ionic current:

$$\frac{dS(t)}{dt} = \alpha \frac{dQ(t)}{dt} = \alpha I_p(t), \quad (2)$$

where the proportionality coefficient  $\alpha$  is the electrochromism efficiency parameter [11].

The electrochromic spot is almost circular in shape, centred on the cathode. This indicates that colour centres are formed under the influence of the field in the region around the cathode, which has almost a cylindrical shape (Fig. 4). Indeed, the distance between the contacts is much greater than the film thickness ( $d = 3 \text{ mm} \gg h = 1 \mu\text{m}$ ). This is the condition for the cylindrical geometry of current distribution from point electrodes. It can be observed, for example, in experiments on probe measurement of thin film conductivity on dielectric substrates [12].

Then we assumed a simplified model for the electrochromic colouration region in the form of a cylinder around the cathode with a radius



**Fig. 4.** Layout of an HVP-based electrochromic film on a dielectric substrate (glass) with point (probe) contacts. Around electrodes of cylindrical geometry, the current lines are shown

$R(t)$  and a height equal to the film thickness  $h$ . The growth of the observed spot is the internal electrochromism reaction (1) process with a moving boundary, which is the lateral surface of this cylinder with an area  $S_L(t) = 2\pi R(t)h$ . We believe that at any given time the concentration of the resulting colour centres inside the cylinder is  $N_s$  and outside the cylinder it is zero. Then the ion current is:

$$I_p(t) = J_p(t) \cdot S_L(t) = qN_s \frac{dR(t)}{dt} \cdot 2\pi R(t)h, \quad (3)$$

where the ion current density  $J_p(t)$  is the product of the ion charge concentration  $qN_s$  ( $q$  is the elementary charge) inside the cylinder by the velocity of its boundary motion ( $dR(t)/dt$ ).

The second equality in (3) can be expressed as:

$$qN_s \frac{dR(t)}{dt} \cdot 2\pi R(t)h = qN_s \frac{dS(t)}{dt} h, \quad (4)$$

which establishes a direct relationship between the ion current and the growth rate of the area of the electrochromic spot (the area of the upper base of the cylinder)  $S(t) = \pi R^2(t)$ :

$$I_p(t) = I(t) - I_{st} = qN_s h \frac{dS(t)}{dt}. \quad (5)$$

We compared (2) and (5) and determined that the electrochromism efficiency parameter was inversely related to the concentration of the formed colour centres  $N_s$ :

$$\alpha = \frac{1}{qN_s h}. \quad (6)$$

Thus, having determined the growth rate of the spot area from the curves in Fig. 2, and the corresponding ion currents by the experiments described in Fig. 3, we obtained the electrochromism efficiency parameters and the concentration of the formed colour centres from relations (5) and (6). The results from the calculation are shown in Table 1. The  $N_s$  values are also compared with the estimated values of

the equilibrium concentration of HVP protons ( $N_o$ ) for all variants of experiments (I–III).

We calculated the  $N_o$  value for the original film (experiment I) based on the HVP chemical formula ( $V_2O_5 \times 1.8H_2O$ ), obtained using X-ray diffraction [5]. Since the volume of the tetragonal unit cell of HVP is  $V_e = a \times b \times c = 1.118 \cdot 10^{-24} \text{ cm}^3$  ( $a = 11.5 \text{ \AA}$ ,  $b = 3.6 \text{ \AA}$ ,  $c = 27 \text{ \AA}$ ), and the number of hydrogen atoms is 18 [10], then  $N_o$  is approximately equal to  $1.6 \cdot 10^{22}$  per  $1 \text{ cm}^3$ . According to the data of thermogravimetric analysis [6], for the fully hydrogenated film (experiment III) with an implantation dose of  $3.5 \cdot 10^{17} \text{ cm}^{-2}$ , this value decreases by  $\sim 2.6$  times. Apparently, this is due to the partial evaporation of interlayer water when the film is heated (to about  $100 \text{ }^\circ\text{C}$  [6]) during hydrogenation.

The sample in experiment II is inhomogeneous: the cathode region is the initial HVP film, and the anode region is the hydrogenated HVP film. Both parts of the film, as determined above, have different concentrations of protons. Inevitably, there must be a diffusion flux near their boundaries to equalize these concentrations. If we take into account the time between the PIII treatment and experiment II (dozens of minutes), as well as the heating of the film subjected to PIII, which also affects the cathode (untreated) region, it becomes clear that such a redistribution of hydrogen is bound to occur. Then, we assumed the average of the concentrations estimated above for variants I and III to be the equilibrium concentration of protons in experiment II.

As can be seen from Table 1, the values obtained for the concentration of the formed colour centres  $N_s$  in all experiments are more than one order of magnitude lower than the equilibrium concentration of HVP protons  $N_o$ . Thus, there are more than enough protons for the IEC reaction (1) even within the cylindrical region of electrochromic spot. It can then be assumed that the mobility of the protons migrating into

**Table 1.** Parameters for electrochromism efficiency and concentration of colouring centres and HVP protons

Parameters	Experiment I	Experiment II	Experiment III
$\alpha, \text{ cm}^2/\text{C}$	130	320	610
$N_s, \text{ cm}^{-3}$	$3 \cdot 10^{20}$	$7.4 \cdot 10^{20}$	$1.4 \cdot 10^{20}$
$N_o, \text{ cm}^{-3}$	$1.6 \cdot 10^{22}$	$1.1 \cdot 10^{22}$	$6.2 \cdot 10^{21}$

the cathode region from the depth of the film is not essential for the kinetics of electrochromism. The factor determining the IEC rate should be the faradaic contact resistance of electrons [13] involved in the electrochemical reaction.

Thus, for the initial and inhomogeneously hydrogenated films (experiments I and II), the concentration of potential colour centres should be the same, since the cathode region in experiment II is not subjected to PIII and is identical to the initial film. However, in variant II, a significantly (almost 2.5 times) higher growth rate and concentration of the colour centres are observed (Table 1). As pointed out in [11], the reason for the increased efficiency of electrochromism after heterogeneous hydrogenation is the decrease in the electron resistance of the anode region of the film subjected to PIII. Consequently, the faradaic conductivity of the IEC reaction increases.

On the other hand, in a film fully treated with PIII (experiment III), internal electrochromism is very weak, with a low concentration of colour centres (Table 1). In our opinion, this is due to the plasma-ion modification of the material, when the action of the proton flux on the film partially restores  $V^{+5}$  to  $V^{+4}$  in HVP. This leads to an increase in the electron (hopping) conductivity of HVP (an increase in the  $V^{+4}$  concentration) and an increase in the total current (see Fig. 3, curve 3). At the same time, the concentration of poly-vanadate colour centres, in which vanadium should be pentavalent, decreases [5].

#### 4. Conclusions

Having analysed the internal electrochromism in HVP, we made the following conclusions

1. A thin-film electrochemical cell with point (probe) contacts can be represented by a simple cylindrical model of ion current distribution. Based on this model, we can assess the reaction rate through the visualisation of the electrochemical reaction, as is the case with electrochromism in HVP. The concentration of the forming reagents (colour centres) can be estimated from the current kinetics. The concentration of colour centres in the HVP xerogel films generally corresponds to a highly disordered material structure with a large number of defects, which can be poly-vanadate group fragments (the oxidation state of vanadium is +5).

2. The determining factor in the kinetics of electrochromism in HVP is not the mobility and concentration of protons migrating from the depth of the film to the cathode region, but the rate of the IEC reaction, which depends on the faradaic contact resistance. Therefore, additional hydrogenation of HVP alone cannot enhance electrochromism, even if we reduce the role of negative PIII factors, such as through the intense heating of the films with partial evaporation of water and reduction of  $V^{+5}$  to  $V^{+4}$ . In our opinion, the IEC rate in HVP could be increased by forming electrochromic cells with increased electronic conductivity. For example, they could have alternating layers of initial HVP and PIII-treated films, as well as other hydrogenated materials with mobile protons and high electron conductivity.

#### Author contributions

P. P. Boriskov – research concept, methodology development, text writing, and final conclusions.  
S. V. Burdyukh – research concept and experiment.  
O. Ya. Berezina – scientific leadership, sample synthesis, and text editing.

#### Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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