Photoelectric polarization and quantum-chemical data about electrochemical films formed in perchlorate alcohol solutions

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Methods

Potentiodinamic, impedance scectroscopy, photo-current and photopotential measurements, chromatography, Raman spectroscopy, IR- и X-ray structural analysis, quantum chemical modeling with the use of B3LYP, IEFPCM, HyperChem Pro, X_α - SW.

Reproduced value considered if average square deviatoin S_x was less than $1{,}6673\cdot10^{-3}$, dispersion $S_x^2<2{,}7799\cdot10^{-6}$, confidence interval α = 0,96-0,98, correlation coefficient r=0,987 – 0,999.

Research objects

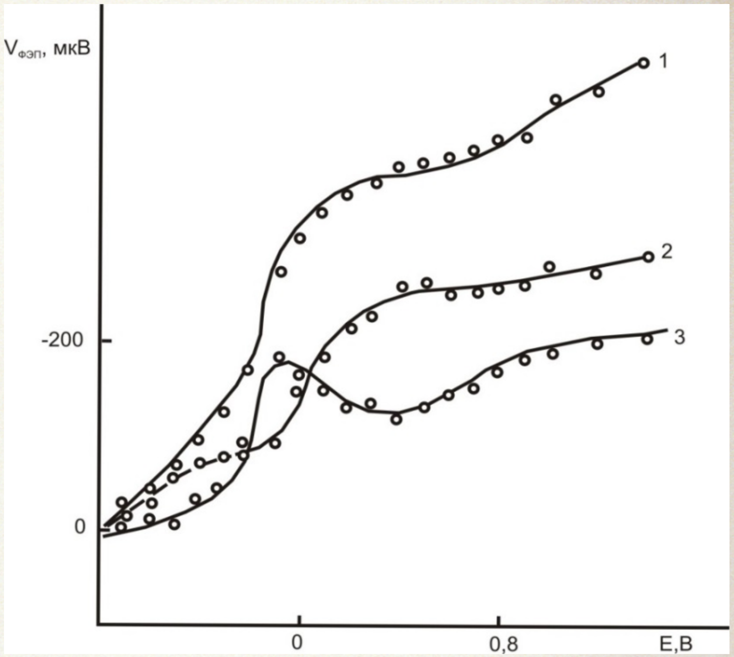
1. Metals: Ti (99,999%), V (99,99%), Nb (99,9999%), Ta (T4), Zr (99,999%),

2. Working environments.

Nonaqueous lithium perchlorate, saturated alcohols (Merk).

Solvents had been distillated and had been absolutized. We defined water ratio every time before experience used chromatography. It was $1\cdot10^{-4}$ % (mol).

Ar had been passed through the cell. Access of air had been excluded.



•**Fig.** The dependence of photoresponce of Ti-electrode from potential in 0,1 M solution:

•1-LiClO4 in ButOH;

•2 – indifferent aqueous K2SO4;

•3- the photoresponces difference, E -dependence.

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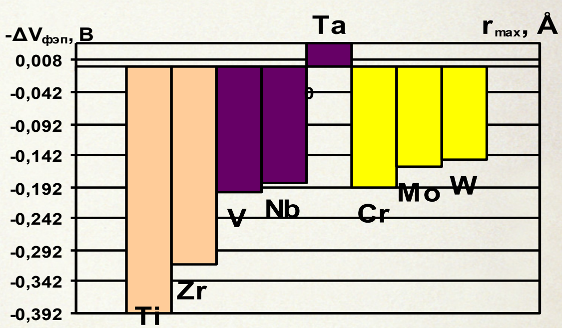


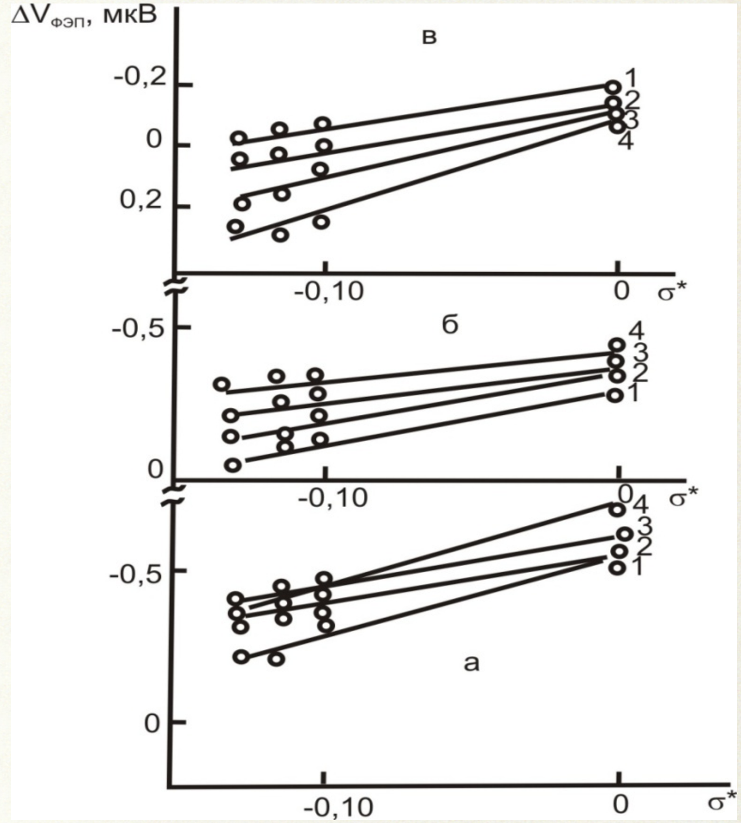


Fig. $\Delta V_{ФЭП}$, σ* – зависимость для а –V; б – Nb; в - Ta в 0,1 M перхлоратных растворах спиртов при потенциалах, В: 1 – $E<E_{кр}$; 2 - $E_{кр}$; 3 – $E>E_{кр}$; 4 –$E>>E_{кр}$.

Smitt D.H., Hertel G.R // J. Chem. Phys. 1969. V. 51. p. 3106.

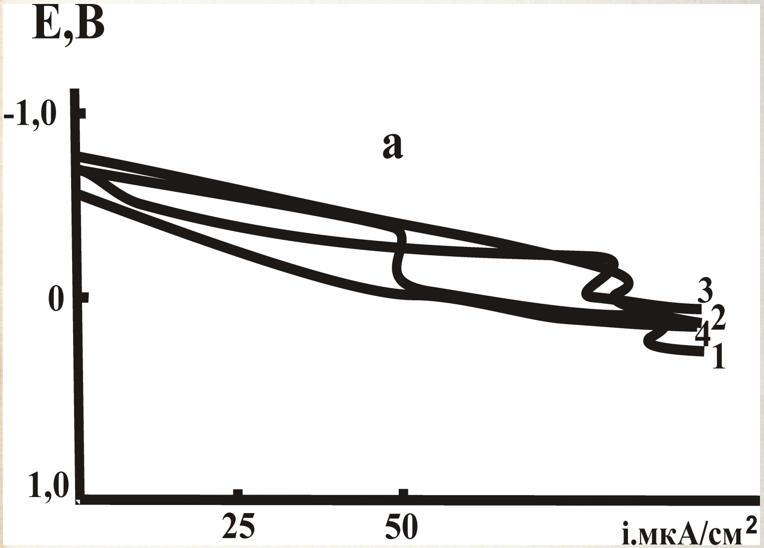


Fig. Anodic potentiodinamic curves for Zr in 0,1M alcohol solutions:

1 – MetOH;

2 – EtOH;

3 – n-PrOH;

4 – n-ButOH.

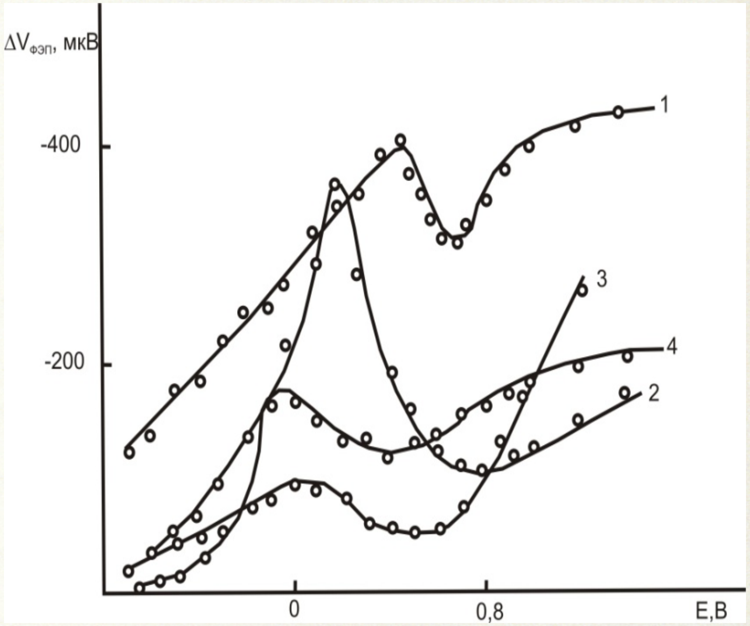


Fig. ΔV_{PEP}, E –dependence for Ti in 0,1 M perchlorate solution: 1 - MetOH; 2 - EtOH; 3 - PrOH; 4 - ButOH.

The meanings of E_c for Ti in 0,1 M perchlorate alcohol solution:

R	Met	Et	Pr	But
E, B	0,43	0,18	0,08	-0,08

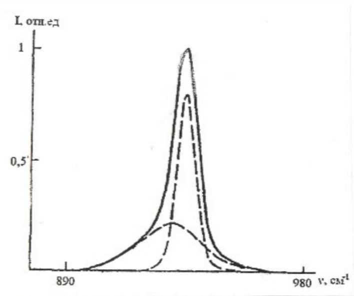
Kofstad P. // J.Electrochem. Soc. 1962. V.109.P.776.

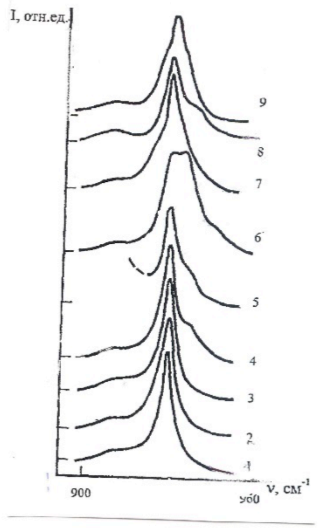
Tabl. 1. Koefficients of stoichiometry *X* and concentration of defects of crystal lattice *N* (10^{20}) for Ti, V, Nb, Ta in 0,1 M perchlorate alcohol solutions

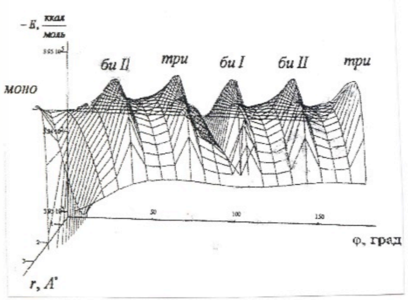
M	R	E, B					
		$E<E_{\text{кр}}$		$E_{\text{кр}}$		$E>E_{\text{кр}}$	
		X	*N*	*X*	*N*	*X*	*N*
Ti	Met	0,9959	5,248	0,9935	8,320	0,9945	7,040
	Et	0,9972	3,584	0,9943	6,656	0,9980	2,560
	Pr	0,9986	1,792	0,9984	2,048	0,9993	0,896
	But	0,9971	3,712	0,9970	3,840	0,9980	2,560
V	Met	0,9979	1,491	0,9967	2,343	0,9970	2,130
	Et	0,9984	1,136	0,9977	1,633	0,9986	0,994
	Pr	0,9987	0,923	0,9981	1,420	0,9995	0,355
	But	0,9992	0,568	0,9990	1,349	0,9997	0,213
Nb	Met	0,9984	0,880	0,9968	1,7 60	0,9974	1,430
	Et	0,9985	0,825	0,9971	1,595	0,9978	1,210
	Pr	0,9992	0,440	0,9987	0,715	0,9996	0,220
	But	0,9992	0,440	0,9992	0,440	0,9996	0,220
Ta	Met	1,0001	0,055	1,0006	0,330	1,0002	0,110
	Et	1,006	0,330	1,008	0,440	1,0003	0,165
	Pr	1,0011	0,605	1,0012	0,660	1,0003	0,165
	But	1,0015	0,825	1,0015	0,825	1,0004	0,220

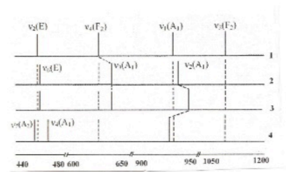
Tabl. 2. Energy (E_t), charge(q_t), length of bonds (l_{C-H}, l_{C-O}, l_{Me-O}), dipole moment (μ) in complex $[MeOHR]^{\circ}$ for d-metals in 0,1 perchlorate ethanol solutions.

Me	E_t, эВ	q_t, Кл	l_{O-H}, Å	l_{C-O}, Å	l_{Me-O}, Å	μ_{C2H5OH}, D	
						μ_1	μ_2
Mo	-8517,97	0,64	1,95	1,40	1,77	1,69	1,92
W	-8224,39	0,58	1,94	1,39	1,79	1,69	1,96









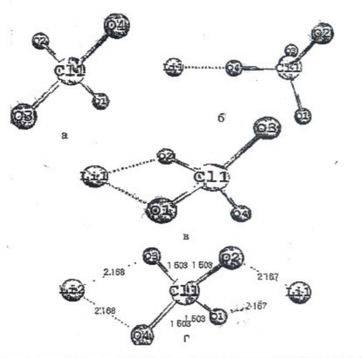


Fig. Strips in Raman-spectras (different cations and solvents), decomposition of vibration’s strip of the perchlorate-ion in ethanol solutions and it’s Potential energy surface.

Fig. The distribution of the vibration frequencies of coordinated perchlorate-ion in Raman-spectras: 1- free ion; 2 – monodentate coordinated ion pair [$Li^+ClO_4^-$]; 3 – triple associate type [$Li^+ClO_4^-\ Li^+$]; 4 – bidentate ion pair [$Li^+ClO_4^-$].

Fig. Configurations perchlorate-ions: a- individual; b – monodentate in ion-pair; c – bidentate in ion-pair; d – triple associate type [Li+ClO4-Li+].

V 1

$$Me + ROH = Me(ROH)_{адс}$$

$$Me(ROH)_{адс} \leftrightarrows Me(OR^{-})_{адс} + H^{+}$$

$$Me(OR^{-})_{адс} \leftrightarrows Me(OR)_{адс} + e \qquad \text{(limiting stage)}$$

$$Me(OR)_{адс} + Me(ROH)_{адс} \leftrightarrows [(Me(OR) \cdot Me(ROH)]_{адс}$$

$$MeOR \cdot Me(ROH) \rightarrow MeOR^{+} + e$$

$$MeOR^{+} \leftrightarrows MeOR^{2+} + e$$

$$MeOR^{2+} \leftrightarrows MeOR^{3+} + e$$

$$MeOR^{3+} + H^{+} \rightarrow Me^{4+} + ROH$$

ClO_4 $[Li^{+}ClO_4^{-}]$ ClO_4^{-}
$[MeOHR]^{\circ}$

V 2

$$Me + ROH \leftrightarrow [Me(OHR)]^{0}_{адс}$$

$$[Me(OHR)]^{0}_{адс} \rightarrow [MeOHR]^{+}_{адс} + e \qquad \text{(limiting stage)}$$

$$[MeOHR]^{+}_{адс} \leftrightarrows [MeOHR]^{2+}_{адс} + e$$

$$[MeOHR]^{2+}_{адс} \leftrightarrows [MeOHR]^{3+}_{адс} + e$$

$$[MeOHR]^{3+}_{адс} \leftrightarrows [MeOHR]^{4+}_{адс} + e$$

$$[MeOHR]^{4+}_{адс}(n-1)ROH \leftrightarrows [Me(ROH)_{n}]^{4+}$$

$$[Me(ROH)_{n}]^{4+} \leftrightarrow Me^{4+} + nROH$$

$$Me + H_2O \underset{K_1'}{\overset{K_1}{\rightleftarrows}} (MeOH)_{ads} + H^{+} + e$$

$$(MeOH)_{ads} \underset{K_2'}{\overset{K_2}{\rightleftarrows}} (MeOH^{+})_{ads} + e$$

$$(MeOH^{+})_{ads} + H^{+} \underset{K_3'}{\overset{K_3}{\rightleftarrows}} (Me^{n+})_{ads} + H_2O$$

$$(Me^{n+})_{ads} + x\,H_2O \underset{K_4'}{\overset{K_4}{\rightleftarrows}} [(Me^{n+})_{aq}]_0$$

$$[(Me^{n+})_{aq}]_0 \xrightarrow{X_5} Me^{n+}(aq)$$

X_5 – diffusion constant

Conclusions

1. The initial stage of surface film's growth on d-metals depends on the metal nature and polarization. The nature of solvent, for example, the structure of organic molecules is of great importance for this process. The fact is that electrochemical adsorption complex is formed on the electrode surface. The thin chemosorption layer is evolved on the electrode with polarization. It has a high electronic conductivity. The main transfer mechanism is tunneling of electrons. This layer determines parameters of oxide films.

2. Anodic films aren't stoichiometric. They are semiconductors, mainly, with electron conductivity. Tantalum oxide is characterized by p- conductivity. The negative value of photoresponce is decreased in alcohol series. It confirms that the structure of organic molecules affects to stoichiometry of adsorption layer. Maximums of photoresponce amplitude, deviation from stoichiometry, concentration of crystal lattice's defects are observed in the area of critical potential.

3. *2p*- and *nd*-orbitals bring the large contribution in the bonding. The states of crystal fields have the influence on the bonding. Chemosorption bond is arised if Fermi-level is lower than the loosening chemosorption state.

4. The perchlorate-ion is a outer-sphere component for surface adsorption complex [MeOHR]°.

Thanks for your attention!