

Yu. M. Artem'ev

CHANGES IN THE ELECTRIC POTENTIALS OF TANTALUM(V) OXIDE ELECTRODES MODIFIED BY W AND Fe UNDER ILLUMINATION

St. Petersburg State University, 199034, St. Petersburg, Russian Federation

Changes in the potentials of electrodes with tantalum(V) oxide layers of ≈ 2 microns thickness under lighting with middle pressure mercury lamp were followed up in test experiments. Electrodes of two types were under investigation: doped by W and doped by Fe. Tantalum oxide layers were obtained by thermal oxide formation on metallic tantalum. W and Fe were contained in the form of surface oxide admixtures. Both types of electrodes revealed photo-potentials which were developed towards the negative region. Such behavior indicated on n-type conductivity of the samples. The effect was observed up to long-wavelength cutoff of UV-range. The greatest values of photo-potential (≈ 270 mV) were observed for the electrodes doped by W under light irradiation of the energy range corresponding to intrinsic absorption of Ta₂O₅. Photo-potentials developed by Fe-doped electrodes were lower more than by order of magnitude. Refs 18. Figs 4.

Keywords: tantalum(V) oxide, surface modification, photopotential, photoelectrochemical hydrogen reduction.

Ю. М. Артемьев

ИЗМЕНЕНИЕ ЭЛЕКТРИЧЕСКОГО ПОТЕНЦИАЛА ТАНТАЛ(V)-ОКСИДНЫХ ЭЛЕКТРОДОВ, МОДИФИЦИРОВАННЫХ W И Fe, ПРИ ОСВЕЩЕНИИ

Санкт-Петербургский государственный университет,
199034, Санкт-Петербург, Российская Федерация

В тестовых экспериментах отслежено изменение потенциала электродов, содержащих ≈ 2 мкм слой оксида тантала(V) при освещении ртутной лампой среднего давления. Исследованы два вида электродов: модифицированных W и Fe. Тантал-оксидные слои получены термическим окислением металлического тантала. W и Fe присутствовали в виде поверхностных оксидных примесей. В обоих случаях фотопотенциал развивался в катодную область, свидетельствуя об n-проводимости образцов. Эффект наблюдался до длинноволновой границы УФ-диапазона. Наибольшие значения фотопотенциала (≈ 270 мВ) зарегистрированы в случае электродов, допированных W, при облучении светом, соответствующим по диапазону энергий, фундаментальному поглощению Ta₂O₅. Значения фотопотенциалов, развиваемых допированными Fe электродами, оказались более чем на порядок ниже. Библиогр. 18 назв. Ил. 4.

Ключевые слова: оксид тантала(V), модифицирование поверхности, фотопотенциал, фотоэлектрохимическое восстановление водорода.

In the recent years various tantalum compounds such as tantalum(V) oxide, tantalates of various metals were under investigation for their potential photocatalytic activity in water dissociation reaction [1–7].

Chemical pure tantalum(V) oxide as photocatalyst isn't useful for practical purposes owing to its considerable band gap value (≈ 4 eV) [8]. The oxide samples absorb only negligible part of Solar irradiation, the range with $\lambda < 310$ nm. Tantalum(V) oxide is isolator by its electro-conductivity value [9]. However, the electronic structure of Ta₂O₅ gives a chance to use the oxide in the base of an active photoelectrode for photoelectrochemical cell for water splitting. The first reason is the high level of conduction-band bottom and, correspondingly, the great value of flat band potential which is higher than TiO₂ level [10] and, consequently, higher than the potential of molecular hydrogen evolution from water

[11]. The second reason is its photo-corrosion resistance both against anodic and cathodic decomposition [12]. In addition, the problem of lack of photoactivity in the range of Solar spectrum and the problem of electro-conductivity shortage are proposed to be resolved in the way of dopants addition.

It was of importance for our study that photo-electrodes were considered as converters of light energy to electricity. Their action is based on internal photoelectric effect within the oxide.

The aim of the study was to predict a possibility of development of the potential sufficient for hydrogen reduction from water by tantalum(V) oxide electrodes modified by W and Fe under illumination.

Potentials were measured for open circuit with the digital voltmeter-pH-meter “pH-150” with high input resistance. Saturated silver chloride electrode was used as the reference electrode. The electrodes were inserted in 0.1N KCl solution with pH = 4.5 at room temperature. Irradiation of middle pressure mercury lamp of DRK-120 type in assembly with OI-18 LOMO illuminator was used. Optical transducers weren't exploited. The distance between lamp and electrode was 25 cm. IR part of irradiation was cut off by 10 cm water filter. Glass filters of standard set were used to select the required light regions.

Electrodes were produced from tantalum metallic ribbon of TVCh (tantalum of high purity) quality with 0.2 mm thickness. A purity of surface layer was ascertained by X-ray fluorescent spectrometric analysis with Spectroscan-006 device. The anode of X-ray tube was made from molybdenum. The following lines were found in the spectrum: 1523 mÅ — the main line, 1327.1, 1284.6, 1138.0, 1099.4 mÅ — trace lines. Tungsten was discovered as the main impurity. The share of tungsten atoms of the number of surface tantalum atoms was determined by the energy dispersive analyzer “Oxford INCA 350” with Si(Li) detector in the structure of the “Zeiss EVO-40EP” electron microscope. This value was 6–7 %.

The electrode working illuminated plate was of $41 \times 15 \text{ mm}^2$ size. Conducting contacts were welded on by the argon welding. Oxide layer was produced by thermal oxidation technique at 800 K in the oxygen flow within 1 h. With the aim to remove surface contaminates the plates were degreased, treated by acid and thoroughly rinsed with twice distilled water. Fairly loose at microscopic level cover was formed in consequence of oxidation (Fig. 1). The electrodes obtained by such a way were designated as W/TOE. A layer thickness wasn't

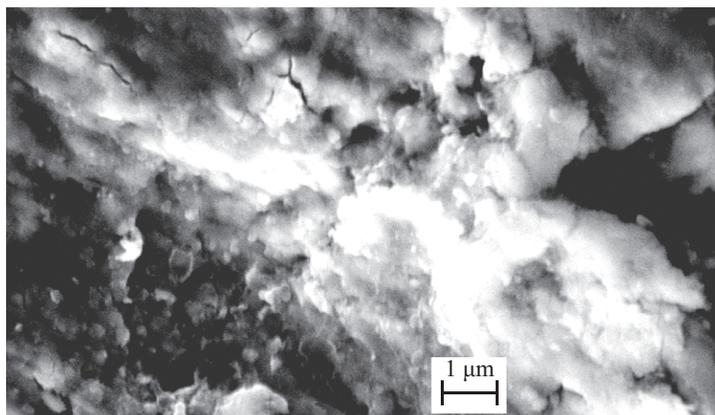


Fig. 1. Representation of tantalum oxide layer obtained with the Zeiss EVO-40EP scanning electron microscope

measured. According to [14] the oxidation of metallic tantalum under similar conditions resulted in the oxide layer of 2 microns thickness.

Oxidized surface was of light-yellow color which could be reasonably related to WO_3 . It was found that if this cover would be removed and the oxidation process would be prolonged the reformed layer would be colorless. Consequently, tungsten as impurity was contained only at the very surface. An appearance of this surface impurity could be explained by specific conditions of tantalum ribbon production. For example, the ribbon could be contaminated in the course of heated rolling on tungsten mill rolls.

DR spectra (Fig. 2) of W/TOE, tantalum(V) oxide obtained by burning of tantalum ribbon in pure oxygen, and WO_3 powder of chemical pure quality were recorded with Lambda 9 UV/VIS/NIR (PerkinElmer) spectrophotometer in reference to BaSO_4 . The spectrum of Ta_2O_5 sample corresponds to characteristic spectra of this compound [11]. The shoulder in the area of 375–450 nm, which correlates with WO_3 absorption band, is clearly seen in the W/TOE spectrum.

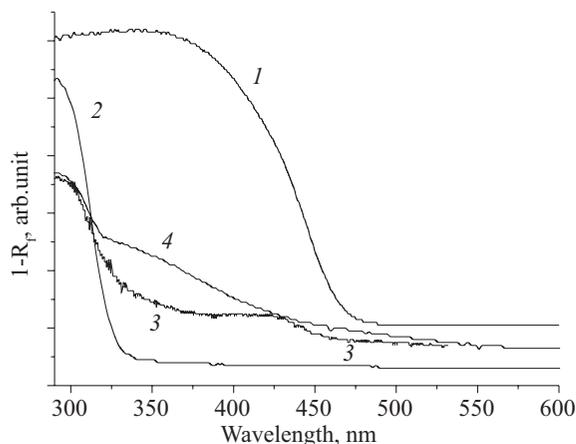


Fig. 2. Diffuse reflectance spectra:

1 — WO_3 powder; 2 — Ta_2O_5 powder; 3 — W/TOE; 4 — Fe/TOE

Potential of W/TOE was shifted to negative region under illumination (Fig. 3). Long wavelength boundary of light action was determined by a poor but appreciable effect observed when ZhS-10 light filter (cut off $\lambda < 390$ nm [15]) was applied.

Potential of W/TOE was developed towards cathodic area and it approached to a maximal value under excitation by UV-light for more than an hour. (UFS-2 filter is transparent for the light range from 270 up to 380 nm. It is an analog of “Schott” BG 11 light-filter.) A comparatively fast return to the rate of the starting potential was observed when the light was cut off. Such behavior was reproduced for light “on-off” cycles and for series of electrodes. It reflected processes occurred at interfaces and within oxide bulk. A study of the processes was out of the frameworks of the present work. The maximal potential change (i. e. photo-potential) which we have registered was about 270 mV. If the irradiation would be prolonged this value could be higher approximately on 30–50 mV. For further discussion let take into account the following. In general, according to [12], the value of semi-conductor electrode photo-potential measured for open circuit is insufficient to estimate a capability of any photoelectrochemical reaction to occur. However in the case of n-type semi-conductor a shift of Fermi level and, approximately, a position of quasi-Fermi level of photo-generated electrons will be determined by photopotential value. Owing to high position of Ta_2O_5 flat band potential for certain illumination rates an electron quasi-level may attain the level of

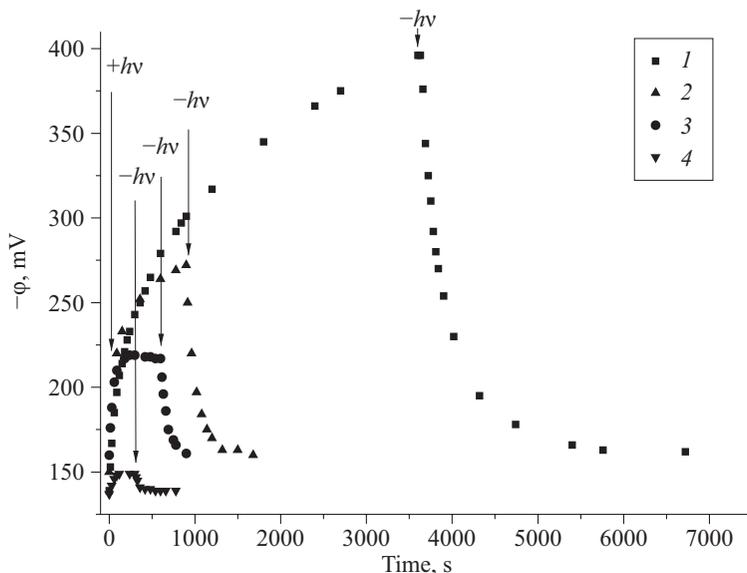


Fig. 3. Change in W/TOE potential in dependence on duration of illumination by DRK-120 when the following light filters were used:

1 — UFS-2; 2 — BS-5; 3 — BS-7; 4 — ZcS-10;
vertical arrows indicate the time points of lighting on ($+hv$) and off ($-hv$)

hydrogen reduction from water and exceed it. Most likely for tantalum(V) oxide a sufficient shift value will be defined by a few units of eV.

When the irradiation corresponded to the intrinsic absorption of Ta_2O_5 (Fig. 2) was cut off with a use of light-filters BS-5 (transparent at $\lambda > 320$ nm) and BS-7 ($\lambda > 360$ nm) the photopotential value was appreciably diminished (Fig. 3). But this value was still rather considerable (for the case of BS-7 filter $\Delta\phi \approx 70$ mV) and it indicated on photoactivity of the electrode out of the range of long wavelength boundary of intrinsic absorption of Ta_2O_5 .

With the aim to produce highly dispersed iron-oxide particles uniformly allocated across the surface of TOE the following procedure was fulfilled. Tantalum(V) oxide layer produced at the first stage was removed mechanically. The electrode was oxidized afresh, cooled, and inserted instantly in the solution of anhydrous iron(III) chloride in absolute ethanol. It was hold there for 1 h in hermetically closed flask. The electrode taken out of the ethanol solution was of light yellow color. Further it was heated at 200 °C for 4 h in the air flow saturated by water vapors. Hydrolysis of iron-oxy- and ethoxy-chloride compounds and their conversion into iron-oxide and iron-hydroxide surface compounds would occur under indicated conditions. At the first step of the treatment iron ethoxy-chloride particles contained in alcohol solution were assumed to interact with impurity water molecules and tantalum-hydroxide groups of the oxide surface. At the second step the hydrolysis process was proposed to complete. The iron content which was ascertained by spectrophotometric technique with o-phenanthroline complex [16] was less than 0.1 wt. %.

Charge transfer band O→Ta was seen in DR spectrum of TOE modified by iron-oxide particles (Fe/TOE) (Fig. 2). An unstructured absorption extended to long wavelength region was observed at $\lambda > 325$ nm. A similar spectrum was gained earlier for bulk samples of tantalum(V) oxide modified in the same way [17]. It was related to the non-uniform iron-oxygen surface particles.

Potential generation at Fe/TOE under light action was investigated under the same conditions like at W/TOE. Potentials moved to the negative area with increasing of lighting time. Maximal values were attained for tens of minutes, but they were appreciably low than in the case of W/TOE (Fig. 4). One among the possible explanations was an enhancement of the recombination of photogenerated electrons and holes, which was surmised for a number of various oxide samples modified by iron [18].

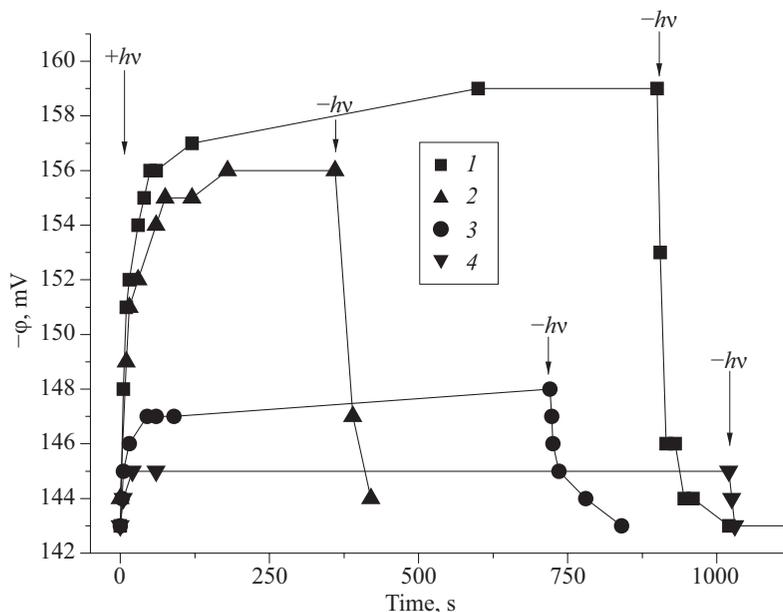


Fig. 4. Change in Fe/TOE potential in dependence on duration of illumination by DRK-120 when the following light filters were used:

1 — UFS-2; 2 — BS-3; 3 — BS-5; 4 — BS-7;

vertical arrows indicate the time points of lighting on (+hv) and off (-hv)

Considerable changes in potentials were observed under illumination through UFS-2 and BS-3 light-filters. BS-3 was transparent at $\lambda > 300$ nm and it slightly reduced a luminous flux in the range of intrinsic absorption of Ta_2O_5 . Therefore the generated photopotentials were lower. The effect was also observed when BS-7 light-filter was used. BS-7 cut off totally the irradiation corresponding to absorption band of tantalum(V) oxide. The effect was obviously caused by absorption on admixtures like iron oxide particles. However the photopotential in this case was inconsiderable ($\Delta\varphi \approx 3$ mV).

Conclusion. The layers of tantalum(V) oxide modified by W and Fe with a thickness about 2 micron were obtained by thermal oxidation of metal tantalum. Photogenerated potentials on electrodes with these layers were developed towards cathodic area. The greatest values of photopotential were observed in the case of electrodes contained W under action of light corresponded to intrinsic absorption of Ta_2O_5 . However the potential values attained were insufficient to reduce hydrogen from water. We assume the W/TOE to be promising in further investigations.

The author thanks Senior Researcher L. B. Gulina for X-ray fluorescent spectrometric analysis and Professor V. P. Tolstoy for the experiments with electronic microscope.

References

1. *Yongfa Zhua, Fang Yua, Yi Man et al.* Preparation and performances of nanosized Ta₂O₅ powder photocatalyst // *J. Solid State Chem.* 2005. Vol. 178. P. 224.
2. *Thammanoon Sreethawong, Supachai Ngamsinlapasathian, Susumu Yoshikawa.* Facile surfactant-aided sol-gel synthesis of mesoporous-assembled Ta₂O₅ nanoparticles with enhanced photocatalytic H₂ production // *J. Molecular Catalysis (A).* 2013. Vol. 374–375. P. 94.
3. *Sen Lin, Lei Shi, Hisao Yoshida, Mingrun Li, Xiaodong Zou.* Synthesis of hollow spherical tantalum oxide nanoparticles and their photocatalytic activity for hydrogen production // *J. Solid State Chem.* 2013. Vol. 199. P. 15.
4. *Kato H., Kudo A.* Photocatalytic water splitting into H₂ and O₂ over various tantalate photocatalysts // *Catalysis Today.* 2003. Vol. 78. P. 561.
5. *Honghui Yang, Xiuru Liu, Zhaohui Zhou, Liejin Guo.* Preparation of a novel Cd₂Ta₂O₇ photocatalyst and its photocatalytic activity in water splitting // *Catalysis Commun.* 2013. Vol. 31. P. 71.
6. *Harun Tiyyisiza, Candace K. Chan.* Preparation of amorphous and nanocrystalline sodium tantalum oxide photocatalysts with porous matrix structure for overall water splitting // *Nano Energy.* 2013. Vol. 2. P. 116–123.
7. *Jing Liu, Jiawen Liu, Zhonghua Li.* Preparation and photocatalytic activity for water splitting of Pt–Na₂Ta₂O₆ nanotube arrays // *J. Solid State Chem.* 2013. Vol. 198. P. 192.
8. *Wachs I. E., Briand L. E., Jehng J.-M. et al.* Molecular structure and reactivity of the group V metal oxides // *Catalysis Today.* 2000. Vol. 57. P. 323.
9. *Kostikova G. P., Kostikov Yu. P.* Chemical processes in the course of oxide doping. St. Petersburg: St. Petersburg University Press, 1997.
10. *Ye J., Zoub Z., Arakawa H. et al.* Correlation of crystal and electronic structures with photophysical properties of water splitting photocatalysts InMO₄ (M = V⁵⁺, Nb⁵⁺, Ta⁵⁺) // *J. Photochemistry and Photobiology (A).* 2002. Vol. 148. P. 79.
11. *Zamaraev K. I., Parmon V. N.* Possible approaches to the development of photo-catalytic solar energy converters // *Russ. Chem. Rev.* 1980. Vol. 49, N 8. P. 695.
12. *Pleskov Yu. V., Gurevich Yu. Ya.* Semiconductor Photoelectrochemistry / ed. by P. N. Bartlett. New York: Consultants Bureau, 1986. 422 p.
13. *Dengwei Jing, Liejin Guo.* Hydrogen production over Fe-doped tantalum oxide from an aqueous methanol solution under the light irradiation // *J. Physics and Chemistry of Solids.* 2007. Vol. 68. P. 2363.
14. *Maeng S., Aze L., Tyson T., Jiang A.* An investigation of structures of thermal and anodic tantalum oxide films // *J. Electrochem. Soc.* 2005. Vol. 152, N 2. P. B60.
15. *Veinberg I.* Catalog of colored glasses. Moscow: Mashinostroenie, 1967. P. 62.
16. *Charlot G.* Les méthodes de la chimie analytique. Analyse quantitative minérale: 4^{ème} édition. Paris: Masson, 1961.
17. *Artem'ev Yu. M., Balakireva E. A.* Oxygen and hydrogen adsorption on tantalum(V) oxide modified by iron-oxygen groups // *Vestn. S.-Peterb. Univ. Ser. 4. Fizika, khimiia.* 2006. Iss. 4. P. 100–102.
18. *Xiaobo Chen, Shaohua Shen, Liejin Guo, Samuel S. Mao.* Semiconductor-based photocatalytic hydrogen generation // *Chem. Rev.* 2010. Vol. 110. P. 6503.

Статья поступила в редакцию 4 февраля 2014 г.

Контактная информация

Артемьев Юрий Михайлович — кандидат химических наук, доцент; e-mail: yuriim54@yandex.ru

Artem'ev Yurii M. — Candidate of Chemistry, Associate Professor; e-mail: yuriim54@yandex.ru