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Modified Electrodes for Photogalvanic Cells

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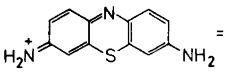
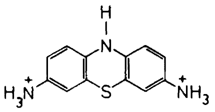
Rates of electron transfer reactions at electrodes modified with the dyes thionine and rhodamine B have been measured. The application of these modified electrodes in photogalvanic cells is considered. The thionine coated electrode is shown to be potentially useful for a wide range of photogalvanic systems. Adsorption from rhodamine B solutions is disadvantageous.

This paper describes investigations of factors which control the rate of electrochemical reactions in photogalvanic systems like eqn. (1), where Th is

$$\mathrm{Th} + 2\mathrm{Fe(II)} \underset{k}{\overset{h\nu,\,3\mathrm{H}^+}{\rightleftharpoons}} \mathrm{L} + 2\mathrm{Fe(III)} \qquad (1)$$


= Th


= L

thionine, and L is leucothionine.

Such systems may be used in photogalvanic cells, which are devices for the direct conversion of solar energy into electrical energy.[1] The absorption of radiation by thionine and the subsequent electron transfer reaction of excited thionine molecules with Fe(II) generates leucothionine and Fe(III). Power may be extracted when the products of this photochemical process react at electrodes (at the same time regenerating the initial reactants). A number of photogalvanic systems involving other redox couples is also known. An important requirement for an efficient cell is that one of the photogenerated products should react selectively and rapidly at one of the electrodes.[1]

Previous papers[2,3] have described a selective electrode suitable for use in iron-thionine photogalvanic cells with photoreaction (1). This electrode was produced by the irreversible adsorption of up to 20 monolayers of thionine at a platinum or SnO_2 electrode. At such a modified electrode, the thionine couple has fast electrode kinetics, but the rate of electron transfer to Fe(III) is slow. The properties of the thionine coated electrode have presently been further investigated by studying the reactions of a series of redox couples at the electrode. The aim is to see whether this modified electrode may have application to photogalvanic systems involving couples other than Fe(II)/Fe(III) and Th/L.

Secondly, a study of electrode properties in the iron-rhodamine B system is described. Strong adsorption of rhodamine B at solid electrodes has been reported.[4,5] The present work considers whether such adsorption modified electrodes are selective electrodes suitable for photogalvanic cells.

EXPERIMENTAL

Experiments were carried out at 25 °C. All potentials are reported with respect to the saturated calomel electrode. The platinum rotating disc electrode was manufactured at the Kjemisk Institutt. The motor, motor controller and potentiostat were from Tacussel. Thionine, *puriss.* grade methylene blue and *purum* grade rhodamine B were supplied by Fluka. The ruthenium(II) tris-(2,2′-bipyridine) was prepared and purified by the method of Burstall.[6] All other chemicals were Analar grade or equivalent.

THIONINE COATED ELECTRODES

Thionine coated electrodes were prepared by potentiostating a clean platinum electrode at +1.5 V for 20 min in a solution containing 10^{-4} M

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Table 1. Kinetic parameters at a thionine coated electrode. QH_2 = hydroquinone; Q = quinone; MB = methylene blue; LMB = leucomethylene blue. All measurements made in 0.5 M H_2SO_4. Reactant concentrations = 1 mM.

Reaction	Uncoated $E_{\frac{1}{2}}$/V	k'_o/cm ks^{-1}	Coated $E_{\frac{1}{2}}$/V	k'_o/cm ks^{-1}	$k'_?$/cm ks^{-1}
Fe(II) → Fe(III) + e	0.45	8.2	0.70	0.30	5.7
Fe(III) + e → Fe(II)	0.42	8.2	0.17	0.15	13.2
$Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e$	0.42	>30[a]	0.52	1.2	6.8
$Fe(CN)_6^{3-} + e \rightarrow Fe(CN)_6^{4-}$	0.42	>30[a]	0.19	0.06	0.37
$Ru(bipy)_3^{2+} \rightarrow Ru(bipy)_3^{3+} + e$	1.02	>30[a]	1.05	5.57	8.7
$Ru(bipy)_3^{3+} + e \rightarrow Ru(bipy)_3^{2+}$	1.02	>30[a]	0.99	1.1	28
$QH_2 \rightarrow Q + 2e + 2H^+$	0.52	0.25	0.52	0.25	–
$Q + 2e + 2H^+ \rightarrow H_2Q$	0.32	0.25	0.27	0.10	–
MB + 2e → LMB	0.17	>30[a]	0.13	0.70	5.8

[a] Reaction was reversible.

thionine and 0.05 M H_2SO_4. These conditions create a reproducible coating of thionine. The thionine modified electrode thus produced remains stable when immersed in other aqueous electrolyte solutions, when stored in air, and even under the low vacuum conditions of an X-ray photoelectron spectrometer.[2]

Various redox couples (Table 1) were studied under identical conditions at both a clean platinum electrode and at a thionine coated electrode. As an example of the effects produced, Fig. 1 shows the current-voltage curves for the reduction of methylene blue at the rotating disc electrode. At the thionine coated electrode the half wave potential has become less positive and the limiting current is reduced from the transport limited value. This shows that an additional rate limiting step appears in the reduction at the coated electrode. The limiting current (i_L) in such a case is decribed by the Koutecky-Levich equation[7] which may be

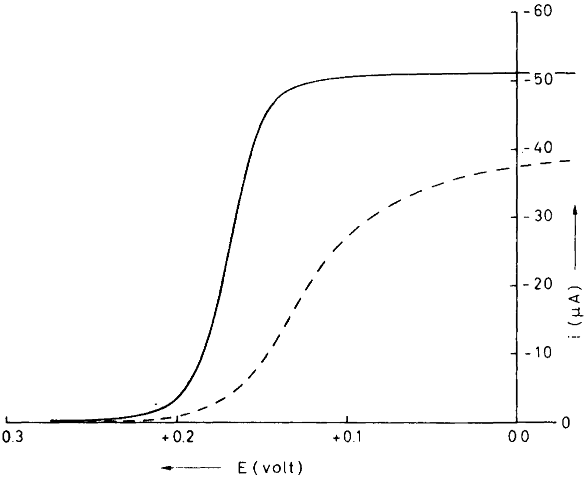


Fig. 1. Current voltage curves for the reduction of methylene blue at an uncoated (——) and at a thionine coated (– – –) Pt electrode. [methylene blue] = 1 mM; 0.5 M H_2SO_4 electrolyte.

written as eqn. (2), where $k'_{D,O}$ is the mass transfer

$$\frac{n[O]AF}{|i_L|} = \frac{1}{k'_{D,O}} + \frac{1}{k'_?} \qquad (2)$$

rate constant for the species (O) involved; $k'_?$ is the heterogeneous rate constant for the additional rate limiting step; n is the number of electrons; $[O]$ is the bulk concentration of species O; A is the surface area of the electrode; and F is the Faraday constant. Thus, unless $k'_?$ is much larger than $k'_{D,O}$ the observed limiting current (i_L) will be below the transport limited value.

At a rotating disc electrode,[8]

$$k'_{D,O} = 1.55\, D_O^{2/3} v^{-1/6} W^{1/2} \qquad (3)$$

where D_O is the diffusion coefficient of O in $cm^2\ s^{-1}$; v is the kinematic viscosity in $cm^2\ s^{-1}$; and W is the rotation speed of the electrode in Hz. Thus, eqn. (2) predicts that a plot of $|i_L|^{-1}$ *versus* $W^{-1/2}$ should be linear. The unknown rate constant, $k'_?$, can be found from the intercept, which corresponds to infinite rotation speed. Fig. 2 shows such a plot for methylene blue reduction.

Rate parameters for the redox couples studied are shown in Table 1. The rate constants for the unknown step were calculated as just described. The standard electrochemical rate constants (k'_o) were calculated from analysis of the current voltage relationship using an expression for the Tafel equation corrected for the effects of transport and electrochemical back reaction.[2]

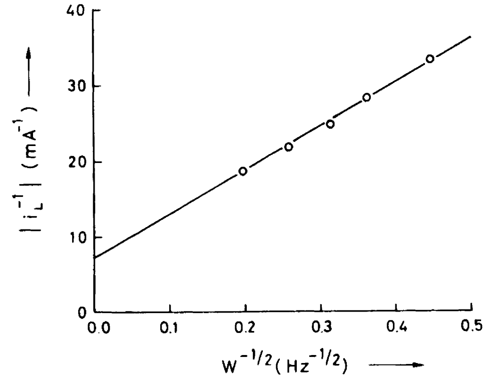


Fig. 2. Koutecky-Levich plot, eqn. (2), for the reduction of methylene blue at a thionine coated electrode.

Except for the case of hydroquinone oxidation, $E_{1/2}$ at the coated electrode is changed from the value at a clean electrode. It becomes more positive for oxidation and less positive for reduction. All of the redox processes except the hydroquinone oxidation have reduced k'_o values at the coated electrode. Further, for a given redox couple the effect on the reduction process is greater than the effect on the oxidation process. This is especially so for the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ couple. However, k'_o for the oxidation of hydroquinone is unaffected by the coating, and k'_o for the reduction of quinone is affected only by a factor of 2.5.

For the hydroquinone/quinone couple $k'_?$ is inaccessibly large. All the other reactions show an additional rate limiting step. For the oxidations, the values of $k'_?$ are very similar. This similarity is remarkable in view of the different charges of the reacting species and their different standard potentials. There is no such similarity for the reduction processes.

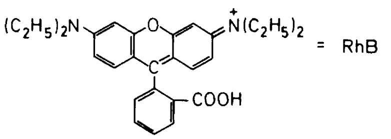
The data in Table 1 show that the thionine coated electrode may find application to photogalvanic systems other than the iron-thionine system. All such systems consist of two redox couples; either two inorganic couples, an inorganic and an organic couple, or two organic couples. If the modified electrode is to be of use, it must allow the oxidation of one couple to be relatively fast whilst hindering the reduction of the other couple, or *vice versa.*

With inorganic-inorganic systems the data show that the thionine coated electrode may be useful even with couples of similar charge transfer properties. This is due to the important observation that the electrode favours oxidation processes over reduction processes. Comparison of the data for $Fe(CN)_6^{3-}$ and $Ru(bipy)_3^{2+}$ shows that the usefulness is enhanced for pairs of unlike couples. This is significant for photogalvanic cells utilizing the well-known photochemical properties of this ruthenium couplex. A major problem with the development of such cells has been the lack of a discriminating electrode.

The iron-thionine system is itself an example of the usefulness of the modified electrode for inorganic-organic systems. The data for hydroquinone/quinone show that organic species other than thionine may be relatively unaffected by the thionine coating. Thus there may be other systems where the organic couple has relatively fast kinetics at the modified electrode whilst the inorganic couple is hindered. Possible organic-organic systems are few due to the lack of organic molecules with cyclable electrode reactions. Unfortunately, the electrode is unsuitable for the thionine-hydroquinone system. However, the hindering of the reduction of methylene blue shows that the modified electrode can discriminate between organic couples.

RHODAMINE B COATED ELECTRODES

Several workers[5,9] have studied the photoelectrochemical properties of rhodamine B (RhB). In particular, Quickenden and Yim[9] have constructed a photoelectrochemical cell based on the iron-rhodamine B system. However, they did not analyse the rate of electron transfer processes at their electrodes. A photogalvanic cell based on this system would have the homogeneous reactions (4), where



$$\mathrm{RhB + Fe(III)} \underset{k}{\overset{\mathrm{LIGHT}}{\rightleftharpoons}} \mathrm{RhB_{OX} + Fe(II)} \qquad (4)$$

light absorbed by the rhodamine B dye drives the photochemical reaction forward. The electrode kinetics of $\mathrm{RhB/RhB_{OX}}$ and Fe(II)/Fe(III) are therefore of importance.

A persistant modification of the electrode surface by rhodamine B could be shown by the effect of treatment on the electrode kinetics of Fe(II) and Fe(III). Modified electrodes were prepared by allowing the platinum rotating disc electrode to stand at open circuit in rhodamine B solution. They were also prepared by potentiostating the electrode at +1.5 V. In this latter case the rhodamine B is oxidised at the electrode surface and the electrode conditions are those which were optimum for thionine coating. The electrodes were then thoroughly rinsed and transferred to an Fe(II) or Fe(III) solution.

The electrode kinetics of Fe(II) and Fe(III) at a rhodamine B modified electrode could be analysed in the same manner as at a thionine coated electrode. Typical data are presented in Table 2. The effects produced by preparation at open circuit and under potentiostatic conditions are similar.

If the rhodamine B were adsorbed in a simple manner, it might be expected to slowly desorb in the Fe(II) and Fe(III) solutions. However, a further change occurs that affects the kinetics of the Fe(II)/Fe(III) couple. This is shown in Fig. 3 for an electrode treated at open circuit in a rhodamine B

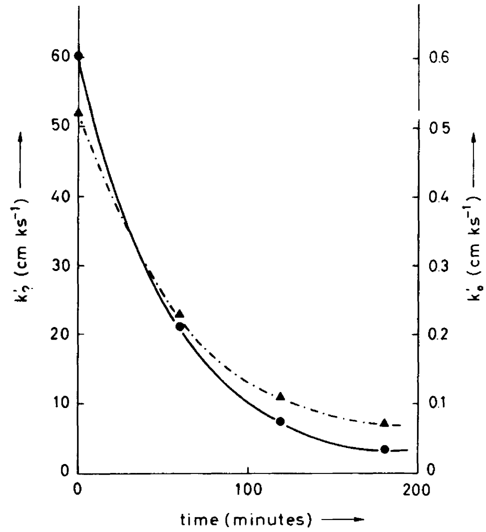


Fig. 3. Variation with time of the rate constants $k'_?$ (▲) and k'_o (●) for Fe(III) reduction at a rhodamine B modified electrode. [Fe(III)] = 1 mM; 0.5 M H_2SO_4 electrolyte.

Table 2. Kinetic properties of Fe(II) and Fe(III) at a rhodamine B modified electrode. All measurements made in 0.5 M H_2SO_4. Reactant concentrations = 1 mM.

Reaction	Treatment	k'_o/cm ks^{-1}	$k'_?$/cm ks^{-1}	$E_{\frac{1}{2}}$/V
Fe(II) → Fe(III) + e	Open circuit, 20 min	0.11	42	0.80
	Potentiostat at +1.5 V, 20 min	0.39	15	0.75
Fe(III) + e → Fe(II)	Open circuit, 20 min	0.60	52	0.32
	Potentiostat at +1.5 V, 20 min	0.25	13	0.22

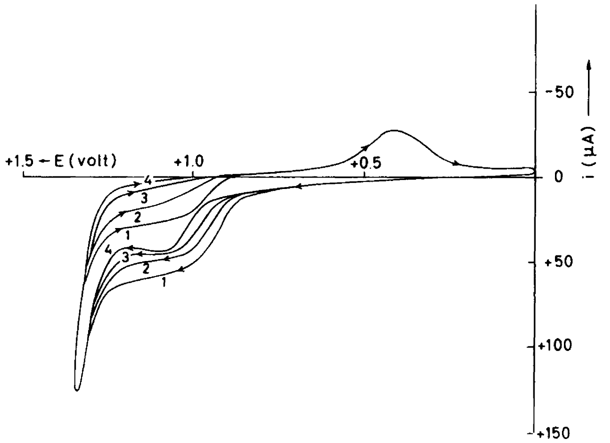


Fig. 4. Four successive voltage sweeps at a Pt electrode. [rhodamine B] = 1 mM; 0.5 M H_2SO_4 electrolyte. First sweep initiated at 0.0 V. Sweep rate = 50 mV s^{-1}.

solution and then transferred to a solution containing Fe(III). The kinetics of Fe(III) reduction were measured with time, the electrode remaining at open circuit between measurements. The values of both k'_o and $k'_?$ successively are drastically diminished. Eventually, the reduction of Fe(III) becomes essentially completely belocked.

However, the modification of the electrode also affects electron transfer from rhodamine B to the electrode. A cyclic voltamogram of rhodamine B at a clean platinum electrode is shown in Fig. 4. The peak at anodic potentials is due to the one-electron oxidation of rhodamine B. The current is decreased with successive sweeps. Oxidation of rhodamine B is not itself the cause of this decrease. Electrodes allowed to stand for a short time at open circuit in rhodamine B solution also showed currents for rhodamine B oxidation below the diffusion limited value. This is clearly unsatisfactory for photogalvanic uses.

An attempt was made to prevent the adsorption of rhodamine B by using a thionine coated electrode. Coating of the electrode should prevent interaction of rhodamine B with the platinum surface while still allowing electron transfer. However, this was unsuccessful.

The effects observed show that if the iron-rhodamine B system is to be used in a photogalvanic cell, a means must be found to prevent the blocking of electrode reactions by the dye. This blocking of the electrode reactions of both couples is likely to be an important reason for the very low efficiency of the cells of Quickenden and Yim.[9]

CONCLUSION

The results show that dye adsorption can be either an asset or a hindrance to the operation of a photogalvanic cell. The most important discovery is that a thionine coated electrode favours oxidation processes over reduction processes. This suggests that it may find application not only in iron-thionine cells[3,4] but also in cells containing two inorganic couples. This would greatly increase the number of viable photogalvanic systems.

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