Study of diamond-like carbon films doped with transition metals and used as cathodes for current creation in water

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Abstract. Properties of diamond-like carbon films (DLCF) on n-Si substrates used as cathodes in Yb – DLCF (n-Si) water electrochemical system have been studied by current creation with water decomposition $H_2O \rightarrow OH^- + H^+$. The current is several times higher after preliminary electrolytic deposition of impurity that contains one of the transition metals (Pd, Pt, Ni, Cr) on DLCF (n-Si) layer, which changes the nature of the catalytic process of water decomposition. The aging effect of DLCF (n-Si) ⟨Me⟩ was observed after 7- to 25-day metal oxidation in air. It is confirmed the change of the electron work function of CDL (n-Si) ⟨Me⟩ electrode and the current change between it and the Yb electrode.

1. Introduction

In the works [1-6], we investigated the phenomenon of current creation in distilled water between two electrodes with different electrochemical potentials, when water is decomposed catalytically in accord with the equation $H_2O \rightarrow OH^- + H^+$ at the electrodes, the voltage difference between which is kept by discharging the ions OH^- and H^+ at them. Using this simple electrochemical system enables one both to obtain the energy at the cost of current creation and using the obtained hydrogen in what follows, the former energy being tens of times higher than the latter one [4]. The energy yield is provided here by the nature of electrode matter itself.

To make this way of getting energy efficient, first, it is necessary to provide a high difference between electrochemical potentials of these electrodes (or between respective electron work functions), while the electrodes should have as high activity in catalytic water decomposition as possible.

In the works [1-6], a high performance as the electrode-anode was demonstrated for ytterbium (Yb), the electron work function of which lies within the range 3.0 to 3.7 eV in dependence of the oxidation degree. In addition, Yb has declaired itself as a good catalyst for water decomposition.

To choose the electrode-cathode, we used various substances (metals, silicon) in the works [1-6], which have the values of the electron work function within the range 4.2 to 5.3 eV. These values can be notably increased via thermal oxidation of the electrodes. At the same time, catalytic activity of cathodes (as to water decomposition) is determined both by cathode material and physico-chemical state of their surface.

In redox reactions, specifically in $H_2O \leftrightarrow OH + H$, transition metals and their oxides play a good role [7]. Their efficiency is considerably increased when they are deposited in a dispersed state (clusters, islands, *etc.*) on a substrate that also possesses catalytic properties or some other ones related with the catalytic process.

The aim of this work was to study the efficiency of possible using the films of transition metals (Pd, Pt, Ni, Cr) as electrodes-cathodes deposited onto a carbon substrate, the latter being a diamond-like carbon film (DLCF). As solid and chemically resistant material, DLCF turned up to be promising for designing devices of vacuum electronics [8] and, in principle, these films are perspective for applying them as catalytically active electrode substrates. DLCF-amorphous material contains carbon in sp^2- and sp^3-hybrid states, hydrogen impurities as well as some other elements, for instance nitrogen, in dependence of a production way.

It determines their structural and electrophysical properties that are useful for electrodes-substrates. It is worth to note that DLCF is one of carbon structure kinds that comprise graphite, carbon fullerenes and nanotubes possessing definite perspectives as hydrogen accumulators [9]. All these properties became a basis to choose them as carrying substrates for deposition of transition metal (Pd, Pt, Ni, Cr) island films onto them and use these bi-layer structures as electrodes-cathodes.

2. Methods of investigation

The method of experimental investigations has been described in the works [1-3] in detail. When two electrodes (Yb anode and DLCF cathode without or with the impurity of transition metal) are simultaneously dipped into distilled water, there arises a potential difference ΔV_k between them, which is, as a rule, smaller than the difference of electron work functions for the electrodes ($\Delta\varphi$). After making to close the external electric circuit at the moment $t = 0$, we measured time dependences for the current $J(t)$. As the area of electrodes S and the distance between them L were different for various pairs, to compare the effective conductivity of respective electrochemical systems we used the values

$$\sigma = J(t) \cdot (L / \Delta V_k S) = AJ(t),$$

where σ is the effective conductivity,

$$A = L / (\Delta V_k S) \ \text{V}^{-1}\text{cm}^{-1}.$$

When the external circuit was supplied with an additional voltage source with $V_0 = 9.7$ V, instead of the value ΔV_k in this formula we used the value $(\Delta V_k \pm V_0)$.

Before the measurements of $\sigma = AJ(t)$ dependences, we determined the electron work function for the used electrodes. With this aim, we used a Pt plate ($\varphi = 5.32$ eV) as a standard electrode, because Pt is the most stable electrode in our electrochemical studies. φ-values for various electrodes were determined via calculations based on measuring the current between Pt and another electrode when the external voltage $V = \pm 9.7$ V was applied in forward and backward directions [1-3]. To calculate the φ-value for electrodes, we used the formula $\varphi = 5.32$ (eV) $- qV(I_1 - I_2) / (I_1 + I_2)$ (eV), where q is the charge of an electron, I_1 and I_2 are the currents in the electrical circuit of this electrochemical system when the Pt electrode has $-V$ or $+V$ potential, respectively. Summarized in Table are the φ-values obtained by us for various states of the electrodes-cathodes. It is noteworthy that all the electrodes were insensitive to solar light.

DLCF films without any impurity of transition metals or with them served as cathodes. These films were obtained on the surface of silicon wafers (n-Si, $\rho = 0.02$ Ohm·cm) by using the method of plasmo-chemical deposition (PE-CVD) in plasma of the high-frequency discharge (13.56 MHz) with the power 175 W and N_2

concentration 20 % in the gas mixture $H_2:N_2:CH_4:Ar = 10:4:3:1$. The gas pressure inside the reactor chamber was 100 Pa. Deposition of the carbon films was carried out onto silicon substrates being at the room temperature due to cooling the bottom electrode with flowing water. The deposition time for DLCF films was 5 min. Their thickness was close to 80 nm, as measured with the profilometer "Dektak".

Deposition of the transition metal impurity onto DLCF was performed via the electrochemical process in a water solution of metal chloride salts (with the concentration $10^{-2} - 10^{-1}$ M), the titanium (Ti) plate being used as the anode. The amount of the deposited metal (mostly present in the form of island films) was calculated in accord with the Faraday law as based on measurements of the current and time of charge transport between Ti and DLCF (n-Si) electrodes.

3. Experimental data and discussion

As seen from Fig. 1, the effective conductivity $AJ(t)$ of the electrochemical system Yb – DLCF(n-Si) without doping the DLCFs with impurities of transition metals is relatively low. The $AJ(t)$ values grow to some extent, if the DLCF(n-Si) structures were annealed during 1 hour in Ar atmosphere at 300 °C, which is obviously caused by better adhesion between DLCF and n-Si after annealing (compare curves 1, $1^{(+)}$, $1^{(-)}$ and 2, $2^{(+)}$, $2^{(-)}$). It is seen that the conductivity grows noticeably after connection of the additional voltage $V_0 = \pm 9.7$ V (curves $2^{(+)}$, $2^{(-)}$), which is indicative of the fact that annealing promotes creation of non-uniformities in DLCFs. These non-uniformities serve to more efficient water decomposition due to higher values of local electric fields at them [2-4], when the voltage between the electrodes Yb and DLCF (n-Si) is increased.
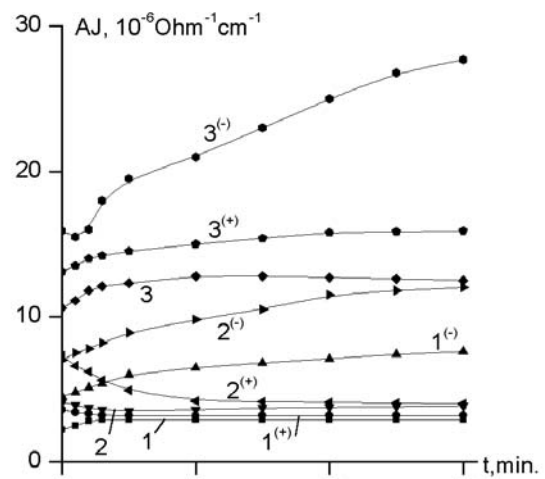

Fig. 1. Time dependences of the efficient conductivity $AJ(t)$ between the electrodes Yb – DLCF (n-Si) in water. *1*, $1^{(+)}$, $1^{(-)}$ – non-annealed DLCF; *2*, $2^{(+)}$, $2^{(-)}$ – annealed DLCF (300 °C, Ar, 1 hour); *3*, $3^{(+)}$, $3^{(-)}$ – doped with Pd ($2.5 \cdot 10^{19}$ cm^{-2}) and annealed DLCF. *1*, *2*, *3* – $V_0 = 0$; $1^{(+)}$, $1^{(-)}$, $2^{(+)}$, $2^{(-)}$, $3^{(+)}$, $3^{(-)}$ – $V_0 = \pm 9.7$ V on the DLCF (n-Si) electrode.

It is also seen from Fig. 1 that at $V_0 = 0$ the values described by curves 1 and 2 only weakly change with time, i.e., DLCFs are relatively stable to current transfer through them. When $V_0 = +9.7$ V at DLCF (n-Si) electrode, the current is decreased with time, while at $V_0 = -9.7$ V on this electrode the current is increased. The main cause for these changes of the current values with time at $V_0 = +9.7$ V is, in our opinion, enrichment with hydrogen (at $V_0 = -9.7$ V) or dehydrogenation (at $V_0 = +9.7$ V) of DLCFs, which changes the electron work function for them and, as a result, promotes some change of the voltage between Yb and DLCF(n-Si) electrode. It has been well confirmed by our following investigations.

The character and values of $AJ(t)$ dependences is considerably changed after deposition of Pd impurity onto DLCF (Fig. 1, curves 3, 3[(+)], 3[(−)]). The DLCF was preliminary annealed. It is seen that the $AJ(t)$ values become several times higher at $V_0 = 0$ after Pd doping, and the $AJ(t)$ dependences (curves 2 and 3) possess different character. First of all, it is indicative of the growth of catalytic activity in water decomposition at the DLCF $\langle$Pd$\rangle$ electrode. The sharp growth of the $AJ(t)$ value (curve 3[(−)]) is caused by electric-field acceleration of water decomposition near the non-uniformities of the DLCF after enrichment of it with hydrogen.

Changes in values and character of $AJ(t)$ dependences with a gradual increase of Pd impurities up to $6 \cdot 10^{18}$ cm^{-2} on the non-annealed structure DLCF (n-Si) are illustrated in Fig. 2 (curves 1 to 4). All the $AJ(t)$ dependences were obtained in conditions, when the external voltage was absent ($V_0 = 0$). In addition, the dependences 5 and 6 were obtained after annealing of

the doped with Pd ($6 \cdot 10^{18}$ cm^{-2}) structure and repeated doping it with Pd ($2.5 \cdot 10^{19}$ cm^{-2}). The curve 6 was measured after 7 days as compared to the curve 5. The considerable decrease of the $AJ(t)$ value is caused by the aging of the DLCF (n-Si) $\langle$Pd, $2.5 \cdot 10^{19}$ cm$^{-2}\rangle$ electrode, that is by Pd film oxidation. It is also confirmed by some growth of φ-values (see Table).

When the electrode DLCF (n-Si) $\langle$Me$\rangle$ is covered with the impurity of Pt, but not of Pd (Fig. 3), we observed the lower rate of aging. Before doping, the Pt-DLCF electrode was annealed. Deposition of Pt ($3 \cdot 10^{18}$ cm^{-2}) resulted in noticeable growth of $AJ(t)$ values (compare the curves 1 and 2). In what following, like to Pd, we observed the aging effect. The curve 3 was obtained after 4 days of aging, curve 4 – after 25 days.

The repeated doping with Pt ($1.6 \cdot 10^{19}$ cm^{-2}) performed some later resulted in changing the curve 4 for the curve 5 ($AJ(t)$ values for it after 60 min from the start of measuring the curve reached up to $14 \cdot 10^{-6}$ Ohm^{-1}cm^{-1}). It is noteworthy that the aging effect was not practically observed after repeated doping. The curve 6 was obtained after 10-day aging, and it practically coincides with the curve 5. Thus, doping the DLCF electrode with Pt results in more positive yield than that with Pd.

Like to Pd deposition, the aging process is fast when the DLCF electrode is covered with a Ni film (Fig. 4). It is described by the curves 1, 2, 3, when the initial structure DLCF (n-Si) (curve 1) is covered with Ni ($1 \cdot 10^{18}$ cm^{-2}) (curve 2) and the aging process lasts 5 days (curve 3). Repeated deposition of Ni ($3 \cdot 10^{18}$ cm^{-2}) resulted in the dependence 4 that "converts" to the dependence 5 after 10-day aging.

Table. Values of the electron work function φ for electrodes in various physico-chemical states.

| Electrode	Electrode notation	φ, eV
Diamond-like carbon film (DLCF): before annealing after annealing	DLCF DLCF[(a)]	5.42-5.00 4.67
DLCF doped with Pd ($2 \cdot 10^{17}$ cm^{-2}) DLCF doped with Pd ($1 \cdot 10^{18}$ cm^{-2}) DLCF doped with Pd ($6 \cdot 10^{18}$ cm^{-2})	DLCF[(Pd)]($2 \cdot 10^{17}$) DLCF[(Pd)]($1 \cdot 10^{18}$) DLCF[(Pd)]($6 \cdot 10^{18}$)	5.48 4.85 4.76
DLCF[(Pd)] ($6 \cdot 10^{18}$ cm^{-2}) after annealing DLCF[(a)] doped with Pd ($2.5 \cdot 10^{19}$ cm^{-2}) after annealing Aged DLCF[(a)][(Pd)]($2.5 \cdot 10^{19}$ cm^{-2})	DLCF[(Pd)][(a)]($6 \cdot 10^{18}$) DLCF[(a)][(Pd)]($2.5 \cdot 10^{19}$) aged	4.96 5.13 5.22
DLCF[(a)] doped with Pt ($3 \cdot 10^{18}$ cm^{-2}) after annealing Aged DLCF[(a)][(Pt)]($3 \cdot 10^{18}$ cm^{-2}) Doped DLCF[(a)][(Pt)]($1.6 \cdot 10^{19}$ cm^{-2}) Aged DLCF[(a)][(Pt)]($1.6 \cdot 10^{19}$ cm^{-2})	DLCF[(a)][(Pt)]($3 \cdot 10^{18}$) aged DLCF[(a)][(Pt)]($1.6 \cdot 10^{19}$) aged	4.76 4.78 5.17 5.18
DLCF[(a)] doped with Ni ($1 \cdot 10^{18}$ cm^{-2}) after annealing Aged DLCF[(a)]($1 \cdot 10^{18}$ cm^{-2}) DLCF[(a)] doped with Ni ($3 \cdot 10^{18}$ cm^{-2}) Aged DLCF[(a)] ($3 \cdot 10^{18}$ cm^{-2})	DLCF[(a)][(Ni)]($1 \cdot 10^{18}$) aged DLCF[(a)][(Ni)]($3 \cdot 10^{18}$) aged	4.73 4.81 4.71 4.79
DLCF[(a)] doped with Cr ($3 \cdot 10^{19}$ cm^{-2}) after annealing Aged DLCF[(a)][(Cr)]($3 \cdot 10^{19}$ cm^{-2})	DLCF[(a)][(Cr)]($3 \cdot 10^{19}$) aged	4.55 4.74
Structure Cr$_3$Si doped with Cr ($1.5 \cdot 10^{19}$ cm^{-2}) Aged structure Cr$_3$Si[(Cr)]	Cr$_3$Si[(Cr)]($1.5 \cdot 10^{19}$) aged	4.51 4.85
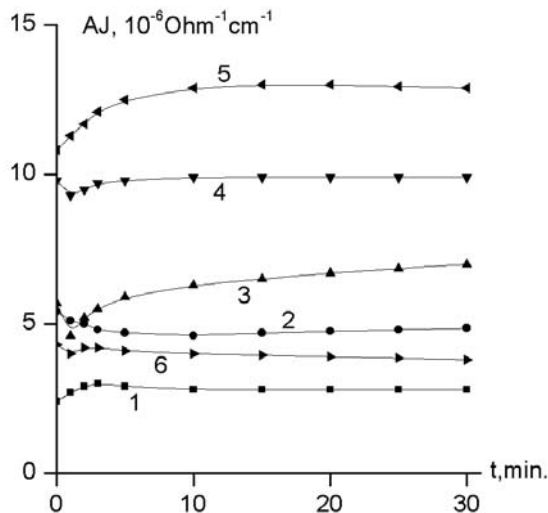
Fig. 2. $AJ(t)$ dependences for Yb – DLCF (n-Si) electrodes at $V_0 = 0$. *1* – non-doped and non-annealed DLCF; *2, 3, 4* – DLCF doped with Pd up to $2 \cdot 10^{17}\,cm^{-2}$, $1 \cdot 10^{18}\,cm^{-2}$, $6 \cdot 10^{18}\,cm^{-2}$, respectively; *5* – DLCF doped repeatedly with Pd ($2.5 \cdot 10^{19}\,cm^{-2}$) DLCF (n-Si) ($6 \cdot 10^{18}\,cm^{-2}$) (*4*) after annealing; *6* – structure 5 after aging.
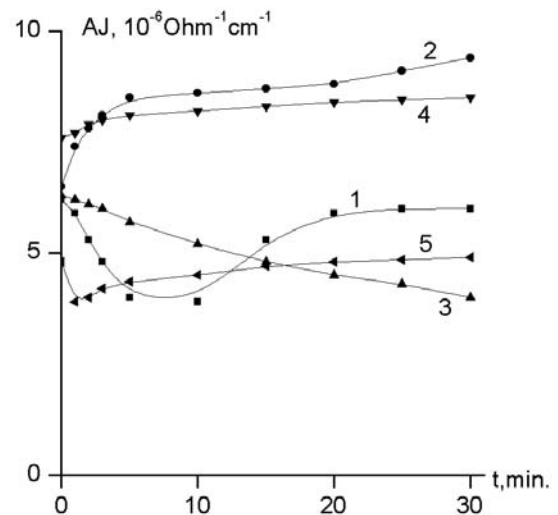

Fig. 4. $AJ(t)$ dependence for Yb – DLCF (n-Si) electrodes at $V_0 = 0$. *1* – non-doped and annealed DLCF (n-Si) structure; *2* – DLCF (n-Si) structure doped with Ni ($1 \cdot 10^{18}\,cm^{-2}$); *3* – structure 2 after 5-day aging; *4* – structure 3 after repeated doping with Ni ($3 \cdot 10^{18}\,cm^{-2}$); *5* – structure 4 after 10-day aging.
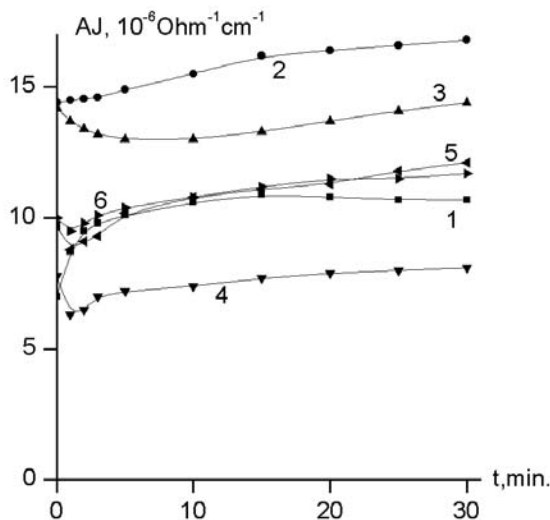

Fig. 3. $AJ(t)$ dependence for Yb – DLCF (n-Si) electrodes at $V_0 = 0$. *1* – non-doped and annealed DLCF (n-Si) structure; *2* – doped with Pt ($3 \cdot 10^{18}\,cm^{-2}$) DLCF (n-Si); *3* – structure 2 after 7-day aging; *4* – structure 2 after 25-day aging; *5* – structure 4 repeatedly doped with Pt ($1.6 \cdot 10^{19}\,cm^{-2}$); *6* – structure 5 after 10-day aging.
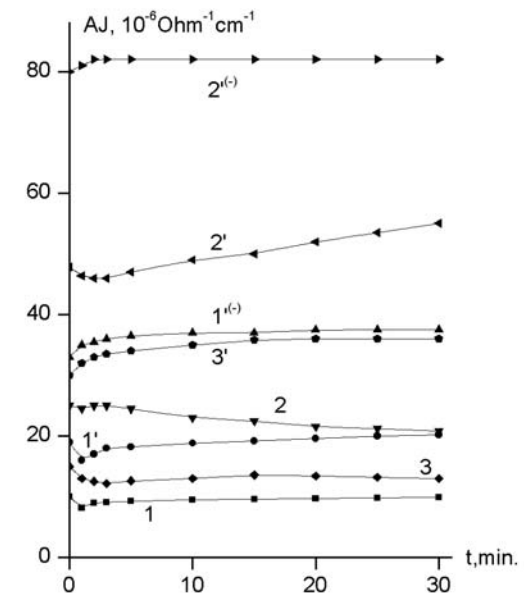

Fig. 5. $AJ(t)$ dependences for Yb – DLCF (n-Si) electrodes (*1, 2, 3*) at $V_0 = 0$ and Yb – Cr₃Si (*1′, 2′, 3′, 1′⁽⁻⁾, 2′⁽⁻⁾*) at $V_0 = 0$ (*1′, 2′, 3′*) and $V_0 = -9.7$ V (*1′⁽⁻⁾, 2′⁽⁻⁾*) on Cr_3Si. *1* – non-doped and annealed DLCF (n-Si); *2* – structure DLCF (n-Si) doped with Cr ($3 \cdot 10^{19}\,cm^{-2}$); *3* – structure 2 after 7-day aging; *1′* – non-doped Cr_3Si structure; *2′* – Cr_3Si structure doped with Cr ($1.5 \cdot 10^{19}\,cm^{-2}$); *3′* – structure 2′ after 7-day aging.

At last, Fig. 5 demonstrates the results of the influence of Cr, as a transition metal, on properties of the DLCF (n-Si) electrode. The annealed structure DLCF (n-Si) described with the curve 1 was covered with the Cr film ($3 \cdot 10^{19}\,cm^{-2}$), which resulted in the dependence 2 that, in its turn, converted into the dependence 3 after 10-day aging of the doped structure. As seen from the comparison of Figs. 1 to 5 demonstrating results of doping with various transition metals, Cr provides the highest $AJ(t)$ values. It means that Cr is a good catalyst for water decomposition $H_2O \rightarrow H^+ + OH^-$. However, oxidation of Cr during the aging process considerably decreases its catalytic activity.

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For comparison, the curves 1′, 2′, 3′ and 1′$^{(-)}$, 2′$^{(-)}$ describe $\Delta J(t)$ dependences obtained after deposition of Cr onto another carrier – electrode, namely, Cr$_3$Si that was investigated in our works [2, 4]. The non-doped electrode Cr$_3$Si was corresponded by the dependence 1′, doped with Cr ($1.5 \cdot 10^{19}$ cm^{-2}) electrode – by the dependence 2′ that after 10-day aging was converted into the dependence 3′. Fig. 5 shows that using chromium silicide as a cathode in combination with Yb anode is much more efficient than using DLCFs as cathodes. It concerns cases both before and after doping them with Cr. However, the aging effect (oxidation of the Cr film) plays its negative role in the case of using Cr$_3$Si as an electrode-substrate as well. Curves 1′$^{(-)}$ and 2′$^{(-)}$ in Fig. 5 were obtained for the case of the voltage $V_0 = -9.7$ V applied to the Cr$_3$Si electrodes and show an essential role of the electric field at the structure non-uniformities inherent to these electrodes when using them for water decomposition.

4. Conclusions

1. Investigated are diamond-like carbon films on n-Si substrates, which serve as cathodes in current creation provided by water decomposition $H_2O \rightarrow OH^- + H^+$ in the electrochemical system Yb – DLCF (n-Si). It has been shown that the efficiency of the DLCF (n-Si) electrode grows to some extent after annealing it at 300 °C. The DLCFs, both non-doped and doped with Pd, Pt, Ni, Cr, turned to be insensitive to solar light.

2. The current J in the system Yb – DLCF ⟨Me⟩, both without any external voltage and with $V_0 = \pm 9.7$ V, is several times higher after deposition one of transition metals (Pd, Pt, Ni, Cr) onto the DLCF. In doing so, the character of time $J(t)$ dependences is changed, which is indicative of the growth of the catalytic activity inherent to the DLCF ⟨Me⟩ electrode and change in the character of electronic processes on it after deposition of a metal film (Me).

3. Oxidation of the metal film Me in air (aging effect during 7 to 25 days) causes the electrodes DLCF ⟨Me⟩ to be unstable, which results in current $J(t)$ decrease in the system Yb – DLCF ⟨Me⟩ under aging. Pt films turned to be the most stable against aging, contrary to Pd and Ni films.

4. Changes in current $J(t)$ values, when doping the DLCF with transition metals and aging the doped films, are indicative of the fact that the main role in these changes is played by changes in the catalytic activity of electrodes DLCF ⟨Me⟩, but not in the electron work function for them (see Table).

5. Using Cr films covering the substrates DLCF (n-Si) and Cr$_3$Si as an example, we have shown that usage of Cr$_3$Si is more promising for current creation in water decomposition.

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