

Electrode Kinetics of Fe(III)/Fe(II) Redox Couple on an Electrodeposited Ruthenium Electrode*

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The heterogeneous electron transfer in $\text{Fe}(\text{CN})_6^{4-/3-}$ and aquo complexes of $\text{Fe}^{3+/2+}$ redox couples have been investigated on a ruthenized platinum electrode in 0.5 mol dm^{-3} sulphuric acid solution. Qualitative voltammetric data measured on a rotating disc electrode showed that a ruthenized platinum layer was a good electronic conductor, which did not block electron transfer in either direction of $\text{Fe}(\text{CN})_6^{4-/3-}$ redox couple. Quantitative electrode kinetic data were obtained using aquo complexes of $\text{Fe}^{3+/2+}$ redox couple on a freshly deposited ruthenium electrode and on an electrode activated to the state of enhanced oxygen evolution from acid solution. The heterogeneous electron transfer rate constant of $3.9 \times 10^{-5} \text{ cm s}^{-1}$ on the unactivated electrode increased by 30% in the case of the activated electrode.

INTRODUCTION

The homogeneous electron transfer processes occur *via* two main mechanisms.¹ In the first, called outer-sphere mechanism, each complex ion retains its own coordination sphere without a chemical change of the reactants. In the second case, in the inner-sphere mechanism, at least one ligand is shared, in the intermediate state, between two complexes. In electrode reactions, a parallelism can be drawn in the sense that the electrode plays a role of one reactant as a source and/or sink of electrons. In pure electron transfer reactions, in the reduction of $\text{Fe}(\text{CN})_6^{3-}$ for example, the electron transfer occurs in the outer Helmholtz plane of the electrical double layer. The rate of electron transfer, in principle, does not depend on the nature of the electrode, provided metallic electrodes are used. However, secondary effects exist,² the capacity of the electrical double layer is potential dependent as well as the specific adsorption of ionic species.³ Consequently, the kinetics of electron transfer in $\text{Fe}(\text{CN})_6^{4-/3-}$ and $\text{Fe}_{\text{aq}}^{3+/2+}$ (aq denotes aquo complex) redox couple will be influenced by the nature of the electrolyte,⁴ by the presence of chloride ions^{5,6} and by the pres-

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ence of impurities, which are a source of various ligands.⁷ In the second class of electrochemical reactions, which take place in the inner part of the Helmholtz layer, strong bonds are formed between the electrode and the reacting species. The hydrogen and oxygen evolution reactions are typical examples of these electrocatalytic reactions, where H and OH radicals are adsorbed on the electrode in the intermediate state. The rate of electrocatalytic reactions strongly depends on the nature of the electrode, and, for example, the rate of the hydrogen evolution reaction varies up to 9 orders of magnitude depending whether platinum or mercury are used.⁸

Several attempts have been made to correlate the electronic properties of metals with their electrochemical behaviour. The point of zero charge, the exchange current densities of hydrogen evolution reaction and Fe(III)/Fe(II) redox couple have been correlated with electronic work functions of metals.⁸⁻¹² However, no definite conclusions have been drawn so far in predicting the electrocatalytic properties of some new material. The situation is even more complex in the case of metal oxides. They exhibit a broad range of conductivity, from insulators via semiconductors to oxides with metallic type of conductivity. This is illustrated by the rate of simple electron transfer of Fe(CN)₆^{4-/3-} redox couple which varies for 18 orders of magnitude whether oxides of metallic conductivity or those of insulating behaviour are used.¹³ In addition, electrochemical activation of some electrode materials by prolonged anodization, cathodization and/or continuous potentiodynamic cycling can change their electrocatalytic properties by secondary effects, *i.e.* by changes in the electrical double layer and/or changes in the surface itself by growing an oxide film. In this connection, an enhancement of oxygen evolution reaction on electrolytically grown hydrous oxide films on iridium,¹⁴ rhodium,¹⁵ nickel¹⁶ and ruthenium¹⁷ was reported. In the case of ruthenium,¹⁷ the electrochemically activated electrode exhibited about eight times higher current density at the same potential in the range of the oxygen evolution reaction; the effect was not due to the increased real surface area, so that it was, therefore, truly electrocatalytic. It was shown¹⁸ that the increased rate of oxygen evolution was accompanied by an increase of electrode dissolution but, nevertheless, only 13% of the enhanced current was due to that dissolution. There are, therefore, some intrinsic factors in improved electrocatalytic properties.

It is the aim of the present paper to examine the electrode kinetic parameters of the Fe(III)/Fe(II) redox couple at, firstly, freshly electrodeposited ruthenium and, secondly, at electrochemically treated ruthenium. It is also our intention to correlate the differences, if any, of the simple electron transfer reaction of Fe(III)/Fe(II) redox couple with electrocatalytic behaviour of two types of electrodeposited ruthenium electrodes. Literature data for the Fe(III)/Fe(II) redox system on ruthenium are rather scarce. Galizzioli *et al.*¹⁹ have determined kinetic parameters of this system at RnO₂ electrodes prepared by thermal parameters of this system at RuO₂ electrodes prepared by thermal decomposition of RuCl₃ on platinum and tantalum substrates. The exchange current density varied by two orders of magnitude, depending on the substrate and calcination temperature. In the case of electrodeposited ruthenium,¹¹ the exchange current density was in the same range as the values obtained with other noble metals.⁹

EXPERIMENTAL

The electrodeposition of ruthenium was carried out either on a platinum disc electrode (0.2 cm² geometrical area) or on a platinum wire electrode (0.25 cm² geometrical area) galvanostatically at 40 mA cm⁻² for 15 min from 1 g dm⁻³ (NH₄)₂RuCl₆ in 0.1 mol dm⁻³ HCl

(Fluka puriss.) solution at room temperature. The rotating disc electrode was rotated at 2500 rotations per minute (rpm) in order to remove hydrogen bubbles which evolved during electrodeposition. This freshly electrodeposited electrode will in further text be referred as a Type A electrode.

The electrochemical set-up consisted of an EG&G Mod. 273/97 potentiostat/galvanostat, a PINE Mod. AFMT135PTPTT platinum disc electrode driven by a PINE Mod. AFMSRXE rotor. Activation of the ruthenium electrode was carried out using a potential-time program which consisted of 45 square-wave (SQW) pulses from -0.2 V to $+0.85$ V *vs.* saturated calomel electrode (SCE) in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. The potential was held for 40 s at each potential value. The electrodes were emersed at 0.85 V and transferred to another cell with iron species, where measurements of electrode kinetics were carried out. The activated electrode will in further text be referred as a Type B electrode. All data in this work were normalized to the geometrical area of electrodes.

A three compartment electrochemical cell, thermostated at 25 ± 0.1 °C with platinum foil as a counter electrode and a SCE as the reference electrode were used. $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{FeSO}_4 \times 7\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3 \times 9\text{H}_2\text{O}$ (Kemika), and sulphuric acid (Fluka) were of analytical grade. Quadruply distilled water was used for solution preparation.

RESULTS

Figure 1 shows cyclic voltammograms of freshly electrodeposited ruthenized platinum at a rotating disc electrode (RDE) and the same electrode subjected to the electrochemical activation procedure as described in the experimental section. The activated electrode exhibits some difference in the hydrogen ionization process at the beginning of the potentiodynamic scan, as well as in the range of surface oxidation from 0.1 V to 1.1 V, but a voltammetrically most significant difference, with relevance to the enhanced oxygen evolution, is in the range from 0.8 V to 1.1 V. The potential excursion in the positive direction was stopped at 1.1 V in order to avoid electrode dissolution¹⁸ which starts at about 1.2 V. There is also a more reversible reduction of the formed oxide, as it was already discussed previously.¹⁸

The voltammetric profiles recorded at the rotating disc electrode are the same as those reported for a quiescent ruthenized platinum and ruthenized titanium wire

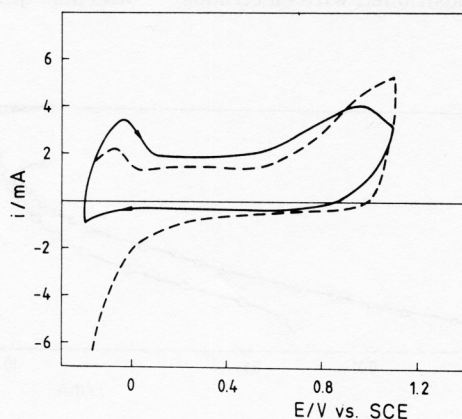
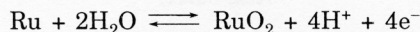


Figure 1. Cyclic voltammograms at a sweep rate of 50 mv s^{-1} in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ of a Type A ruthenized platinum electrode (full line) and of an activated (Type B) electrode (dashed line).

electrodes.^{17,20} This is what can be expected, because both processes, oxide formation and reduction, are surface processes independent of the rotation speed. Only hydrogen ionization in a positive scan between -0.2 V and 0.0 V could be partly influenced by the rotation speed due to the dissolution of hydrogen into ruthenium. However, this problem is not of interest for the present work. The primary concern is the electrode in its oxidative state, particularly in the range where the greatest difference between the two electrodes was detected. This is, as seen from Figure 1, between 0.8 V and 1.1 V.

The enhanced electrocatalytic activity in the oxygen evolution reaction at the activated ruthenium electrode is about one order of magnitude, as seen from the Tafel polarization plot in Figure 2, but is not due to an increase of the real surface area. If this should be the case, the current over the entire potential range of the cyclic voltammogram in Figure 1 would be higher. More precisely, the currents for both hydrogen ionization and the initial stage of surface oxidation between 0.2 V and 0.7 V, which proceeds as²¹



would be higher. As a matter of fact, the current for oxide formation is smaller, probably due to some dissolution of ruthenium and/or incomplete reduction of the previously formed oxide. The sharp decrease of current after 1.32 V looks like electrode passivation. However, this is not the case. The ruthenized layer dissolves, the true electrochemical area is smaller, the solution is colored by dissolved ruthenium species, as it was also observed by other authors.^{22,23} Finally, as anodic polarization proceeds, the cyclic voltammetric profile of platinum shows up. It should be pointed out that the use of a rotating disc electrode in gas-evolving reactions offers some advantage in the sense that detachment of gas bubbles is more facile at a rotating electrode. However, the similarity of polarization data for the oxygen evolution reaction at a ruthenized wire electrode and those in Figure 2 show that the detachment of bubbles from vertically positioned wire electrodes^{17,20} was also quite satisfactory, and led to no complications.

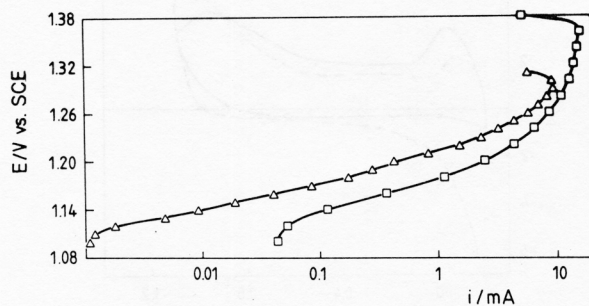


Figure 2. Potentiostatic polarization plot for the oxygen evolution reaction from 0.5 mol dm^{-3} H_2SO_4 on a rotating disc electrode (rotation speed 2500 rpm) of a (Δ) Type A ruthenized platinum electrode and (\square) Type B electrode.

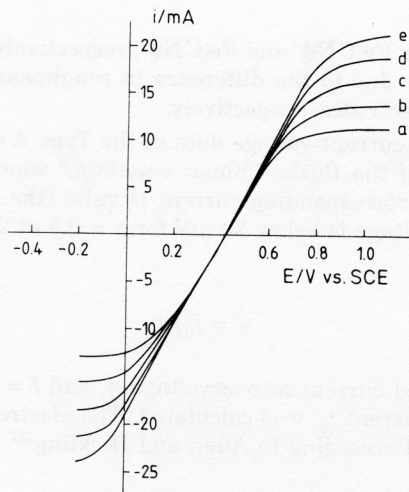


Figure 3. Current-potential curves at a sweep rate of 10 mV s^{-1} of a $\text{Fe}(\text{CN})_6^{4-/3-}$ redox couple in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ on the Type A ruthenized platinum rotating disc electrode at (a) 2500; (b) 3600; (c) 4900; (d) 6400 and (e) 8100 rpm.

From the family of current-voltage curves for $\text{Fe}(\text{CN})_6^{3-}$ reduction and $\text{Fe}(\text{CN})_6^{4-}$ oxidation at a RDE in the range of rotation speeds from 2500 to 8100 rpm (Figure 3) it can be seen: firstly, that the potential range is exactly the same as that in which ruthenium oxide formation and reduction take place, *i.e.* between -0.2 V and 1.1 V . Secondly, it is evident that over the entire potential range there is an absence of blocking effect either on $\text{Fe}(\text{CN})_6^{4-}$ ion oxidation or on $\text{Fe}(\text{CN})_6^{3-}$ ion reduction. The rather sloping directions of the curves are, however, qualitative evidence for a quasi-reversible electron transfer. The plot of limiting currents vs. the square root of rotation speeds (Figure 4) showed linear dependence, as predicted by the Levich equation for mass-transport control.²⁴ Data are in excellent agreement with those for $\text{Fe}(\text{CN})_6^{4-/3-}$ reduction and oxidation at a gold rotating disc electrode.²⁵ These authors also observed the same increase of reduction current, which is obviously a result of the difference in diffusion coefficients,²⁶ which are $7.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$

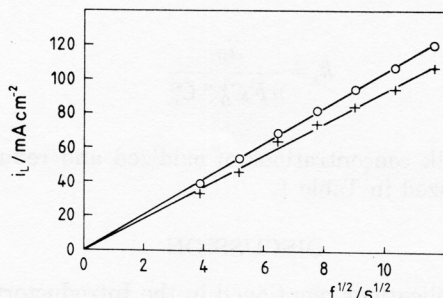


Figure 4. Limiting currents vs. the square root of rotation speed on a RDE of a Type A ruthenized platinum for (o) reduction of $\text{Fe}(\text{CN})_6^{3-}$ and (+) oxidation of $\text{Fe}(\text{CN})_6^{4-}$ in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$.

and $8.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$, respectively. Differences in absolute current magnitudes are due to the difference in roughness factors of the gold and ruthenized platinum electrodes, respectively.

Figure 5 shows the current-voltage data of the Type A electrode in the low field approximation region of the Butler-Volmer equation,⁸ where a linear dependence of overvoltage and the corresponding current is valid (the relative error is smaller than 2.5% if the overvoltage is below 20 mV for $\alpha = 0.5$ at 25 °C). In the case of one electron reaction:

$$i = i_0 f \eta$$

where i is the measured current at overvoltage η , and $f = F/RT$. From the slope of i vs. η , the exchange current i_0 , was calculated. The electrochemical transfer coefficient, α , was calculated according to Allen and Hickling:²⁷

$$\alpha = \frac{\ln i_0 - \frac{\ln i_0}{1 - \exp(nf\eta)}}{nf\eta}$$

The heterogeneous electron transfer rate constant, k_s , was calculated according to Randles:²⁸

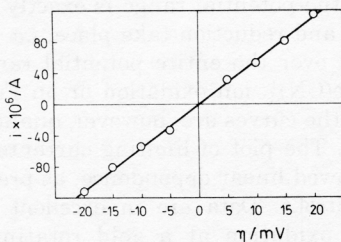


Figure 5. Current-potential data for $\text{Fe}^{3+/2+}$ redox couple on the Type A ruthenized platinum electrode in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 25 °C.

$$k_s = \frac{i_0}{nF C_0^{1-\alpha} C_r^\alpha}$$

where C_o and C_r are bulk concentrations of oxidized and reduced species, respectively. Data are summarized in Table I.

DISCUSSION

Despite various complications mentioned in the Introductory section that might influence the kinetics of electron transfer of $\text{Fe}(\text{CN})_6^{4-/3-}$ and $\text{Fe}_{\text{aq}}^{3+/2+}$ redox couple including adsorption of hexacyanoferrate,²⁹⁻³¹ the presence of chloride^{5,6} and sulphate³² and double layer corrections, most of them will cancel out while comparing the rate

TABLE I

Electrode kinetic data of $Fe^{3+/2+}$ redox couple on Type A and Type B ruthenized platinum electrodes in $0.5 \text{ mol dm}^{-3} H_2SO_4$

0.212 mol dm ⁻³ Fe ₂ (SO ₄) ₃ · 9H ₂ O; 0.113 mol dm ⁻³ FeSO ₄ · 7H ₂ O			
Electrode	$i_0 \cdot 10^4 \text{ A cm}^{-2}$	α	$k_s \cdot 10^5 \text{ cm s}^{-1}$
Type A	5.78	0.51	$3.85 \pm 0.3^*$
Type B	7.51	0.50	$5.03 \pm 0.2^*$

* average of four measurements

of electron transfer of the unactivated Type A ruthenium electrode to the activated Type B electrode. Voltammetric and particularly electrocatalytic differences between these two types of electrodes are evident in Figures 1 and 2. Undoubtedly, the oxide/electrolyte interface is modified to an electrocatalytically more active state in the oxygen evolution reaction; some secondary effects are changed in the case of the activated electrode. The probing of the surface state with electron transfer of $Fe(CN)_6^{4-/3-}$ redox couple, as seen from Figure 3, shows that the ruthenized platinum electrode in oxidative and reductive states behaves as a good electronic conductor, which is one of the main requirements for a good electrocatalyst. The electron transfer is not blocked in either the oxidative or reductive state. In this connection, a parallelism can be drawn by the results reported by Gottesfeld *et al.* using electrolytically grown hydrous oxide films on the iridium electrode³³ in acid solution and on the rhodium electrode³⁴ in alkaline solution. On the oxide-free electrodes, both electrode processes, reduction and oxidation of $Fe(CN)_6^{4-/3-}$ redox couple, exhibited a linear Levich-type behaviour at the limiting current plateaux. When a hydrous oxide film was grown, some blocking of $Fe(CN)_6^{3-}$ reduction was observed. These authors explained the process in a way that the electron transfer in a oxidation process at an oxide-covered electrode occurred on the oxide/electrolyte interface while in the reduction process the charge transfer took place at the metal substrate surface. In the case of the TiO₂ electrode, as reported by Beaz *et al.*, the oxidation of $Fe(CN)_6^{4-}$ was blocked,³⁵ the electrode behaved as a semiconductor. Compared to these results, the electrodeposited ruthenium layer is a better electronic conductor. These results, as well as those in Figure 3, are of qualitative nature only. Lack of quantitative data in the literature for the electron transfer of $Fe(CN)_6^{4-/3-}$ redox couple in acid solution is obviously due to the acid catalyzed aquation of hexacyanoferrate ions and, therefore, due to their instability. The recommended pH range³⁶ is 4–12.

The quantitative data on the simple outer-sphere electron transfer on electrodeposited ruthenium electrodes have been obtained using aquo complexes of Fe^{3+} and Fe^{2+} ions. The rate of electron transfer in $Fe_{aq}^{3+/2+}$ redox couple, as seen from Table I, is about 30% faster on the Type B electrode. The experimental error is below 10% and, therefore, the difference detected experimentally is significant. The rate of oxygen evolution is about one order of magnitude faster on the Type B electrode (Figure 2). These two rates cannot be directly compared, not only due to the differences in their mechanism, namely outer-sphere mechanism in the case of electron transfer in $Fe_{aq}^{3+/2+}$ redox couple and inner-sphere mechanism in the case of oxygen evolution reaction but also due to the environment where these two reactions occur. The reduc-

tion/oxidation processes of the $\text{Fe}_{\text{aq}}^{3+/2+}$ redox couple occur on the »geometrical« area of the porous electrode layer. In other words, the relatively large aquo complexes of Fe^{3+} and Fe^{2+} ions cannot penetrate deep inside the electrode pores. More precisely, the electrode reaction does not take place at the geometrical surface area of the platinum substrate. The roughness factor of the ruthenized RDE, calculated on the basis of the data in Figure 4 and the Levich equation,²⁴ is 8. In the case of oxygen evolution, water molecules, as a source of oxygen and OH-groups, from which oxygen is evolved, diffuse much easier inside the pores. Moreover, they are present inside the pores from the very beginning of the electrodeposition process. Therefore, the oxygen evolution also takes place inside the pores; a concept of threedimensional electrocatalysis was already proposed by Burke and O'Sullivan³⁷ in the case of hydrous oxide film on iridium electrode. The question which arises from the data in the present work, and which concerns us primarily from the electrocatalytic point of view, is why the electron transfer on the $\text{Fe}_{\text{aq}}^{3+/2+}$ redox couple and oxygen evolution reaction are faster on the Type B electrode. We propose a simple model which starts from the evidence that the anodically formed hydrous oxide film contains surface OH-groups. Namely, the presence of an increased amount of OH-groups on the Type B electrode was detected by X-ray photoelectron spectroscopy.³⁸ Since OH-groups are intermediates in oxygen evolution reaction,³⁹ obviously more favorable surface sites have been created by electrochemical activation in the case of the Type B electrode. The increased amount of water was also detected by thermogravimetric measurements in the case of the Type B electrode.⁴⁰ Bringing all these evidences together, a more hydrated environment has been created in the case of the Type B electrode, which led to electrocatalytically more efficient conditions. As far as the electron transfer in $\text{Fe}_{\text{aq}}^{3+/2+}$ redox couple is concerned, surface OH-groups, as electron donor ligands, may act as bridging ligands between the electrode and Fe^{3+} and Fe^{2+} ions, and accelerate the electron transfer.⁴¹ Although the hydrous ruthenium oxide film is nonstoichiometric, containing both oxygen and OH-groups, we shall consider here, for the sake of simplicity, only pure RuO_2 surface sites. By electrochemical activation, an increased amount of OH-groups is created, which enable a faster electron transfer in the $\text{Fe}_{\text{aq}}^{3+/2+}$ redox couple for the reasons mentioned before. Inspection of the heterogeneous rate constant, k_s , of the $\text{Fe}^{3+/2+}$ redox couple, as seen from Table II, shows: firstly, that the rate of electron transfer is smaller on the oxide covered electrodes. This is not surprising, bearing in mind that oxides are poorer electronic conductors. Secondly, it is evident that the rates of electron transfer differ significantly in the case of the pure noble metal electrodes. It was found that the presence of chloride ions accelerates the electron transfer of $\text{Fe}^{3+/2+}$ redox couple,^{5,6} the same problem was discussed more recently by Hung and Nagy.⁴² They found that in the carefully controlled »chloride free« solution the rate of electron transfer was significantly slower. In the case of the ruthenized platinum electrode in this work, the rate constant is comparable to the results obtained by those authors⁴² and also to the results on rhodium oxide electrode.⁴³ But, we could hardly think about a chloride free solution in our work. The electrodeposition of ruthenium was carried out in 0.1 mol dm^{-3} HCl solution and, therefore, some chloride ions could be present in the pores throughout the experiment with iron species. The chlorine evolution reactions occur at more positive potentials.¹⁷ Therefore, the relatively low rate of electron transfer is due to the oxide covered ruthenium electrode in the first place, rather than to a chloride free solution.

TABLE II

Electrode kinetic data of Fe^{3+/2+} redox couple on various electrodes and supporting electrolytes

Type A electrode	Electrolyte	Conc. mol dm ⁻³	$k_s \cdot 10^4$ cm s ⁻¹	Reference
Au	HClO ₄	0.5	0.22	42
Pt	HClO ₄	1.0	24	44
Pt	H ₂ SO ₄	0.5	333	45
Pt	H ₂ SO ₄	1.0	43	46
Pt	H ₂ SO ₄	0.5	70	47
SnO ₂	HClO ₄	1.0	0.02	48
Rh/Rh-oxide various coverages	HClO ₄	0.5	4.6 ± 0.16	43
Ruthenized platinum Type A	H ₂ SO ₄	0.5	0.39	This work

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SAŽETAK

Elektrodna kinetika redoks-para Fe(III)/Fe(II) na rutenijevoj elektrodi

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Istraživan je heterogeni prijenos elektrona između $[\text{Fe}(\text{CN})_6]^{4-/3-}$ i akva-kompleksa $\text{Fe}^{3+/2+}$ na ruteniziranoj platinskoj elektrodi u 0.5 mol dm^{-3} sumpornoj kiselini. Kvalitativni voltametrijski podaci mjereni na rotirajućoj disk-elektrodi pokazali su da je rutenizirani elektrodni sloj dobar vodič elektrona, koji nije blokirao prijenos elektrona kod nijedne ionske vrste u redoks-paru $[\text{Fe}(\text{CN})_6]^{4-/3-}$. Kvantitativni kinetički podaci dobiveni su upotrebom redoks-para $\text{Fe}^{3+/2+}$ na svježe doponiranoj rutenijevoj elektrodi, te na elektrodi u stanju povećane aktivnosti u elektrokemijskom razvijanju kisika iz kisele otopine. Heterogena konstanta brzine prijenosa elektrona iznosila je na neaktiviranoj rutenijevoj elektrodi $3,9 \cdot 10^{-5} \text{ cm s}^{-1}$, a porasla je za 30% u slučaju aktivirane rutenijeve elektrode.