

## Photoelectrochemical Behaviour of $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ at Passive Iron Electrodes in Borate Solution

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Effects of illumination on the reactions of the  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  couple at passive iron electrodes in a borate buffer at pH 8.1 have been studied. The rate of oxidation of  $\text{Fe}(\text{CN})_6^{3-}$  is markedly increased on illumination, whereas the reduction of  $\text{Fe}(\text{CN})_6^{4-}$  is not affected. Photovoltaic and photogalvanic explanations of the observed effects are discussed. Best accordance is found with a photogalvanic mechanism involving excitation and reaction of  $\text{Fe}(\text{CN})_6^{4-}$  adsorbed on the electrode surface.

A passivating oxide layer, typically 1–5 nm thick, may be formed on iron electrodes in aqueous solution.<sup>1–12</sup> It was early proposed that the layer was a bilayer of  $\text{Fe}_3\text{O}_4$  at the metal surface and  $\gamma\text{-Fe}_2\text{O}_3$  at the oxide/electrolyte interface.<sup>1,2</sup> A subsequent model describes the layer on the basis of a stoichiometry of  $\text{Fe}_3\text{O}_4$  which can change to a deficient structure  $\text{Fe}_{2.67}\text{O}_4$ .<sup>3,4</sup> The presence of  $\text{Fe}_3\text{O}_4$ ,  $\gamma\text{-Fe}_2\text{O}_3$ , or both, has been confirmed by electron diffraction.<sup>5</sup> However, the exact nature of the layer is still a matter of controversy.

A semiconductor model has been shown to be consistent with the properties of the layer.<sup>8–12</sup> For example, the potential dependence of the differential capacitance of passive iron electrodes<sup>9</sup> and the low exchange current density and asymmetric transfer coefficients of the  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  redox couple at such electrodes<sup>8,12</sup> are consistent with this model. The model describes the layer as an n-type semiconductor with high donor density. The semiconductor nature of the layer suggests that photoelectrochemical measurements may be

enlightening. Firstly, they may help elucidate the nature of fundamental processes at the layer. Secondly, the layer may show properties of interest for the photochemical conversion of solar energy into electrical or chemical energy.

Photoelectrochemical measurements have previously been made at polycrystalline iron oxide layers produced by thermal oxidation<sup>10,13</sup> or chemical vapour deposition.<sup>14</sup> A brief description has also been given of photocurrent measurements at a passive layer in aqueous solution with no redox couple added.<sup>10</sup> The present paper reports a systematic investigation of photocurrent and photovoltage measurements at passive iron electrodes in a slightly alkaline borate solution containing  $\text{Fe}(\text{CN})_6^{4-}$  and/or  $\text{Fe}(\text{CN})_6^{3-}$ .

### EXPERIMENTAL

The iron electrodes (Goodfellow) were specified as >99.998% purity. The cylinder of iron was sealed in KEL-F, and a planar face of the cylinder formed the electrode surface. Measurements were made in a solution of 0.5 M  $\text{H}_3\text{BO}_3$  and 0.1 M KOH (pH 8.1) with varying concentrations of  $\text{K}_4\text{Fe}(\text{CN})_6$  and/or  $\text{K}_3\text{Fe}(\text{CN})_6$ . Experiments were carried out at 25 °C. All potentials are reported with respect to the saturated calomel electrode.

Before each experiment, the electrode surface was first mechanically polished. It was then etched for 1 min in 20%  $\text{HNO}_3$  solution, rinsed with distilled water, and transferred to the test solution. It remained at open circuit for 20 min while deoxygenation of the solution took place. A potential of 0.8 V was then applied. A rapid, almost exponential, decay in the current occurred. After 20 min at 0.8 V, the electrodes showed quite reproducible current–voltage and photocurrent–voltage behaviour, except for slow changes by

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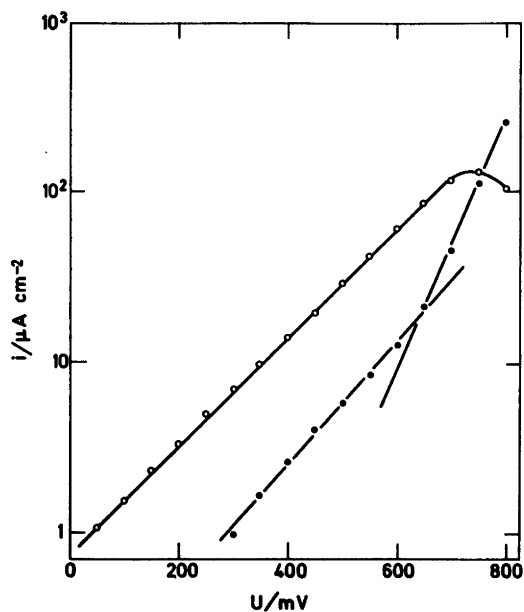


Fig. 1. Anodic dark current (●) and photocurrent (○) vs. electrode potential ( $10^{-2}$  M  $\text{K}_4\text{Fe}(\text{CN})_6$ , white light).

ageing. The polarization measurements were made potentiostatically by stepwise changes, mostly from high to low potentials.

In the photoelectrochemical measurements, light from a 250 W tungsten halogen lamp was focused and then directed *via* a quartz rod so that the electrode surface was completely illuminated. The relative intensity of the light could be varied by means of neutral density filters, and the wavelength could be varied using interference filters of bandpass 10 nm. Light intensity was measured using a Metrologic Photometer.

## RESULTS

Typical quasi-stationary current–voltage and photocurrent–voltage curves for a passive iron anode in the presence of  $\text{Fe}(\text{CN})_6^{4-}$  are shown in Fig. 1. The anodic dark current was directly proportional to the concentration of  $\text{K}_4\text{Fe}(\text{CN})_6$  in the range  $10^{-3}$  to  $10^{-1}$  M. The slope of the current–voltage curve shows a break at about 0.65 V. The mean value of the apparent transfer coefficient ( $\alpha_+$ ) was found to be  $0.23 (\pm 0.03)$  at potentials below 0.65 V and  $0.38 (\pm 0.05)$  at higher potentials. The photocurrent ( $i_p$ ) has been taken as the difference between the currents measured under illumination

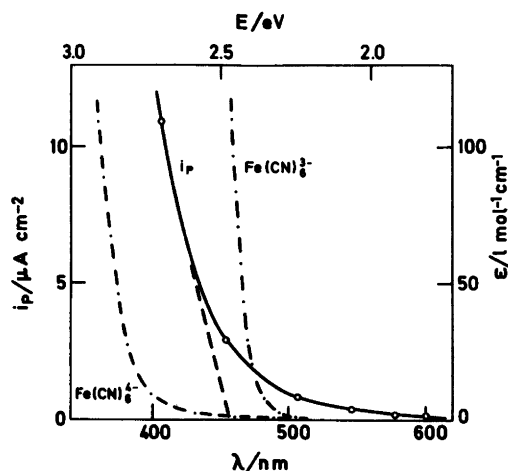


Fig. 2. Anodic photocurrent vs. wavelength and energy of light (0.6 V,  $3 \times 10^{-3}$  M  $\text{K}_4\text{Fe}(\text{CN})_6$ , constant light flux). Also, low-energy absorption edges of  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Fe}(\text{CN})_6^{3-}$  in solution.

and in the dark. In the absence of  $\text{K}_4\text{Fe}(\text{CN})_6$ , mainly transient photocurrents occurred, so that the relatively large steady photocurrents are due to the presence of  $\text{K}_4\text{Fe}(\text{CN})_6$ . The slope of the photocurrent–voltage curve was independent of the  $\text{K}_4\text{Fe}(\text{CN})_6$  concentration in the range  $10^{-3}$  to  $10^{-1}$  M. The mean slope was  $330 (\pm 30)$  mV/decade, yielding an apparent transfer coefficient ( $\alpha'_+$ ) of 0.18 ( $\pm 0.02$ ). The maximum in the photocurrent–voltage curve of Fig. 1 is due to the limiting diffusion of  $\text{Fe}(\text{CN})_6^{4-}$ .

The dependence of the photocurrent on the wavelength of the incident light is shown in Fig. 2. The experimentally measured photocurrents have here been corrected to allow for the variation in the intensity of the incident light at each wavelength. Such corrected plots show a slight dependence on the electrode potential at which measurements were made. With increasingly positive potential the photocurrent rises at longer wavelengths. It was difficult to produce a reliably corrected plot at wavelengths below 400 nm, since very little light was available and absorption by  $\text{Fe}(\text{CN})_6^{4-}$  in the solution becomes appreciable. The pathlength of light in the solution was 0.5 cm. The long wavelength absorption limits of  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Fe}(\text{CN})_6^{3-}$  in the solution are also shown in Fig. 2.

The dependence of the photocurrent on the  $\text{K}_4\text{Fe}(\text{CN})_6$  concentration is shown by a log–log plot in Fig. 3. The measurements were made with 507 nm

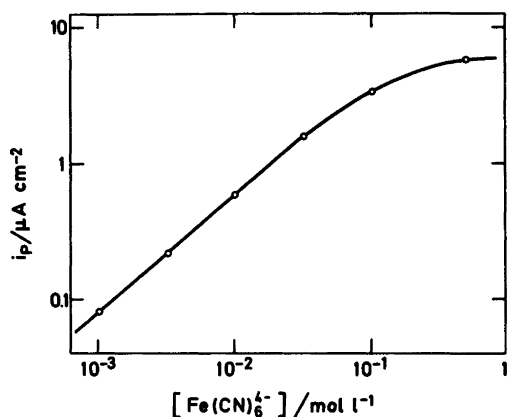


Fig. 3. Anodic photocurrent vs. concentration of  $K_4Fe(CN)_6$  (0.4 V, light of 507 nm and flux  $2.5 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ ).

light, a wavelength at which dissolved  $K_4Fe(CN)_6$  shows very small absorption (Fig. 2). Nevertheless, it was necessary to make a correction of 5% for such absorption at the highest concentration. The slope of the linear part of the log-log curve is 0.85. The dependence of the photocurrent on the light intensity has also been measured and is shown in Fig. 4.

No photoeffect was observed on the reduction of  $Fe(CN)_6^{3-}$ . This cathodic reaction showed a Tafel slope of about  $-100 \text{ mV/decade}$ , corresponding to a cathodic transfer coefficient ( $\alpha_-$ ) of about 0.6. The currents showed an essentially first order dependence on the  $K_3Fe(CN)_6$  concentration.

With both  $K_4Fe(CN)_6$  and  $K_3Fe(CN)_6$  present, the passive iron electrode assumed a well-defined open-circuit potential. This potential generally was

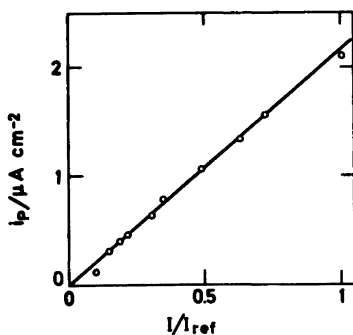


Fig. 4. Anodic photocurrent vs. light flux (0.4 V,  $3 \times 10^{-2} \text{ M } K_4Fe(CN)_6$ , light of 507 nm, reference flux  $2.5 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ ).

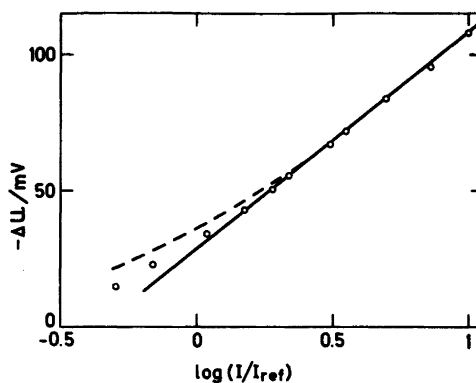


Fig. 5. Photovoltage at open circuit vs. relative light flux ( $10^{-2} \text{ M } K_4Fe(CN)_6$ ,  $10^{-2} \text{ M } K_3Fe(CN)_6$ , white light,  $I_{ref} = I_{max}/10$ ).

identical to that of a platinum wire in the same solution. When the electrode at open circuit was illuminated, a photovoltage was generated. The dependence of this photovoltage on the light intensity is shown in Fig. 5. The photovoltage has here been taken as the difference between the stationary potentials under illumination and in the dark. In the dark, the open-circuit potential of the passive iron electrode in the solution of Fig. 5 was 0.186 V. It became less positive under illumination.

#### AGEING

In order to determine the dependence of the photoeffects on applied potential, wavelength of light, light intensity and reactant concentration, the electrodes were prepared in a reproducible way. The absolute value of photocurrents and photovoltages depended on the exact nature of the electrode pretreatment and the electrochemical treatment during the course of the experiment. For example, when a passivated electrode was left at open circuit in a solution containing both  $10^{-2} \text{ M } K_4Fe(CN)_6$  and  $10^{-2} \text{ M } K_3Fe(CN)_6$ , slow changes occurred both in the dark current and in the photoresponse. These changes were not significant during the course of a normal experiment (up to 3 h). After 50 h, however, the photovoltage had increased by 35% and the photocurrent had decreased to 45% of their initial values. Changes with time have also been measured during capacitance studies of passive iron electrodes.<sup>9</sup> It was then suggested that aged passive layers may have decreased donor concentration due to improved crystallization.

## DISCUSSION

The present observations under dark conditions compare well with previous results.<sup>8,11,12</sup> From a comparison with data<sup>12</sup> applying to various passive layer thicknesses, it appears that the passive layers of the present work are 2.0–2.5 nm thick.

Both the present and previous work<sup>8,11,12</sup> show a distinctly asymmetric behaviour of the  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  couple at passive iron electrodes in slightly alkaline solution. The transfer coefficient (or potential dependence) is here low for the anodic and high for the cathodic reaction. This largely matches expectations<sup>15</sup> for reactions transferring electrons to or from the conductance band of a semiconductor electrode. Under the present conditions, therefore, the  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  reactions seem to occur mainly by such a conductance-band mechanism at the semiconducting passive layer.<sup>8</sup> Since only small Tafel-slope changes appear on illumination (Fig. 1), this conclusion applies to the reactions both in the dark and under illumination.

The present results show that the anodic oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  is markedly affected by illumination, whereas the cathodic reduction of  $\text{Fe}(\text{CN})_6^{3-}$  is not. This difference indicates that heating is not a cause of the illumination effects observed. Furthermore, the anodic photocurrent largely obeys a Tafel law (Fig. 1). It also exhibits an essentially linear dependence on the light intensity (Fig. 4), but not on the  $\text{K}_4\text{Fe}(\text{CN})_6$  concentration (Fig. 3). These observations should be contrasted to a recent report<sup>13</sup> that no photocurrent appears under similar conditions at sintered and flame produced iron oxide electrodes.

The present photocurrent observations and Tafel data lead to eqn. (1) for the photovoltage response

$$\Delta U = -\frac{2.3 RT}{(\alpha_- + \alpha'_+)F} \log \left[ \frac{I}{I_0} \left( 1 - \exp\left(-\frac{F\Delta U}{RT}\right) \right)^{-1} \right] \quad (1)$$

( $\Delta U$ ) expected at open circuit in the presence of both  $\text{K}_4\text{Fe}(\text{CN})_6$  and  $\text{K}_3\text{Fe}(\text{CN})_6$ .<sup>16</sup> Here,  $\alpha_-$  and  $\alpha'_+$  are the apparent transfer coefficients of the cathodic current and the anodic photocurrent, respectively, and  $I_0$  is a suitable reference intensity of light. This equation applies well to the present photovoltage data (Fig. 5). The limiting straight line in Fig. 5 gives values of  $\alpha_- + \alpha'_+$  (by its slope) and  $I_0$  (by its intercept at  $\Delta U = 0$ ). With these values, eqn. (1) yields the stipulated curve diverging at low light intensities from the straight line in Fig. 5. The value thus

obtained for  $\alpha_- + \alpha'_+$  (0.85) compares with that obtained from Tafel data (0.8).

Photoelectrochemical effects generally are photovoltaic (originating from photogeneration of electron-hole pairs in a semiconductor) or photogalvanic (originating from photoexcitation of a solution species). The applicability of these two possibilities to the present case is separately considered below.

## PHOTOVOLTAIC CONSIDERATIONS

Photovoltaic effects are expected mainly on processes involving minority carriers of a semiconductor.<sup>15,17</sup> At passive iron electrodes, where the minority carriers are holes in the valence band of the passive layer,<sup>8–12</sup> this should be on anodic processes occurring by a valence-band mechanism. The anodic oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  at passive iron, however, seems to occur mainly by a conductance-band mechanism both in the dark and under illumination (see above). This prevents a photovoltaic explanation of the photoeffects observed.

At a semiconductor electrode, a possible photovoltaic effect should appear at light energies exceeding the band gap of the semiconductor.<sup>15,17</sup> For passive layers on iron, the band gap is lower than 2 eV,<sup>9,11</sup> whereas the presently observed photoeffects appear first at light energies above 2.5 eV (Fig. 2). Also this makes a photovoltaic explanation unlikely in the present case.

## PHOTOGALVANIC CONSIDERATIONS

Light is absorbed also on photoexcitation of  $\text{Fe}(\text{CN})_6^{4-}$ . An anodic photocurrent will result if this excitation is followed by electron transfer from excited species to the electrode, most likely to the conductance band of the passive layer.

From values for the light intensity and for the extinction and diffusion coefficients of  $\text{Fe}(\text{CN})_6^{4-}$  in solution, an unrealistically long lifetime (about 4 s) is obtained for its excited species to account for the photocurrents observed. Also, the photocurrent occurs at longer wavelength than light absorption by  $\text{Fe}(\text{CN})_6^{4-}$  in solution (Fig. 2). These observations, together with the observed concentration dependence of the photocurrent (Fig. 3), call for considerations of excitation and reaction of  $\text{Fe}(\text{CN})_6^{4-}$  adsorbed at the passive iron electrode.

The photocurrent curve of Fig. 3 may then be taken as reflecting the adsorption isotherm for  $\text{Fe}(\text{CN})_6^{4-}$  at passive iron. It accordingly shows the approach to adsorption saturation. This opens for a simple estimation of the extinction coefficient presently required of  $\text{Fe}(\text{CN})_6^{4-}$  in its adsorbed state. In the wavelength region 500–400 nm, this coefficient becomes  $10^2 - 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ , which is about two orders of magnitude larger than for  $\text{Fe}(\text{CN})_6^{4-}$  in solution. This would indicate an intensity increase and/or a red shift in the low-energy absorption edge of  $\text{Fe}(\text{CN})_6^{4-}$  on adsorption, (Fig. 2). This may reflect a symmetry lowering by adsorption, since symmetry lowering generally produces such effects on d–d adsorption bands of transition-metal complexes.<sup>18</sup>

A photogalvanic explanation, involving excitation and reaction of adsorbed  $\text{Fe}(\text{CN})_6^{4-}$ , is thus in accordance with the present results. This explanation is supported by further evidence for adsorption being a step in the oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  at semi-conducting oxide electrodes.<sup>19</sup> A similar explanation applies also to photoeffects on the oxidation of  $\text{Ru}(\text{bipy})_3^{2+}$  at tin oxide electrodes.<sup>20</sup>

## CONCLUSION

The present results agree with previous ones that the reactions of the  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  couple at passive iron electrodes in slightly alkaline solution mainly occur by a conductance-band mechanism. They further show that illumination markedly stimulates the anodic reaction of this couple, and that this occurs without any sign of a valence-band mechanism appearing. The latter prevents a photovoltaic explanation of the photoeffects observed. Good accordance is found with a photogalvanic explanation involving excitation and reaction of adsorbed  $\text{Fe}(\text{CN})_6^{4-}$  species, if quite large changes in the absorption spectrum of  $\text{Fe}(\text{CN})_6^{4-}$  on adsorption are accepted.

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