

# Electron Transfer Reactions of the Hexacyanoferrate Redox Couple at Passive Niobium

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The electron transfer reaction of the  $\text{Fe}(\text{CN})_6^{3/4-}$  couple on passive niobium has been studied and reaction orders have been determined at different pH values. The solution chemistry appears to explain the fractional reaction orders found. Anodic oxidation is very slow and the exchange current density is extremely low. Comparisons have been made with measurements on other metals, especially passive Ti.

## Nomenclature

$j_+$	anodic current density
$j_-$	cathodic current density
$j_p$	passive (ionic) current density
$j_0$	exchange current density
$j_e$	electronic current density
$F$	Faraday constant
$U$	electrode potential (SCE)
$\delta$	oxide film thickness
$b_+$	anodic Tafel slope
$b_-$	cathodic Tafel slope
$\alpha_+$	anodic transfer coefficient
$\alpha_-$	cathodic transfer coefficient
$k_+$	anodic rate constant
$k_-$	cathodic rate constant

The primes refer a parameter to its quasi-stationary state after 20 h stabilization.

## Introduction

The kinetics of electron transfer reactions (ETR) at oxide-covered metal electrodes has been the subject of several investigations, most of which are well reviewed.<sup>1,2</sup> Most studies on ETR at passive metal electrodes have been performed with passive titanium electrodes.<sup>2–6</sup> At passive niobium the hexacyanoferrate(II)/(III) redox couple has been most thoroughly investigated.<sup>7,8</sup> The cathodic Tafel curve [for reduction of hexacyanoferrate(III)] was found to exhibit a shoulder. Its appearance was explained by transition from direct elastic to elastic resonance tunneling as the rate-determining step of electron transfer.<sup>7,8</sup> The literature seems scarce with respect to data for oxidation of hexacyanoferrate(II) at passive niobium. Data for the influence of the concentration of reactant ions and the nature of the

supporting electrolyte on the rate of ETR on passive niobium also seem scarce.

A recent contribution from our laboratory concerns ETR of the hexacyanoferrate couple at passive titanium electrodes.<sup>4</sup> The rate of electron transfer was demonstrated to depend on the electrode potential, the solution pH, the thickness of the passive film and the way of growing the passive film to a given thickness. According to these results, electron exchange mainly occurs with the metal through thin passive films (< 4.5 nm) or with the conduction band in the oxide of thicker films. The reactions show a rather strange dependence on the concentration of hexacyanoferrate(II) and -(III) [eqn. (1)].

$$j_+ = F(k_+[\text{red}]^{-0.5})[\text{red}] \quad (1a)$$

$$j_- = F(k_-[\text{red}]^{-0.5})[\text{ox}] \quad (1b)$$

The corrosion and passive behaviour of niobium has previously been studied by stationary and transient polarization measurements in solutions of various pH.<sup>9</sup> The intention of the present paper is to investigate the oxidation of hexacyanoferrate(II) and the reduction of hexacyanoferrate(III) at passive niobium. Measurements of the influence of [ox] and [red], and of the influence of the supporting electrolyte, on the rate of electron transfer are emphasized.

## Experimental

The electrochemical experiments were performed on niobium (99.9%, Goodfellow) sheet electrodes with an area of about 4.5 cm<sup>2</sup>. Reductions of the area by the etching were corrected for. The cell was thermostatted at 25°C. Both the reference electrode (SCE) and the counter electrode (Pt) were immersed directly into the cell solution. Just before use or reuse, the electrode was etched in a mixture containing 8 M HNO<sub>3</sub> and 14 M HF for about 30 s, rinsed twice in doubly distilled water and washed in a

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**Table 1.** Reaction orders ( $n$ ) of the cathodic reduction and the anodic oxidation at various pH values and stabilization potentials ( $U'$ ) at a constant concentration (0.005 M) of the actual reaction product. The concentration of the reactant ranges from 0.005 to 0.10 M.

pH	$U'/V(\text{SCE})$	$n$
Cathodic reduction		
2.0	-0.14	0.81
3.0	0.00	0.85
5.1	0.00	0.78
Anodic oxidation		
2.0	1.06	0.89
3.0	0.40	0.85
5.1	0.40	0.90

portion of the cell solution. This procedure removes all fluoride from the electrode surface.<sup>9</sup> Electrolytes were made from AR quality salts with water twice distilled in a quartz apparatus. In the cell they were deoxygenated and stirred with purified nitrogen bubbling. The measurements were made in stagnant solution under a stream of nitrogen. Three different series of test solutions were used:

0.15 M  $\text{KHSO}_4$  + 0.35 M  $\text{K}_2\text{SO}_4$  (pH 2.0)

0.01 M  $\text{NaHSO}_4$  + 0.49 M  $\text{Na}_2\text{SO}_4$  (pH 3.0)

0.50 M  $\text{K}_2\text{SO}_4$  + 0.01 M  $\text{CH}_3\text{COOH}$   
+ 0.017 M  $\text{CH}_3\text{COOK}$  (pH 5.1)

into which various amounts of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  were dissolved in the cell after formation and stabilization of the passive film. The film was formed by a potentiodynamic scan (usually  $0.2 \text{ mV s}^{-1}$ ) from the corrosion potential to the chosen stabilization potential ( $U'$ ). It was held there for 20 h before measurements.

Current transients were obtained by applying a square potential pulse from the stabilization potential of duration 10 s and reading the current at the end of the pulses. Between the pulses a period of about 5 min was allowed to retain the pre-pulse state. In order to determine the net rate of ETR, potential pulses were applied first in the absence of the redox system and then in its presence.

## Results

**Equilibrium data.** When the passive niobium electrode was switched to open circuit after measurements at a chosen stabilization potential in a solution containing 0.01 M  $\text{Fe}(\text{CN})_6^{3/4-}$ , the potential dropped quite slowly to a value which seemed to become more positive with increasing film thickness. However, a stationary value was not reached, even after several hours. The potential of the niobium electrode under these conditions was always more negative than the corresponding equilibrium potential at a platinum

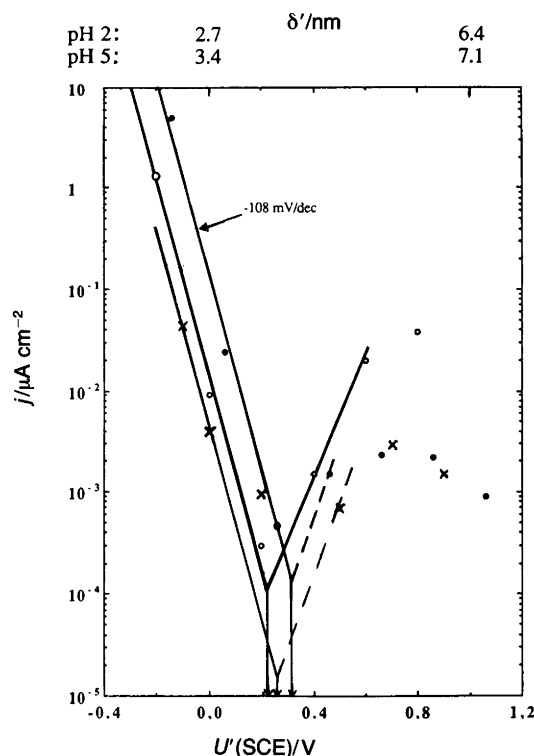
electrode. The equilibrium potential at the platinum electrode was attained within a few seconds and was stable at  $0.314 \pm 0.002 \text{ V}(\text{SCE})$  at pH 2.0,  $0.225 \pm 0.002 \text{ V}(\text{SCE})$  at pH 3.0 and at  $0.256 \pm 0.002 \text{ V}(\text{SCE})$  at pH 5.1. These values are valid for 0.01 M concentrations of the redox couple.

**Stationary data.** When one or both parts of the redox couple were added to the cell solution, the current density on the electrode changed to a new value ( $j' = j_e' + j_p'$ ). The electronic current density,  $j_e'$ , varied with the stabilization potential ( $U'$ ) and pH, but was essentially unaffected by the scan rate of film formation. Fig. 1 shows the values of  $j_e'$  as a function of  $U'$  and pH. Scales for the quasi-stationary film thickness ( $\delta'$ ) of the passive film are adopted from previous work [eqn. (2)].<sup>9</sup>

$$\delta' = 3.7 [U'(\text{V}) + 0.60 + 0.06 \text{ pH}] \text{ nm} \quad (2)$$

The cathodic reaction rate ( $j_{-}' = j_e'$ ) exhibited essentially a Tafel relationship with slope  $-0.10 \pm 0.01 \text{ V dec}^{-1}$ . The anodic reaction, which is slow even at very positive potentials, seems to behave symmetrically near the equilibrium potential. At more positive potentials, the anodic current density attains a maximum and tends to decrease at potentials positive to 0.8 V(SCE).

In Fig. 2 some results of the effects of [ox] and [red] on the rate are presented. The results fit the following rate



**Fig. 1.** Stationary electronic current density ( $j_e'$ ) versus stabilization potential ( $U'$ ) and pH for passive Nb electrodes. [ox] = [red] = 0.01 M. ●, pH 2; ○, pH 3; X, pH 5.1.

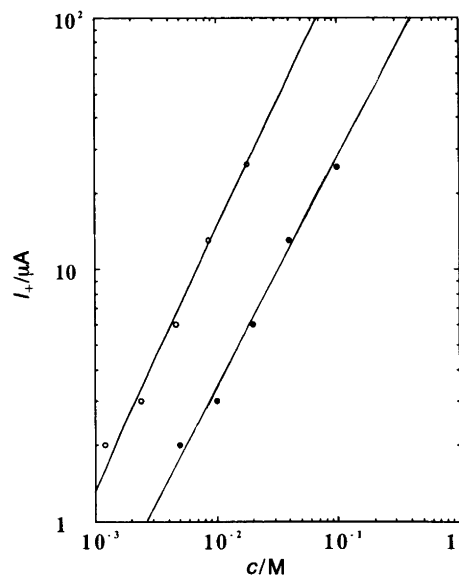


Fig. 2. Anodic current as a function of concentration of added  $\text{K}_4[\text{Fe}(\text{CN})_6]$  at pH 5.1 at  $U' = 0.40 \text{ V(SCE)}$  (filled circles). Empty circles denote calculated actual concentrations of free hexacyanoferrate(II) ions when assuming:  $f_{\text{KFe}(\text{CN})_6^{3-}} = 20f_{\text{Fe}(\text{CN})_6^{4-}}$ ,  $f_{\text{KSO}_4^-} = f_{\text{SO}_4^{2-}}$ ,  $f_{\text{K}^+} = 0.5$ ,  $K_{\text{ass}}(\text{K}_2\text{SO}_4) = 9.1$  (Ref. 17). The reaction order then obtained is one.

$$j_+' = Fk_+[\text{red}] \quad (3a)$$

$$j_-' = Fk_-[\text{ox}] \quad (3b)$$

equations [eqn. (3)] for [ox] and [red] between 0.005 and 0.10 M. In these equations  $k_+$  and  $k_-$  are rate constants depending on  $U'$ ,  $\delta'$  and pH. Unlike titanium, the rate constants depend only slightly on the concentrations of ox and red.

Addition of cesium ions to the solution decreased  $j_+'$  by a factor of 10 when  $[\text{Cs}^+]$  was raised to equal  $[\text{Na}^+]$  in 0.10 M  $\text{Na}_4[\text{Fe}(\text{CN})_6]$  at pH 3.9.

**Transient data.** The anodic branch of the Tafel plot yielded very uncertain information on the anodic Tafel slope and the exchange current density ( $j_0$ ) (Fig. 3).  $j_0$  was determined from the cathodic data and the reversible potential measured with the Pt electrode. Those values of  $j_0$  are quite uncertain. However, the exchange current density seems to decrease with increasing film thickness (and potential). Exchange current density between 1 and 100  $\text{pA cm}^{-2}$  were evaluated. At pH 2.0 and 3.0 the cathodic Tafel slope ( $b_-$ ) seems to be quite independent of  $U'$ , having a value of about  $-0.10 \text{ V dec}^{-1}$ . At pH 5.1, the slope seems to decrease from  $-0.12$  to  $-0.08 \text{ V dec}^{-1}$  from  $U' = -0.10$  to  $U' = 1.20 \text{ V(SCE)}$ .

## Discussion

The cathodic polarization data in Fig. 3 agree well with the data obtained by Heusler and Yun<sup>8</sup> at pH 1.7. Because of an increase in the delay after large cathodic potential pulses

to retain the original state before a new pulse could be applied, we have not performed steps to more negative potentials than  $-0.4 \text{ V(SCE)}$ . Accordingly, we are not able to confirm the shoulder in the cathodic polarization curve found by Heusler and Yun.

The present measurements show that the electron exchange is extremely low ( $< 10^{-10} \text{ A cm}^{-2}$ ) for the hexacyanoferrate couple on passive Nb. Therefore, it was difficult to obtain reliable anodic polarization data and further to obtain the dependence of  $j_0$  on the film thickness. In order to determine the mechanism of electron exchange, we need reliable data for both transfer coefficients ( $\alpha_+$  and  $\alpha_-$ ) and for  $j_0$  versus film thickness.<sup>2</sup> As long as we only have data for  $\alpha_-$  and some estimates of  $j_0$ , it is impossible to determine the mechanism of electron transfer, but it is likely that the electron exchange is with the conduction

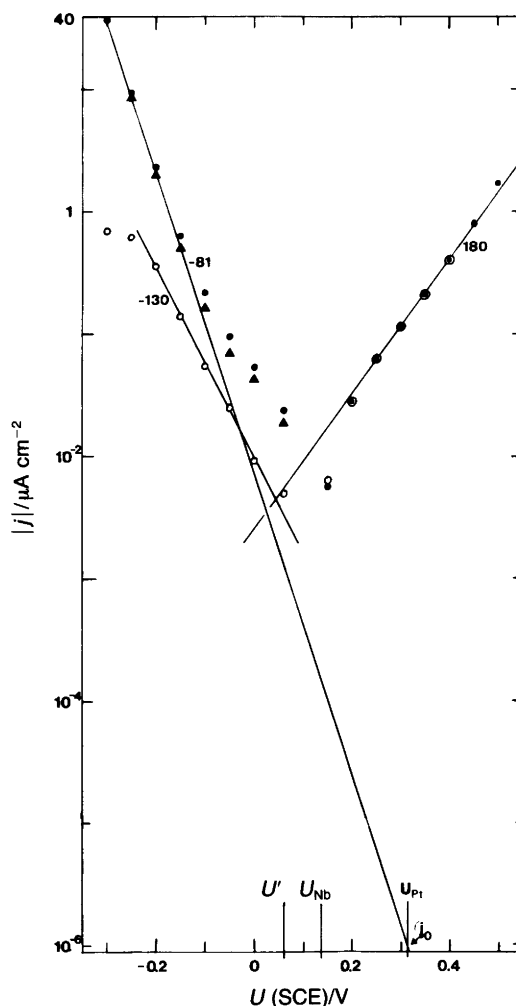


Fig. 3. Example of current transients obtained by square potential pulses from a stabilization potential [ $U' = 0.060 \text{ V(SCE)}$ ] in the absence (empty circles) and presence (filled circles) of 0.01 M of the redox couple. The filled triangles show the net current density of reduction of hexacyanoferrate(III). Tafel slopes [ $\text{mV(dec}^{-1}\text{)}$ ] are shown on the curves.  $U_{\text{Nb}}$  and  $U_{\text{Pt}}$  mean the open-circuit potentials of Nb and Pt, respectively, in the presence of the redox couple.  $j_0$  is the exchange current density. The solution is 0.15 M  $\text{KHSO}_4 + 0.35 \text{ M K}_2\text{SO}_4$ .

band of the passive film, since our films are too thick for direct elastic tunneling, at least above 0.2 V(SCE).

**Reaction orders.** The reaction orders are close to one for the directly observed data. However, the pure first-order mechanism is hidden by the solution chemistry of the hexacyanoferrate ions. It is well reviewed by Sharpe<sup>10</sup> and may even explain the strange reaction orders observed on titanium.<sup>4</sup> One should note the weakness of the two last dissociation steps of hexacyanoferrous acid. According to this, addition of hexacyanoferrate(II) in excess of the buffer capacity of an acid solution increases the pH. However, this causes only small changes in pH for a 0.10 M addition to the buffer solutions with pH 2.0 and 5.1, but the buffer with pH 3.0 suffers and increase in pH to 3.9. Owing to weak protonation of  $\text{Fe}(\text{CN})_6^{4-}$  at pH 5.1, this solution is used as an example for calculation of actual concentrations of free hexacyanoferrate(II) ions in the solution (Fig. 2).

The important feature of ion pairing between the alkali metal ions and the hexacyanoferrate(II) ion can then be considered alone. This means that when the salts are added to the solution, not only may the pH change, but also certainly the concentration of potassium ions. This will decrease the activity of hexacyanoferrate(II) ions, and hence the reaction will appear less than first order in the directly observed data. The anodic electron transfer will also decrease by addition of the hexacyanoferrate(III) salt, owing to the increased concentration of potassium ions. However, this effect is small. The effect is enhanced by addition of cesium ions, because the ion-pairing tendency increases from Li to Cs.<sup>10,11</sup> As reported in the present work, this indeed is readily observable.

However, it is impossible to carry out accurate calculations of activities of the different solution species in order to find a quantitative explanation of the deviation from first-order dependence. This is due to the lack of data for the activity coefficients for  $\text{Fe}(\text{CN})_6^{3/4-}$  at high ionic strengths, where the Debye-Hückel limiting law breaks down.<sup>12,13</sup> In spite of this, an attempt has been made in Fig. 2, based on assumptions of the values for the activity coefficients according to the Debye-Hückel law, which shows that this explanation may be correct. The deviation from first-order dependence of the anodic ETR on the concentration of hexacyanoferrate(II) ions may also be due to changes in the background passive current density during the measurements. However, this effect can be considered small according to previous measurements of the passive current density on Nb.<sup>9</sup>

The above arguments will not explain the half-order dependence found on titanium.<sup>4</sup> However, adsorbed hexacyanoferrate ions may react with metal ions leaving the oxide surface during the dissolution process. A stable titanium(IV) hexacyanoferrate(II) exists and may therefore be precipitated on the surface, blocking the ETR. A similar precipitation is not known for niobium. Precipitation on the oxide surface would affect both the anodic and the cathodic ETR, which is seen for titanium,<sup>4</sup> but not for

niobium. One should note that Peter *et al.*<sup>14</sup> found fractional orders on gold electrodes without being able to give a good explanation. Ammar *et al.*<sup>15</sup> found 0.7–0.8 order on passive tin.

The dependence of the cathodic current density on the concentration of hexacyanoferrate(III) may be treated as above, although hexacyanoferric acid is stronger than hexacyanoferrous acid, and hexacyanoferrate(III) ions show a much weaker tendency to associate with alkali metal ions than hexacyanoferrate(II) ions.<sup>10</sup> However, reaction orders of <0.77 have not been observed either on Ti or on Nb. The influence of hexacyanoferrate(II) on the cathodic reaction on Nb is negligible except at pH 2, where the small increase in pH due to addition of hexacyanoferrate(II) ions may explain the effect. The cathodic reaction proceeds faster at low pH, which may be due to  $\text{HFe}(\text{CN})_6^{2-}$  being one of the electroactive species.

The reported effect of addition of cesium ions suggests that the metal hexacyanoferrate(II) complex is not electroactive. This seems to contradict the results of Peter *et al.*,<sup>14</sup> but is supported by equilibrium potential measurements made by Kolthoff and Tomsicek.<sup>16</sup> Their measurements showed that the activity of the reduced species decreased more than the activity of the oxidized one, when an excess of alkali metal ions was added. The effect was most pronounced for addition of CsCl.

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