New hydrogen-sensitive films based on V_2O_5 and WO_3 with Pt catalyst

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Optical properties of the films of vanadium and tungsten oxides in a gas atmosphere, containing hydrogen, have been investigated. Films have been synthesized by electrodeposition and chemical deposition from aqueous solutions. Vanadium (V) oxide films and tungsten (VI) oxide films with a platinum catalyst reversibly change their color being exposed to hydrogen. The present work show promising use for such films as sensitive optical elements for gas sensors.

Introduction

Today in modernization of industry an important role belongs to automatization of production processes based on computer technology, robotic systems and devices for different purposes. Nowadays demand increase is observed for gas analyzers required for technological processes control, as well as gas sensors for industrial emissions of toxic and hazardous substances due to growth of industrial production. Improvement of many of these processes, their fail-safety and environmental safety determined by reliability and response speed of automatic analytical instruments based on gas sensors, both standalone as well as part of control systems. Presently interest increased for use of metal oxides as a material for gas sensors. These materials are characterized by changes in optical properties due to the reversible chemisorption of reactive gases on the surface.

Results and discussion

Vanadium (V) oxide films and tungsten (VI) oxide films with a platinum catalyst are capable to reversibly change color interacting with hydrogen. For example, a film of vanadium (V) oxide in a hydrogen atmosphere alters from green to yellow. While interacting with oxygen the vanadium (V) oxide film exposed to air changes color back to green. This effect can be explained by the following reactions:

$$H_2 \xrightarrow{Pt} 2H^+ + 2e^- \qquad (1)$$

$$xH^+ + V_2O_5 \rightarrow H_xV^V{}_{1-x}V^{IV}{}_xO_5 \qquad (2)$$

(green) (yellow)

$$H_xV^V{}_{1-x}V^{IV}{}_xO_5 + 0{,}5xO_2 \leftrightarrow V_2O_5 + 0{,}5xH_2O \qquad (3)$$

(yellow) (green)

Absorption spectrum of vanadium (V) oxide film is shown on fig. 1. Light absorption under the hydrogen exposure decreases in the visible region of the spectrum and increases in the near infrared part.

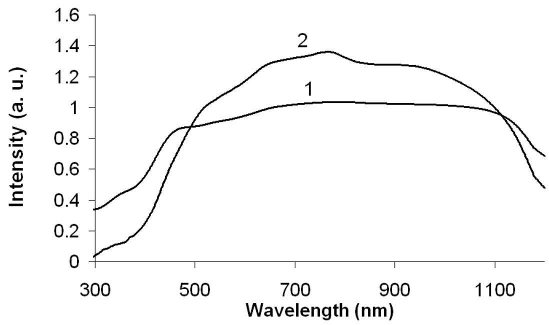


Fig.1. The absorption spectrum of V_2O_5 in air (1) and hydrogen (2) atmosphere

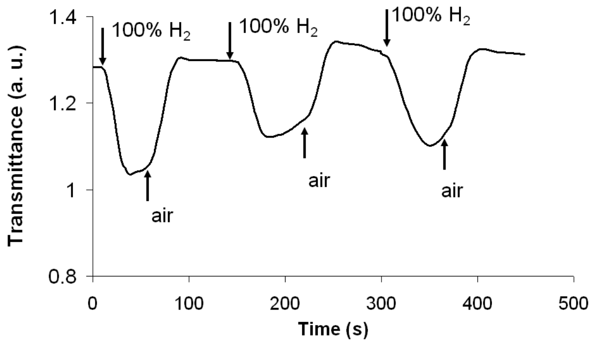


Fig.2. Optical response (λ = 750 nm) when exposed to 100% hydrogen and air.

Measurement of the optical response of the film at λ = 750 nm (Fig. 2) showed that this process is reversible. Moreover, it was found that the reduction reaction with hydrogen as shown at Fig. 2 and the reverse air oxidation both have the same rate. The equilibrium of reaction 3 with the appearance of oxygen quickly shifted toward the formation of a green V_2O_5. Such films are sensitive to the appearance of atmospheric oxygen and hydrogen. They can be used to control gas cylinder containing hydrogen for the traces of oxygen.

Similar processes occur on the films of tungsten (VI) oxide:

$$H_2 \xrightarrow{Pt} 2H^+ + 2e^- \quad (4)$$

$$xH^+ + WO_3 \rightarrow H_xW^{VI}_{1-x} W^{V}x\ O_3 \quad (5)$$

(transparent) (blue)

$$H_xW^{VI}_{1-x} W^{V}_{x} O_3 + 0,5xO_2 \rightarrow WO_3 + 0,5xH_2O \quad (6)$$

(blue) (transparent)

Unlike the film of vanadium oxide, the tungsten oxide film is more sensitive to the appearance of hydrogen in air. If an explosive gas mixture of hydrogen and oxygen forms, this film changes its color to blue. Moreover, the hydrogen content in gas mixture with oxygen affects both the intensity of staining and the speed of the process. Fig. 3 shows absorption spectra of Pt/WO_3 film. As could be seen on fig. 3 increasing of hydrogen content in gas mixture alters intensity of light absorption (increases in the visible region). Maximum staining of films of tungsten (VI) oxide appears in the near-IR region at low concentrations of hydrogen. Increasing hydrogen content by volume leads to shifting of the gasochromic staining maximum in visible light region. Therefore WO_3 film's color changes from transparent to blue.

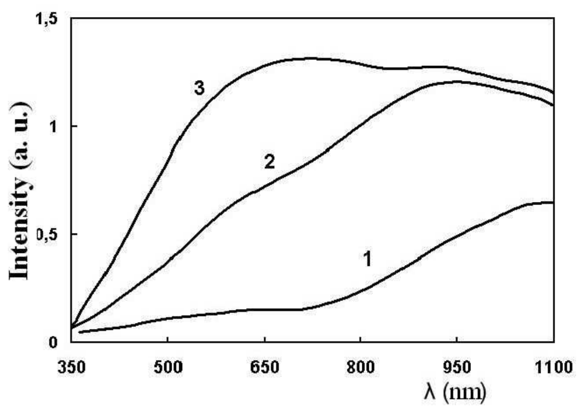


Fig.3. Light absorption spectra of Pt/WO_3 film in hydrogen-air mixture with following H_2 content by volume: 4% (1), 30% (2) and 100% (3)

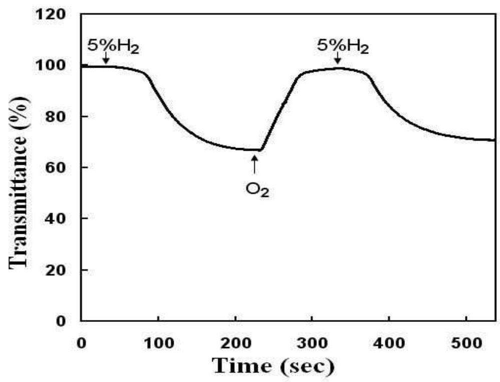
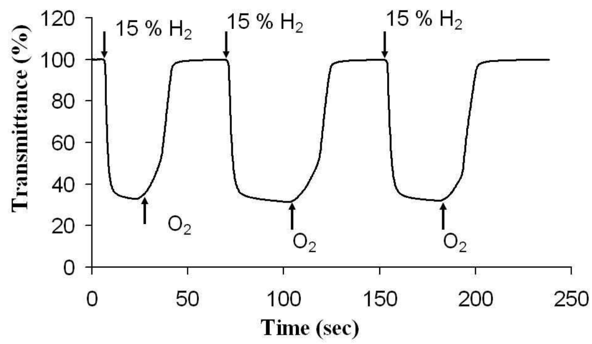


Fig.4a and 4b. Time dependence of the optical response of the Pt/WO_3 film in two cycles of staining when exposed to gas mixture containing air with 5% and 15% H_2 by volume (respectively) followed by bleaching by oxygen from air.



Increasing of hydrogen content by volume in air also affects the performance of dyeing processes of Pt/WO_3 film. As can be seen at Fig.4a and Fig.4b the rate of dyeing and bleaching of Pt/WO_3 film increases in 5 times after increasing of hydrogen content from 5% to 15% by volume.

Conclusions

It is shown that the green Pt/V_2O_5 films change their color to yellow in hydrogen atmosphere. When exposed to oxygen from air, they change color back to green within 10 seconds. Pt/WO_3 electrodeposited films are more sensitive to hydrogen. Their staining speed and color contrast increases several times when exposed to hydrogen mixed with air (≥ 5 vol.%). The resulting films are promising as sensitive material for gas sensors for detecting of explosive concentrations of hydrogen in air and gas storage tanks and cylinders.

Experimental part

Gasochromic films of vanadium and tungsten oxides have been prepared by electrochemical and sol-gel deposition. Vanadium (V) oxide films were deposited on SnO_2 by sol-gel method, followed by heat treatment at temperature of 150° C. Thereafter, the films of vanadium (V) oxide were covered by electroplating a thin (20-30 nm) layer of the Pt catalyst. WO_3 films were prepared by cathodic deposition of the electrolyte containing sodium tungstate and sulfuric acid. [1] The application of a platinum catalyst coating on the film V_2O_5 and WO_3 was carried out by the contact exchange between the charged surface of oxide and $(PtCl_6)_2^{2-}$ complex ions in the 5% solution of platinum chloride acid H_2PtCl_6. This technique allows us to use the deposition of platinum on the surface active sites and monitor its quantity [2]. The resulting films were tested for hydrogen sensitivity for Pt/V_2O_5, Pt $/WO_3$ in a sealed gas cell.

Hydrogen was produced by electrochemical decomposition of water in a sealed cell of low pressure. Gas mixtures were prepared in sealed containers and tested by setting depicted in diagram (Figure 6). In laboratory experiments, display unit often combined through the ADC to a PC for recording the spectra and kinetics of gasochromic coloration.

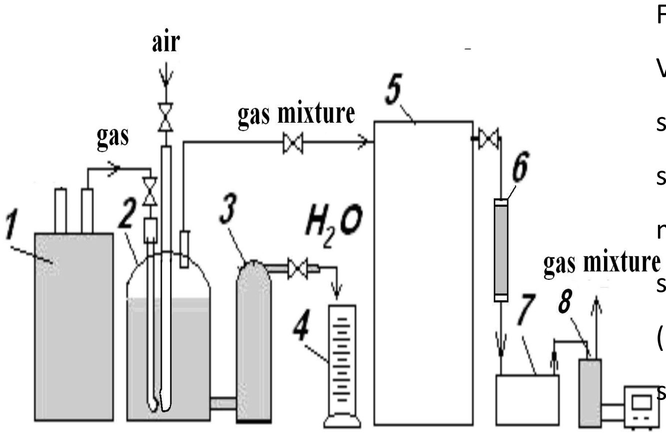


Fig. 1. Apparatus for studying gasochromic effects in V2O5/Pt, WO3/Pt films where: 1 - gas generator, 2 - sealed glass cylinder for preparation of the gas sample, 3 - auxiliary cylinder filled with water, 4 - measuring cylinder, 5 - a device for selection and storage of the gas samples, 6 - drainage column (P_2O_5 powder), 7 - compressors, 8 - the optical sensor on the basis of the test films with the display unit.

References

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