# PHOTOGALVANIC CELLS*

W. JOHN ALBERY and ANDREW W. FOULDS

*Department of Chemistry, Imperial College, London SW7 2AY (Gt. Britain)*

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## Summary

The theory of the operation of the ideal photogalvanic cell for solar energy conversion is described and the crucial kinetic characteristics that the system must possess are deduced for the homogeneous kinetics, the mass transfer and the electrode kinetics. Existing iron—ruthenium and iron—thionine systems are discussed with respect to the ideal characteristics. In the case of the iron—ruthenium system the kinetics of the thermal back reaction are too rapid and the cell does not have differential electrode kinetics. The iron—thionine system satisfies many of the criteria. A thionine-coated electrode possesses the necessary differential electrode kinetics. Sulphonated thionine is to be preferred to ordinary thionine in that it is more soluble. The performance of the iron—thionine cell with respect to the ideal cell is analysed and discussed.

## 1. Introduction

A typical photogalvanic cell [1], shown in Fig. 1, consists of a thin layer of electrolyte (about $10^{-2}$ - $10^{-1}$ cm thick) contained between two
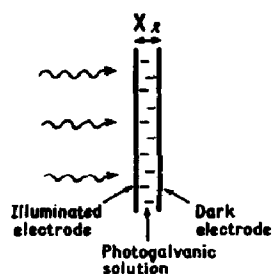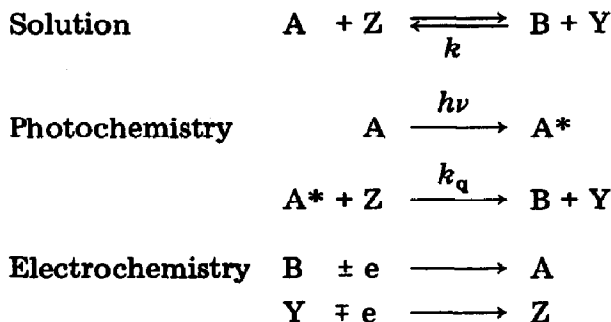


Fig. 1. Thin layer photogalvanic cell of thickness $X_1$.

parallel electrodes. The solar radiation enters the cell through a semi-transparent electrode and is trapped in the electrolyte. The high energy products of the photochemical reaction diffuse to the electrode where they react, driving electrons around an external circuit. The simplest system for such a cell consists of two redox couples A, B and Y, Z. The reaction scheme is

$$\text{Solution} \qquad A + Z \; \underset{k}{\rightleftharpoons} \; B + Y$$

$$\text{Photochemistry} \qquad A \; \xrightarrow{h\nu} \; A*$$

$$A* + Z \; \xrightarrow{k_q} \; B + Y$$

$$\text{Electrochemistry} \quad B \; \pm e \; \longrightarrow \; A$$

$$Y \; \mp e \; \longrightarrow \; Z$$

We shall first describe the general theoretical analysis of the system and then apply the analysis to the iron–ruthenium and the iron–thionine system.

## 2. Theory of the A, B/Y, Z systems

The theoretical analysis of this system has been presented in a series of papers by Albery and Archer [2 - 7]. The differential equation that describes the concentration profile of B across the cell in the steady state is

$$D\frac{\partial^2[B]}{\partial x^2} + g - k[Y][B] = 0 \tag{1}$$

where

$$g = \phi I \epsilon [A] \tag{2}$$

$D$ is the diffusion coefficient of B, $x$ is the distance across the cell, $\phi$ is the quantum efficiency for the generation of B, $I$ is the flux of photons and $\epsilon$ is the natural extinction coefficient of A. The first term describes the transport of B by diffusion, the second term the generation of B by the photochemical reaction and the third term the loss of B by the thermal back reaction with Y. We do not assume that the cell is uniformly illuminated but rather that the light intensity obeys the Beer–Lambert law:

$$I = I_0 \exp(-\epsilon[A]x) \tag{3}$$

where $I = I_0$ at $x = 0$.

We have also examined cases where the solution is bleached and the Beer–Lambert law does not hold. However, in all such cases the photogalvanic cell is less efficient because B is generated too far from the illuminated electrode. Hence for efficient operation the concentration of A is not significantly perturbed from its value in the dark.

It is now convenient to introduce the characteristic lengths given in Table 1.

TABLE 1

Characteristic lengths

| Name | Symbol and equation | Description |
|---|---|---|
| Cell length | $X_1$ | Distance between electrodes (see Fig. 1) |
| Absorbance length | $X_\epsilon = \dfrac{1}{\epsilon[A]}$ | Light is mainly absorbed in this distance (see eqn. (3)) |
| Generating length | $X_G = \left(\dfrac{D}{\phi\epsilon I_0}\right)^{\frac{1}{2}}$ | Average distance A diffuses in light of irradiance $I_0$ before being converted to B |
| Reaction length | $X_k = \left(\dfrac{D}{k[Y]}\right)^{\frac{1}{2}}$ | Average distance B diffuses before being converted to A |

The detailed analysis [5, 6] shows that for a successful cell we require

$$10X_\epsilon \approx X_G \approx \tfrac{1}{2}X_k < \tfrac{1}{2}X_1 \tag{4}$$

The condition that $X_G$ be an order of magnitude greater than $X_\epsilon$ ensures that A can diffuse into the region where the light is being absorbed and so prevent the solution becoming bleached. The condition that $X_k$ is 20 times $X_\epsilon$ ensures that B when it is generated can diffuse to the illuminated electrode before being destroyed by reaction with Y. The condition for $X_1$ ensures that the photogenerated B is at best twenty times more likely to react on the illuminated electrode rather than on the dark electrode.

In eqn. (4) we find that $X_G$ is God-given; taking His values we obtain the value of $X_G$ in Table 2. From eqn. (4) and Table 1 we then obtain ideal values for the other lengths and conditions for [A] and $k[Y]$.

TABLE 2

Conditions for an ideal photogalvanic cell

$X_G$ = $10^{-3}$ cm for $D = 10^{-5}$ cm$^2$ s$^{-1}$, $\epsilon = 10^8$ cm$^2$ mol$^{-1}$, $I_0 = 1.6 \times 10^{-7}$ mol cm$^{-2}$ s$^{-1}$ and $\phi = 1$

$X_\epsilon$ = $10^{-4}$ cm, so [A] = $10^{-1}$ M

$X_k$ = $2 \times 10^{-3}$ cm, so $k[Y] = 40$ s$^{-1}$

$X_1$ > $2 \times 10^{-3}$ cm

## 3. Electrode kinetics

Next we consider the conditions required for the electrode kinetics. A species at an electrode may either react on the electrode or may be lost by reaction in the bulk of the solution or by diffusing away from the electrode. The balance between electrochemical destruction and loss in the solution is found by comparing the electrochemical rate constant $k'$ and the ratio $D/X$ where $X$ is a characteristic length [8]. Because they describe a rate of reaction per unit area in terms of a concentration in moles per unit volume, electrochemical rate constants have dimensions of cm s$^{-1}$. If $k' > D/X$ then the species will be more likely to react on the electrode rather than diffuse away or react in the bulk of solution. In contrast, if $k' < D/X$ the species will be more likely to be lost in the solution by diffusion or by reaction rather than react on the electrode. For the ideal photogalvanic cell $X_k < X_1$ so B is more likely to be destroyed by reaction with Y rather than diffusing to the dark electrode. Hence the characteristic length for B is $X_k$. However, the concentration of Y is assumed to be greater than that of B so that any destruction of Y by B makes a negligible perturbation to the concentration of Y. Hence for Y the characteristic length is $X_1$. In Table 3 we give the conditions for the electrode kinetics of the ideal cell.

TABLE 3

Ideal electrochemical rate constants

| Couple | Illuminated electrode | Dark electrode |
|---|---|---|
| A/B | $k'_B > \dfrac{D}{X_k} \approx 5 \times 10^{-3}$ cm s$^{-1}$ | $k'_B[B] \ll k'_Y[Y]$ |
| Y/Z | $k'_Y[Y] \ll k'_B[B]$ | $k'_Y > \dfrac{D}{X_1} \approx 5 \times 10^{-3}$ cm s$^{-1}$ |

Of the photogenerated species the illuminated electrode selects B rather than Y. This selection is essential or else the electrode merely catalyses the back reaction:

$$\left. \begin{array}{c} B \pm e \rightarrow A \\ Y \mp e \rightarrow Z \end{array} \right\} \ B + Y \rightarrow A + Z$$
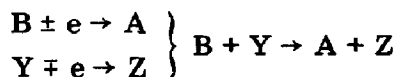
The potential of this electrode will be close to the standard electrode potential of the A, B couple (in the particular medium). Hence in Table 3 the value of $k'_B$ will be close to the standard electrochemical rate constant for the A, B couple (the value of $k'$ at $E = E^\circ$). At the dark electrode we require that the flux of B be much smaller than that of Y, thereby ensuring that B reacts

on the illuminated electrode and Y on the dark electrode. This could be achieved by having another selective electrode where $k'_B \ll k'_Y$. However, it is simpler to satisfy the condition in eqn. (3). If $X_1 > 20 \, X_\epsilon$ then B will react on the illuminated electrode where it is made rather than diffuse to the distant dark electrode. Any homogeneous reaction of Y with B will further reduce the flux of B at the dark electrode. The condition for the Y, Z couple on the dark electrode ensures that Y is destroyed on that electrode, which will be close to the standard electrode potential of the Y, Z couple in the particular medium. Hence $k'_Y$ is close to the standard electrochemical rate constant of the Y, Z couple. If the conditions in Table 3 can be fulfilled the current will be generated at a potential close to the difference $\Delta E^\circ$ in the standard electrode potentials of the two couples. This is essential for a successful photogalvanic device. If identical electrodes are used then the cell functions as a concentration cell [4]. The current is delivered at a potential of only about $RT/F$ (59 mV) and such devices are useless.

The photogenerated species B and Y correspond to the hole–electron pair generated in a semiconductor electrode. To obtain a flow of current B and Y must be separated. In the semiconductor this is done by band bending. In a successful photogalvanic cell the separation must be achieved by differential electrode kinetics. The secret of success is to prevent Y which is generated at the illuminated electrode from reacting there and to force it instead to diffuse across the cell and react on the dark electrode.

However, the blocking of the Y, Z couple on the illuminated electrode poses one of the most severe problems. Assuming that the cell traps photons with energy greater than 1.8 eV [6] and that 0.7 eV is lost in the generation of B + Y, the ideal cell would have $|\Delta E^\circ|$ of about 1.1 V. In terms of the standard electrochemical rate constant $k'_{Y,o}$ of the Y, Z couple on the illuminated electrode we then find

$$k'_{Y,o} < \frac{D}{X_1} \exp\left(-\frac{\alpha |\Delta E^\circ| F}{RT}\right) \approx 2 \times 10^{-12} \text{ cm s}^{-1} \tag{5}$$

where we have taken $\alpha = \frac{1}{2}$ and $\Delta E^\circ = 1.1$ V. This condition corresponds to extremely slow electrochemical kinetics and may not be able to be fulfilled. Therefore the reaction of Y on the illuminated electrode will probably in practice limit the voltage produced by the cell.

### 4. The concentration profiles

We can now calculate the concentration profiles of the different species right across the ideal cell [5]. These are shown for an ideal cell operating at its optimum power point in Fig. 2. The Beer–Lambert profile for the light means that it is all absorbed close to the illuminated electrode. The light does not penetrate across the cell and the concentration of the photogenerated B passes through a maximum where the light is being absorbed; 95% of B
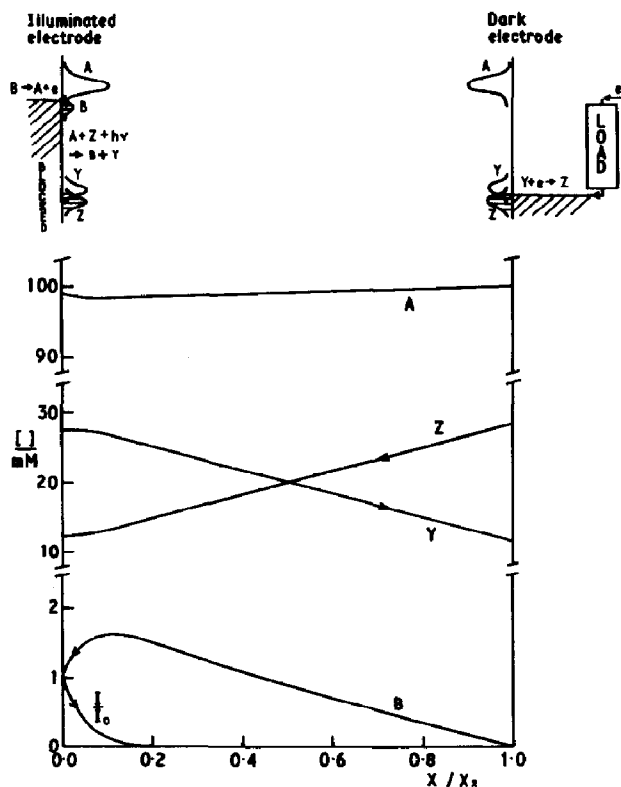
Fig. 2. Concentration profiles for the ideal photogalvanic cell at the optimum power point. The illuminated electrode is on the left-hand side. Note that B is plotted on ten times the scale of the other species. A schematic energy diagram is also shown.

diffuses to the illuminated electrode and reacts there electrochemically. The remaining 5% is destroyed by reaction with Y in the bulk of the cell or eventually on the dark electrode. The concentration of A is plotted on a different scale but in fact the minimum in the A profile where it is consumed in the photochemical reaction is the mirror image of the maximum in the B profile. The photochemical reaction also converts Z to Y near the illuminated electrode while Y is returned to Z at the dark electrode. The transport by diffusion of Y and Z across the cell in opposite directions requires a concentration gradient which must be equal to that of B at the illuminated electrode. However, the greater length of $X_1$ compared with $X_e$ means that the difference in concentration across the cell for both Y and Z must be larger than that of photogenerated B. This difference $\Delta c$ is calculated as follows. For the ideal cell the flux of electrons, of Y and of Z should all be close to $I_0$. Hence

$$D\Delta c/X_1 = I_0 \tag{6}$$

where $\Delta c = [Y]_0 - [Y]_{X_1} = [Z]_{X_1} - [Z]_0$. The concentration of Y and Z half way across the cell are the same as their concentrations $[Y]_D$ and $[Z]_D$

in the absence of light. Using values of $I_0 = 1.6 \times 10^{-7}$ mol cm$^{-2}$ s$^{-1}$, $D = 10^{-5}$ cm$^2$ s$^{-1}$ and $X_1 = 2 \times 10^{-3}$ cm we find from eqn. (4)

$$\Delta c = 3 \times 10^{-2} \text{ M} \tag{7}$$

It is necessary for the concentrations of Y and Z in the dark to be greater than $\frac{1}{2} \Delta c$ or otherwise there will be no Y to react at the dark electrode and no Z at the illuminated electrode.

The presence of Z at the illuminated electrode is essential to trap the excited species A*. The quantum efficiency for the production of B from A will only approach its maximum value if

$$k_q [Z]_0 \tau > 10$$

where $\tau$ is the lifetime of A* in the absence of Z. At the dark electrode we would like [Z] to be as small as possible since this will produce a larger voltage from the cell. Hence, balancing these considerations, we obtain the following condition for the concentration of Z

$$[Z]_D \approx \Delta c + 10/k_q \tau \tag{8}$$

In Fig. 2 we also show the type of schematic energy diagram used in discussing photovoltaic cells. The diagram shows the importance of blocking the Y, Z couple on the illuminated electrode.

## 5. Ideal power output

The ideal photogalvanic cell would have a power conversion efficiency [5] of 18% and this compares favourably with efficiencies for semiconductor solar cells. As shown in Fig. 2, nearly all the photons that are trapped are converted through B into current at the illuminated electrode, which is delivered at about $\Delta E^\circ$. The fill factor of this type of cell could be as high as 0.7 to 0.8. Hence the power output per unit area $W/A$ is given by

$$W/A = 0.8 F \phi I_0 \Delta E^\circ \approx 140 \text{ W m}^{-2} \tag{9}$$

These estimates may be compared with the best power conversion efficiency that has been obtained so far by Hall *et al.* [9]. They used the iron–thionine system in 50 vol.% aqueous acetonitrile; the efficiency was only 0.03%.

## 6. The A, B, C system

The iron–thionine system [10 - 14] is more complicated than the simple A, B/Y, Z system we have discussed so far. The organic couple is a two-electron redox system and hence we have to consider the scheme

$$2Z + A \underset{k_{-1}}{\overset{g}{\rightleftharpoons}} Z + B + Y \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C + 2Y$$
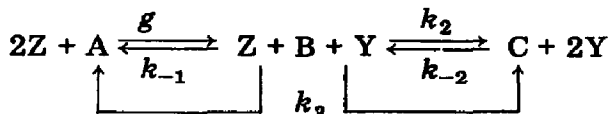
In the case of thionine A represents thionine, B semi-thionine and C leucothionine:
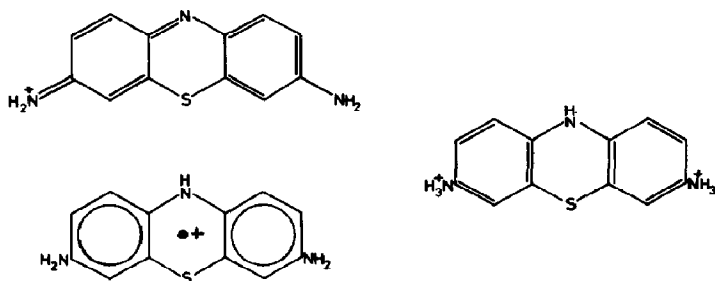


We have carried out a general analysis of the A, B, C system [15] and have shown that there are six different mechanisms for the photochemical generation of C. However, only two out of the six mechanisms are important in the iron–thionine system and we shall restrict our discussion to them.

Previous work [12, 13] shows that leucothionine is formed by the disproportionation reaction B + B rather than by the reaction with Z ($k_2$). The species B is an intermediate and is too unstable to reach the electrode. We are therefore interested in the production of leucothionine (C) and so define a "quantum efficiency" $\phi_C$ where

flux producing C = $\phi_C \, g$

For a photostationary state where C is being destroyed on an electrode instead of reacting with Y we find

$$\phi_C = \frac{1}{2 + k_{-1}[Y]/k_3[B]} \qquad (10)$$

If $k_{-1}[Y] \gg k_3[B]$ then most of the photogenerated B returns to A by reaction with Y, $\phi_C$ is very small and the cell is inefficient. However, if $k_3[B] \gg k_{-1}[Y]$ then B is destroyed by the disproportionation reaction and half of the photogenerated B becomes C; $\phi_C$ reaches its optimum value of $\frac{1}{2}$. Hence we require

$$\frac{2k_3[B]}{k_{-1}[Y]} > \frac{2k_3 g}{k_{-1}^2[Y]^2} > 1 \qquad (11)$$

or by substitution from eqn. (2)

$$[Y] < \left( \frac{2\phi I_0}{X_\epsilon} \frac{k_3}{k_{-1}^2} \right)^{\frac{1}{2}} \qquad (12)$$

Note firstly that the fate of B depends upon the irradiance; because of its bimolecular nature, the desirable disproportionation reaction is favoured by

high intensity. In characterizing possible cells it is important to realize that the mechanism will change with the irradiance. Secondly, a small value of $X_\epsilon$ makes eqn. (12) easier to satisfy. This is because the smaller the distance in which B is formed the more likely it is to disproportionate.

We wish to emphasize that semithionine (B) is present only in much smaller concentrations than either thionine or leucothionine. One can show using typical values [13] that

$$\frac{[B]}{[C]} = \frac{k_{-2}[Y]}{k_3^{1/2} g^{1/2}} \approx 10^{-3}$$

This conclusion has also been reached by Wildes and Lichtin [16, 17] and by Ferreira and Archer [18]. Some authors [19 - 21], however, still try to explain their results assuming that semi-thionine is the principal photo-generated species.

## 7. The conditions for the concentrations of A, Y and Z

We first consider the concentration of Y. The concentration of Y should be as large as possible for generating as large a voltage as possible at the dark electrode and it must also be sufficiently large to prevent concentration polarization:

$$[Y]_D > \frac{1}{2} \Delta c$$

However, it must not be so large as to destroy either B or C. Hence we obtain from Table 1

$$[Y]_D = \frac{40}{k} - \frac{1}{2} \Delta c \tag{13}$$

and for the A, B, C system from eqn. (12)

$$[Y]_D = \left( \frac{\phi I_0}{5 X_\epsilon} \frac{k_3}{k_{-1}^2} \right)^{\frac{1}{2}} - \frac{1}{2} \Delta c \tag{14}$$

Substitution of eqn. (7) in eqns. (13) and (14) give the following conditions for the homogeneous rate constants:

$$k < 10^3 \text{ M}^{-1} \text{ s}^{-1} \tag{15}$$

and

$$k_{-1}^2 / k_3 < 300 \text{ M}^{-1} \text{ s}^{-1} \text{ for } X_\epsilon = 10^{-4} \text{ cm} \tag{16}$$

or

$$< 30 \text{ M}^{-1} \text{ s}^{-1} \text{ for } X_\epsilon = 10^{-3} \text{ cm} \tag{17}$$

We now list the conditions for the concentrations of A, Y and Z in the ideal cell.

A should be as large as possible to shorten $X_\epsilon$, so that firstly photons are trapped close to the illuminated electrode and secondly for the A, B, C system the disproportionation reaction is as efficient as possible; from Table 1 $[A] \approx 10^{-1}$ M.

Y should be as large as possible but it is constrained by whichever of eqn. (13) or eqn. (14) gives the smaller value.

Z should be as small as possible but is constrained by eqn. (8).

## 8. The iron—ruthenium system

This system is an example of the A, B/Y, Z system where A is $Ru(bpy)_3{}^{2+}$, B is $Ru(bpy)_3{}^{3+}$, Y is $Fe^{2+}$, Z is $Fe^{3+}$ and bpy is bipyridyl. Lin and Sutin [22] measured the photopotentials produced by this system using a concentration cell with two identical platinum electrodes. We have further investigated the system using the semi-transparent rotating disc electrode [23]. The rotation of the electrode allows one to study the current—voltage characteristics of the system in the steady state with defined mass transport to the electrode. Furthermore the thickness of the diffusion layer (about $10^{-2}$ cm) conveniently matches the lengths in Table 2. For these reasons we believe that this technique is ideally suited for the study of photogalvanic cells. Since we are interested in producing power the full current—voltage curve must be measured. The measurement of photopotentials on their own can be most misleading. For instance by bleaching a concentration cell, one can produce a large photopotential but as soon as a significant current is passed the concentration difference is destroyed and with it the potential.

Typical current—voltage curves for the iron—ruthenium system are shown in Fig. 3. There is no variation with rotation speed because $X_k$ is smaller than the thickness of the diffusion layer. We have shown [23] that for these conditions the photoelectrochemical collection efficiency $N_{h\nu}$ is given by

$$N_{h\nu} = \frac{\text{flux of electrons}}{\text{flux of photons}} = \frac{X_k}{X_\epsilon} \ll 1$$

From the value of $N_{h\nu}$ we find that in 0.5 M HCl $k \approx 5$ M$^{-1}$ $\mu$s$^{-1}$. This value is very similar to that found by Lin and Sutin in 0.5 M $H_2SO_4$ using stopped flow or flash photolysis. The value of the rate constant is nearly a thousand times larger than the condition of eqn. (15). Hence $X_k \ll X_\epsilon$ and most of the photogenerated Ru(III) is lost by reaction with $Fe^{2+}$ before it reaches the electrode. By changing the ligands on the ruthenium the rate constant can be decreased [24].

However, there is an even more serious objection to this simple type of cell. The iron—ruthenium system has not yet got a selective electrode. The
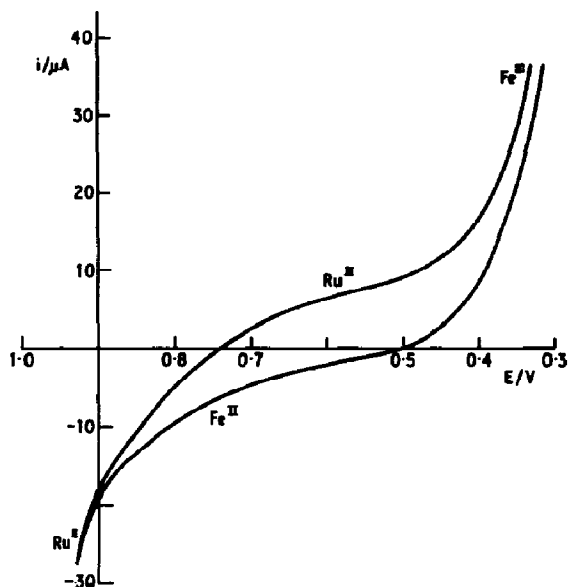
Fig. 3. Typical current–voltage curves — lower curve unilluminated, upper curve illuminated — for the iron–ruthenium system measured on a semi-transparent rotating disc electrode.

data in Fig. 3 were obtained in $Cl^-$ media when the iron couple is irreversible. Thus the illuminated electrode discriminates between Ru(III) and Fe(II). However, the dark electrode would not be able to handle Fe(II) at $E^o_{Fe^{3+},Fe^{2+}}$. The potential of the dark electrode would be close to that of the $E^o_{Ru^{3+},Ru^{2+}}$ and the cell would develop very little voltage difference. Choosing a medium (like $SO_4^{2-}$) where the iron couple is more reversible would solve the problem of the dark electrode. But now the illuminated electrode would no longer discriminate between Ru(III) and Fe(II) and would therefore catalyse the back reaction. The victims of Henry VII always found Morton's fork uncomfortable.

## 9. The iron–thionine system — homogeneous kinetics

The great advantage of the iron–thionine system and similar A, B, C/Y, Z systems is that because of the difference between the one-electron outer sphere inorganic couple Y, Z and the two-electron organic couple A, C it may be possible to obtain the necessary selection of B and Y on the two electrodes. A disadvantage is that the homogeneous reaction scheme is more complicated and must be properly characterized. Extensive investigations of the homogeneous rate constants have been carried out by Hatchard and Parker [12], by Lichtin and coworkers [14, 15] and by Ferreira and Harriman [13]. We have also measured the crucial kinetic parameters by analysing the photostationary state [15] as a function of $[Fe^{2+}]$, $[Fe^{3+}]$ and the irradiance.

We can show that

$$\left(\frac{[Fe^{3+}]}{[C]}\right)^{\frac{1}{2}} = \left(\frac{k_3}{k_2}\right)^{\frac{1}{2}} \frac{\epsilon}{k_{-1}} \chi - \frac{k_{-2}^{\frac{1}{2}} k_3^{\frac{1}{2}}}{k_{-1}} \tag{18}$$

where

$$\chi = \frac{[A]I_0}{[C][Fe^{3+}](1 + \tau k_q/[Fe^{2+}])}$$

Figure 3 shows a plot of eqn. (18) where by taking $\tau k_q = 5$ data at three different concentrations of $Fe^{2+}$ all lie on a common straight line. From the gradient and intercept the other crucial kinetic parameters can be calculated. The straight line also confirms the A, B, C scheme where the $k_2$ step is ignored and B is treated as an intermediate.

Results for the critical homogeneous kinetic parameters for the iron–thionine system are collected in Table 4. In general the system satisfies the conditions for homogeneous kinetics. The concentrations of $Fe^{2+}$ and $Fe^{3+}$ needed to prevent concentration polarization will in the case of $Fe^{2+}$ trap A* and in the case of $Fe^{3+}$ will not destroy either B or C. For the ideal cell

TABLE 4

Homogeneous kinetic parameters for the iron–thionine system

| $T$ (°C) | Medium | A* + Z $(k_q\tau)^{-1}$ (mM) | B + B vs. B + Y $(k_{-1}^2/k_3)$ $(M^{-1} s^{-1})$ | C + Y $k_{-2}$ ($M^{-1}ms^{-1}$) | Reference |
|---|---|---|---|---|---|
| 20 | 0.05 M $H_2SO_4$ | 1.7 | 2.6 | 0.26 | 12 |
| 25 | $H_2SO_4$ pH 2 | 2.1 | 3.4 | 0.3 | 14 |
| 25 | 0.05 M $H_2SO_4$ | 5 | 8 | 0.76 | Our work |
| 25 | 0.2 M $K_2SO_4$ pH 2.5 | 1.0 | 0.73 | 2.6 | 18 |
| 25 | 50% AN | 0.25 | 0.21 | 0.58 | 14 |
| 25 | 0.05 M† $H_2SO_4$ | 0.9 | 0.6 | 0.3 | Our work |
| Conditions required | | <10 | <≈30 | <≈1 | |
| Eqn. no. | | (8) | (17) | (15) | |

† A is disulphonated thionine in this case.

the $k_{-2}$ condition is the more severe. But this assumes that $X_\epsilon$ is smaller than $10^{-3}$ cm. If $X_\epsilon$ is about $10^{-2}$ cm then the $k_{-1}^2/k_3$ condition will be equally severe.

The ideal cell requires $X_\epsilon \approx 10^{-4}$ cm or [A] $\approx 10^{-1}$ M. The low solubility of thionine in aqueous solution means that $X_\epsilon \approx 10^{-1}$ cm and this is one of the main reasons why such cells are so inefficient. The major advantage of the 50% aqueous acetonitrile mixture favoured by Lichtin [14] is that thionine is more soluble and $X_\epsilon$ is reduced to about $10^{-2}$ cm. Even so the light penetrates right through the cell. Lichtin and coworkers have devised a multilayer cell [26] to absorb more of the solar radiation. However, this arrangement does not solve the problem of the kinetic constraints. Too large a value of $X_\epsilon$ means that first C does not reach the electrode, secondly it is harder for B to disproportionate and thirdly photogeneration of C at the dark electrode requires differential electrode kinetics at that electrode or else the cell will become a miserable concentration cell. For these reasons we believe that it is essential to reduce $X_\epsilon$ still further.

We have recently synthesized a disulphonated derivative of thionine that has a solubility in aqueous solution of $10^{-2}$ M, thereby reducing $X_\epsilon$ to $10^{-3}$ cm. The absorption characteristics are similar to that of thionine ($\lambda_{max}$ = 588 nm, $\epsilon_{max}$ = 5.6 $\times$ $10^7$ cm$^2$ mol$^{-1}$). An important advantage is that up to concentrations of $10^{-3}$ M we find no evidence of any dimer formation. The electrochemical characteristics are very similar to those of thionine. In 0.05 M $H_2SO_4$ the standard electrode potential is 0.45 V (with respect to the normal hydrogen electrode) and on a rotating disc electrode the couple is reversible. As given in Table 4 the homogeneous kinetic parameters not only satisfy the necessary conditions but also are more favourable than those for thionine. Indeed we find that under the same conditions the sulphonated thionine gives a more bleached photostationary state than ordinary thionine. We hope that further ingenuity in the design and synthesis of new dye molecules will furnish us with an even more ideal A, B, C system.

## 10. The iron–thionine system — electrode kinetics

As discussed above one must prevent Y, Z reacting on the illuminated electrode. Hall *et al.* [26] have used an undoped $SnO_2$ electrode and have shown that the electrode kinetics for the $Fe^{3+}/Fe^{2+}$ couple are significantly slower. In our work we have found that thionine can be irreversibly adsorbed onto electrodes made of either platinum or $SnO_2$ (doped with Sb). The electrode is held at 1.1 V for about 10 min. Ring–disc electrode studies show that during this time about 20 monolayers of thionine are consumed by the disc electrode. When such an electrode is removed from the thionine solution washed and placed in 0.05 M $H_2SO_4$, the cyclic voltammogram in Fig. 5 shows that again about 20 monolayers of thionine are present. An electron spectroscopy for chemical analysis (ESCA) spectrum of the thionine-coated Pt electrode shows the signals expected for thionine but no Pt signal is seen.
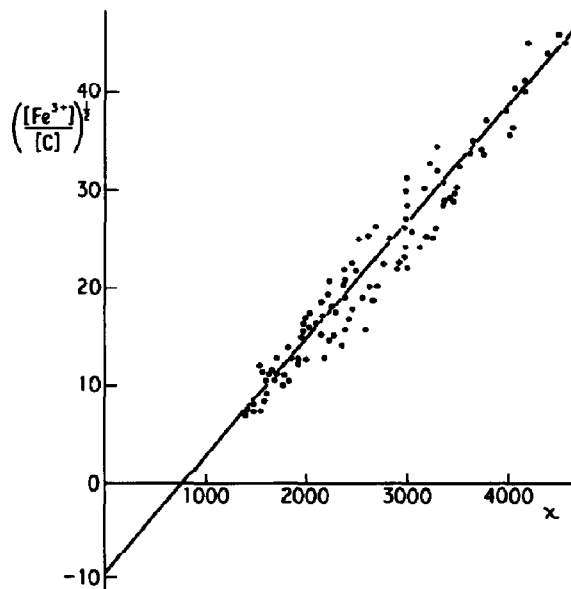
Fig. 4. Plot of eqn. (18) for the iron–thionine system in 0.05 M $H_2SO_4$. The concentration of thionine, A, in the dark was 7.8 $\mu$M throughout; $[Fe^{2+}]$ was varied from 0.5 to 50 mM and $[Fe^{3+}]$ from 0.01 to 5 mM. The irradiance was varied over a factor of 10.
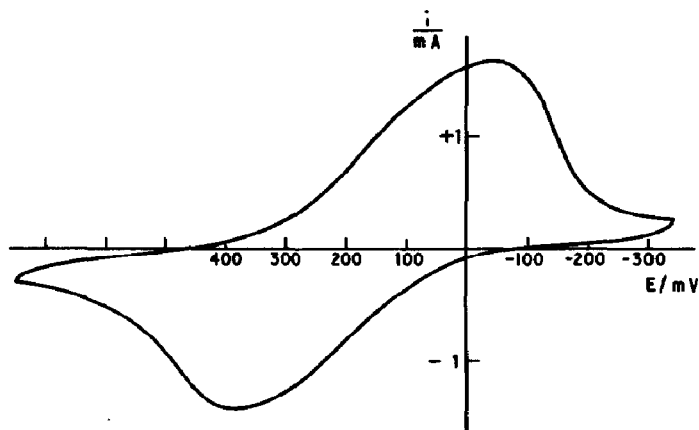


Fig. 5. Cyclic voltammogram of a thionine-coated $SnO_2$ electrode on a quartz plate of area 4 $cm^2$. The scan speed was 100 mV $s^{-1}$. The electrode was immersed in 0.05 M $H_2SO_4$ containing no thionine.

The electrode kinetics of the thionine-coated electrode are rather remarkable. Typical current–voltage curves on a rotating thionine-coated disc electrode are shown in Fig. 6. The electrode kinetics of the thionine/leucothionine couple are fast and fulfil the conditions required for the A, B couple in Table 3. By contrast the thionine layer blocks the reaction of the $Fe^{3+}/Fe^{2+}$ couple. The blocking is not as effective as the ideal requirement
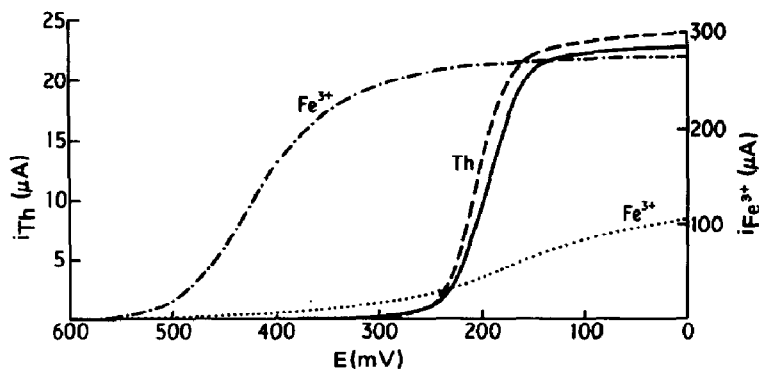
Fig. 6. Current–voltage curves for the reduction of $Fe^{3+}$ and of thionine on a rotating Pt disc electrode with and without thionine coating. Without coating: $Fe^{3+}$ —·—·; thionine ----. With coating: $Fe^{3+}$ ........; thionine ———. The coating makes little difference to the fast electrode kinetics for the thionine/leucothionine couple but suppresses the reduction of $Fe^{3+}$.

of eqn. (5) but given the smaller $\Delta E^\circ$ of the cell it is effective enough to prevent the $Fe^{3+}$ being reduced at the potentials of the illuminated electrode. Hence the thionine-coated electrode is an ideal differential electrode for the iron–thionine cell.

## 11. Conclusions

As discussed above, whereas the ideal cell should have a power conversion efficiency of 18%, the best practical cell to date has an efficiency of only 0.03% [9] which is a factor of 600 smaller than the ideal. We can roughly apportion the factor of 600 as follows:

| | |
|---|---|
| fill factor | 2.5 |
| cell voltage | 7 |
| absorption of radiation | 4 |
| $X_\epsilon/X_k$ | 8 |

The more soluble sulphonated thionine should reduce the $X_\epsilon/X_k$ factor to 2. An even more soluble dye would still be desirable. The absorption band of thionine absorbs about 13% of the insolation spectrum or about 25% of the photons that should be absorbed in the ideal cell. Low energy photons have to be rejected because the voltage developed from them would be too low. The factor of 4 may be reduced by the use of sensitizers such as rhodamine 6G [27]. The main problem remaining is that the iron–thionine cell develops too low a cell voltage. This leads directly to the unfavourable factor of 7 and indirectly to the factor of 2.5 in the fill factor. If the cell voltage is low then the alteration in the concentration of C at the illuminated electrode makes a significant change in the voltage developed by the cell. The low voltage arises from the small difference between the standard electrode potentials

for the two couples. We have investigated a number of different iron complexes with more positive values of $E_Y^\circ$ but so far the results have been disappointing. We are also examining the system at higher pH since the voltage developed should increase by 0.18 V for each unit of pH. The thionine-coated illuminated electrode has sufficient selection between $Fe^{3+}$ and leucothionine for the cell to develop about 0.5 V. It is probably unlikely that the full 1.1 V will be able to be developed. This is because first the back reaction for a system which has such a large $\Delta E^\circ$ will probably be too fast and secondly it will be difficult to achieve the necessary blocking of the Y, Z couple. This means that a realistic aim would be to increase the cell voltage to 0.5 V.

We have concentrated on the iron-thionine system firstly because it is the most successful system to date and secondly because it has been the most studied. What is clear is that the performance of any photogalvanic cell depends on the photochemistry, the homogeneous kinetics, the mass transport and the electrode kinetics of the system. These must be studied separately in order to understand the factors that limit the performance of the cell, and to see how far any particular system meets the conditions set out in the first part of this paper.

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