

## XPS STUDY OF $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O$ XEROGELS INTERCALATED WITH HYDROQUINONE

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Layered nanocomposites of  $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O$  gels are synthesized by using sol-gel technology. Then an aqueous solution of hydroquinone (HQ) was mixed with the formed gel in molar ratio 0.33 : 1 and 0.17 : 1 respectively. In this way the  $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O/2HQ$  and  $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O/HQ$  gels were synthesized. The valences of vanadium and titanium ions in the investigated compounds are studied by means of X-ray photoelectron spectroscopy (XPS) before and after etching the samples with  $Ar^+$  ions for 15 min (3 keV, current density  $10 \mu A cm^{-2}$ ). XPS analysis results show that independent of the hydroquinone intercalation degree (one or two hydroquinone) and  $Ar^+$  ion etching the ions of titanium are in stable 4+ states. Vanadium ions in all cases (one or two hydroquinone, before and after etching) are in  $V^{3+}$ ,  $V^{4+}$ , and  $V^{5+}$  states. The increase in quantity of hydroquinone in the samples leads to higher concentration of  $V^{3+}$  and  $V^{4+}$  ions. The concentrations of lower valence vanadium ions increase after  $Ar^+$  ion etching of the samples.

**Keywords:** vanadium hydrates, sol-gel technology, hydroquinone, XPS

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### 1. Introduction

The mobile structure of vanadium pentoxide xerogels is composed of  $V_2O_5$  blocks linked by strongly bonded water molecules [1, 2]. Embedding various ions and radicals between V–O layers it is possible to produce many nanocomposites by simple sol-gel technology methods [3–7]. Some physical properties of layered nanocomposites of  $V_{1.67}Me_{0.33}O_{5\pm\delta}\cdot nH_2O$  (Me = Mo or Ti) xerogels intercalated with hydroquinone (HQ) were described in [8]. It was shown that the electrical conductivity of xerogels intercalated with hydroquinone increases with the hydroquinone amount in them [8]. The electronic part of the conductivity of vanadium pentoxide based xerogels is defined by the electron hopping between vanadium ions in different valence states [9] and depends of the vanadium ion reduction ratio  $C = c^{4+}/(c^{4+} + c^{5+})$ , where  $c^{4+}$  and  $c^{5+}$  are the concentrations of  $V^{4+}$  and  $V^{5+}$  ions respectively.

It is known that the X-ray photoelectron spectroscopy (XPS) method allows determining the valence states of various ions and their concentrations [10].

Moreover, using the  $Ar^+$  ion etching of the investigated compounds during XPS experiments, it is possible to change the chemical states of ions in hydrated vanadium compounds [11].

The aim of this work was the determination of vanadium and titanium valence states in  $V_{1.67}Me_{0.33}O_{5\pm\delta}\cdot nH_2O$  xerogels intercalated with hydroquinone.

### 2. Experiment

The vanadium pentoxide powder ( $V_2O_5$ , purity 99.9%, “Sigma–Aldrich”), titanium dihydride ( $TiH_2$ , purity 99.7%, “Atlantic Equipment Engineers”), hydrogen peroxide ( $H_2O_2$ , purity 99%, “Standard”), and hydroquinone ( $C_6H_4(OH)_2$ , purity 99%, “Sigma–Aldrich”) were used as the starting materials to produce nanocomposites.  $V_2O_5$  and titanium dihydride were taken in molar ratio 1.67 : 0.33 and dissolved in hydrogen peroxide at 273 K temperature. Then the solution was heated at 333–334 K and exposed at this temperature until peroxide complexes of vanadium and titanium fully decomposed and  $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O$

Table 1.  $V_{1.67}Ti_{0.33}O_{4.85} \cdot nH_2O$ /HQ gel titanium region fitting parameters.

| Peak                 | Binding energy, eV | FWHM, eV | RA*, % | G/L**, % |
|----------------------|--------------------|----------|--------|----------|
| As-grown             |                    |          |        |          |
| Ti 2p <sub>3/2</sub> | 458.31             | 1.81     | 68.1   | 31       |
| Ti 2p <sub>1/2</sub> | 464.03             | 2.37     | 31.9   | 31       |
| After etching        |                    |          |        |          |
| Ti 2p <sub>3/2</sub> | 458.28             | 2.33     | 66.4   | 30       |
| Ti 2p <sub>1/2</sub> | 463.98             | 3.24     | 33.6   | 30       |

\* RA is relative area of the peak.

\*\* G/L is Gaussian/Lorentzian ratio.

Table 2.  $V_{1.67}Ti_{0.33}O_{4.85} \cdot nH_2O$ /2HQ gel titanium region fitting parameters.

| Peak                 | Binding energy, eV | FWHM, eV | RA, % | G/L, % |
|----------------------|--------------------|----------|-------|--------|
| As-grown             |                    |          |       |        |
| Ti 2p <sub>3/2</sub> | 458.36             | 2.02     | 71    | 37     |
| Ti 2p <sub>1/2</sub> | 463.99             | 2.58     | 29    | 37     |
| After etching        |                    |          |       |        |
| Ti 2p <sub>3/2</sub> | 458.51             | 2.33     | 67    | 40     |
| Ti 2p <sub>1/2</sub> | 464.23             | 3.07     | 33    | 40     |

Table 3. Vanadium–oxygen region fitting parameters of  $V_{1.67}Ti_{0.33}O_{4.85} \cdot nH_2O$ /HQ gel.

| Peak                                   | Binding energy, eV | FWHM, eV | RA, % | G/L, % |
|--|--------------------|----------|-------|--------|
| As-grown                               |                    |          |       |        |
| V 2p <sub>3/2</sub> (V <sup>5+</sup> ) | 517.06             | 1.74     | 25    | 16     |
| V 2p <sub>3/2</sub> (V <sup>4+</sup> ) | 515.91             | 1.74     | 10    | 16     |
| V 2p <sub>3/2</sub> (V <sup>3+</sup> ) | 514.86             | 1.74     | 1     | 16     |
| O 1s (O <sup>2-</sup> )                | 529.81             | 1.78     | 46    | 16     |
| O 1s (OH <sup>-</sup> )                | 531.45             | 1.78     | 11    | 16     |
| O 1s (H <sub>2</sub> O)                | 532.76             | 1.78     | 7     | 16     |
| After etching                          |                    |          |       |        |
| V 2p <sub>3/2</sub> (V <sup>5+</sup> ) | 516.68             | 2.02     | 11    | 24     |
| V 2p <sub>3/2</sub> (V <sup>4+</sup> ) | 515.29             | 2.02     | 18    | 24     |
| V 2p <sub>3/2</sub> (V <sup>3+</sup> ) | 514.51             | 2.02     | 10    | 24     |
| O 1s (O <sup>2-</sup> )                | 530.02             | 2        | 49    | 24     |
| O 1s (OH <sup>-</sup> )                | 531.89             | 2        | 10    | 24     |
| O 1s (H <sub>2</sub> O)                | 532.52             | 1.43     | 2     | 24     |

gel was formed. An aqueous solution of hydroquinone was mixed with the formed gel in molar ratio 0.33:1 and 0.17:1 respectively. In this way the  $V_{1.67}Ti_{0.33}O_{5\pm\delta} \cdot nH_2O$ /2HQ and  $V_{1.67}Ti_{0.33}O_{5\pm\delta} \cdot nH_2O$ /HQ gels were synthesized. These gels were applied on the Ni pad and dried in an air. The thickness of the formed layers was about 0.01 mm.

XSAM 800 (Kratos Analytical, UK) was used to record the X-ray photoelectron spectra. A non-monochromatized Mg K $\alpha$  (1253.6 eV) radiation source

Table 4. Vanadium region fitting parameters of  $V_{1.67}Ti_{0.33}O_{4.85} \cdot nH_2O$ /2HQ gel.

| Peak                                   | Binding energy, eV | FWHM, eV | RA, % | G/L, % |
|--|--------------------|----------|-------|--------|
| As-grown                               |                    |          |       |        |
| V 2p <sub>3/2</sub> (V <sup>5+</sup> ) | 517.15             | 1.7      | 15    | 31     |
| V 2p <sub>3/2</sub> (V <sup>4+</sup> ) | 515.92             | 1.7      | 19    | 31     |
| V 2p <sub>3/2</sub> (V <sup>3+</sup> ) | 514.75             | 1.7      | 4     | 31     |
| O 1s (O <sup>2-</sup> )                | 529.87             | 1.83     | 45    | 31     |
| O 1s (OH <sup>-</sup> )                | 531.37             | 1.83     | 12    | 31     |
| O 1s (H <sub>2</sub> O)                | 532.97             | 1.71     | 5     | 31     |
| After etching                          |                    |          |       |        |
| V 2p <sub>3/2</sub> (V <sup>5+</sup> ) | 517.29             | 2.03     | 11    | 24     |
| V 2p <sub>3/2</sub> (V <sup>4+</sup> ) | 516.35             | 2.03     | 19    | 24     |
| V 2p <sub>3/2</sub> (V <sup>3+</sup> ) | 515.22             | 2.03     | 14    | 24     |
| O 1s (O <sup>2-</sup> )                | 530.29             | 1.89     | 48    | 24     |
| O 1s (OH <sup>-</sup> )                | 531.84             | 1.89     | 6     | 24     |
| O 1s (H <sub>2</sub> O)                | 532.79             | 1.89     | 2     | 24     |

excited the photoelectrons at 15 kV, 300 W. During the spectrum analysis the working pressure was below 10<sup>-7</sup> Pa in the analysis chamber. The analyzer used with an energy resolution  $\Delta E/E = 0.08\%$  in steady retarding mode.

Using KRATOS DS800 data system the photoemission data has been collected and processed. The multiple photoelectron spectra were separated into several peaks setting the peak position: binding energy (BE), area (A), width (FWHM), and Gaussian/Lorentzian (G/L) ratio, after the Mg K $\alpha$  source satellites and background deduction. The accuracy of the relative intensities and BE of the measured lines were about 10% and 0.1 eV respectively. The random C 1s line the BE of which should have been equal to 284.6 eV was used for the correction of the charging effects. After Shirley background subtraction, a non-linear least squares curve fitting routine with a Gaussian/Lorentzian product function was used for the analysis of XPS spectra.

The Ar<sup>+</sup> ion bombardment at 3 keV for 15 min with current density 10  $\mu A cm^{-2}$  was used to study the influence of ion sputtering on chemical states of metals.

### 3. Results and discussion

Figure 1 shows typical XPS spectra of titanium region for  $V_{1.67}Ti_{0.33}O_{5\pm\delta} \cdot nH_2O$ /HQ gel (a) before and (b) after Ar<sup>+</sup> ion etching. XPS spectra for  $V_{1.67}Ti_{0.33}O_{5\pm\delta} \cdot nH_2O$ /2HQ gel are similar. Titanium peaks consist of two Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> components the parameters of which are given in Tables 1 and 2. For both gels (with one and two hydroquinone), before

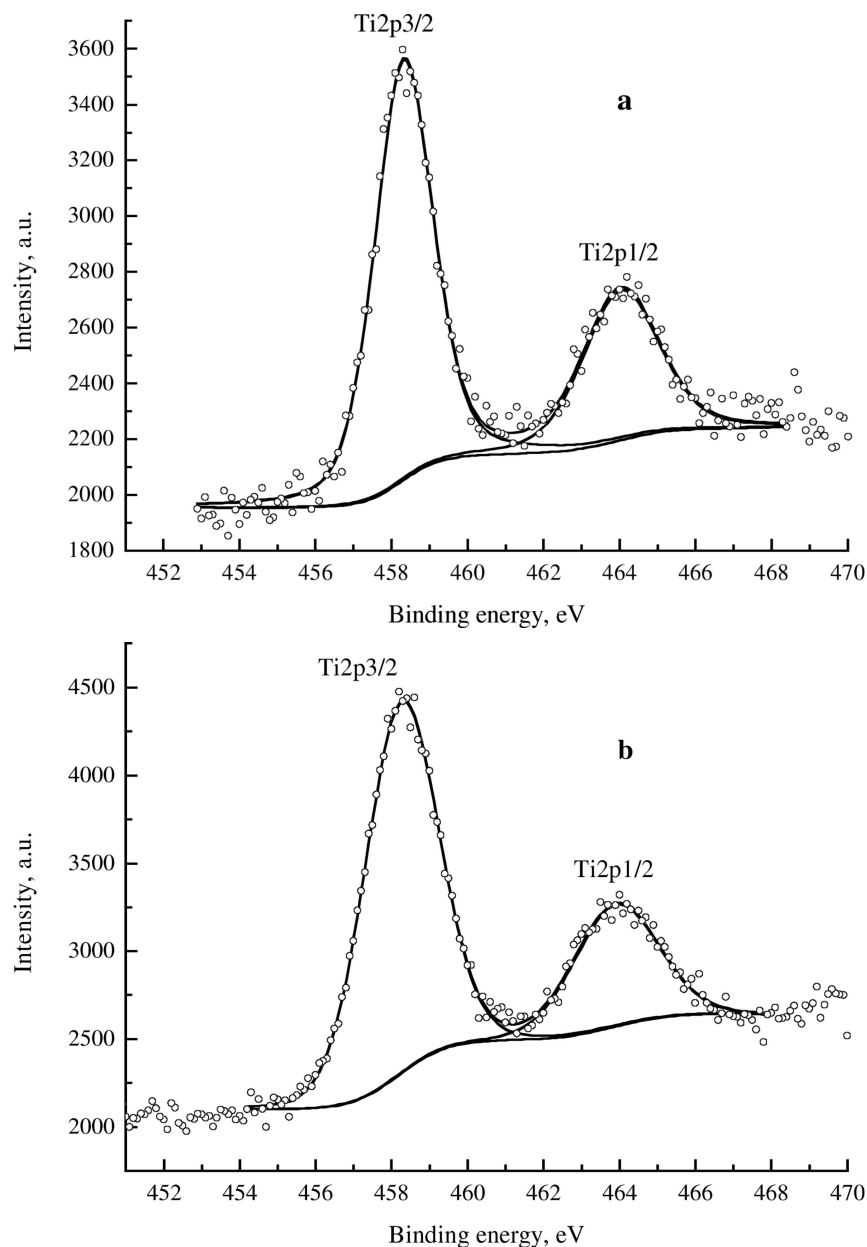


Fig. 1. XPS spectra of  $V_{1.67}Ti_{0.33}O_{4.85} \cdot nH_2O$ /HQ gel titanium region (a) before and (b) after the etching.

as well as after the  $Ar^+$  ion bombardment, the binding energies of Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$  peaks are  $\sim 458$  and  $\sim 464$  eV respectively. The values of BE are typical of titanium dioxide [12, 13]. This fact shows that independent of the hydroquinone intercalation degree and  $Ar^+$  ion etching the ions of titanium are in stable  $4+$  states. The similar stable states of Ti ions were observed in vanadium–titanium hydrates [14, 15].

The vanadium–oxygen region in XPS spectra of investigated compounds with one and two HQ are shown in Figs. 2 and 3 ((a) before and (b) after  $Ar^+$  ion bombardment) and the fitting components are presented in Tables 3 and 4 respectively. In all cases the V 2p peaks consist of three pairs of lines (see Figs. 2 and

3). The binding energies of three V  $2p_{3/2}$  peak components are  $\sim 517$ ,  $\sim 516$ , and  $\sim 515$  eV (see Tables 3 and 4) that correspond to  $5+$ ,  $4+$ , and  $3+$  valence states of vanadium [13, 16–18]. The  $V^{3+}$  ions exist in all investigated compounds before as well as after the  $Ar^+$  ion bombardment. It is necessary to notice that in vanadium–titanium hydrated compounds the  $V^{3+}$  ions appear only after the  $Ar^+$  ion etching of the samples [14]. From the relative area of the V  $2p_{3/2}$  peak  $V^{3+}$ ,  $V^{4+}$ , and  $V^{5+}$  components, which are presented in Tables 3 and 4, we can calculate the reduction ratio of various valence states of vanadium ions,  $C_i = c^i / (c^{3+} + c^{4+} + c^{5+})$ , where  $i = 3+, 4+, 5+$  and  $c^{3+}$ ,  $c^{4+}$ ,  $c^{5+}$  are the concentrations of

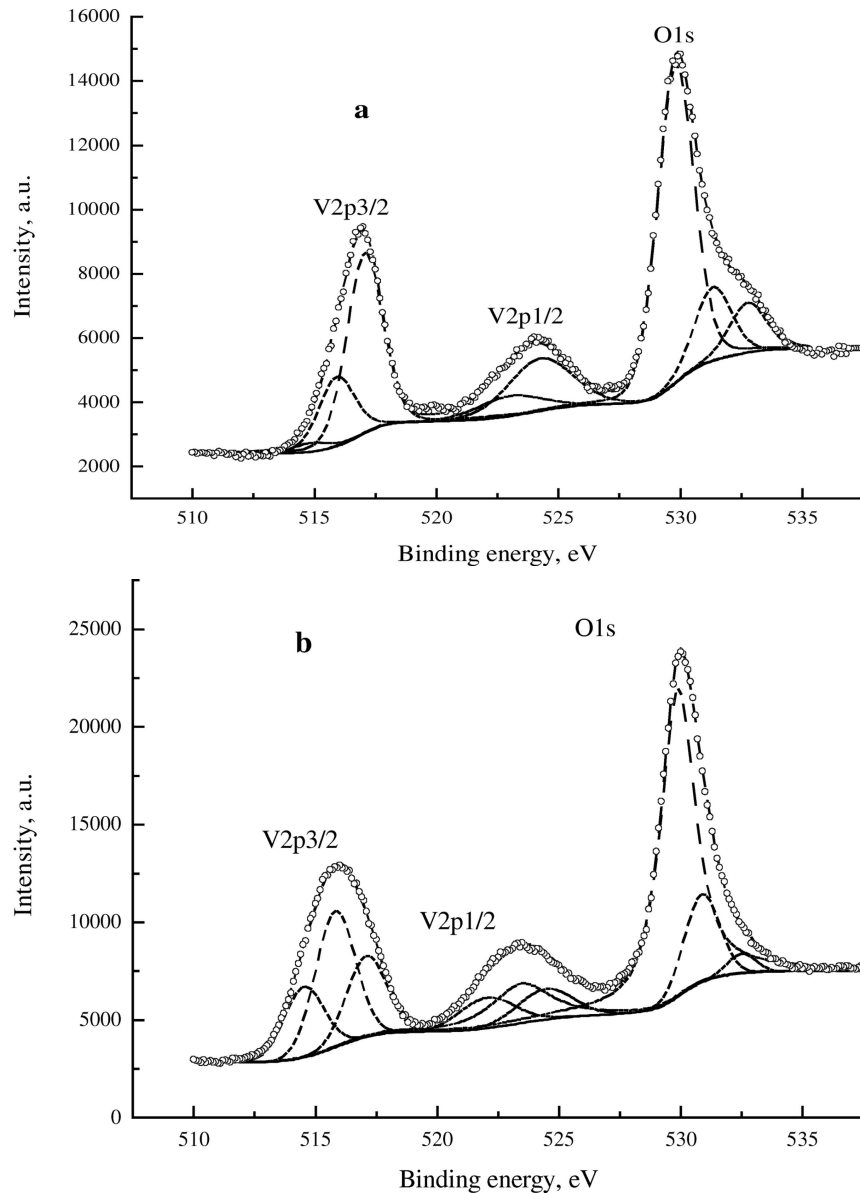


Fig. 2. XPS vanadium–oxygen region spectra of  $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O/HQ$  gel (a) before and (b) after the etching.

$V^{3+}$ ,  $V^{4+}$ ,  $V^{5+}$  ions respectively. These concentrations are proportional to the relative area of corresponded fitting components [10]. Figure 4 shows the calculated reduction ratios for  $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O/HQ$  and  $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O/2HQ$  compounds before (as-grown) and after the  $Ar^+$  ion etching of the samples. From the results presented in Fig. 4 it follows that the concentration of lower valence vanadium ions increases with the hydroquinone concentration and after the  $Ar^+$  ion etching. Thus it is possible to speak about vanadium–oxygen bonding relaxation when the hydroquinone is intercalated in the vanadium–titanium hydrates.

#### 4. Conclusions

X-ray photoelectron spectra of  $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O/2HQ$  and  $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O/HQ$  (HQ is hydroquinone) gels, produced by using sol-gel technology methods, are presented. The valences of vanadium and titanium ions in the investigated compounds are studied by means of X-ray photoelectron spectroscopy (XPS) before and after etching the samples with  $Ar^+$  ions for 15 min (3 keV, current density  $10 \mu A cm^{-2}$ ). XPS analysis results show that independent of the hydroquinone intercalation degree (one or two HQ) and the  $Ar^+$  ion etching the ions of titanium are in stable  $4+$  states. Vanadium ions in all cases (one or two hydroquinone, before and after etching) are in  $V^{3+}$ ,  $V^{4+}$ , and

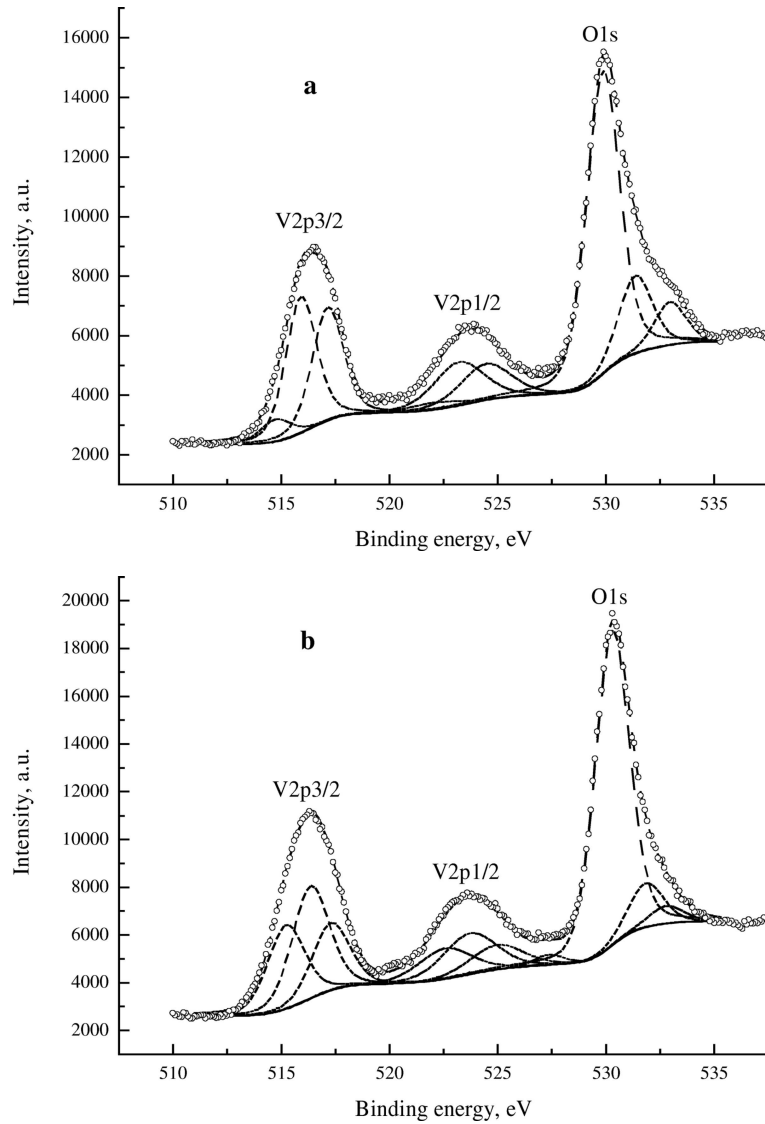


Fig. 3. XPS vanadium region spectra of  $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O/2HQ$  gel (a) before and (b) after the etching.

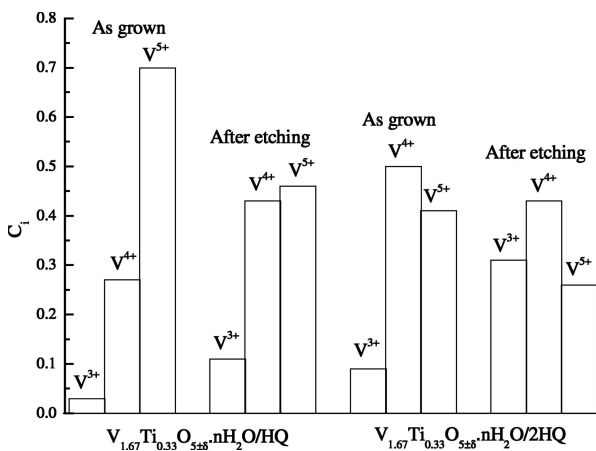


Fig. 4. Reduction ratio  $C_i$  for  $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O/HQ$  and  $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O/2HQ$  hydrates before (as-grown) and after the  $Ar^+$  ion etching of the samples.

$V^{5+}$  states. The increase in quantity of hydroquinone in the samples leads to the growth of concentration of  $V^{3+}$  and  $V^{4+}$  ions. The concentrations of lower valence vanadium ions increase after the  $Ar^+$  ion etching of the samples.

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## $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O$ KSEROGELIŲ, INTERKALIUOTŲ HIDROCHINONU, RENTGENO FOTOLEKTRONINIŲ SPEKTRŲ TYRIMAS

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### Santrauka

Pateikti  $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O/2HQ$  ir  $V_{1.67}Ti_{0.33}O_{4.85}\cdot nH_2O/HQ$  (HQ – hidrochinonas) gelių, gautų naudojant zolio ir gelio technologiją, Rentgeno fotoelektronų spektrai. Tyrinčiuose junginiuose vanadžio ir titano jonų valentingumas analizuotas remiantis Rentgeno fotoelektronų spektroskopija (RFS) prieš ir po bandinių išdininimo  $Ar^+$  jonais, trukusį 15 min (3 keV, srovės tankis

$10 \mu A cm^{-2}$ ). RFS analizės rezultatai parodė, jog, nepriklausomai nuo hidrochinono interkaliavimo laipsnio (vienas ar du HQ) ir išdininimo  $Ar^+$  jonais, titano jonai yra stabiliose 4+ būsenose. Vanadžio jonai visais atvejais (vienas ar du HQ, prieš ir po išdininimo) yra  $V^{3+}$ ,  $V^{4+}$  ir  $V^{5+}$  būsenose.  $V^{3+}$  ir  $V^{4+}$  santykinė koncentracija didėja, didėjant HQ kiekiui geliuose bei po bandinių išdininimo  $Ar^+$  jonais.