

CCA-678

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Conference Paper

## Kinetics of Redox Reactions on $\text{TiO}_2$ and $\text{NiO}$ Single Crystals and Oxidized Metal Surfaces\*

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Received November 2, 1971

Kinetics of  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  redox reaction couple on oxidized Ti, Ni and on  $\text{TiO}_2$  and  $\text{NiO}$  single crystals has been studied by fast methods of polarization and current measurements. From experimental values of the exchange-currents and transfer coefficients  $\alpha$  and  $\beta$ , and knowing the reaction mechanism, the potential distribution in the metal-oxide film — electrolyte system for Ti has been evaluated. It has been shown, that the main difference in properties of passive oxide films on Ni and Ti lies in the character of potential distribution at the oxide-solution interface.

To investigate the nature of passive surface and to establish regularities of metal dissolution from the passive state it is of interest to study electrochemical properties of a passive metal surface. There are a number of papers concerned the investigation of properties of passive layers on metals<sup>1-7</sup>. Most authors proceed from the semiconductor nature of the oxide film, formed on the passive metal surface. The electrochemical behavior of metals covered with a thin semiconductor film has theoretically been considered and the quantitative connection between the values of transfer coefficients of redox reactions and the potential distribution in this system has been established<sup>8</sup>.

To characterize properties of the passive metal surface<sup>8</sup>, we have studied the kinetics of redox reactions on the oxidized metals and analysed fundamental kinetic parameters. From these data, knowing the reaction mechanism, the potential distribution in the metal-oxide film—electrolyte system has been evaluated and conclusions have been drawn with regard to the properties of the oxide film.

Ti and Ni passivated to different degrees, and compact single crystals of  $\text{TiO}_2$  and  $\text{NiO}$ , with a known concentration of free carriers, have been studied.  $\text{TiO}_2$  (a rutile modification, *n*-type) with the concentration of free electrons  $10^{18} \text{ cm}^{-3}$  and  $\text{NiO}$  (*p*-type) with hole concentration  $10^{20} \text{ cm}^{-3}$  have been used. 1 *N*  $\text{Na}_2\text{SO}_4$  with *pH* = 5.6 for Ti and *pH* = 10.6 for Ni was employed as a supporting solution. Under these conditions a stable passive state of these metals in a wide potential range was ensured and no chemical dissolution of oxide films took place.

\* Based on a lecture presented at the 22nd Meeting of the International Society of Electrochemistry, Dubrovnik, Yugoslavia, September 1971.

The ferri-ferrocyanide ionic couple with a one-electron transfer step was used as a model redox system. Measurements were carried out on rotating electrodes in argon atmosphere, at 25°. To maintain the oxidation state of electrode constant during measurements, fast methods of polarization and current measurements were used.

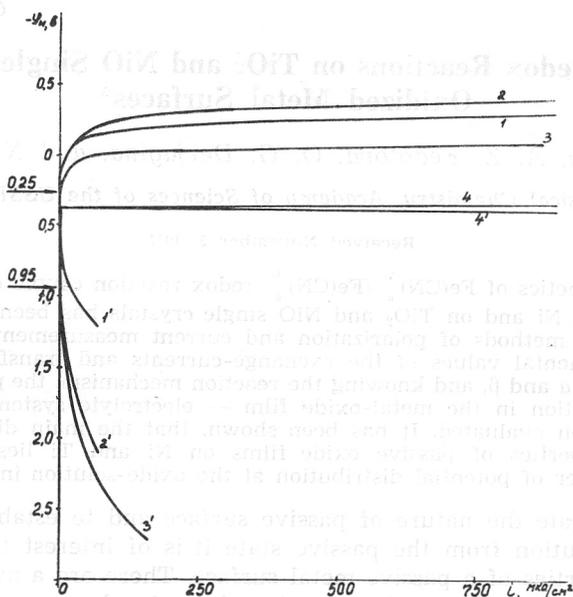


Fig. 1. The  $\varphi$ - $i$  plot (60 v/min) for Ti oxidized at +0.25 v (1, 1'); +0.95 v (2, 2'); TiO<sub>2</sub> (3, 3') and Pt (4, 4') in 1 N Na<sub>2</sub>SO<sub>4</sub> + 0.0025 N K<sub>3</sub>Fe(CN)<sub>6</sub> + 0.15 N K<sub>4</sub>Fe(CN)<sub>6</sub>; 25° C.

Fig. 1 shows nonsteady current-potential curves characterizing the rate of redox reactions of a  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  couple on compact TiO<sub>2</sub> electrode and on Ti, oxidized at a potential of +0.25 v and at +0.95 v\*. The cathodic reduction of  $\text{Fe}(\text{CN})_6^{3-}$  ions on Ti and TiO<sub>2</sub> is shown to have a low overvoltage and the same Tafel slopes as on Pt electrode ( $b \sim 0.12$  v).

Anodic oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  ions on Ti and TiO<sub>2</sub> is greatly inhibited and depends on the degree of electrode oxidation.

Table I presents values of kinetic parameters of the redox reaction of  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  ions for Ti, rutile and Pt. It follows, from the Table, that a passive titanium surface (as well as that of TiO<sub>2</sub>) is characterized by the low exchange current of the redox reaction (4—5 orders of magnitude less than on Pt) and by the low value of the apparent anodic transfer coefficient.

Special experiments on the TiO<sub>2</sub> electrode showed that mainly electrons from the conduction band participate in these redox reactions.

In this case, the reaction rate of anodic oxidation of solution ions is determined by the potential drop value in the Helmholtz layer. Therefore, if the main part of the potential drop is localized not in the Helmholtz layer but

\* The potentials are referred to NHE.

TABLE I

Kinetic Parameters of the  $\text{Fe}(\text{CN})_6^{3-} + e \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$  Reaction for Ti and  $\text{TiO}_2$ 

Electrode	Film forming potential (volts)	Initial film thickness Å	Exchange current ( $i_0$ ) $\text{A/cm}^2$	Transfer coefficients	
				$\alpha$	$\beta$
Ti	+ 0.25	37	$0.43 \times 10^{-7}$	0.53	0.20
Ti	+ 0.95	55	$0.10 \times 10^{-7}$	0.53	0.08
$\text{TiO}_2$	+ 0.25	—	$0.25 \times 10^{-7}$	0.59	0.05
Pt	—	—	$0.87 \times 10^{-3}$	0.52	0.48

in the oxide, the anodic reaction rate should be very low and only slightly depending on the electrode potential.

Measuring the electrode differential capacity on the  $\text{TiO}_2$  electrode in 1 N  $\text{Na}_2\text{SO}_4$  the linear dependence  $1/C^2 - \varphi$  has been obtained (Fig. 2). Hence, according to Shottky, the whole potential drop, under conditions of anodic polarization, actually localizes in the space charge region of  $\text{TiO}_2$ , which accounts for the great inhibition of anodic oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  ions on this electrode.

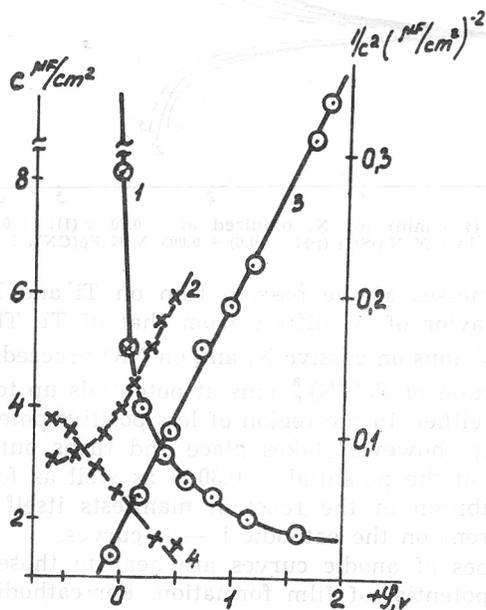


Fig. 2. The  $C-\varphi$  (1, 2) and  $1/C^2-\varphi$  (3, 4) plots for  $\text{TiO}_2$  and  $\text{NiO}$  respectively in 1 N  $\text{Na}_2\text{SO}_4$  25° C.

Assuming that the mechanism of these reactions on passive Ti is the same as that for rutile and using experimental values of exchange-current and transfer coefficients  $\alpha$  and  $\beta$ , obtained for passive Ti, we made an attempt to evaluate, the portion of the potential drop in the passive film and in the

ionic region of the double layer. We evaluated also the concentration of free electrons in the surface layer of the film-solution interface.\*

This evaluation has shown that at anodic polarization of Ti, passivated at potential 0.25 v, the potential drop in oxide film is equal to 60% and increases when Ti was passivated at a more positive potential (0.95 v). The concentration of free electrons in oxide decreases at the contact with the electrolyte from  $7 \times 10^6$  at the passivation potential of 0.25 v to  $4 \times 10^5$  at potential 0.95 v.

Similar measurements have been carried out on a Ni electrode, the compact oxide of which possesses hole conductivity.

Fig. 3 shows cathodic and anodic reaction rates on the passive Ni surface and on the NiO single crystal in the same redox medium. The passive films on Ni were produced at the potentials + 0.30 v, + 0.50 v and + 0.70 volts.

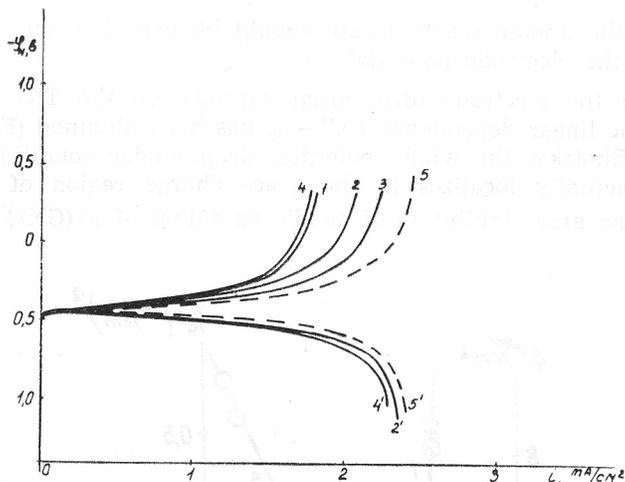


Fig. 3. The  $\phi$ - $i$  plot (4 v/min) for Ni oxidized at + 0.30 v (1); + 0.50 v (2, 2'); + 0.70 v (3); NiO (4, 4') and Pt (5, 5') in 1 N  $\text{Na}_2\text{SO}_4$  (pH = 10.6) + 0.005 N  $\text{K}_3\text{Fe}(\text{CN})_6$  + 0.005 N  $\text{K}_4\text{Fe}(\text{CN})_6$ ; 25° C.

At close thicknesses of the passive film on Ti and Ni (of the order of 30–50 Å) the behavior of Ni differs from that of Ti. The anodic oxidation reaction of  $\text{Fe}(\text{CN})_6^{4-}$  ions on passive Ni and on NiO proceeds with no inhibition. The cathodic reduction of  $\text{Fe}(\text{CN})_6^{3-}$  ions at potentials up to + 0.35 v is practically not inhibited either. In the region of less positive potentials the inhibition of cathodic reaction, however, takes place and turns out to be stronger for the film produced at the potential + 0.30 v as well as for NiO electrode. In this case, the inhibition of the reaction manifests itself as the decrease of the »limiting« current on the cathodic  $i - \phi$  curves.

The Tafel slopes of anodic curves are near to those of Pt and are independent of the potential of film formation. For cathodic curves the slopes change in the process of polarization, that is, they increase at a potential  $< + 0.35$  v.

Thus, the data obtained show that independently of the passivation degree, at potentials more positive than + 0.35 v the surface of passive Ni

\* In our calculation we have admitted that the potential in the film changes linearly.

TABLE II

Kinetic Parameters of  $\text{Fe}(\text{CN})_6^{3-} + e \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$  Reaction for Ni and NiO

Electrode	Film forming potential (V)	Initial film thickness, Å	Exchange current ( $i_0$ ), A/cm <sup>2</sup>	Transfer coefficients	
				$\alpha$	$\beta$
Ni	+ 0.30	41	$0.4 \times 10^{-3}$	0.26	—
Ni	+ 0.50	47	$0.3 \times 10^{-3}$	0.53—0.21	0.48
Ni	+ 0.70	—	$0.5 \times 10^{-3}$	0.58—0.22	—
NiO	+ 0.50	—	$0.2 \times 10^{-3}$	0.58—0.32	0.41
Pt	—	—	$0.4 \times 10^{-3}$	0.52	0.48

and NiO behaves itself as an effective inert metallic electrode with respect to redox reactions in the system of  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  ions.

The absence of inhibition of the anodic oxidation reaction on NiO and the value of anodic coefficient close to 0.5, independently of the reaction mechanism, indicate the localization of the potential in the Helmholtz layer under these conditions. Evidently, the potential redistribution and the increase of the part of potential drop in the oxide occur at potentials, less than + 0.35 v.

In the case when the valent electrons participate in the cathodic reaction, the increase of the portion of the potential drop in the solid phase may be the cause of the  $\alpha$  coefficient decrease.

Our supposition is confirmed by the data on the capacity measurement on the NiO electrode in 1 N  $\text{Na}_2\text{SO}_4$  (Fig. 2). We have observed the linear dependence of  $1/C^2 - \varphi$  in the narrow region of potentials, namely from + 0.35 v to - 0.30 v, *i. e.*, just where the inhibition of cathodic reduction of  $\text{Fe}(\text{CN})_6^{3-}$  ions on the NiO electrode takes place.

Comparison of the electrochemical behavior of the NiO electrode and the Ni passive surface allows to admit that for Ni in the potential range of + 0.35 to - 0.30 v the main potential drop is also localized in an oxide film. This accounts for the peculiarity of electrochemical behavior of such electrodes.

We have also studied the redox reaction of oxygen reduction and  $\text{OH}^-$  ions oxidation on passive Ni and NiO electrodes. The equilibrium potential of this reaction at pH = 10.6 is close to that of the  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  couple. The overvoltage of the cathodic reaction on Pt is, however, higher and, therefore cathodic reaction for oxygen proceeds in the potential range of 0 to - 0.30 v, *i. e.*, in the range where the main potential drop is localized in the oxide. As a result, on NiO and passive Ni the reaction of oxygen reduction is inhibited sharply up to potentials from - 0.50 to - 0.60 v. (Fig. 4).

The kinetics of Ti and Ni anodic oxidation in 1 N  $\text{Na}_2\text{SO}_4$  at various potentials have been investigated together with the study of properties of oxide layers. The analysis of  $i-t$  curves (Fig. 5) shows that the current change with time is generally different for Ti and Ni. The curves for Ti plotted in double logarithmic coordinates give a straight line with slope (K) close to minus unity. The latter shows the fulfilment of the logarithmic law of Ti oxidation and the availability in the film of an electric field controlling its growth.

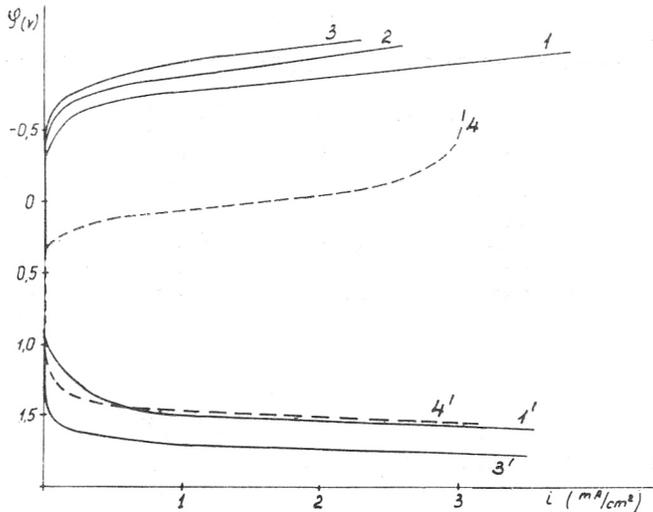


Fig. 4. The  $\varphi-i$  plot for Ni oxidized at +0.50 v (1) and the real curve of  $O_2$  reduction for Ni (2); NiO (3) Pt (4) in 1 N  $Na_2SO_4$  (pH = 10.6); atm  $O_2$  25° C.

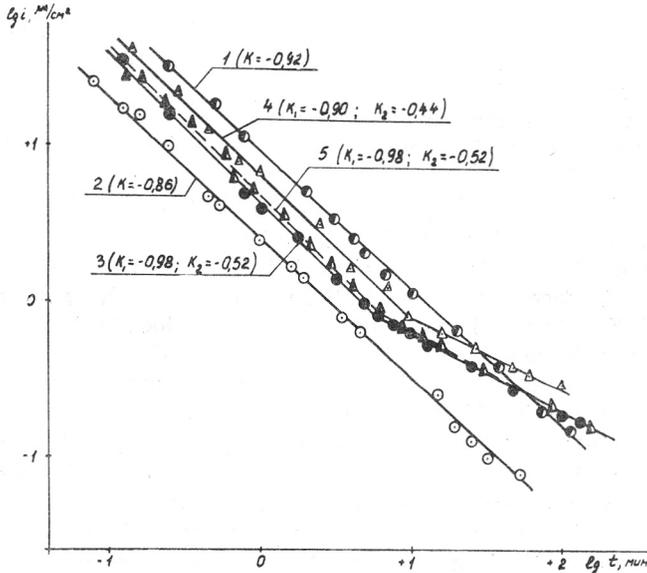


Fig. 5. The  $lg i-lg t$  plot for Ni at +0.30 v; (1) in 1 N  $Na_2SO_4$ ; (2) +0.50 v; (3) +0.70 v; (4) for Ti at +0.25 v; (5) +0.70 v (without stirring).

For Ni the fulfilment of the logarithmic oxidation law is observed during film formation at +0.30 v, while the film growth at more positive potentials (0.5 and 0.7 v) obeys the logarithmic law only in the initial period (during the first 5—7 minutes) and then it is replaced by the parabolic one. The change of the slope of  $lgi-lgt$  straight lines ( $K_2 = -0.5$ ) corresponds to the latter. Diffusion becomes, in this case, the limiting stage of film growth. The absence

of the effect of solution stirring (Fig. 5, curve 4) leads to the assumption that the diffusion of the particles controlling the growth of the oxide film takes place in the solid phase. The above mentioned differences in kinetics and the mechanism of the Ti and Ni oxidation are in accordance with the data on the estimation of potential distribution in these systems.

Thus, the main difference in properties of a passive oxide film on Ni and Ti lies in the character of the potential distribution at the oxide-solution interface. It is the difference in the potential distribution at the interface that is responsible for the difference in the electrochemical behavior of passive Ti and Ni.

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## IZVOD

**Kinetika redoks reakcija na monokristalima TiO<sub>2</sub> i NiO i na oksidiranim površinama metala**

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Mjereni su kinetički parametri za elektrokemijsku redoks reakciju  $\text{Fe}(\text{CN})_6^{3-}$  na elektrodama od Ti, TiO<sub>2</sub>, Ni, NiO i Pt da bi se pronašao mehanizam prijenosa naboja. Ustanovljeno je da je za TiO<sub>2</sub> (kao p-tip poluvodičkog oksida) brzina reakcije oksidacije uvjetovana razlikom potencijala lokaliziranog u sloju prostornog naboja oksidne faze. Za NiO je utvrđeno da je najveći dio ukupnog pada potencijala lokaliziran u Helmholtzovom sloju, i da stoga ponašanje NiO slično onom inertnih metalnih elektroda, npr. platine. Pokazano je da se razlike u elektrokemijskom ponašanju pasivnih oksidnih slojeva mogu uspješno interpretirati razlikama u lokalizaciji potencijala u pojedinim dijelovima graničnih slojeva.

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Priljeno 2. studenoga 1971.