KINETICS OF REDOX REACTIONS ON TiC ELECTRODES COVERED WITH A SURFACE OXIDE

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The rates of reduction and oxidation of hexacyanoferrate(III) and hexacyanoferrate(II) ions, respectively, as well as the rate of reduction of chinone on TiC electrodes were measured using method of linearly increasing electrode potential. The rate of these electrochemical reactions depends on the state of electrode surface and diminishes with increase of the surface oxide thickness. The slope of polarization curve is on oxide-covered electrodes, particularly at higher current densities, considerably greater than on oxide-free electrodes. Experimental results have been explained with use of a model which suggests energetic barrier for the electron transfer through the oxide layer and dependence of concentration of layer electrons on the layer thickness and simultaneously on the concentration of electroactive ions in the solution.

The kinetics of redox reactions is largely influenced by state of the electrode surface, especially by degree of coverage the electrode with surface oxide. Our study of kinetics of redox reactions on the TiC electrodes aims at elucidating state of the electrode surface in the region of potentials, where rapid oxidation of the surface on the one hand and evolution of hydrogen on the other have not taken place as yet, *i.e.* in the region of potentials from -0.2 to $+0.4$ V (s.c.e.). For the study of kinetics of redox reactions in this potential region, titanium carbide is a very suitable material, since undamaged TiC is up to potentials of 0.45 V (s.c.e.) very stable, corrosion current density in 1m-KCl is very small ($i_{cor} = 0.5$ $\mu A/cm^2$), and has a relatively high hydrogen overvoltage[1]. Kinetics of redox reactions, with respect to the potential region available, has been studied in hexacyanoferrate(III)-hexacyanoferrate(II) and quinone--hydroquinone systems.

EXPERIMENTAL

For measurements of the polarization curves, potentiostat Wenking 61 RS in connection with supply of linearly increasing voltage, was employed. The potential-current curves were recorded by $x-y$ plotter ENDIM 2200. The measuring electrode was used in the form of a rotating electrode, the platinum electrode was a conventional disc electrode of effective surface area 2 mm in diamater. The TiC electrode, which was made of $TiC_{0.96}$ single crystals, had for constructional reasons an approximately rectangular shape. Number of electrode rotations was usually

1440 r.p.m. As reference electrode, saturated calomel electrode (s.c.e.) was employed. As auxiliary electrode, platinum electrode was used. The solutions were prepared from reagents of R.G. purity; quinone and hydroquinone were repurified by sublimation. Moreover, the solutions with quinone contained a buffer solution consisting of $0.01M\text{-}Na_2HPO_4 + 0.01M\text{-}NaH_2PO_4$ (pH 6·25).

The electrodes were before the measurement ground with coarse grained boron carbide powders and polished with fine grained diamond paste to achieve mirror-like lustre. Before each measurement of the polarization curve, the fresh surface, unless otherwise stated, was renewed by repolishing with corundum paste. The electrode was after repolishing rinsed with water and put under voltage into the solution to be measured so quickly that the time from the end of polishing to putting into the solution should not exceed 10 s. The beginning of measurements of the polarization curves studied by redox reactions was always in a cathodic region of potentials and the whole curve was measured potentiodynamically with the rate of potential increase of $0.004\ Vs^{-1}$. After a multiple measuring the polarization curve on a new surface, the electrode was oxidized at selected potential for a time interval chosen beforehand. After the oxidation having been finished, the polarization curve was again measured in the same way. In the measurement of the rate of cathodic and anodic reactions, or that of the effect of electroactive compound concentration on the kinetics of the reaction on the electrode oxidized in the same way, the potentiodynamic curve of reduction was after oxidation of the electrode first measured in the original solution, afterwards the electrode was taken out and immediately put into the $0.01M\text{-}K_4FeCN_6 + + 1M\text{-}KCl$ solution to prevent its further oxidation by air oxygen; the solution in the vessel was changed and the polarization curve measured in a new solution. In order to find, whether the electrode surface was not considerably changed during these operations, the polarization curve was again measured in the original solution. For further processing, only those results were taken into account, for which course of the polarization curves in the same solution at the beginning and at the end of the whole series was maintained without obvious changes.

For measuring the charge of the electrode oxidation and its effect on rate of the electrode reaction, the electrode was ground in the way described above, and immediately electrochemically oxidized at a selected potential ($+0.3$ V against s.c.e., usually) in the basic electrolyte, *i.e.* without an electroactive compound, and value of the charge was obtained directly by integration of the current passing. The oxide film thickness was calculated from

$$d_{ox} = QM/4F\ rh \qquad (1)$$

provided that the charge passing in the anodic oxidation is spent only to produce TiO_2 and the layer produced does not dissolve any more; values $h = 4.25\ \text{g cm}^{-3}$ and $r = 3$ were taken into calculation for layer density and coefficient of roughness, respectively.

RESULTS

Reduction of hexacyanoferrate(III) ions on freshly prepared surface of titanium carbide electrode at current densities $i \lesssim 0.5i_L$ proceeds, similarly as on the platinum electrode, so quickly that it is controlled merely by diffusion, as unambiguously follows from logarithmic analysis of the polarization curve (Fig. 1). At current densities $i \gtrsim 0.5i_L$, a small, but still apparent deviation from theoretical course of the diffusion-controlled process, takes place. If surface of the TiC electrode,

however, is exposed even for a very small period of time (about 30 s) to air oxygen, or if the electrode is oxidized by the procedure described above, the rate of reduction considerably decreases. Relation between current and potential can be, from a certain minimum current density upwards, expressed by a well-known equation for irreversible reactions

$$\log |i|/|i_L - i| = \log c_0\, Fk/|i_L| - \alpha'\, F(E - E^0)/2.3RT. \qquad (2)$$

Value of the charge transfer coefficient α', however, is considerably smaller than it is usual with metal electrodes. After attaining a certain degree of oxidation, its value was no longer changed and varied between $0.11 - 0.22$.

As an example of irreversibly proceeding reaction, reduction of quinone has been studied. Logarithmic analysis of the polarization curves (Fig. 2) shows the slope b of the polarization curve to be 0.072 ($\alpha' = 0.82$) on a new surface of the TiC electrode, which is, according to Vetter[2], a value equal also for a platinum electrode. The rate constants of reduction of 0.01M quinone in the given medium were equal to $k = 3.3$. $. 10^{-6}$ and $k = 1.74 . 10^{-6}$ for the platinum and TiC electrodes, respectively. At
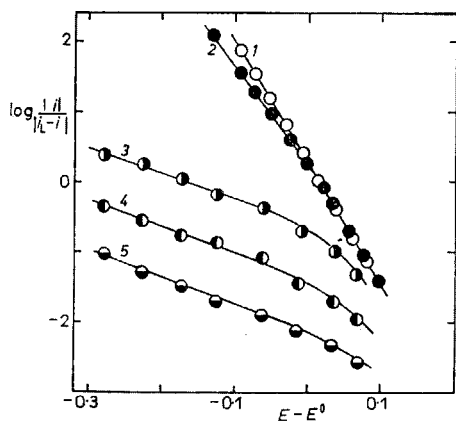

FIG. 1

Dependence between $\log |i|/|i_L - i|$ and $(E - E^0)$ in Solution 0.01M-$K_3Fe(CN)_6$ + $+ 1$M-KCl

1 Platinum electrode; *2* freshly ground TiC electrode; *3, 4, 5* TiC electrode oxidized at $E = +0.3$ V for: *3* 15 min; *4* 45 min; *5* 60 min.
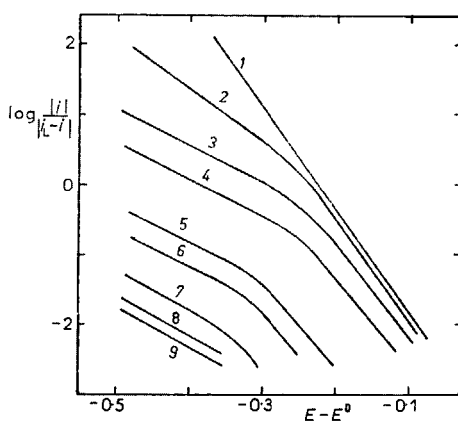
FIG. 2

Dependence between $\log |i|/|i_L - i|$ and $(E - E^0)$ in Solution 0.01M-Quinone + $+ 0.01$M-Na_2HPO_4 + 0.01M-NaH_2PO_4 + $+ 1$M-KCl

1 Platinum electrode; *2* freshly ground TiC electrode; *3, 4* TiC electrodes oxidized at $E = +0.13$ V for: *3* 5 min; *4* 55 min; *5—9* TiC electrodes oxidized at $E = +0.3$ V for: *5* 4 min; *6* 8 min; *7* 23 min; *8* 44 min; *9* 67 min.

higher current densities $(i \gtrsim 0.5i_L - 0.6i_L)$ deviation of the polarization curves to a new linear dependence of lower value of coefficient α' takes place even on the electrodes polished very carefully and for a long time. With the increasing oxidation of the electrode surface the curves are shifted at constant potential towards lower current densities, the constant value of coefficient α' being maintained. For lower current densities, the slope of the polarization curves returns even on these oxidized electrode to the slope of the polarization curve of an original nonoxidized electrode.

Fig. 3 presents rates of cathodic reduction and anodic oixdation in the hexacyano-ferrate(III)–hexacyanoferrate(II)system on the electrode having equal degree of surface oxidation. It follows from the figure given that cathodic as well as anodic current densities are for the corresponding potential difference $E - E°$ approximately the same.

Dependence of the rate of reduction on the concentration of quinone was at equal potential E established in quinone solutions on the electrode oxidized to the same degree. In the region of current densities having normal value of the charge transfer coefficient $\alpha' = 0.82$, dependence $[(\partial \log |i|/|i_L - i|): \partial \log c_{0,0}]_E = 1$; in the region of lower value of coefficient α', the given dependence has only somewhat lower value (0.88). The influence of the oxidation degree of the surface electrode (expressed
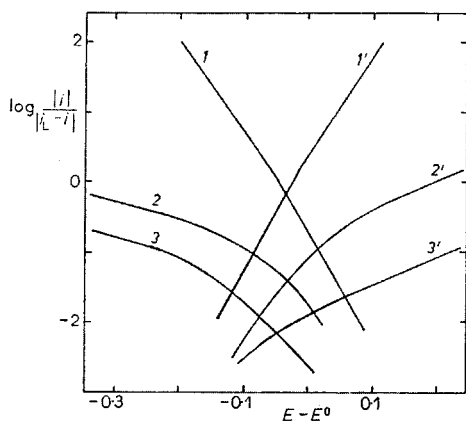

FIG. 3

Dependence between $\log |i|/|i_L - i|$ and $(E - E^0)$ in Solutions $0.01\text{M-K}_3\text{Fe(CN)}_6 +$ $+ 1\text{M-KCl}$ and $0.01\text{M-K}_4\text{Fe(CN)}_6 + 1\text{M-KCl}$ at Equal Oxidation Degree of the Electrode

1, 1′ Freshly ground TiC electrode; *2, 2′* TiC electrode oxidized at $E = 0.4$ V for 14 min; *3, 3′* oxidized for 18 min.
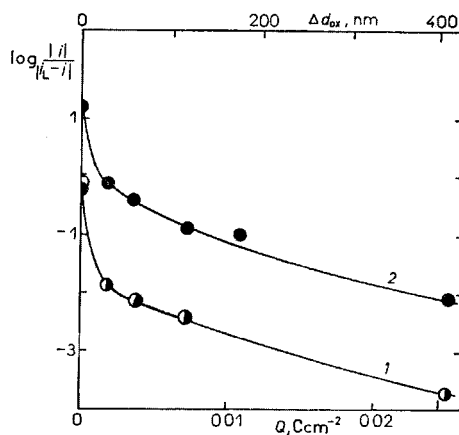
FIG. 4

Dependence of $\log |i|/|i_L - i|$ on Charge during Oxidation

1 at $(E - E^0) = -0.55$ V $(\alpha' = 0.8)$ (○ value found on the platinum electrode); *2* at $(E - E^0) = -0.75$ V $(\alpha' = 0.3)$.

both by quantity of the electric charge passed through the electrode surface unit, and by an increase of oxide layer thickness Δd_{ox}) on the rate of quinone reduction expressed by $\log |i|/|i_L - i|$ is shown in Fig. 4. The upper curve holds for potential difference $E - E^0 = -0.750$ V, i.e. for the region of lower coefficient α', the lower curve belongs to the potential at $E - E^0 = -0.550$ V with normal coefficient α'.

DISCUSSION

Inhibition of studied redox reactions on surfaces of the TiC electrodes oxidized at potentials $E > 0.0$ V (S.C.E.) or by air oxygen may be explained by formation of the oxide layer. Presence of the oxide layer in this region of potentials was already earlier proved by an independent impedance method[3]. It is well-known that the oxide layer on the electrode surface always causes a decrease the rate of the electrode reaction, even though the considered way of the charge transfer through the oxide layer can be different. Schultze and Vetter[4,5] developed for the electrode reactions occurring on the surface of very thin layers of noble metal oxides a theory of the charge transfer through the insulating layer by means of tunnel effect. It follows from this theory, however, that coefficient of the charge transfer, α', does not change in the reaction taking place on the surface and it is therefore apparent that this theory does not satisfy for redox reactions on oxidized TiC electrodes. Neither the Kuzněcov and Dogonadze[6] theory, the validity of which was experimentally verified, for example, on oxide-covered titanium electrodes[7], does not satisfy, since this theory anticipates an oxide layer with the band structure having distinct semiconductive properties. The Meyer model[8], according to which the oxide layer represents a further energetic barrier complies relatively best with the course of redox reactions. Total potential gradient consists of the voltage drop E_1 given by the ion transfer through the Helmholtz layer and voltage drop E_2 for electron transfer through the oxide layer. The current density of cathodic reaction proceeding at a potential sufficiently higher than is the equilibrium potential, so that the rate of reversed reaction can be neglected, may be expressed by equation

$$i_1 = -k_1' \, Fc_{0,p} \exp\left(-\alpha \, FE_1/RT\right). \tag{3}$$

The current density through the oxide layer can be expressed by analogous equation

$$i_2 = -k_2' \, Fc_e \exp\left(-\beta \, FE_2/RT\right). \tag{4}$$

It is evident that

$$i = i_1 = i_2 \quad \text{and} \quad E = E_1 + E_2. \tag{5}$$

By combining equations (3) and (5) a relationship for the dependence of current

on potential may be obtained

$$i = - Fk'_3 \, c_e^{\alpha/(\alpha+\beta)} c_{0,p}^{\beta/(\alpha+\beta)} \exp\left(-\alpha\beta E \, F/(\alpha+\beta) \, RT\right), \qquad (6)$$

where

$$k'_3 = k'_1{}^{\beta/(\alpha+\beta)} k'_2{}^{\alpha/(\alpha+\beta)} . \qquad (7)$$

If the electrode reaction proceeds at such a rate that effect of diffusion cannot be neglected, the surface concentration $c_{o,p}$ can be then expressed by relation

$$c_{o,p} = c_{o,o}(i_L - i)/i_L . \qquad (8)$$

By introducing (8) into (6) and taking the logarithm, equation

$$\log |i|/|i_L - i|^{\beta/(\alpha+\beta)} = \log Fk'_3 + \log (c_{0,o}/|i_L|)^{\beta/(\alpha+\beta)} + \log c_e^{\alpha/(\alpha+\beta)} -$$
$$- (\alpha\beta E \, F/(\alpha+\beta) \, 2{\cdot}3RT) , \qquad (9)$$

is obtained, which represents a complicated dependence between the left side of equation containing current density, and potential. Nevertheless, simple linear dependences between $\log |i|/|i_L - i|$ and E have been found experimentally. A simple equation satisfying experimental results can be achieved, provided that concentration of electrons in the oxide layer depends on concentration of the electroactive compound

$$c_e = k_e c_{0,p} . \qquad (10)$$

The assumption defined by equation (10) does not, for the time being, follow from a suitable corresponding model of the oxide layer, but it is a result of a mere formal treatment of fundamental equations, which allows description of kinetics of the reactions on oxide-covered electrodes. Likewise Meyer[8] generally anticipated possible dependence of concentration carriers in the oxide layer on the concentration of the electroactive compound. Equation (10) can be essentially regarded as expression of an equilibrium between the electron localized in the oxide surface layer and the electron level of the electroactive compound. By introducing equations (8) and (10) into equation (6) we obtain simple relation

$$\log |i|/|i_L - i| = \log Fk'_4 c_{0,o}/|i_L| - \alpha\beta E \, F/(\alpha+\beta) \, 2{\cdot}3RT , \qquad (11)$$

where

$$k'_4 = k'_3 k_e^{\alpha/(\alpha+\beta)} . \qquad (12)$$

Relating constant k'_4 to standard potential of the redox reaction, equation (11) changes

into the equation (2) quoted, where

$$\alpha' = \alpha\beta/(\alpha + \beta) .\tag{13}$$

At low current densities, the electron conductivity of the layer may sometimes be so great that, at the given Faradaic current, the voltage drop in the oxide layer, E_2, equals zero. In this case, we can write using equation (4) for the current density through the i_p layer:

$$i_p = -k_2' \, Fc_e = -k_2'k_e \, Fc_{0,p} = -k_2'k_e \, Fc_{0,0}(i_1 - i_p)/i_L ;\tag{14}$$

by further treatment we obtain for i_p

$$i_p = -k_d k_2' k_e \, Fc_{0,0}/(k_d + k_2'k_e \, F),\tag{15}$$

where $k_d = i_L/c_{0,0}$.

Since $E_2 = 0$, $E = E_1$, the polarization curve will be in this region controlled by equation (3) with usual coefficient α, this fact being at low current densities really observed. In addition, equation (14) shows that the current density, for which conversion to usual polarization curve takes place, depends not only on the oxidation degree of the electrode (on the k_2' and c_e values), but on the concentration, $c_{o,p}$, of the electroactive compound as well. It follows from equation (15) that dependence betweeen i_p and concentration should have shape

$$(\partial \log |i_p|/\partial \log c_{o,o}) \, k_2' = 1 .$$

Validity of this relationship has not been hitherto studied in a more detail, but the measured polarization curves show this value to approach unity (more accurately 0.88).

The inhibiting effect of the oxide layer becomes evident in a decrease of the current density of electrode reaction, while dependence between $\log (|i|/|i_L - i|)_E$ and charge of oxidation is of analogous course for both parts of the polarization curve. However, there is some difference consisting in the fact that with small thicknesses of the oxide layer (on the freshly ground electrodes) the rate of the electrode reaction is slower only at higher current densities and only from a certain thickness of the oxide layer, d_{ox}^k, the electrode reaction begins to slow down more considerably, even at lower current densities.

This means that the oxide layer influences constant k_1 of its own electrode reaction only after reaching a certain value of d_{ox}^k. Unlike this, at higher current densities, effect of the potential drop due to a decrease of concentration c_e of charge carriers in the layer, is applied even for small thicknesses of the oxide layer, $i.e.$ on the electrodes

measured immediately after polishing. It follows from the logarithmic analysis of the polarization curves, on which a characteristic break-down appears at higher current densities, that the employed method of polishing does not lead to the oxide--free electrode surface. And since electrochemical methods do not make it possible to determine the starting thickness of the oxide layer, d_{ox}, more accurately, the oxide layer increase d_{ox} only and not the real thickness of the oxide film can be obtained using the charge of oxidation.

Behaviour of TiC electrodes covered with the film of surface oxide produced either by oxidation with air oxygen at room temperature or by electrochemical oxidation at potentials $E \leqq +0.4$ V (s.c.e.) distinctly differs from the behaviour of the oxide semiconductive layers with a sufficiently broad energetic gap, as are, for example, oxide layers on titanium[7] and niobium[9]. The great value of the rate constant of the electrode reaction, which is close to a value for metal electrodes, shows the $TiC_y—O_x$ oxide layer represents transition between metallic and semiconductive electrodes. The nonoxidized carbon (oxidation of carbon takes place at potentials as high as $E > 0.6$ V) (ref.[10]) represents an efficient donor of electrons and has an effect on electrochemical properties of the oxide layer.

LIST OF SYMBOLS

$c_{0,0}$	volume concentration of electroactive ox-form
$c_{0,p}$	surface concentration of electroactive ox-form
c_e	concentration of charge carriers in the oxide electron layer
d_{ox}	oxide layer thickness
E_1	difference of potentials between electrode surface and solution
E_2	difference of potentials in the oxide layer
h	oxide layer density
i, i_1, i_2	current densities
i_L	limiting current density
i_p	current density at $E_2 = 0$
k_{1-4}, k_e	rate constants
$k \ldots$	rate constant of the electrode reaction, related to standard potential of redox reaction
M	molecular weight of TiO_2
Q	charge of oxidation of electrode surface unit
r	roughness coefficient
α	coefficient of charge transfer through the Helmholtz layer
β	coefficient of charge transfer through the oxide layer

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