

CHALCOPYRITE
PHOTOELECTROCHEMISTRY

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By

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ABSTRACT

A considerable amount of electrochemical research has been committed to the study of chalcopyrite, but as voltammetry indicates several surface layer transformations which are difficult to ascribe to particular reactions, cyclic photocurrent voltammetry, photocurrent spectroscopy and impedance spectroscopy were employed to elucidate the nature of the product layers formed on chalcopyrite under a wide range of conditions. Naturally occurring samples of chalcopyrite were used throughout, once it was established that consistent solid state and electrochemical data were obtained from them. The investigation was related to the predictions of a potential-pH diagram calculated from critically assessed thermodynamic data: for example, the formation of n-type CuFeO_2 under oxidising conditions is thermodynamically feasible.

In alkaline solutions photocurrent voltammetry indicated the formation of a complex photo-active film on cycling to oxidising potentials. Analysis of the photocurrent spectrum at 0.7 V vs S.C.E. suggested behaviour very similar to that of n-type Fe_2O_3 formed on iron electrodes, though under less oxidising potentials the composition of the chalcopyrite oxidation products was more complex. It is believed a ternary oxide of copper and iron gives rise to the observed photocurrents, and overlays chalcopyrite which is metal-depleted. The photoelectrochemical behaviour of this oxide interphase is shown to be extremely sensitive to the imposed potential regime, especially near 0.2 V and 0.4 V. Moreover, the progress of oxidation is demonstrated to depend very much on the semiconducting nature of the oxide at the oxide/electrolyte interface.

Photocurrent and photo-voltage spectra for chalcopyrite below its rest potential at pH 9.2 (-0.2 V) are presented. The "white" light photocurrent response was stable over several days allowing for photocurrents under monochromatic light to be recorded by employing slow spectral sweeps. A threshold energy for the electronic transition responsible of about 3.3 eV was obtained. Though chalcopyrite has been reported to be a degenerate semiconductor with a 0.5 eV band-gap, the photocurrent spectra above 3.3 eV resemble absorption spectra, and suggest a similar phase to chalcopyrite prevailing at potentials as low as -1.0 V vs S.C.E.. Photoelectrochemical data was also obtained for bornite, Cu_5FeS_4 , and chalcocite, Cu_2S , and compared with that for chalcopyrite.

Photocurrent and impedance data are presented for chalcopyrite in acid conditions, in which it is unlikely that oxides are stable, and yet photo-activity arising from a passivating phase was again observed over a wide potential range.

Although it was not possible to determine the exact composition of chalcopyrite oxidation and reduction products, this work enabled the behaviour of chalcopyrite to be more easily interpreted. The previous widely held view that chalcopyrite forms heterogenously distributed and well known products is discredited, whilst, for instance, the reversibility of mild oxidation of chalcopyrite can now be more clearly understood.

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nec deus intersit nisi dignis vindice nodus inciderit

Horace

TABLE OF CONTENTS

	Page
ABSTRACT	i
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	v
LIST OF FIGURES	viii
LIST OF TABLES	xv
LIST OF SYMBOLS	xvi
INTRODUCTION	1
CHAPTER 1. A LITERATURE REVIEW	3
1.1. CHALCOPYRITE	3
1.1.1. Physical structure	3
1.1.2. Thermochemistry and related sulphides	6
1.2. CHALCOPYRITE IN HYDROMETALLURGICAL PROCESSES	9
1.2.1. Froth flotation	9
1.2.2. Pressure leaching	11
1.3. THE ELECTROCHEMISTRY OF CHALCOPYRITE	13
1.3.1. New stability and metastability diagrams for the copper - sulphur - iron - water system	13
1.3.2. Chalcopyrite in acid solutions	21
1.3.3. Chalcopyrite in alkaline solutions	24
1.4. PHOTOELECTROCHEMISTRY	25
1.4.1. Semiconductor/electrolyte interfaces	26
1.4.2. The semiconductor/electrolyte interface illuminated: the photoelectrochemical effect	29
1.5. IMPEDANCE SPECTROSCOPY	33

CHAPTER 2.	EXPERIMENTAL	36
2.1.	ELECTROLYTES	36
2.2.	THE WORKING ELECTRODE	36
2.2.1.	Fabrication from mineral samples	36
2.2.2.	Surface preparation	37
2.3.	THE ELECTROCHEMICAL CELL	38
2.4.	INSTRUMENTATION	39
2.4.1.	For photoelectrochemical experiments	39
2.4.2.	For a.c. impedance spectroscopy	43
2.4.3.	For other experiments	44
CHAPTER 3.	RESULTS OF PRELIMINARY INVESTIGATIONS ON TWENTY CHALCOPYRITE SAMPLES	45
3.1.	The Hall Effect	45
3.2.	Resistivity measurements	45
3.3.	Microprobe analysis	45
3.4.	X-ray crystallography	48
3.5.	Rest potentials and the atmospheric oxidation of chalcopyrite	48
3.6.	Photocurrent and dark current transients in acid solutions	54
3.7.	Photocurrent and dark current transients in alkaline solutions	81
CHAPTER 4.	ELECTROCHEMICAL BEHAVIOUR OF CHALCOPYRITE IN ACID SOLUTIONS	95
4.1.	Oxidation	96
4.2.	Reduction	107
CHAPTER 5.	REDUCTION OF CHALCOPYRITE IN ALKALINE SOLUTIONS	116
5.1.	Chalcopyrite at potentials negative of the rest potential	116
5.2.	Under mildly oxidising conditions	130

5.3.	Bornite under reducing conditions	132
5.4.	Chalcocite at its rest potential	132
CHAPTER 6.	OXIDATION OF CHALCOPYRITE IN ALKALINE SOLUTIONS	134
6.1.	Introduction	134
6.2.	n-type hematite; α -Fe ₂ O ₃	136
6.3.	p-type Cu ₂ O.	141
6.4.	Photocurrent spectra of chalcopyrite at oxidising potentials	145
6.5.	Cyclic photovoltammetry on cp at oxidising potentials	163
6.6.	Coulometry	172
6.7.	Cyclic voltammetry	178
6.8.	The photo-electrochemistry of other sulphides in alkaline solutions	182
CHAPTER 7.	CONCLUSIONS	185
	Future work	188
APPENDICES		190
Appendix 1	Thermodynamic data for the Cu-Fe-S-H ₂ O systems at 298 K	190
Appendix 2	Computer programs	194
Appendix 3	Photographic plates	215
REFERENCES		217

LIST OF FIGURES

- Figure 1.1.1.1.** Unit cell of chalcopyrite showing two octahedral hole vacancies.
- Figure 1.1.1.2.** Interatomic bond lengths (pm) and angles in CuFeS_2 .
- Figure 1.1.1.3.** SCF- $X\alpha$ ground state orbital eigenvalues for CuS_4^{7-} , $R = 0.2302$ nm and FeS_4^{5-} , $R = 0.2258$ nm (from [33]).
- Figure 1.1.2.1.** Phase relations in the condensed Cu - Fe - S system at 600 °C, 400 °C and 25 °C (estimated).
- Figure 1.3.1.1.** Potential - pH diagram for Cu - Fe - S - water system for 298 K and dissolved copper, iron and sulphur activities of $10^{-4.01}$, 10^{-4} , and $10^{-3.99}$, respectively.
- Figure 1.3.1.2.** Potential - pH diagram for Cu - Fe - S - water system at 298 K, excluding all sulphur (VI) species and pyrite, and for dissolved copper, iron and sulphur activities of $10^{-4.01}$, 10^{-4} , and $10^{-3.99}$, respectively.
- Figure 1.4.1.** The Semiconductor/Electrolyte junction under polarisation.
- Figure 1.4.2.1.** Light absorption and energy redistribution in a semiconductor.
- Figure 1.4.2.2.** The semiconductor/electrolyte junction, SC/EL, under illumination.
a n-type semiconductor at potentials anodic of the flat-band potential,
b p-type semiconductor at potentials cathodic of the flat-band potential.
- Figure 1.5.1.** A trace of the alternating current response I to an alternating applied potential difference E .
- Figure 1.5.2.** The Randle's equivalent circuit.
- Figure 1.5.3.** Frequency dependent impedance response at constant potential for equivalent circuit shown in **Figure 1.5.2**.
- Figure 2.2.1.** Mineral electrode arm and mount.
- Figure 2.3.1.** Photoelectrochemical cell.
- Figure 2.4.1.1.** Photoelectrochemical apparatus.
- Figure 2.4.1.2.** Dummy cell used before undertaking photoelectrochemical experiments.
- Figure 2.4.1.3.** Output of 150 W xenon lamp vs photon energy and wavelength. Slit width 3mm.
- Figure 2.4.3.1.** Electrochemical cell employed in certain voltammetric experiments.
- Figure 3.5.1.** Time dependence of mineral open circuit potential in 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$.
- Figure 3.5.2.** Cathodic reduction curve for chalcopyrite in 0.3 M Na_2SO_4 , pH 7.2. Sweep rate 50mV s^{-1} .

- Figure 3.5.3.** Voltammogram of chalcopyrite from the rest potential to -1.0 V in 0.3 M Na₂SO₄ pH 12.16 50mV s⁻¹.
- Figure 3.5.4.** Voltammogram of chalcopyrite from the rest potential to -1.0 V in 0.3 M Na₂SO₄ pH 2 50mV s⁻¹.
- Figures 3.6.1-13.** Dark (top) and photo- (bottom) current responses to positive (left) and negative (right) potential excursions from 0 V vs. S.C.E at pH 1. Sweep rate = 50 mV s⁻¹. The results were presented for electrodes fabricated from cp of diverse origin, namely 1a, 2a, 5, 6, 7, 9, 10, 11, 12, 16, 19, 21 and 22, respectively. See Table 3.3.1.
- Figure 3.7.1.** Electrode 22. Dark (top) and photo- (bottom) current responses to positive (left) and negative (right) potential excursions from -0.2 V vs. S.C.E. at pH 9.2. Sweep rate = 50 mV s⁻¹
- Figure 3.7.2-6.** Dark (top) and photo- (bottom) current responses to positive (left) and negative (right) potential excursions from -0.2 V vs. S.C.E. at pH 9.2. Sweep rate = 5 mV s⁻¹. Results were presented for several different electrodes fabricated from cp of diverse origin, namely 22, 9b, 12, 16 and 22 respectively. See Table 3.3.1.
- Figure 4.1.1.** Electrode 22. Dark current, **a**, and photocurrent response, **b**, following a positive potential excursion from 0 V vs S.C.E. in 0.1 M HClO₄. 50 mV s⁻¹.
- Figure 4.1.2.** log(I) vs E for positive excursions from 0 V at 5 mV s⁻¹ and 50 mV s⁻¹ in 0.1 M HClO₄ + 0.5 M NaClO₄, pH 1.
- Figure 4.1.3.** Impedance data obtained for chalcopyrite electrode 22K in 0.1 M HClO₄ and 0.5 M NaClO₄ at applied potentials between -0.1 V and 0.8 V stepped positively 100 mV. 20 data points per frequency decade, 10 to 65000 Hz. One minute lapse before measurements to allow the current to reach a steady state.
- a:** At 0.0 V, plotted in the complex plane showing theoretical values obtained using the parallel RC circuit described in the text.
- b:** Impedance data between -0.1 V and 0.3 V plotted in the complex plane,

- c: Similar plots for the entire range of potentials,
d: $Z(\text{real})$ and $Z(\text{imag})$ vs $\omega^{-1/2}$ indicative of the Warburg impedance operative at the low frequency limit for higher potentials.
- Figure 4.2.1.** Electrode 22q. Dark current, **a**, and photocurrent, **b**, response to a positive potential excursion from 0 V to ever widening potential limits at pH 0.67. (2 M H_2SO_4). Sweep rate = 5 mV s^{-1} .
- Figure 4.2.2.** Continuation of experiment represented in **Figure 4.2.1**.
- Figure 4.2.3.** Photocurrent transients for chalcopyrite immersed in 1 molar HClO_4 and swept to varying positive potential limits. Sweep rate 5 mV s^{-1} .
- Figure 4.2.4.** Spectral photocurrent response of chalcopyrite electrode 22, following the same regime used to obtain **Figure 4.2.1**, only at pH 2.1.
- Figure 4.2.5.** See 4.2.1. Photon energy vs $(i_{\text{ph}}h\nu)^n$ indicates $n = 2$, indirect electron transition.
- Figure 5.1.1.** Cottrell plot of dark current transients for cp at increasingly negative stepped potentials.
- Figure 5.1.2.** Photocurrent magnitude vs photon energy for cp in 0.1 M borax solution, pH 9.2, at increasingly negative stepped potentials.
- Figure 5.1.3.** Photocurrent phase angle vs photon energy for cp as 5.1.2.
- Figure 5.1.4.** $(h\nu\Phi)^{1/2}$ vs photon energy, $h\nu$, for cp as 5.1.2.
- Figure 5.1.5.** Photocurrent threshold energies for cp vs potential V , calculated from plots of $\{V_{\text{ph}}h\nu/P\}^{1/2}$ vs $h\nu$ under galvanostatic control, and $\{h\nu\Phi\}^{1/2}$ vs $h\nu$ and $\Phi^{1/2}$ vs $h\nu$ under potentiostatic control.
- Figure 5.1.6.** Photo-voltage magnitude normalised for the lamp power output V_{ph}/P vs photon energy $h\nu$ for cp in 0.1 M borax solution, pH 9.2, under cathodic followed by anodic constant currents.
- Figure 5.1.7.** Photo-voltage phase angle vs photon energy for cp as 5.1.6.
- Figure 5.1.8.** $(V_{\text{ph}}h\nu/P)^{1/2}$ vs photon energy, $h\nu$, for cp as 5.1.6.
- Figure 5.1.9.** Averaged magnitudes and phase angles of photocurrents as a function of potential. The averaged spectral values have not been normalised for the flux output of the xenon lamp, to indicate their size relative to "white" light photocurrents.
- Figure 5.1.10a.** Variation with time I_{tot} , I_{ph} and θ after stepping the potential from -0.8 to -0.875 V vs S.C.E. as described in the text.
b, detail of I_{tot} vs t , upon closing the shutter.

- Figure 5.1.11.** Variation with time V_{tot} , V_{ph} and θ from the onset of applying $-2.4 \mu\text{Acm}^{-2}$ as described in the text.
- Figure 5.1.12.** $(I_{\text{ph}} \cdot \sin\theta/P)^2$ vs potential.
- Figure 5.2.1.** Photocurrent spectrum for chalcopyrite electrode just anodic of its rest potential, -0.036 V in 0.1 M borax, pH 9.2.
- Figure 5.2.2.** Indirect electron transition plot for cp as 5.2.1, and then shortly after reducing the potential to -0.3 V .
- Figure 5.3.1.** Photocurrent spectrum parameters i_{tot} , Φ , and θ vs $h\nu$ for bornite electrode in 0.1 M borax solution at an applied potential of -0.3 V .
- Figure 5.4.1.** Indirect electron transition plot for Cu_2S at its rest potential of -0.07 V in 0.1 M borax.
- Figure 6.1.1.** $i_{\text{ph}} \cdot \sin\theta$ and i_{tot} vs V , for cp electrode in 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$ linearly swept between potential limits of $+0.8$ and -1.2 V , two cycles, 5 mV s^{-1} . Also depicted is the variation in capacitance under stepped potentiostatic control obtained from impedance spectral data following one stepped sweep to -1.2 V and $+0.8 \text{ V}$. 110 s per 0.5 V step.
- Figure 6.2.1.** i_{ph} and i_{tot} vs V , for iron electrode in 0.1 M sodium tetraborate linearly swept between potential limits of $+0.8$ and -1.0 V , two cycles, and $+1.0$ and -1.0 V , 1 cycle.
- Figure 6.2.2.** Plots of Φ and $\{\Phi \cdot h\nu\}^n$ vs $h\nu$ for cp electrode in 0.1 M sodium tetraborate maintained at 0.7 V following a potential excursion from -0.2 V to and from -1.2 V at 5 mV s^{-1} . 60 nm s^{-1} monochrometer sweep rate. 1 s lock-in time constant.
- Figure 6.2.3.** Plots of Φ and $\{\Phi \cdot h\nu\}^n$ vs $h\nu$ for cp electrode in 0.1 M sodium tetraborate maintained at 0.6 V following a potential excursion from -0.2 V :
a, to and from -1.2 V at 5 mV s^{-1} ;
b, to -1.2 V at 0.1 mV s^{-1} and from -1.2 V at 5 mV s^{-1} .
 60 nm s^{-1} monochrometer sweep rate. 1 s lock-in time constant.
- Figure 6.3.1.** Detail of 6.1.1, showing initial response of i_{tot} , i_{ph} and θ to the swept potential.
- Figure 6.3.2.** Total current and photocurrent response of a high purity Cu electrode to potential excursions between -0.8 and 0.8 V at pH 9.2. Sweep rate 5 mV s^{-1} .

- Figure 6.3.3.** Plots of Φ and $\{\Phi \cdot hv\}^{1/2}$ vs $h\nu$ for the copper electrode in 0.1 M sodium tetraborate alternately maintained at 0.0 and -0.3 V after 8 minutes at each potential. Two spectra are presented at each potential to illustrate the consistency of the results. 1 nm s^{-1} monochromator sweep rate. 1 s lock-in time constant.
- Figure 6.3.4.** **a** and **b**, heterogenous vs **c** and **d**, homogenous oxide product formation on a cp electrode shown in cross section, in alkaline solutions. The direction of photocurrent indicated is for photo-generated electrons. Photo-generated holes will move in the opposite direction.
- Figure 6.4.1.** **a**, photocurrent conversion efficiency, Φ , and **b**, photocurrent phase angle θ vs photon energy $h\nu$, for cp in 0.1 M sodium tetraborate at constant applied potentials stepped positively from the rest potential. 60-90 minutes per step. 0.1 nm s^{-1} monochromator sweep rate. 30 s lock-in time constant. $0.3 \text{ }\mu\text{V}$ lock-in sensitivity.
- Figure 6.4.2.** The vectorial modification of **a**, Φ , and **b**, θ vs photon energy $h\nu$, between spectra recorded at -0.275 V and subsequent more positive potentials for cp in 0.1 M sodium tetraborate as shown in **Figure 6.4.1**.
- Figure 6.4.3.** Plots of **a**, $\{\Phi\}^{1/2}$ vs $h\nu$ and **b**, $\{\Phi \cdot \sin\theta\}^{1/2}$ vs $h\nu$ for spectra presented in **Figure 6.4.1**.
- Figure 6.4.4.** **a**, photocurrent conversion efficiency, Φ , and **b**, phase angle θ vs photon energy $h\nu$, for cp in 0.1 M sodium tetraborate at constant applied potentials stepped positively from 0.1 V in continuation of experiment described in **Figure 6.4.1**. Same parameters.
- Figure 6.4.5.** Plots of **a**, $\{\Phi\}^{1/2}$ vs $h\nu$ and **b**, $\{\Phi \cdot hv\}^{1/2}$ vs $h\nu$ for spectra presented in **Figure 6.4.4**.
- Figure 6.4.6.** Comparison of "white" light and chromatic **a**, photocurrent magnitude, and **b**, phase angle θ vs applied potential for cp in 0.1 M sodium tetraborate at constant applied potentials stepped positively from -0.275 V as described under **Figures 6.4.1-4**.

- Figure 6.4.7.** a, correlation coefficients and b, threshold energies vs applied potential for cp electrode in 0.1 M sodium tetraborate. Derived from spectral data obtained as follows:
 A, At 0.03 V after 12 hr maintained at this potential and then after a further 1 hr at -0.3 V. See also **Figures 5.2.1** and **2**.
 B, At 0.6 V following a slow excursion to -1.2 V, **Figure 6.2.3b**.
 C, As described in **Figure 6.4.1** (* **Figure 6.4.2**).
 D, As described in **Figure 6.4.4**.
 E, From photo-voltage measurements under constant applied currents.
- Figure 6.4.8.** Electronic energy level diagram for the idealised structure of the cp electrode in 0.1 M sodium metaborate solution at various potentials. b vs a shows all the possible effects of increasing the potential from 0.025 V in the experiment during which photocurrent spectra were recorded (see **Figure 6.4.6**). The results conform only to the increase in oxide layer thickness, whereby the effects of band bending in a are exaggerated. The principle source of photocurrent generation is illustrated. All diagrams pertain to the model presented in **Figure 6.3.4d**.
- Figure 6.5.1.** $I_{ph} \cdot \sin\theta$ vs applied potential for cp electrode in 0.1 M sodium tetraborate solution under "white" light following potential excursions from -0.2 V to -0.5 V, then successively to and from:
 3: 0.3 V; 4: 0.4 V; 5: 0.5 V; 6: 0.6 V; 7: 0.7 V.
 Potential sweep rate 5 mV s^{-1} .
- Figure 6.5.2.** I_{tot} vs applied potential, during experiment pertaining to **Figure 6.5.1**.
- Figure 6.5.3.** a, I_{tot} and b, $I_{ph} \cdot \sin\theta$ vs applied potential, for cp electrode in 0.1 M sodium tetraborate solution under "white" light. 5 mV s^{-1} sweep rate.
- Figure 6.5.4.** The time dependence of a, I_{ph} and b, θ at succeeding positive constant potentials, applied for 180 s, following potential excursions to -0.6 V. Cp electrode in 0.1 M sodium tetraborate solution under "white" light.
- Figure 6.5.5.** The potential dependence of a, I_{tot} and $I_{ph} \cdot \sin\theta$ and b, θ , during negative-going potential sweeps to -0.6 V from the positive potential limit, as in **Figure 6.5.4**. 10 mV s^{-1} sweep rate.

Figure 6.6.1. Cottrell type plots of I_{tot} vs $t^{1/2}$ for cp electrode in 0.1 M sodium tetraborate solution under "white" light. **a** at increasing positive potentials maintained for 180 s and **b**, at -0.6 V following sweep from these positive potentials. See also **Figure 6.5. 4 - 5** and **6.6.2**.

Figure 6.6.1. Plots of $\ln(I_{\text{tot}})$ vs $\ln(t)$ for cp electrode in 0.1 M sodium tetraborate solution under "white" light. **a** at increasing positive potentials maintained for 180 s and **b**, at -0.6 V following sweep from these positive potentials. See also **Figure 6.5.4-5** and **6.6.2**.

Figure 6.6.2. Cottrell type plots of I_{tot} vs $t^{1/2}$ for cp electrode in 0.1 M sodium tetraborate solution under "white" light at positive potentials positive of the rest potential, maintained for 300 s, then stepped positively 0.1 V.

Figure 6.6.3. **a**, Total cathodic charge Q_c and anodic charge Q_a passed for cp under xenon light in 0.1 M borax solution vs positive potential excursion limit. This potential was maintained for 180 s. There followed a negative-going potential sweep at 10 mV s^{-1} to the annotated negative potential limits. These potentials were maintained until $I_{\text{tot}} > -0.1 \mu\text{A per cm}^2$.

b, $Q_c:Q_a$ vs positive potential excursion limit, as described above, and for Cu_2S (chalcocite). The "corrected" values pertain to certain experiments in which the cathodic currents took $> 1 \text{ hr}$ to reach $-0.2 \mu\text{A cm}^{-2}$. Cottrell-type plots were linear in this range, allowing an additional cathodic charge to be considered by integration of the function

$$I = mt^{1/2} + c \text{ with respect to time.}$$

Figure 6.8.1. **a**, cyclic voltammogram for polished bornite electrode in de-oxygenated buffer solution at pH 9.2, commencing near the rest potential -0.3 V. 5 mV s^{-1} sweep rate.

b, "White" light photocurrent response of bornite under conditions described above.

Figure 6.8.2a, cyclic voltammogram for polished chalcocite electrode in de-oxygenated buffer solution at pH 9.2, commencing near the rest potential -0.3 V. 5 mV s^{-1} sweep rate.

b, "White" light photocurrent response of chalcocite under conditions described above.

LIST OF TABLES

Table 1.3.1.1.	Gibbs energies of formation of chalcocite and covellite.
Table 3.3.1.	Mineral specifications. BM = British museum; GBL = Gregory, Botley and LLoyds Ltd, London. cc = chalcocite, bn = bornite
Table 3.3.2.	Specifications of chalcopyrite 22.
Table 3.5.1.	*: predicted range of stability according to metastability diagram in the Appendix.
Table 3.5.2.	Surface oxidation of chalcopyrite in atmosphere.
Table 4.1.1.	Calculated layers of chalcopyrite required for oxidation to various end products over increasingly positive potential ranges to account for observed dark currents at two different sweep rates. For the reaction $aX \rightleftharpoons ne + products$, the number of layers required is $V_{ma}/\{nF(V_c)^{1/3}\}$. * At 1.00 V, S and SO_4^{2-} formed in ratio 6:1. See text.
Table 4.1.2.	R_{so} , R_{ct} , f_{max} , C_{dl} and the surface fractal dimension deduced from impedance data obtained for chalcopyrite in 0.1 M $HClO_4$ and 0.5 M $NaClO_4$ at applied potentials between -0.1 V and 0.8 V stepped positively 100 mV.
Table 4.1.3.	R_{so} , R_{ct} , f_{max} , C_{dl} and the surface fractal dimension deduced from impedance data obtained for chalcopyrite in 0.1 M $HClO_4$ and 0.5 M $NaClO_4$ at applied potentials between 0.7 V and 0.0 V stepped negatively 100 mV.
Table 4.1.4.	R_{ct} , f_{max} , C_{dl} and the surface fractal dimension deduced from impedance data obtained for chalcopyrite in 2 M H_2SO_4 at applied potentials between 0.5 V and -0.1 V stepped negatively 50 mV following potential step excursion from 0.0 V to -0.7 V to 0.65 V. 0.050 mV per step. 120 s per step.
Table 4.2.1.	R_{ct} , f_{max} , C_{dl} and θ deduced from impedance spectroscopy obtained for chalcopyrite electrode in 2 M H_2SO_4 at applied potentials stepped negative from 0.0 V to -0.65 V. 0.050 V per step. 120 s per step.
Table 4.2.2.	Total cathodic and anodic charge passed in experiment pertaining to Figures 4.2.1 and 2; cp in 2 M H_2SO_4 . 5 mV s^{-1} .
Table 5.2.1.	Correlation for indirect electron transition and photoemission plots observed just above the rest potential of cp in 0.1 M $Na_2B_4O_7$; data obtained at 0.036 V.
Table 6.1.1.	Threshold energies for various photo-active phases that could form oxidatively on cp.

LIST OF SYMBOLS

Roman

$a(X)$	Activity of solution species X
ac	alternating current
C_H	The capacitance of the Helmholtz double layer, Fm^{-2}
C_{dl}	electric double layer capacitance, Fm^{-2}
C.E.	counter electrode
C_{sc}	Space charge capacitance, Fm^{-2}
d_{sc}	the Debye length, m
d	passive film thickness, m
D	the diffusion coefficient of minority carriers, m^2s^{-1}
e	electron
e	electronic charge, $1.602 \times 10^{-19} C$
E	Electrochemical potential, V
EL	electrolyte
$E(x), E_s, E_z$	Electric field in a SC at distance x from the SC/EL and normal to the electrode surface. $E_s = E(0)$. $E_z = E$ at a specified x in a product layer or interphase. Vm^{-1}
E_{bg}	the band gap energy, equal to $E_c - E_v$, where E_c and E_v are the electronic conduction and valence band edge energies respectively, eV
F	Faraday constant, $86485 C mol^{-1}$
h	positive charge carriers
h	Planck constant, $6.602 \times 10^{-34} J Hz^{-1}$
i_{ph}	photocurrent, A
i_{tot}	potentiostatically measured time averaged total current passing through W.E. under chopped light, A
I	Dark current, A
I_o	the incident photo flux, Jm^{-2}
j	the steady-state photocurrent, A
$j(t)$	photocurrent as a function of time t, A
k_i, k_f	wave vector of electronic energy level before and after photo-induced transition
k	Boltzmann constant, $1.38 \times 10^{-23} J K^{-1}$
K	Equilibrium constant for a chemical reaction

k_p	the rate constant for hole capture, s^{-1}
L	The diffusion length of the minority carriers, m
M	metal
n	Faradays per mole of substance oxidised or reduced
n_0, p_0	bulk electron and hole densities, respectively, m^{-3}
n_i	the intrinsic carrier density of an intrinsic semiconductor, m^{-3}
$n(x), p(x)$	the electron and hole densities in a SC at distance x from the SC/EL. $n_s = n(0)$ and $p_s = p(0)$, m^{-3}
N_D, N_A	donor and acceptor densities in a doped SC, m^{-3}
p_s	the surface hole density, m^{-3}
$p(X)$	partial pressure of dissolved gaseous species X , Nm^{-2}
Q_a, Q_c	Total anodic and cathodic charge passed through electrode, $mA\ cm^{-2}$
Q_{sc}	The total space charge, $C\ m^{-2}$
N_s	surface state density, m^{-2}
R	the reflectivity of the surface underneath a passive film
R	Gas constant, $8.314\ J\ K^{-1}\ mol^{-1}$
R_0	ohmic resistance within the solution, $\Omega\ m^2$
R_{ct}	charge transfer resistance, $\Omega\ m^2$
R.E.	reference electrode
S.C.E.	standard calomel electrode
SC	semiconductor
T	temperature in degrees K
t	life-time of minority carriers, s
U_{Ga}	the Galvani potential, V
U_{fb}	the flatband potential, V
U_{sc}	The potential drop across the entire space charge layer, V
$U(x)$	Electric potential in a SC at distance x from the SC/EL, V
V_{ph}	photo-voltage, V
V_m	Molar volume of species X , $m^3\ mol^{-1}$
$V_c(X)$	Volume of the unit cell of species X , m^3
W.E.	working electrode
Z	impedance response, comprising real and imaginary components
<i>Greek</i>	
α	absorption coefficient

ϵ_0	Dielectric constant in a vacuum, 8.854×10^{-12}
ϵ	Dielectric constant in a medium relative to vacuum
η	the quantum efficiency
$\Delta G_f^\circ(X)$	Standard Gibbs energy of formation of species X, kJ mol^{-1}
ΔU_E	the externally applied potential, V
ν	Photon frequency, Hz
$\rho(x)$	excess charge of density at distance x from a SC/EL or M/EL
f_{∞}	steady-state trap occupancy under illumination
f_0	trap occupancy in the dark
τ	the relaxation time for excess minority carriers in the surface state, s
θ	phase angle of impedance or photocurrent response, °
ω	frequency of applied potential modulation used in impedance spectroscopy, Hz

INTRODUCTION

Many naturally occurring metal sulphides are semiconductors. Fabricated into electrodes their behaviour in aqueous solutions can be investigated electrochemically. Typically this entails the measurement of an electric current response to a swept potential applied between the electrode and a reference electrode. Changes in potential limits and sweep rate, and in the hydrodynamic regime can be interpreted with reference to potential-pH and activity-pH diagrams. Extractive metallurgists supplement this information by analysing the electrolyte for solution species and the electrode surface to identify bulk solid product phases formed. However, after mild electrochemical treatment the concentrations of solubilised species in the bulk solution are often undetectable and surface phases formed will be of the order of monolayers thick.

The objective of this project was to use photocurrent spectroscopy to characterise the products of chalcopyrite oxidation. Chalcopyrite, CuFeS_2 (cp) is the chief source of the six million tons of copper produced annually. As with other sulphides, the electrochemical potential and pH determines cp's chemical behaviour in solution. This is of industrial importance not only in froth flotation, the principle means by which sulphide minerals are concentrated from their ores [1-3], but also in oxidative [4-11] or reductive [12,13] leaching.

The froth flotation of cp depends on a mixed potential being established by the reduction of dissolved atmospheric oxygen and the oxidation of suitable surfactants on the mineral surface. It is this tendency to oxidise spontaneously in oxygenated environments that hinders the study of chalcopyrite surface chemistry; air-formed oxide, sulphate or sulphur product phases begin to overgrow metal sulphides as soon as they are removed from the electrochemical cell. The literature on chalcopyrite electrochemistry in both acid and alkaline solutions has focused increasingly on its passivation, attributed to the formation of semiconducting films [14-16]. These could be altered all too easily by the removal of the electrode from solution exposing it to traces of oxygen, or by placement in a vacuum. *Ex-situ* techniques are frustrated and information provided by X-ray photoelectron spectroscopy, for example, is not unambiguous [17]. Several interpretations have been reported for the behaviour of chalcopyrite in acid [6,10,11,15,18-22]. In alkali, there was disagreement as to whether a copper polysulphide, a metal deficient sulphide, or covellite plus sulphur formed under conditions of collectorless flotation [2,3,11,23]. It seems conventional voltammetry reveals too many plausible products from the electrolysis of cp, even discounting the formation of phases for which no thermodynamic data are available.

There is a need to characterise chalcopyrite surface phases *in situ*, particularly under conditions relevant to froth flotation. As will be seen, chalcopyrite voltammetry indicates several surface layer transformations which are difficult to ascribe to particular reactions. In this work cyclic photocurrent voltammetry, photocurrent spectroscopy and impedance spectroscopy have been employed to further the understanding of them.

Photocurrent techniques depend on an effect first observed by Becquerel [24]. When an exposed semiconducting surface of an electrode is polarised in aqueous solutions, and irradiated with light of sufficient photon energy, electron-hole pairs are generated, and separate due to a potential gradient which extends into the electrode's interior. For n-type semiconductors and anodic polarisation, the electrons pass into the external circuit, which usually requires a lock-in technique to enable low photocurrents to be resolved from the large background dark currents. Meanwhile the holes migrate to the solid solution interface and oxidise solution species such as xanthate ions, or oxidatively decompose the lattice itself, forming oxide surface phases in neutral and alkaline solutions. Holes may also recombine with electrons before reaching the interface, or at surface recombination centres. The dependence of the photocurrent on photon energy enables the band gap of the surface phase to be determined, and the applied potential at which no photocurrent is obtained defines its characteristic flat band potential. Hence, in principle, the identity of a surface phase may be established from these two material properties, by reference to independent experiments with the bulk phases. In general the properties of phases only monolayers thick deviate from those of bulk materials, requiring photocurrent spectra to be measured as a function of time and film thickness. Conveniently, p-type copper [25,26] and n-type iron [27,28] oxides on their respective metal substrates are photoactive, and can be detected photoelectrochemically as photoactive phases on cp.

CHAPTER 1. A LITERATURE REVIEW

1.1. CHALCOPYRITE

1.1.1. Physical structure

Formal oxidation states in cp have long been a point of contention; both Cu(I)Fe(III)S_2 and Cu(II)Fe(II)S_2 are conceivable. It is interesting that chalcopyrite and cytochrome oxidase have equal molar ratios copper and iron. The enzyme is essential to all aerobic forms of life, each of four copper (II) atoms ferrying an electron from iron (II) heme groups to complexed dioxygen in concerted complete reduction to water. No doubt oxidation of chalcopyrite (cp) in air does not proceed so elegantly, but the variable oxidation states of copper and iron may be relevant to its concentration by froth flotation and subsequent copper extraction by leaching.

Brocher and Pauling [29], having identified the unit cell of chalcopyrite **Figure 1.1.1.1**, from X-ray crystallography data, favoured the formal oxidation states Cu(I)Fe(III)S_2 on account of chalcopyrite's bond lengths. They stress the covalent character of this wurtzite-like structure (see, for instance, reference [30] by Pauling). CuFeS_2 is just one of many ternary phases which exhibit complex temperature dependent transformations and meta-stability. Many have structures based on the wurtzite-like structure of CuFeS_2 shown below.

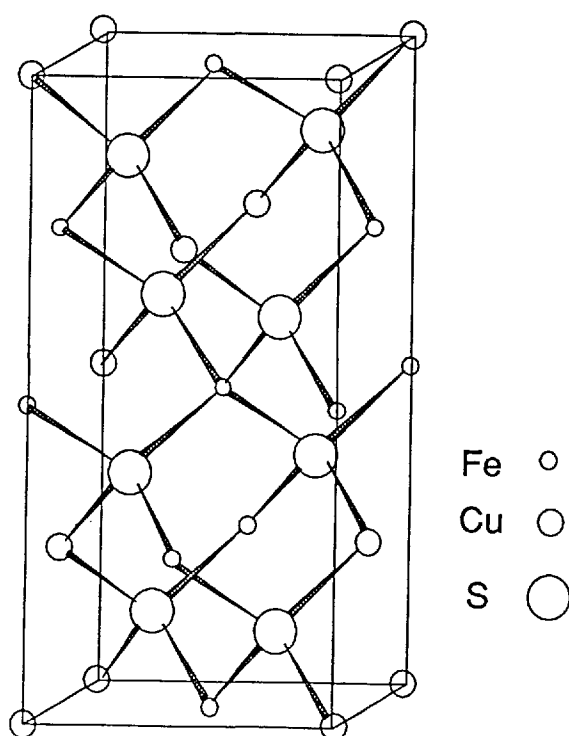


Figure 1.1.1.1. Unit cell of chalcopyrite showing two octahedral hole vacancies.

This structure is found in IB-III A-VIA₂ compounds of Cu and Ag (except oxides), IIB-IVA-VA₂ compounds of Zn, Cd, Hg (except nitrides), and is defective in IIB-III A₂-VIA₄ compounds. Most are semiconductors.

Sulphides related to chalcopyrite such as talnakite, $\text{Cu}_9\text{Fe}_8\text{S}_{16}$ have the same basic structure but with a proportion of octahedral vacancies filled.

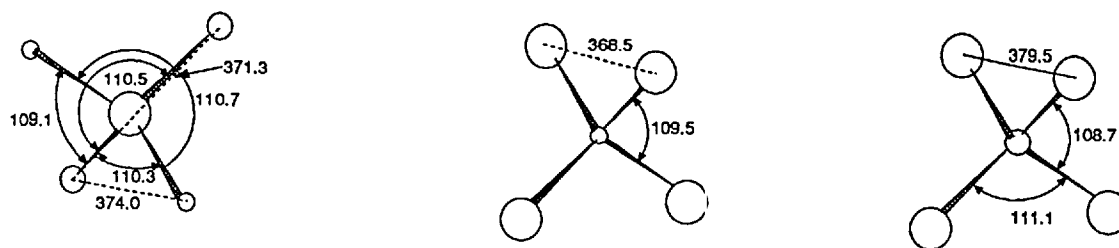


Figure 1.1.1.2. Interatomic bond lengths (pm) and angles in CuFeS_2 . Note distortion of Cu tetrahedra, implying Cu(II) oxidation state e_g degeneracy splitting.

Hall and Stewart [31] further identified the bond angles, as shown in **Figure 1.1.1.2**. Note that Fe is tetrahedrally arranged amongst S atoms whilst the Cu Tetrahedron suffers some distortion, which occurs only with Cu(II), where two copper 3d orbitals of e_g symmetry, namely $d(x^2)$ and $d(y^2 - z^2)$, share one hole and lose their degeneracy by Jahn-Teller distortion. The Cu(I) state would imply full 3d orbital occupancy, no holes, no degeneracy and no distortion.

In contrast, neutron diffraction, Mössbauer and X-ray photoelectron spectroscopy (XPES) [32] all suggest the configuration Cu(I)Fe(III)S_2 . This was assumed by Vaughan *et al.* [33], who compared the results of X-ray emission and X-ray photoelectron spectroscopy with self-consistent-field $X\alpha$ scattered wave molecular orbital calculations on the CuS_4^{7-} and FeS_4^{5-} clusters to deduce electronic energy levels in chalcopyrite. The results of these calculations are illustrated in **Figure 1.1.1.3**.

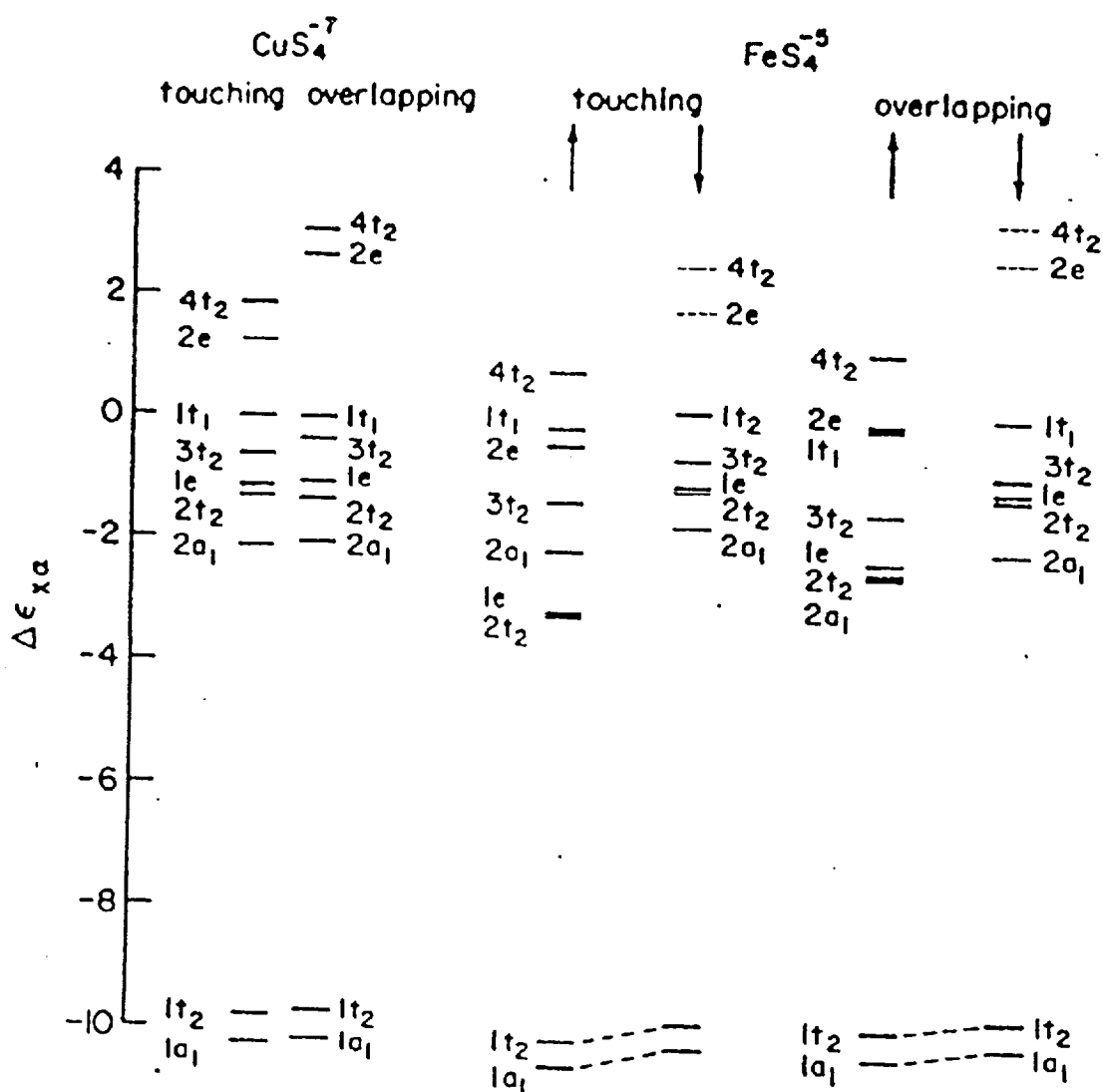


Figure 1.1.1.3. SCF-X α ground state orbital eigenvalues for CuS_4^{7-} , $R = 0.2302$ nm and FeS_4^{5-} , $R = 0.2258$ nm (from [33]).

Here the localised tetrahedra FeS_4^{5-} and CuS_4^{7-} ion clusters are considered in which metal and sulphur atoms are touching and overlapping by about 25 %. In the case of iron, high spin and low spin configurations are considered. CuS_4^{7-} has a full complement of d electrons residing on copper; effectively the ion is spherically symmetrical and so it is little affected by the tetrahedral crystal field splitting of 3d orbital $4t_2$ and $2e$ symmetry groups, in contrast to those of iron. For low spin iron these "crystal field" anti-bonding orbitals are empty; metal d electrons are likely to contribute little to M-S bonding, electrons being provided by the four S^{2-} ions. The reported bandgap for cp of 0.6 eV [34,35] and the broad optical absorption spectrum commencing at 0.6 eV [36] is attributed to electron transfer from the highest occupied energy levels - $4t$ and $2e$ on the Cu cluster - to the low spin empty levels

Cu cluster - to the low spin empty levels on iron. However, the ground state iron atom is high spin and antiferromagnetic, the Néel temperature being 823 K. Groups designated $1a_1$ and $1t_2$ are predominantly S 3s non-bonding. $2a_1$, $1t_1$, $2t_2$, $1e$ and $3t_2$ correspond predominantly to occupied sulphur 3p non-bonding orbitals, the $3t_2$ and $2a_1$ groups containing metal s and p character and the $3a_2$ group (not shown) to empty metal-sulphur anti-bonding orbitals. Taking into account interactions of adjacent tetrahedra, all the discrete levels (except the high spin Fe 2e and $4t_2$ levels) broaden into a continuum of many centre, one-electron orbitals. Very little is known about the unoccupied levels. CuL α , CuK $\beta_{2,5}$, SK $\beta_{1,3}$, and SL $_{2,3}$ M XES valence region energies are consistent with the above diagram for CuS $_4^{7-}$ (overlapping) but FeL α XES indicated that the calculations exaggerate Fe 3d orbital stability. This may be in part a saturation of the sulphur valencies, or mixing with Cu 3d.

It can be seen that chalcopyrite may behave as a semi-conductor. Natural chalcopyrite is frequently degenerate. The resistivity is typically 2 Ω m [37]. The behaviour of chalcopyrite during flotation and leaching is frequently accounted for in terms of its semiconductive nature, which in turn is influenced by impurities and the related phases described below.

1.1.2. Thermochemistry and related sulphides.

α -chalcopyrite, CuFeS $_2$, is just one of many stable phases in the Cu-Fe-S system, which also involves many metastable equilibria, ex-solutions, non-quenchable phases and non-stoichiometry [38]. Moreover, many of these have compositions close to α -chalcopyrite: they can be viewed as forming by the filling of octahedral holes in the chalcopyrite lattice, (see Figure 1.1.1.1). Examples are haycockite, Cu $_4$ Fe $_5$ S $_8$, commonly associated with nickel, talnakite or β -chalcopyrite, Cu $_9$ Fe $_8$ S $_{16}$ and mooihoekite or γ -chalcopyrite, Cu $_9$ Fe $_9$ S $_{16}$. At high temperatures this region of the system is dominated by an intermediate solid solution (iss), having a face centred cubic lattice. Phase diagrams [38] at 200, 400, and 600 °C are shown in Figure 1.1.2.1.

When heated, α -chalcopyrite undergoes a phase transition at 557 °C [39] to form the iss, pyrite, FeS $_2$, and sulphur. The iss, if cooled, forms β -chalcopyrite, which upon heating transforms twice before forming the iss at 525 °C. If heated beyond about 800 °C, both α - and β -chalcopyrite form γ -chalcopyrite which slowly transforms back to α -chalcopyrite at room temperature, though it too, if heated, exhibits a structural change before transforming to the iss at 230 °C.

Only upon quenching around the cubanite composition, CuFe_2S_3 , is the iss structure retained. At 600 °C, the iss also contains a zone in the haycockite composition that is quenched to form a primitive cubic structure, itself slowly transforming to face centred cubic upon annealing at 100 °C (or 200 °C, depending on composition). From the γ -chalcopyrite region, upon quenching, α -chalcopyrite forms, along with γ -chalcopyrite and the cubic structure above having an additional X-ray reflection at 0.52 nm. In this region there are many metastable equilibria and Cabri [38] points out the difficulty in distinguishing between phases of very similar crystallography and identifying high temperature boundaries between unquenchable phases where equilibration is too rapid, or identifying them at low temperature where it is too slow.

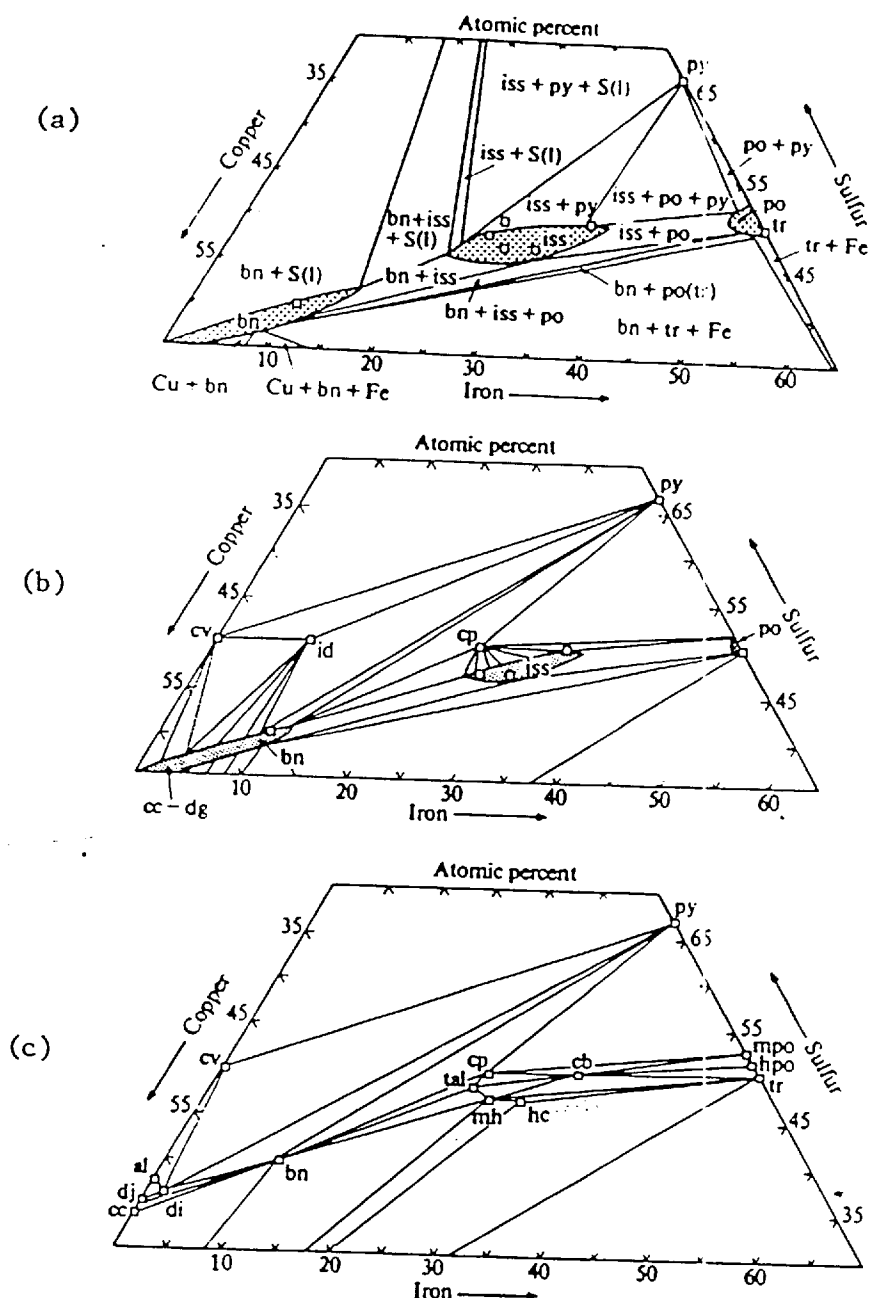


Figure 1.1.2.1. Phase relations in the condensed Cu - Fe - S system at: (a), 600 °C; (b), 400 °C; and (c), 25 °C (estimated). py:pyrite, po:(hexagonal and monoclinic) pyrrhotite, Fe_{1-x} , tr:triolite, FeS , bn:bornite, Cu_5FeS_4 , cv:covellite, CuS , al:anilite, Cu_7S_4 , dj:djurlite, $Cu_{1.96}S$, cc:chalcocite, Cu_2S , dg:digenite, Cu_9S_5 , hc:haycockite, $Cu_2Fe_5S_8$, mh:mooihoekite, $Cu_9Fe_9S_{16}$, tal:talnakite, $Cu_9Fe_8S_{16}$, cb:cubanite, $CuFe_2S_3$, id:idaite, Cu_3FeS_4 . Reproduced from [38].

It is indeed, precisely this conundrum that frustrates chalcopyrite synthesis. Even at 400 °C, a boundary occurs between the iss and chalcopyrite at the Cu=Fe join [39], where $\log(S_2) = -9$, and at the sulphur-rich limit, between chalcopyrite and pyrite + bornite, where $\log(S_2) = -5$. Both pyrite and bornite are active within these limits. It is not surprising then to find in geological assemblages pyrite and bornite, Cu_5FeS_4 , and under the prevailing pressures of formation, even - very commonly - pyrrhotite, FeS_{1-x} . Nonetheless, homogeneous and near stoichiometric samples of natural chalcopyrite can be found, while attempts at synthesis result in porous products with compositions $CuFeS_{1.96}$ at best [40]. Therefore the main thrust of this work will concentrate on high purity specimens of diverse origin such that consistent electrochemical behaviour may emerge and the effect of impurities correlated.

1.2. CHALCOPYRITE IN HYDROMETALLURGICAL PROCESSES

Most of what we know about cp electrochemistry has evolved from mechanistic studies on the hydrometallurgical extraction of copper and froth flotation. It follows that these industrial methods provide a convenient introduction to the work described later.

1.2.1. Froth flotation.

Mineral particles and gangue make up an ore body. Following crushing and grinding, froth flotation of an aqueous pulp can be used to separate and recover chalcopyrite from its ore body. In the vigorously agitated alkaline solution, 10 - 100 μm chalcopyrite particles are rendered hydrophobic by adsorption of a surfactant. Air bubbles may be used to "collect" the hydrophobic particles, which float to the surface of an aqueous pulp, and are trapped in the froth layer generated by a frother such as pine oil. The froth is then recovered by mechanical means.

The attachment of bubbles to mineral particles depends on the mineral surface hydrophobicity; ultimately the difference between mineral-air and mineral-solution surface tensions must be greater than the air-solution surface tension [41] for a bubble to begin to adhere to the mineral surface. A finite contact angle is the thermodynamic requirement tested experimentally. Bubble attachment also largely governs collection efficiencies. Oxygen must be present [1], and upon this discovery it was suggested [1] that electrochemical half-reactions occur at the mineral surface:



where X^- signifies the collector, an oxidisable short-chain surfactant and frequently a pseudohalogen such as diethyldithiophosphate, DTP or a xanthate, dialkyldithiocarbonate. Dissolved oxygen is reduced and the surfactant is oxidised on the semiconducting mineral surface by a mixed potential electrochemical mechanism to produce the chemisorbed X_2 or X^- and render the surface hydrophobic (see **Appendix 1 Figure**). This has since been verified by extensive investigations [2,3,42-3]: for cp an electrode potential of some 0.2 volts vs S.C.E. is observed at which the anodic and cathodic currents arising from (1.2.1.1) and (2) are equal. Each half-cell reaction can be studied independently. Thus, Rand [44] recorded cyclic voltammograms of chalcopyrite, arsenopyrite, pyrite, bornite, galena and chalcocite with and without oxygen present. He found the O_2 requirement in flotation followed the order of activation controlled currents in the Tafel region of these minerals. One anomaly, galena, could be explained by its inherent floatability.

For chalcopyrite, a number of different collectors are used, according to which other sulphides are found in the mineral slurry. For example, if bornite were present, chalcopyrite could be selectively floated by using diisopropyl dithiophosphate. To separate pyrite, N-ethyl-O-isopropyl dithiocarbamate would be preferable. Here iron's weak affinity for aliphatic nitrogen would be exploited. On the whole, chalcopyrite floats more readily than other copper and iron sulphides. Ackerman et al. [45] reported some correlation between semiconductor type and the readiness of collectors to chemisorb on the mineral surface; p-type minerals tend ultimately to form M-X bonds, whilst n-type effect the oxidation of X^- right through to X_2 . Photoelectrochemical studies will prove fruitful in this respect.

The effectiveness of flotation also depends on pH. Surfactant oxidation is pH independent, mineral oxidation is not, so at high pH mineral oxidation produces a hydrophilic oxide or hydroxide surface, while at lower pH values, surfactant oxidation becomes relatively competitive for certain minerals rendering them selectively hydrophobic and hence floatable. Elucidating the nature of the passivating film formed on cp under conditions pertinent to flotation would lead to improved cp flotation selectivity and recovery. Because of the scale of such processes, even small improvements would yield large economic benefits.

Chalcopyrite also floats in the presence of air and no collector [43,46] at potentials as low as -0.1 V vs S.C.E.. The rate of flotation increases at +0.2 V and reaches a maximum at 0.6 V. Gardener and Woods identified the surface products as covellite (CuS) and sulphur, and ferric hydroxide in alkali, or ferrous ions in acid. The sulphur, of at least 6 atoms thickness renders particles hydrophobic. In fact, any oxidants of sufficient

potential will float chalcopyrite under laboratory conditions, although this behaviour is less marked with real ore bodies. Chalcopyrite may also be floated in reducing conditions [3]. However, many reports concerning chalcopyrite flotation are contentious, as for instance the purported suppression of flotation by sodium sulphide [47,48]. Implications for mineral process engineering should be cautiously surmised.

1.2.2. Pressure leaching.

Dissolution of a mineral is termed leaching. None of the leachants mentioned below have been employed extensively, but interest in them is liable to increase as alternatives to high temperature oxidation in air by roasting, a process that to date has resulted in the emission of huge tonnages of sulphur dioxide, the destructive effects of which are yet to be realised. One of the most promising leachants is iron (III) chloride, as used in the Haver Wong process [49,50]. The ore must first be finely ground in a ball mill to maximise the chalcopyrite surface area. Leaching is hampered by the formation of a passive film being generated on the chalcopyrite surface (see Section 1.3.2). That this is an electrochemical process is suggested by comparable rates of dissolution in potentiostatic electrochemical oxidation, and by oxidants generating the same potentials [51-55].

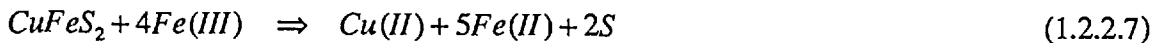
Possible processes that contributing to the total current are anodic, i_a :



and cathodic, i_c :



and a potential established such that i_c and i_a are equal and opposite. In fact the metal ions form chlorine complexes such as $CuCl_2^-$, for clarity not shown in equations (2-5). The overall reaction equation is approximately [57]:



but it is sensitive to prevailing conditions. Thus a mixture of Fe(II) and (III) chloride leach chalcopyrite faster than either individually [51]. This is because ferric chloride complexes chloride ions, thereby lowering CuCl_2^- formation and decreasing the contribution of Cu(I) in reaction (1.2.2.8) to $i_a(\text{total})$, which in turn raises the corrosion potential, enhancing $i_a(\text{chalcopyrite})$. Indeed, Hirato *et al.* [58] have shown that CuCl^+ and CuCl_2^- ions are the key electro-active species present in CuCl_2 leaching. An assessment of iron and copper chloride aqueous equilibria correlates with both of the above observations [59]. Fe(III) sulphate leaching is some four times slower than Fe(III) chloride at 80-90°C [60] and is inhibited by sulphate addition [4]. Firstly, oxidation by the Fe(III) aquo ion is not so reversible as by Fe(III) chloride complexes. Secondly, the end product, copper sulphate [57], is not an effective oxidant at the chalcopyrite surface [61], whereas copper (II) chloride is.

Leaching kinetics support the electrochemical interpretation. Dissolution of chalcopyrite by Fe(III) sulphate follows solely parabolic kinetics [62]. As the passive film thickens, electron transfer via transport through the film is retarded [63]. In contrast, with Fe(III) chloride the rate soon becomes paralinear as the more effective oxidant is generated [51]. Dutrizac [61] found only $(\text{Fe}^{3+})^{0.12}$ dependence of iron concentration in sulphate, but a greater dependence in chloride. In copper(II) chloride solutions, the rate of chalcopyrite leaching is initially linear, and then increases [59], presumably with increasing CuCl^+ ion activity. Fe(II) chloride addition to Fe(III) chloride has little affect upon the leaching rate [4]. This may be due to a limited supply of holes on the chalcopyrite surface limiting the oxidation of Fe(II) ions.

It is worth noting at this point that the leaching of synthetic chalcopyrite may be up some fifteen times faster than high grade natural specimens [57], because of its porosity. It is up to ten times faster if the mineral has inclusions of silver sulphide or pyrite [64]. These provide zones for unpassivated cathodic half cell reactions, raising the corrosion potential, and thus i_a . This is probably due to the morphology of the product layer affecting the oxidant reduction kinetics.

Leaching of chalcopyrite is also effected by thiobacillus ferrooxidans. In this case sulphate, not sulphur, is produced:



The rate is found to be proportional to the bacillus population [65]. The bacilli are assisted by certain collectors [66]. They have a marked preference for chalcopyrite from certain origins [67] and it should be ascertained whether semiconducting properties are

influential. Biological leaching has some potential in the extraction of copper from low grade ores like 'porphyro copper' deposits found in igneous rock intrusions. Leaching is also possible with ammonia and oxygen under high pressure [50].

1.3. THE ELECTROCHEMISTRY OF CHALCOPYRITE;

It is seen from the above that two hydrometallurgical processes involving cp are of an electrochemical nature; they confirm the preliminary findings of Plaskov and Bessimov [1]. Indeed, mineral electrochemistry has continued in many investigations. Some of them pertaining to cp are described below. Mineral electrochemistry can be conducted under so wide a range of conditions, it can afford such varied products and can be interpreted in such diverse ways that a review needs some common base on which previous investigations can be compared. Thermodynamically stable products forming on mineral electrodes as a function of applied potential and pH are aptly described by potential-pH diagrams [68-80]. Therefore these stability diagrams are presented in this chapter even though they are calculated using recently published data, and so quite different from previously published diagrams. Acid and alkaline electrochemistry of cp is quite clearly divided in the literature, so they are explored separately in the subsequent Sections 1.3.2 and 3 with regard to the stability diagrams described below.

1.3.1. New stability and metastability diagrams for the copper - sulphur - iron - water system.

The chief objective of thermodynamic calculations is to predict electrochemical behaviour. Potential-pH diagrams for stable systems indicate only thermodynamic possibilities, but where a certain reaction is known to be kinetically inhibited, the products can be excluded from the calculations. Then diagrams can be produced with metastable phases or species revealed and may provide a better prediction of the kinetic behaviour of a particular system.

Potential-pH diagrams are calculated using the van't Hoff isotherm and Nernst equation:

$$\Delta G^{\circ}(\text{reaction}) = \sum \Delta G^{\circ}(\text{products}) - \sum \Delta G^{\circ}(\text{reactants}) = -nFE^{\circ} \quad (1.3.1.1)$$

$$E = E^{\circ} + \frac{RT}{nF} \ln K \quad (1.3.1.2)$$

$$\Delta G^{\circ} = -RT \ln K \quad (1.3.1.3)$$

$$K = a(\text{ox})/a(\text{red})$$

where E° is the standard electrode potential for each reaction, n is the number of electrons transferred, F the Faraday constant, and a the activity of contributing solution species. Calculations were executed using a computer package developed by Davis and Barry [81-82] using the data given in Appendix 1, which includes the most recently published, critically assessed thermodynamic data [83-87]. Parentheses indicate activities in all the equations quoted here. The thermodynamics of stable and metastable S-H₂O [88], Cu-S-H₂O [89] and Fe-S-H₂O [90] systems are to be reported elsewhere.

The value for $\Delta G_f^\circ(S^{2-})$ of 86.31 kJ mol⁻¹ [83] has been questioned recently with regard to the oxidation of S²⁻ to polysulphides by trace quantities of air in cells wherein the equilibrium constant for the reaction $HS^- \rightleftharpoons H^+ + S^{2-}$ was measured. The pK value for this reaction is then not 13.01 but between 17 and 19 [91,92], corresponding to $\Delta G_f^\circ(S^{2-})$ of some -120 kJ mol⁻¹. This value is adopted in the present work, so S²⁻ ions do not appear on the stability diagrams in the range of pH 0-14.

The Cu-Fe-S-H₂O system is complicated by the non-stoichiometry and metastability of copper sulphides. Potter's [86] values for the Gibbs energies of formation for the stable copper sulphides Cu₂S (chalcocite), Cu_{1.96}S (djurlite), Cu_{1.934}S (digenite), Cu_{1.75}S (anilite) Cu_{1.4}S (blue-remaining covellite) and CuS (covellite) were used in the calculation of the potential-pH diagram shown in Figure 1.3.1.1.

Koch and McIntyre [87] determined ΔG_f° values for each of the Cu-S phases, i.e. Cu_{1.95-1.91}S, Cu_{1.86-1.80}S, Cu_{1.68-1.65}S, Cu_{1.40-1.36}S and CuS, which enables a thermodynamic exploration of metastable copper sulphides formed by Cu₂S oxidation [89,93]. However, their value of -43.3 kJ mol⁻¹ for CuS leads to its absence from potential-pH diagrams which consider the stable Cu_{2-x}S phases. Woods *et al* [93] appears to have exacerbated this problem in their calculation of Gibbs energies of formation from potential differences measured by Koch and McIntyre [87], using a value of -85.6 kJ mol⁻¹ for Cu₂S as a reference point. Their values for the Gibbs energies of formation of CuS and Cu_{1.38}S, -63.1 and -47.0 kJ mol⁻¹, respectively, appear to be in error, since their data source gives values corresponding to -64.0 and -43.3 kJ mol⁻¹, respectively. In view of Table 1.3.1.1 Koch and McKintyre's [87] Gibbs energies of formation of metastable sulphides were used in the calculations, though their relatively low value for covellite was excluded, as covellite has been positively identified as a chalcopyrite oxidation product.

	$\Delta G_f^\circ(Cu_2S) / \text{kJ mol}^{-1}$	$\Delta G_f^\circ(CuS) / \text{kJ mol}^{-1}$
IUPAC [83]	-81.3	-52.8
NBS [94]	-79.5	-53.1

Table 1.3.1.1. Gibbs energies of formation of chalcocite and covellite.

The Gibbs energies of formation of chalcopyrite and bornite are not well established either. These sulphides are difficult to synthesise and natural specimens are often metal-rich, such as mooihoekite ($\text{Cu}_9\text{Fe}_9\text{S}_{16}$), talnakite (β -chalcopyrite, $\text{Cu}_9\text{Fe}_8\text{S}_{16}$) and haycockite ($\text{Cu}_4\text{Fe}_3\text{S}_8$), which are stable at low temperatures [38].

As mentioned above, the Cu-Fe-S system is complex, exhibiting metastable equilibria, ex-solutions, non-quenchable phases and non-stoichiometry. Chalcopyrite itself transforms from a tetragonal to cubic structure at 545 °C [20], above this temperature decomposing to sulphur, bornite and pyrite (FeS_2). Determination of $\Delta G = RT \ln p(\text{S})$ as a function of temperature requires knowledge of the temperature dependent extent of catenation of gas phase molecular sulphur species. Bartholome's approach was to assume mineral abundances in natural assemblages would bear out low temperature equilibria, and using available sulphur partial pressure data for specific ternary associations, obtained ΔG values of -190 ± 15 and $-370 \pm 25 \text{ kJ mol}^{-1}$ for chalcopyrite and bornite, respectively [95]. Young [96] formalised Bartholome's method by writing inequalities in Gibbs energies for successive reactions involving a progressive loss of sulphur as predicted by the phase diagrams of Kullerud [97], yielding the values $\Delta G_f^\circ(\text{CuFeS}_2) = -201.7 \pm 19.0 \text{ kJ mol}^{-1}$ and $\Delta G_f^\circ(\text{Cu}_5\text{FeS}_4) = -362.2 \pm 21.6 \text{ kJ mol}^{-1}$. He also utilised the dissociation pressure data of Merwin and Lombard [98] to obtain values of -172.1 and $-335.0 \text{ kJ mol}^{-1}$, respectively.

In the diagrams presented here, the critically assessed and consistent values of Pankratz, Mah and King were adopted [85], who used data from these and other sources [96-100] to obtain self-consistent data over a range of temperatures, and chose the values $\Delta G_f^\circ(\text{CuFeS}_2) = -190.58$ and $\Delta G_f^\circ(\text{Cu}_5\text{FeS}_4) = -392.72 \text{ kJ mol}^{-1}$. However, reported values for chalcopyrite vary between -170 and -200 kJ mol^{-1} [85,95,96,101,102], so for the hypothetical reaction:



the standard potential E° is uncertain by some 0.2 V.

Zones of stability are affected by the predesignated dissolved activities of copper, iron and sulphur species, $a(\text{CuX})$, $a(\text{FeX})$ and $a(\text{SX})$ respectively, which were chosen to be appropriate activities in the experimental work reported subsequently. In view of the uncertainties in the thermodynamic data used in the calculations, these diagrams should be interpreted cautiously.

Similar diagrams published on this system [103-106] have used different data and all based on dominant sulphur solution species activity but using activities as high as 10^{-1} , pertinent to the study of the hydrometallurgy of copper-iron sulphide ores [105]. Suffice to say an infinite number of such diagrams could be constructed for every chosen set of Gibbs energy values, but a predominance region for chalcopyrite appears using this data only when $a(\text{SX}) > a(\text{FeX}) > a(\text{CuX})$ as above, or $a(\text{FeX}) > a(\text{SX}) > a(\text{CuX})$.

Figure 1.3.1.1 is a potential - pH diagram calculated from all the Gibbs energy of formation values for stable species included in the Appendix, and dissolved activities $a(\text{CuX})$, $a(\text{FeX})$ $a(\text{SX})$ of $10^{-4.01}$, 10^{-4} , and $10^{-3.99}$, respectively. At any given pH and potential, the diagram shows the predominant copper, iron and sulphur phases, compounded from Cu, Fe, S and water, from Fe, S and water and from S and water, respectively.

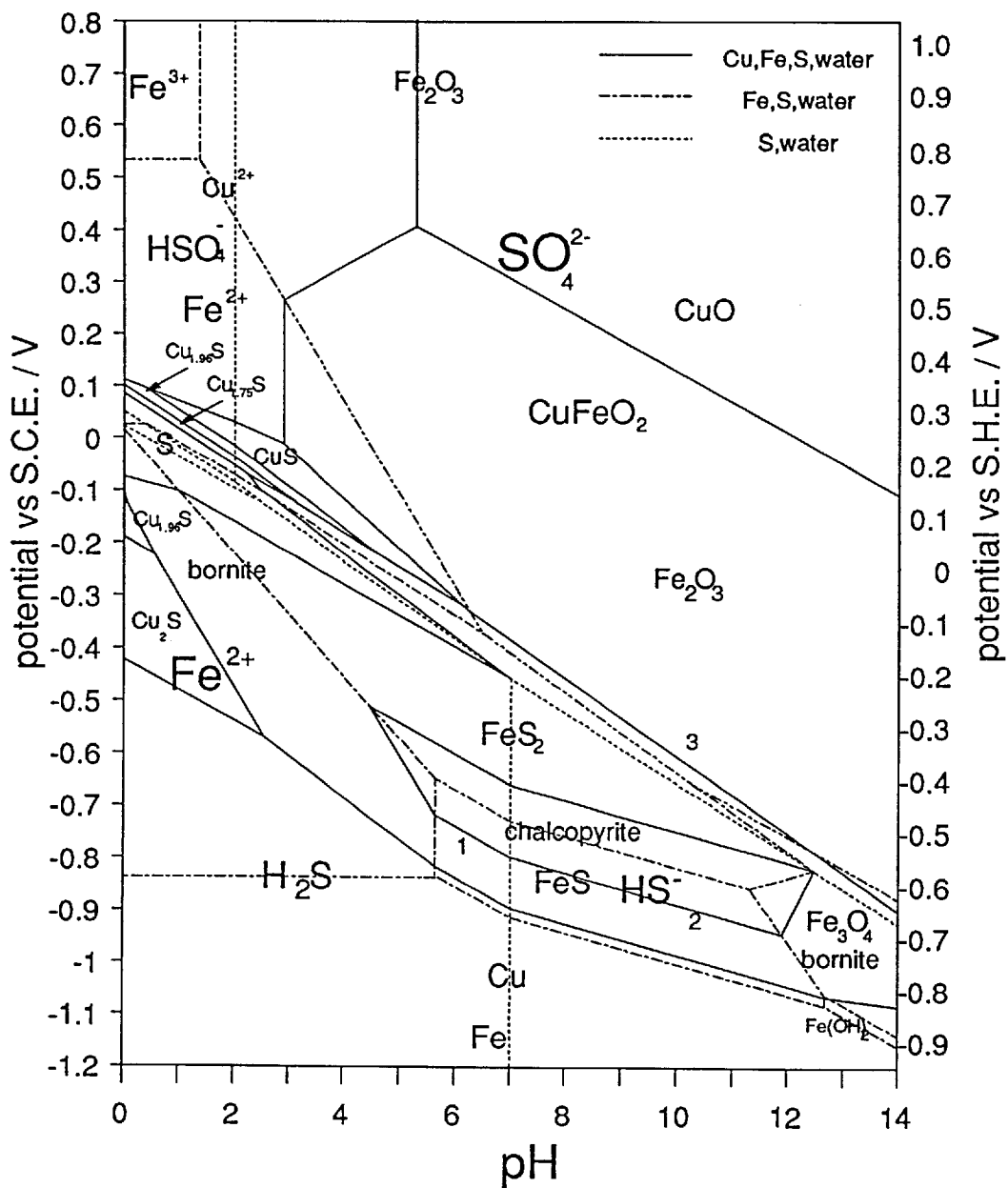
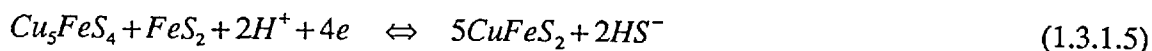
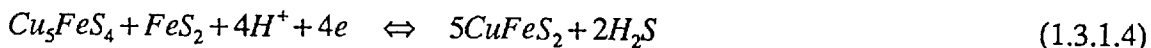


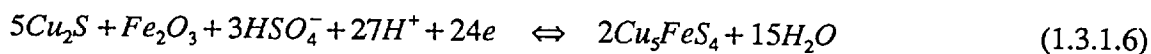
Figure 1.3.1.1. Potential - pH diagram for Cu - Fe - S - water system for 298 K and dissolved copper, iron and sulphur activities of $10^{-4.01}$, 10^{-4} , and $10^{-3.99}$, respectively.

Figure 1.3.1.1 includes a large region of stability for copper ferrite or delafossite (CuFeO_2) at higher potentials, a phase not considered by previous authors. It also shows thermodynamic stability of analite and djurlite, and excludes a stability region for aqueous sulphide ions at $\text{pH} > 13$, for the reasons discussed above. In the diagram each line marks a phase boundary, indicating equilibria between two predominant phases of copper (solid lines), iron (dotted-broken lines) and sulphur (dotted lines). Thus the lines marked 1 and 2 refer to:

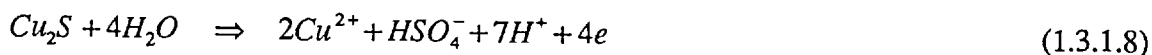
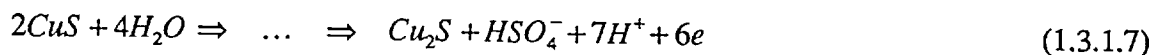


but pyrite has not been detected in any of the leaching or oxidative electrochemical experiments on chalcopyrite reviewed to date in either acid [6,10,11,15,18-22] or alkaline [2,3,11,23] conditions. Pyrite is also noted for its slow hydrothermal nucleation [12], and such a transformation would require complex rearrangement of sulphur and iron atoms. Therefore pyrite was excluded from the construction of subsequent, metastability diagrams.

Also Figure 1.3.1.1 predicts sulphate formation from all sulphides except for CuS forming sulphur at low pH. For example, at the phase boundary marked 3, in the absence of delafossite:



In fact sulphate formation is known to be kinetically inhibited [4], and chalcopyrite has been shown to form sulphur over the whole pH range under anodic conditions [2,6,10,11,23,107-108]. Sulphate forms with sulphur at elevated potentials in molar ratios reported to be 10:1 in molar sulphuric acid [10], and 6:1 in molar perchloric acid [5] at 1.09 V vs S.H.E.. Page [11] assigned the onset of sulphate formation using a chalcopyrite electrode in a buffered solution of pH 7 at 0.6 V, and peak currents due to sulphate formation at 0.9 V at pH 9.2, and 0.5 V at pH 13. Figure 1.3.1.1 also predicts increasingly copper-rich sulphides plus sulphate to form at increasing potentials, ultimately forming copper ions:



As discussed elsewhere [89], this is not the course of electrochemical oxidation of chalcocite under laboratory conditions; again sulphur is produced, with copper (I) oxide or hydroxide. Therefore sulphate was not considered in the metastability diagram **Figure 1.3.1.2**, in which pyrite was also excluded, and the metastable copper sulphides of Koch and MacKintyre [87] replace the intermediate sulphides identified by Potter [86]. **Figure 1.3.1.2** shows an extended region of stability of pyrrhotite, chalcopyrite and bornite due to exclusion of pyrite, and of CuS due to exclusion of S (VI) species. This diagram predicts the behaviour of chalcopyrite more faithfully, especially in acid, as the next section will confirm.

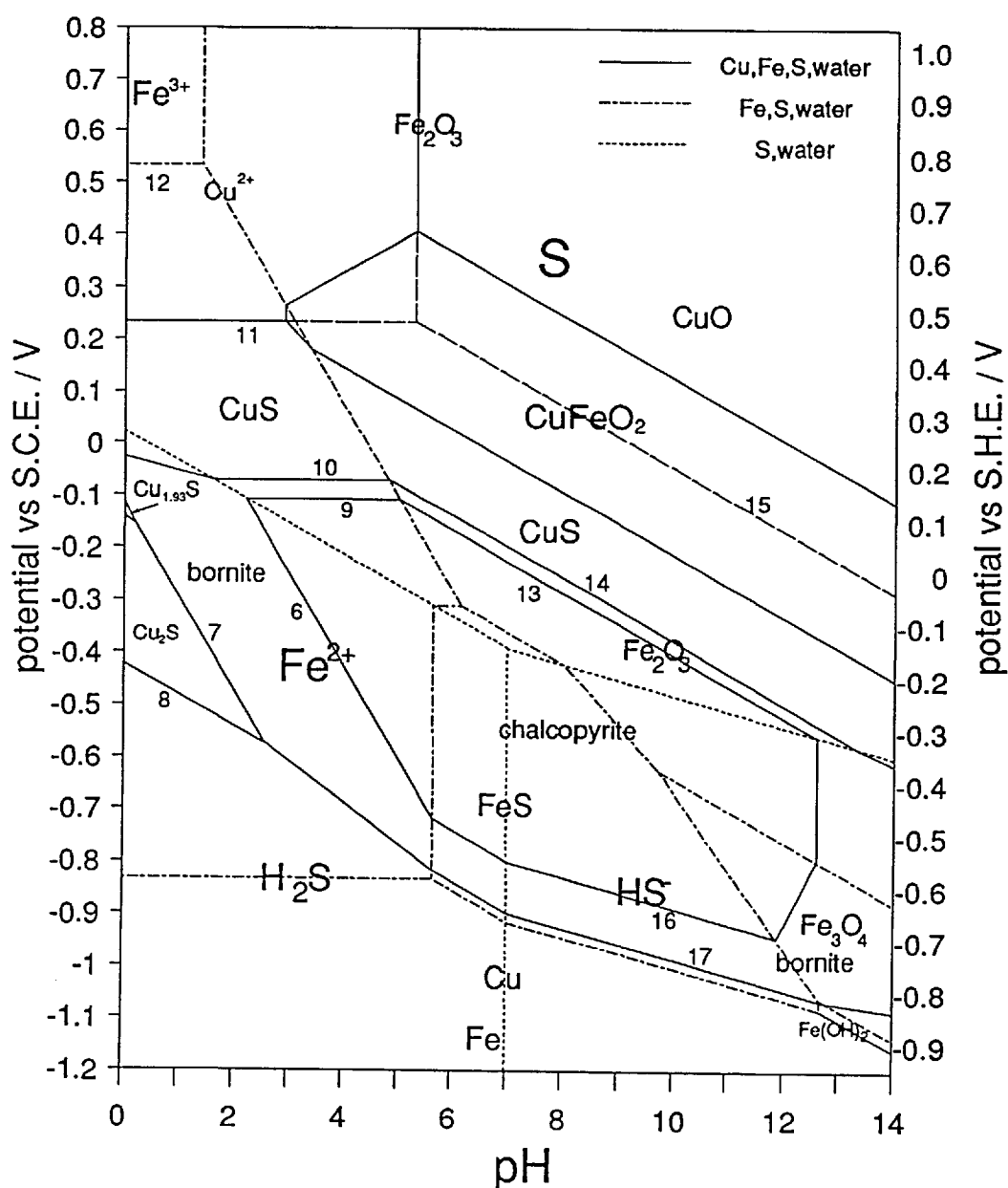


Figure 1.3.1.2. Potential - pH diagram for Cu - Fe - S - water system at 298 K, excluding all sulphur (VI) species and pyrite, and for dissolved copper, iron and sulphur activities of $10^{-4.01}$, 10^{-4} , and $10^{-3.99}$, respectively.

1.3.2. Chalcopyrite in acid solutions.

The initial oxidation of chalcopyrite in acid solution involves preferential dissolution of iron [6,8,9,19,109-110], which has been explained in terms of the formation of bornite [7,11], of a metal deficient copper-iron sulphide [111], or a metal-deficient copper sulphide such as $\text{Cu}_{0.8}\text{S}_2$ [6,10,11]. This phase is known to have a passivating effect [14,15], and recently certain semiconducting properties have been confirmed [16].

Its formation when freshly polished cp electrodes are subjected to applied potentials between 0.2 and 0.6 V gives rise to a 'prewave' - called so because it precedes the much stronger and unpassivated currents at higher potentials. It deserves discussion, not least because it illustrates the complexity of cp electrochemistry. What gives rise to this current?

Linge [62] studied the action of ferric nitrate on chalcopyrite by considering that the reaction:



lowers the potential of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple, so the original potential can be maintained by potentiometric titration against ferric ions. He chose nitrate as opposed to sulphate to avoid iron complexation. After various time intervals (Fe^{2+}) and (Cu^{2+}) were monitored. In agreement with other work [19], he found that initially iron was leached preferentially, but for each 3 electron transfer from chalcopyrite to Fe^{3+} ions, he deduced ejection of ions from chalcopyrite of total charge +6. Charge balance must have been restored by proton adsorption at cation sites, for sulphide dissolution is discounted as no H_2S was observed. He concluded that a metal-deficient protonated sulphide phase forms before subsequent sulphur film production. Linge also showed that ion migration through this film does not limit the reaction rate as that would require a far greater tortuosity through the film than is realistic.

On the latter point, Linge was supported in a paper by Parker et al. [57], who investigated a number of oxidants. They found sulphur removal from a corroded chalcopyrite surface does not affect the reaction rate. They proposed that underneath it lie surface layers of a copper sulphide, which slows transport of reactants and products, slows electron transfer to oxidants and hole supply to reductants, rendering redox couples irreversible on the chalcopyrite surface.

McMillan, MacKinnon and Dutrizac [15] interpreted anodic passivation as being caused by a solid electrolyte interphase, though again, electron transfer was identified as a critical step and their p-type chalcopyrite sample (with 18 % impurities) exhibited negligible currents in the 0.2 to 0.6 V region with 0.3 M Fe(III) sulphate.

Biegler and Swift [5] identified an anodic current wave on potential sweeps of freshly polished chalcopyrite that proceeds its dissolution at >0.8 V vs S.C.E.. It was further investigated by Biegler and Horne [107] who discovered two prewave peaks at 0.04 and 0.14 V in the absence of oxidants. These were neither affected much by the specimen's

origin, nor by the acidity. Only at pH > 11 were these prewaves obscured. They found the product to be stable and the prewave was not restored after return to the rest potential, in contrast to the observations of Parker et al. at 80 °C [84].

Biegler and Horne also performed cyclic sweeps between -0.25 and 0.35 V and suggested:

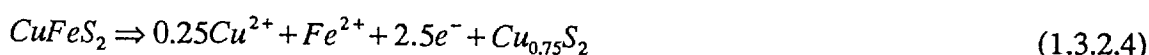


$$E / V = 0.25 - 0.0144 \log(\text{Fe}^{2+}) + 0.0397 \log(\text{Cu}^{2+})$$



$$E / V = 0.278 + 0.0591 \log(\text{Cu}^{2+})$$

as possible candidates for current peaks on the return cathodic sweeps at 0.17 and 0.34 V, having varied Cu(II) concentration with and without rotating the chalcopyrite electrode. Fe(III) addition had little effect. Moreover, a second anodic sweep produced a peak at 0.28 V which they assigned to the reverse of reaction (1.3.2.3). A second peak at 0.55 V is seen to involve fresh dissolution of chalcopyrite, with $E^\circ [\text{Fe(III)/(II)}] = 0.52 \text{ V vs S.C.E.}$. By considering the relative total charges passed in the anodic region, they concluded:



interpreting $\text{Cu}_{0.75}\text{S}_2$ to be $0.75 \text{ CuS} + 1.25 \text{ S}$.

Industrial leaching of copper from chalcopyrite by oxidising solutions has stimulated much interest, ensuring that most electrochemical studies of chalcopyrite are undertaken in acid solutions. Granted sulphur, not sulphate forms, anodic excursions from the rest potential generate products predicted from Figure 1.3.1.2. According to that figure the above consensus that iron dissolves preferentially from the chalcopyrite surface can be attributed to:



$$E / V = 0.019 + 0.0296 \log(\text{Fe}^{2+})$$

in agreement with Warren et al. [110]. The product, as described above, is not well characterised, but most authors agree that covellite then forms:



$$E / V = 0.356 + 0.0148 \log(\text{Cu}^{2+}) + 0.0148 \log(\text{Fe}^{2+})$$

consistent with the diagram, and reports from Warren and Baur *et al.* [9]. However Linge [62] suggested:



$$E / V = 0.231 + 0.0296 \log(Fe^{2+})$$

The covellite is then itself oxidised at higher potentials.

Oxidative chalcopryrite leaching has been effected by reduction of iron (III) sulphate in sulphuric acid [6,15,61]:

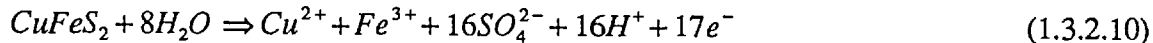


but the reaction is almost irreversible [15]; it is weakly dependent on $a(Fe^{2+})$ unless complexing chloride is introduced [61]. Moreover, Page [11] was unable to detect Fe^{2+} ions formed by chalcopryrite oxidation at low pH using a modified ring-disc electrode.

At potentials exceeding 0.7 V, passivating layer production begins to be over-ridden by unbridled dissolution as in the net reaction (1.3.2.9), and sulphate formation by reaction (1.3.2.10) at last emerges:



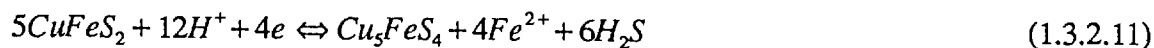
$$E / V = 0.483 + 0.118 \log(Fe^{3+}) + 0.118 \log(Cu^{2+})$$



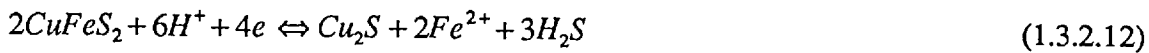
$$E / V = 0.394 - 0.0556pH + 0.0035 \log(Fe^{3+}) + 0.0035 \log(Cu^{2+})$$

At 1.09 V, sulphur and sulphate form in reported ratios ranging from 6:1 in 1 M perchloric acid, to 10:1 in 1 M sulphuric acid [5,110], though there are clearly difficulties detecting the small quantities of both species involved.

It is remarkable that **Figure 1.3.1.2** predicts bornite formation upon both oxidation and reduction of chalcopryrite, with sulphur taking up the change in oxidation state. In cathodic excursions, bornite has been detected [112], but then so have a myriad of other cp reduction products. At increasingly negative potentials the following reactions are predicted to occur in acid electrolytes:



$$E / V = -0.259 - 0.1773pH - 0.0591 \log(Fe^{2+}) - 0.088 \log(H_2S)$$



$$E / V = -0.412 - 0.0886\text{pH} - 0.0295\log(\text{Fe}^{2+}) - 0.443\log(\text{H}_2\text{S})$$

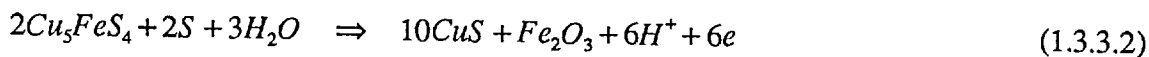
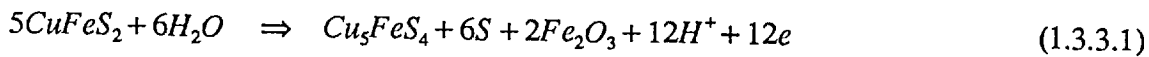


$$E / V = -0.438 - 0.1183\text{pH} - 0.0295\log(\text{Fe}^{2+}) - 0.0591\log(\text{H}_2\text{S})$$

Chalcocite (Cu_2S) has been identified by X-ray diffraction as a reduction product of chalcopyrite electrolysed in 1 M HClO_4 , and further reduction by reaction (1.3.2.7) occurred below -0.4 V [5]. Biegler [112] did detect djurlite, $\text{Cu}_{1.97}\text{S}$, in certain instances. He also notes [107] that a prewave appeared on the initial cathodic sweep of freshly polished chalcopyrite at -0.1 V. MacLeod and Muir [13] determined the products of reduction of chalcopyrite by Cu(I) to be a chalcocite layer on bornite, on copper-rich chalcopyrite, on unreacted chalcopyrite. This is consistent with Figure 1.3.1.2: it can be seen that the metastable sulphides, Cu_{2-x}S , are thermodynamically stable over a wide pH range, and at potentials where a series of small current peaks have been observed during voltammetric sweeps at pH 1. In fact these peaks will be shown below to occur in solutions up to at least pH 7.

1.3.3. Chalcopyrite in alkaline solutions.

The collectorless flotation of chalcopyrite can be achieved in the laboratory by applying positive potentials to electrodes immersed in alkaline solutions. From Figure 1.3.1.2, the following reactions are predicted:



Whilst sulphur formation has been cited as being essential for chalcopyrite flotation [109], and voltammograms interpreted accordingly [23], recent investigations using X-ray photoelectron spectroscopy have suggested the formation of a metal-deficient sulphide or polysulphide [113]. Also ferric hydroxide is understood to form electrochemically [11,23,109], and at potentials some 0.06 V higher than the reversible potential for reaction (1.3.3.1). Likewise cyclic voltammetry has revealed a current peak assigned to oxidation of CuS to cupric hydroxide [11,109], whereas Figure 1.3.1.2 predicts in the absence of delafossite, the reaction:



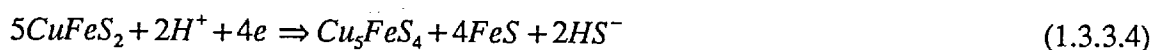
occurring at potentials some 0.07 V lower.

Delafossite is unlikely to form from the oxidation products indicated in the diagram, having a structure quite different from these products (see e.g. [114-116]), but in alkaline solutions it has shown an anodic photoelectrochemical effect [117] very similar to that of oxidised chalcopyrite, as will be described in Chapter 6.

In following sections a photoactive film is reported to form on chalcopyrite in alkaline conditions with properties resembling n-type Fe_2O_3 , though the hydroxide may coexist as outer layer of a duplex film. It is notable that Figure 1.3.1.2 contains no region of stability for Cu_2O even in the absence of sulphate and delafossite formation.

Reaction (1.3.3.1) is not predicted by Buckley, Hamilton and Woods in their thermodynamic consideration of chalcopyrite oxidation in the absence of pyrite and sulphate formation in alkali [17]. In the same paper, their investigation of bornite oxidation precluded sulphur formation. Instead XPS and voltammetry suggested the oxidation products were Cu_5S_4 and an iron oxy-hydroxide such as goethite, FeOOH .

There is scant information about the reductive decomposition of chalcopyrite in alkali. According to Figure 1.3.1.2 the reaction:



is followed by:



1.4. PHOTOELECTROCHEMISTRY

From the above it can be seen that cp electrochemistry has been studied extensively, and with good reason. However the complexity of the system has confounded the confident description of surface phases; we do not have a detailed picture on a molecular level of the interfacial processes occurring at the cp/electrolyte interface. Results of *ex-situ* spectroscopic techniques like LEED and XPES applied to electrochemical processes such as electrocatalysis, corrosion and adsorption [118-124] tend to be ambiguous; physical and chemical changes in the electrode surface can occur when the applied potential is removed, or during the transfer of electrodes from an aqueous environment to a vacuum chamber *via* even a controlled gaseous atmosphere rather than air, or upon subjecting the specimen to ultra-high vacuum, thereby desorbing adsorbed product layers, as has been observed with anodically formed sulphur [125]. In the case of cp, such investigations are few.

In principle non-electrochemical techniques can be used *in-situ* to provide information complementary to that from conventional electrochemical experimental methods. A better understanding of complex minerals such as chalcopyrite could result from such an approach. It may even yield unexpected benefits. The electroluminescence of zinc sulphide is a familiar example of this [126-128], and several metal sulphides are used in ion-selective electrode systems [129]. Photoelectrochemical solar energy conversion devices have led to interest in semiconducting metal sulphides [130-151] as possible photo-electrodes. Copper and iron sulphides - including cp [152,153] - are also being investigated for use in high performance batteries [154-159]. Ellipsometry, photocurrent spectroscopy, specular reflectance spectroscopy and electrode impedance measurements have been shown to be powerful techniques in revealing the mechanism of passivation of metals and semiconductors, electron transfer at semiconductor electrodes, various complex electrochemical reactions and electro-crystallisation [160-166]. All these techniques are easily coupled with conventional electrochemical techniques. They provide an opportunity to monitor and correlate different but closely related phenomena occurring at the semiconductor/electrolyte interface. This is described below.

1.4.1. Semiconductor/electrolyte interfaces

Early investigations into the characteristics of semiconductor/electrolyte (SC/EL) interfaces involved germanium and silicon, and refinements of various semiconductors have added to the understanding of this double layer [167-186]. How the double layer affects the chemistry of SC/EL interfaces has been well reviewed [162,163,187-188].

If a semiconductor is immersed in an electrolyte containing a redox couple, electrons will flow from one to the other until their Fermi levels are the same. Thereby a net layer of excess charge of density $\rho(x)$ resides near the surface, a space charge, generating an electric potential $U(x)$ according to Poisson's equation:

$$\left(\frac{d^2U}{dx^2} \right) = \frac{\rho(x)}{\epsilon\epsilon_0} \quad (1.4.1.1a)$$

or:

$$\left(\frac{d^2U}{dx^2} \right) = -\frac{e(n_D - n_A - n(x) + p(x))}{\epsilon\epsilon_0} \quad (1.4.1.1b)$$

in which x is the distance from the surface, n_D and n_A are the donor and acceptor densities respectively, and $n(x)$ and $p(x)$ the electron and hole densities as they vary with distance x from the electrode surface.

The gradient of this potential - the field $E(x)$ - is manifest in the bending of the bands of the semiconductor at the surface, **Figure 1.4.1**. Clearly, the potential profile on the solid side of a SC/EL interface is significantly different from a metal/electrolyte (M/EL) interface. In a semiconductor there are fewer charge carriers of energy close to the Fermi level E_F , so ρ at any depth x is restricted in the semiconductor as compared with a metal (see below), and the curvature of the potential is more gradual, *i.e.* the electric field extends much further into the bulk. Indeed, the space charge layer and potential drop, U_{sc} , across it may extend 300 nm into the SC interior. **Figure 1.4.1** also conveys the charge distribution. The situation is complicated if the electrolyte is a very dilute solution in which the countercharges are not only located essentially at the outer Helmholtz layer but are distributed over a certain distance into the electrolyte forming a Gouy diffuse layer. The SC/EL systems considered here are only those in which the ion concentrations are sufficiently large, so that any space charge in the electrolyte can be neglected. As in M/EL interfaces, a Helmholtz layer exists, across which there is a fixed potential difference U_H , but the charge on the semiconductor surface is determined by the free charge carriers (electrons and holes), not by the electrons only, as on the metal surface. In either case, on the EL side of the interface will be ions of opposite charge to that on the SC side.

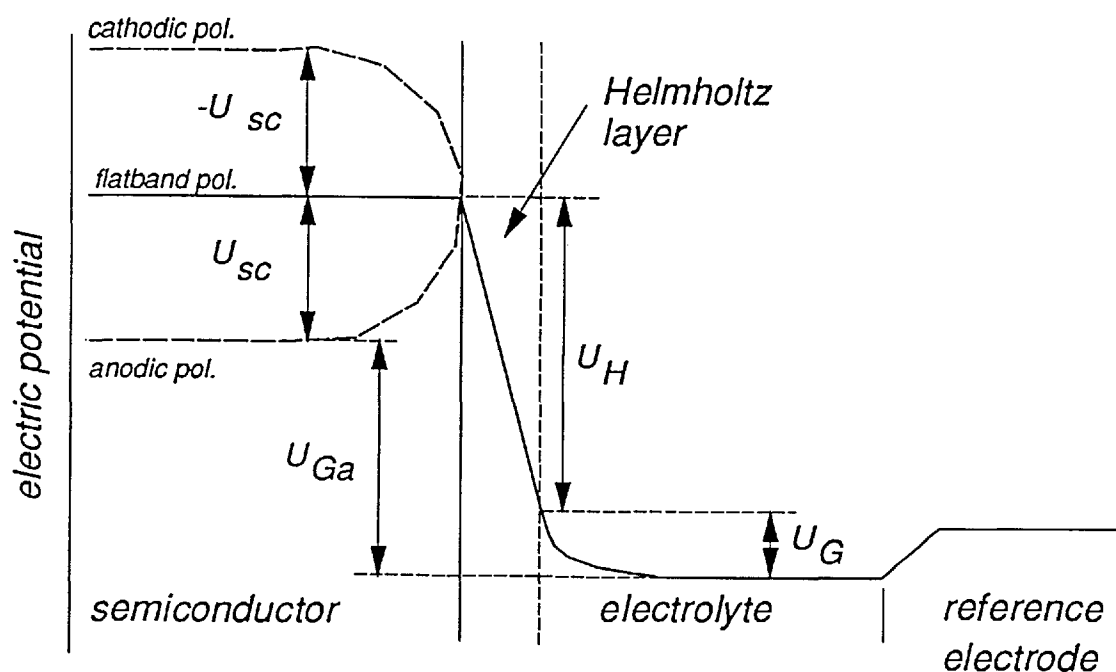


Figure 1.4.1. The Semiconductor/Electrolyte junction under polarisation.

The extent to which ρ is restricted can be determined from the Boltzmann distribution:

$$n = N_C \exp\left(-\frac{E_C - E_F}{kT}\right) \quad (1.4.1.2)$$

where, in this case n is the electron density in the conduction band of energy E_C and density of states N_C . A similar equation can be written for holes p in the valence band of energy $E_F - E_V$ from the Fermi level. Assuming the surface and bulk of the semiconductor are in equilibrium (E_F is constant) the electron density at the surface, $n(0)$ or n_s , relative to the bulk n_0 from (101) is:

$$n_s = n_0 \exp\left(\frac{-eU_{sc}}{kT}\right) \quad (1.4.1.3)$$

Likewise the hole density at the surface p_s relative to the bulk p_0 :

$$p_s = p_0 \exp\left(\frac{eU_{sc}}{kT}\right) \quad (1.4.1.4)$$

In equilibrium holes and electrons must fulfil the condition:

$$n_s p_s = n_0 p_0 = \text{constant} = n_i^2 \quad (1.4.1.5)$$

where n_i is the intrinsic carrier density of the semiconductor.

The potential gradient at the surface, the field, $E(0)$ or E_s , is produced by the total space charge, Q_{sc} :

$$Q_{sc} = \epsilon \epsilon_0 E_s \quad (1.4.1.6)$$

and may be obtained by single integration of the Poisson equation (1.4.1.1) and from (1.4.3 - 5):

$$E_s = \left(\frac{dU_{sc}}{dx}\right)_{x=0} = \left(\frac{2kT}{\epsilon \epsilon_0}\right)^{\frac{1}{2}} \left\{ p_0 \left[\exp\left(\frac{eU_{sc}}{kT}\right) - 1 \right] + n_0 \left[\exp\left(\frac{-eU_{sc}}{kT}\right) - 1 \right] - \left(\frac{e}{kT}\right) (N_A - N_D) U_{sc} \right\}^{\frac{1}{2}} \quad (1.4.1.7)$$

The co-existence of a Helmholtz layer and space charge layer at the SC/EL interface may complicate the effect of an externally applied potential on the characteristics of the double layer, and therefore on the electrode processes. However, experimental and theoretical investigations reveal that in semiconductor electrodes where carrier concentrations are low, the externally applied potential ΔU_E is equivalent to the Galvani potential, U_{Ga} [163], and appears only across the space charge layer, whilst U_H remains fixed [169,171,172,182]:

$$\Delta U_E = \Delta U_{sc} \quad (1.4.1.8)$$

Therefore any change in applied potential can be seen to charge the SC surface as a capacitor, C_{sc} defined:

$$C_{sc} = \frac{dQ_{sc}}{dU_{sc}} \quad (1.4.1.9)$$

The capacitance of the Helmholtz double layer, C_H , can be ignored, because $C_H \gg C_{sc}$. The expression for C_{sc} from (1.4.1.6) and (7) is rather complex, but under two circumstances it can be simplified. For intrinsic semiconductors, where $n_o = p_o = n_i$:

$$C_{sc} = \frac{2e^2 \epsilon \epsilon_o n_i}{kT} \cosh\left(\frac{eU_{sc}}{2kT}\right) \quad (1.4.1.10)$$

and for heavily doped semiconductors:

$$\frac{1}{C_{sc}^2} = \left(\frac{2}{\epsilon \epsilon_o N_D e} \right) \left(U_{sc} - \frac{kT}{e} \right) \quad (1.4.1.11)$$

Equation (1.4.1.11) is often called ^{the} Mott-Schottky equation. It is valid only in the exhaustion region, i.e. for space charges in which the majority carrier density at the surface is smaller than the corresponding bulk concentration ($n_s < n_o$ for n-type and $p_s < p_o$ for p-type electrodes).

The thickness of the space charge layer for doped semiconductors, W , can be derived from (1.4.1.11) using the relation $W = \epsilon \epsilon_o / C_{sc}$:

$$W = \left(\frac{2\epsilon \epsilon_o U_{sc}}{eN_D} \right)^{1/2} \quad (1.4.1.12)$$

assuming U_{sc} is much larger than kT/e . From (1.4.1.11) the flatband potential U_{fb} can also be obtained, which is the potential at which there is no band bending and the space charge capacitance passes through a minimum.

1.4.2. The semiconductor/electrolyte interface illuminated: the photo-electrochemical effect.

Considering a p-type semiconductor, when the surface is irradiated, electrons may be excited from valence to conduction bands, provided the photon energy, $(h\nu)$, exceeds the bandgap energy, $E_g = E_C - E_V$. When there is no lattice vibration - phonon - contribution to this transition it is termed 'direct', Figure 1.4.2.1b(1). The electron will have an unchanged momentum immediately following the transition in accordance with the

Franck-Condon principle. It will then relax to achieve minimum conduction band energy, E_v , as shown. This may involve a change in wave vector k , Figure 1.4.2.1b(2), and therefore phonon interaction.

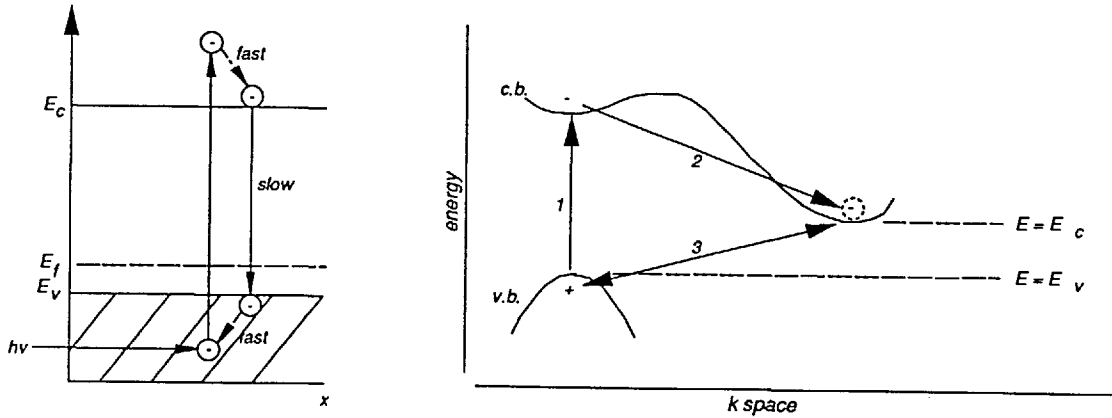


Figure 1.4.2.1. Light absorption and energy redistribution in a semiconductor.

Direct return to the valence band may thence be inhibited by lack of a valence hole with the same wave vector. Recombination may proceed via the indirect, quantum mechanically disallowed transition (k_i not equal to k_f), Figure 1.4.2.1b(3), only with phonon collaboration. Thus this step is much slower [189] and it is possible for an electron-hole pair to become entirely separated in the non-uniform electric field. Likewise the reverse process - indirect excitation of electrons from band edge to band edge - can be far less probable than direct 'vertical' transitions requiring greater energy; band gaps measured thermally are then smaller than those deduced from light experiments [190]. These probabilities are reflected in absorption coefficients, α , for various transitions. For direct transitions [191,192]:

$$\alpha_{hv} = \frac{A(h\nu - E_g)^{\frac{1}{2}}}{h\nu} \quad (1.4.2.1)$$

whilst for indirect transitions:

$$\alpha_{hv} = \frac{A(h\nu - E_g)^2}{h\nu} \quad (1.4.2.2)$$

For n-type semiconductors, photo-excitation of electrons from the valence to the conduction band generates holes in the valence band; the same arguments apply. Whatever the electronic excitation in the semiconductor, it disturbs the equilibrium of energy distribution of electrons and holes. They accumulate near the band edges until a steady state is reached between recombination and generation of electron-hole pairs.

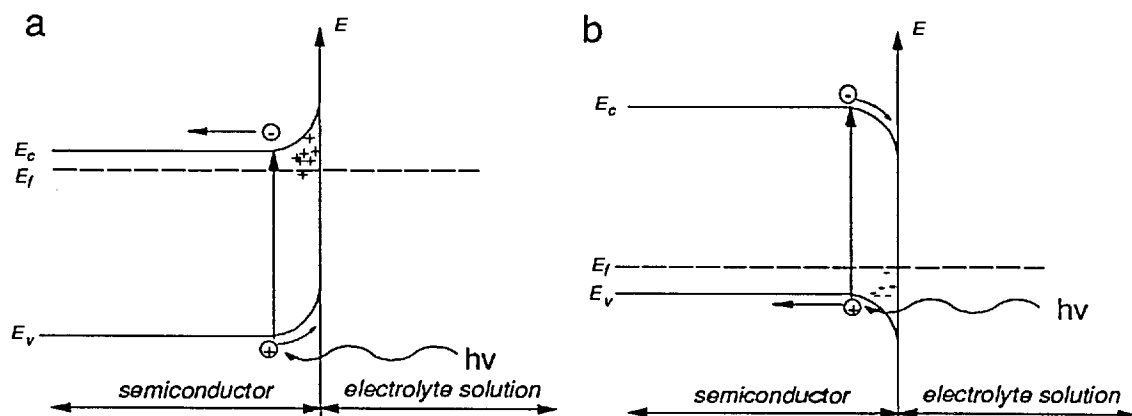


Figure 1.4.2.2. The semiconductor/electrolyte junction, SC/EL, under illumination.

a n-type semiconductor at potentials anodic of the flat-band potential,

b p-type semiconductor at potentials cathodic of the flat-band potential.

Upon irradiation electron-hole pairs generated in the SC are separated by the field gradient within the space charge layer as shown in Figure 1.4.2.2. This may extend several hundred nanometers into the electrode surface. Holes move towards the surface in n-type SC, (a), leading to photo-oxidations. Electrons move towards the surface in p-type SC, (b), inducing photo-reductions. The theory of the depletion region is common to p-n, M/SC and SC/EL junctions, but the mechanism of interfacial charge transfer at SC/EL interfaces is significantly different; the capture of minority carriers at the surface results in an electrochemical charge-transfer reaction. Therefore it is important that any theory of the illuminated SC/EL interface takes into account the characteristics of any electrochemical charge transfer reactions involved. The delay of a photo-response is one measure of the kinetics of charge transfer, and using the lock-in technique described below, it can be evident from signal responses not having phase angles equal to 0° or 180° . This phenomenon was not investigated until the pioneering work by Brattain and Garrett on the germanium/electrolyte interface in 1954 [189], which was followed by work on various SC/EL systems from then on [139,143,193-212].

Assuming there is no recombination and charge transfer at the SC/EL interface is not rate determining, the photocurrent of a crystalline semiconductor i_{ph} is given by [213,214]

$$i_{ph} = e\eta h\nu_0 \left\{ 1 - \exp \left[-\frac{\alpha W}{1 + \alpha L} \right] \right\} \quad (1.4.2.3)$$

where η the quantum efficiency, and I_0 the incident photo flux disregarding any reflections at the electrode/electrolyte interface. The diffusion length of the minority carriers, L , is expressed by the equation

$$L = (D\tau)^{\frac{1}{2}} \quad (1.4.2.4)$$

where D is the diffusion coefficient of the minority carriers and τ their life-time.

In passive films, if the film thickness d is smaller than W , this equation becomes:

$$i_{ph} = e\eta hI_o [1 - \exp(-\alpha d)] [1 + R \exp(-\alpha d)] \quad (1.4.2.5)$$

where R is the reflectivity of the surface underneath the film, varying between 0 and 1. As long as the absorption coefficient and film thickness are small, the exponent can be expanded and the photocurrent becomes proportional to both α and d . This has been demonstrated for TiO_2 [215]. The same applies to semiconductor surfaces and equation (1.4.2.4): for small d_{sc} , i_{ph} is proportional to the absorption coefficient, α , and by virtue of (1.4.2.1), a plot of $(i_{ph} hv)^{1/2}$ vs hv should yield a straight line for indirect transitions, and a plot of or $(i_{ph} hv)^2$ vs hv yield a straight line for direct transitions, from which bandgaps can be deduced.

Equation (1.4.2.4) can also be considered with regard to U_{fb} . If $\alpha W \ll 1$,

$$i_{ph} = (\text{constant} \cdot \alpha W)^{\frac{1}{2}} \quad (1.4.2.6)$$

and U_{fb} can be obtained from a plot of i_{ph} vs $U^{1/2}$.

Recombination of charge can occur at the neutral or space charge regions, or at surface sites on the semiconductor. Taking into account this surface recombination and assuming that the surface states are located at a discrete energy in the band gap and that they communicate preferentially with the semiconductor, Peter et al. [208] derived an expression for the steady state photocurrent response. For a p-type semiconductor,

$$j_{\infty} = I_o \left(1 - \exp \frac{-\alpha W}{1 + \alpha L_n} \right) - k_p p_s N_s (f_{\infty} - f_o) \quad (1.4.2.7)$$

where j_{∞} is the steady-state photocurrent, k_p is the rate constant for hole capture, p_s the surface hole density, N_s surface state density, L_n the diffusion length for electrons, f_{∞} the steady-state trap occupancy under illumination, and f_o the trap occupancy in the dark.

For a transient photocurrent response [115]:

$$\frac{j(t) - j_{\infty}}{j(o) - j_{\infty}} = \exp(-t/\tau) \quad (1.4.2.8)$$

where $j(t)$ is the photocurrent decay, $j(o)$ is the photocurrent at $t = 0$, and τ the relaxation time for excess minority carriers in the surface state equal to $(k_p p_s)^{1/2}$.

1.5. IMPEDANCE SPECTROSCOPY

Consider the dashed line in **Figure 1.5.1** as a section of any current profile vs a swept potential sufficiently small to be considered a linear and reversible response, typically spanning a few millivolts. If, instead, the potential is fixed at a point on this section, and then a superimposed alternating potential is applied, an alternating current response described by the ellipse in the figure will result, leading the potential by a phase angle given by:

$$\sin \chi = \frac{DD'}{AA'} \quad (1.5.1)$$

and of magnitude determined by the electrode's impedance at this potential, equal to:

$$|Z| = \frac{AA'}{BB'} \quad (1.5.2)$$

The current through the electrode is determined not only by an ohmic resistance within the solution, R_{so} , but also by an ohmic charge transfer resistance R_{ct} and the charging and discharging of an electric double layer capacitance C_{dl} at the electrode surface. To a first approximation R_{ct} and C_{dl} are in parallel: each electron comprising the current must either pass through the layer or contribute to its charge or discharging. The equivalent circuit for this most simple scenario is then as shown in **Figure 1.5.2**.

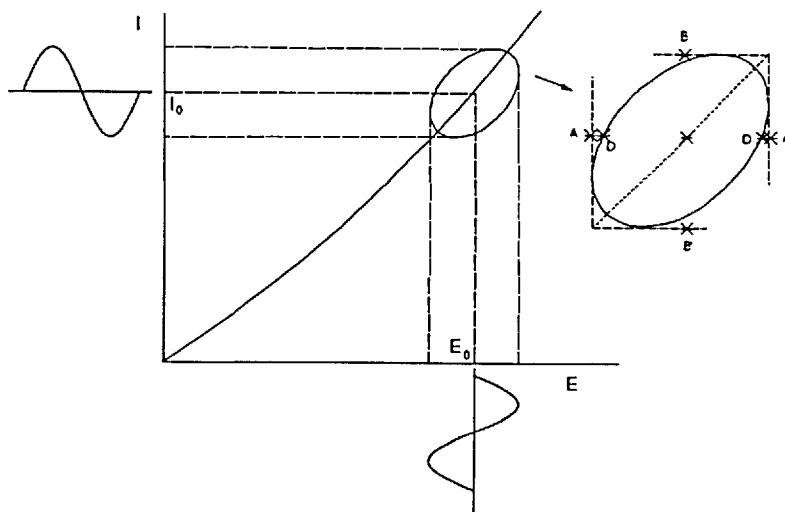


Figure 1.5.1. A trace of the alternating current response I to an alternating applied potential difference E .

The overall impedance Z , a function of the alternating potential frequency, ω , is defined as E/I . In this case:

$$E(\omega) = R_{so} + \frac{1}{1/R_{ct} + i\omega C} = R_{so} + \frac{R_{ct} - i\omega CR_{ct}^2}{1 + \omega^2 C^2 R_{ct}^2} \quad (1.5.3)$$

The real and imaginary parts of this equation correspond to real and imaginary impedances Z_{real} and $Z_{\text{imaginary}}$, and can be represented on an Argand diagram known as a Nyquist plot, as shown in Figure 1.5.3.

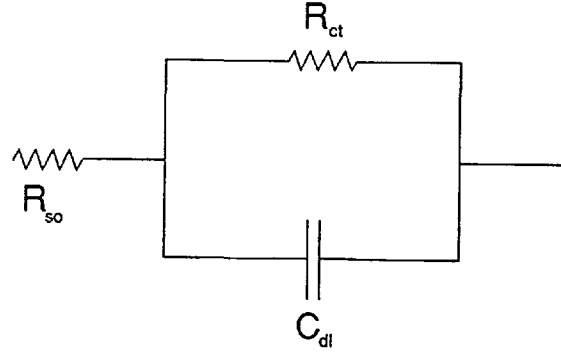


Figure 1.5.2. The Randle's equivalent circuit.

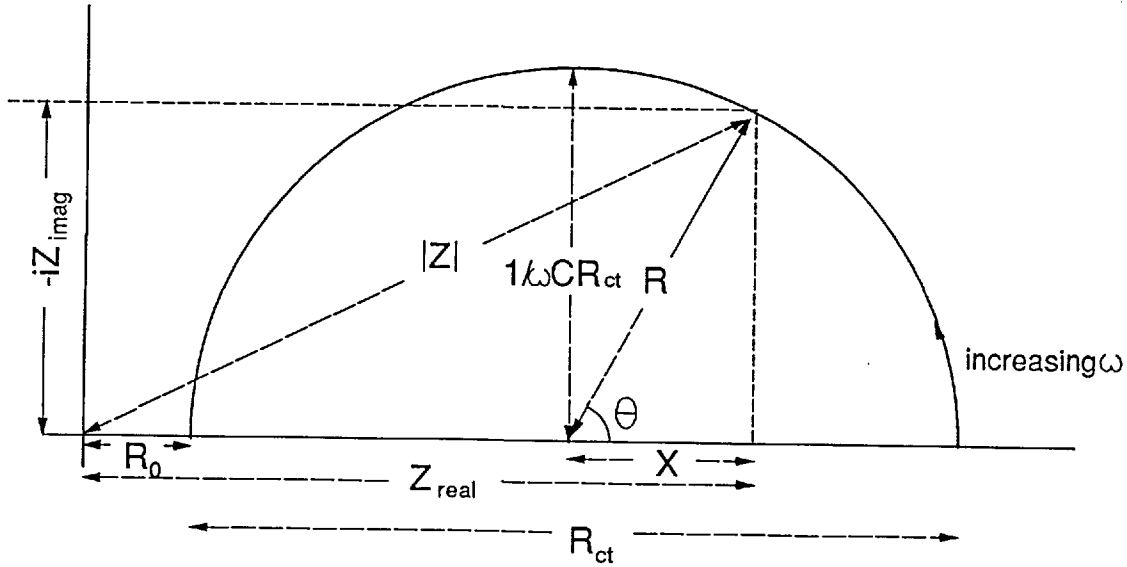


Figure 1.5.3. Frequency dependent impedance response at constant potential for equivalent circuit shown in Figure 1.5.2.

Consider the parameter X in the diagram.

$$X = Z_{real} - R_0 - \frac{1}{2}R_{ct} \quad (1.5.4)$$

and so

$$\cos \theta = \frac{X}{R_{ct}/2} = \frac{1 - \omega^2 C^2 R_{ct}^2}{1 + \omega^2 C^2 R_{ct}^2} \quad (1.5.5)$$

When $\cos \theta = 1$, $\omega = \text{zero or infinity}$, *i.e.* approaching very low or high alternating potentials the capacitive contribution to impedance dwindle, as would be expected. At the point of maximum capacitive contribution to the impedance, $\cos \theta = 0$, so $C = 1/\omega R_{ct}$. Therefore impedance spectroscopy provides a method of determining the interfacial capacitance of an electrode as well as the charge transfer resistance R_{ct} for a slow Faradaic process. For more complicated electrode surfaces more complicated plots are obtained.

In most instances when semicircular frequency dependence of Z was observed, curve fitted semicircles appeared to be depressed by a so called constant phase element, C.P.E., and could be said to have been rotated by a constant phase angle, θ . The C.P.E. can arise in two respects, and be modelled by two different equivalence circuits accordingly. In the first, the element may be considered to be in parallel with the capacitor. This is the case when diffusion is important, and is physically impeded by a porous film or membrane. Depressions of the semicircle may then be very large according to the relative effects of the C.P.E. and C_{dl} . In the second instance, and one frequently encountered in this work, θ is smaller, up to 15° [216]. It has been explained [217] in terms of fractal surface roughness of the electrode. The Mandelbrot-type 'fractal dimension' [218], D , is then:

$$\theta = \frac{\pi(D-2)}{2(D-1)} \quad (0 < \theta < \pi/4) \quad (1.5.6)$$

and the impedance is proportional to a factor of the form:

$$\frac{1}{1 + \lambda(i\omega)^{\frac{1}{1-D}}} \quad (1.5.7)$$

with λ the Cole Cole transfer function [33]. These equations provide the basis for the computer equation used in the **Appendix 2** to model impedance spectroscopic data whereby values for C_{dl} and R_{ct} were determined.

CHAPTER 2. EXPERIMENTAL

2.1. ELECTROLYTES

After cleaning in deionised water, flasks and cells were rinsed in doubly distilled water of resistivity 18 Mohm cm^{-1} from a "Milli-Q" water purifier (Millipore Ltd). Solutions were prepared with this water too, using reagent grade chemicals as follows:

- pH = 1.00: $0.1 \text{ mol HClO}_4 \text{ (as 61 \% solution) dm}^{-3}$,
pH = 2.20: $0.05 \text{ mol KH phthalate} + 0.0495 \text{ mol HClO}_4 \text{ (as 61 \% solution) dm}^{-3}$,
pH = 3.90: $0.05 \text{ mol KH phthalate} + 0.0014 \text{ mol HClO}_4 \text{ (as 61 \% solution) dm}^{-3}$,
pH = 5.60: $0.05 \text{ mol KH phthalate} + 0.038 \text{ mol NaOH dm}^{-3}$,
pH = 7.00: $0.1 \text{ mol KH}_2\text{PO}_4 + 0.582 \text{ mol NaOH dm}^{-3}$,
pH = 9.2: $0.05 \text{ mol Na}_2\text{B}_4\text{O}_7 \text{ dm}^{-3}$.
pH = 11.70: $0.025 \text{ mol Na}_2\text{HPO}_4 + 0.0162 \text{ mol NaOH dm}^{-3}$.

Prior to use, all solutions were purged with "white spot" grade oxygen-free nitrogen (BOC Ltd.) for 1 hour prior to use. After every experiment the electrochemical cell was emptied, rinsed with aliquots of water and then with fresh electrolyte, with which it was then refilled.

Three different sodium sulphate aqueous solutions were taken as electrolytes, i.e. neutral, basic and acidic sodium sulphate solutions, which were prepared from Na_2SO_4 , NaOH and H_2SO_4 . Their pH values were 7.2, 12.16 and 1.95 respectively.

2.2. THE WORKING ELECTRODE

2.2.1. Fabrication from mineral samples.

A number of chalcopyrite samples - in large part kindly provided by the British Museum (Natural History) - were used in the first instance to ensure consistent results could be obtained using naturally occurring samples, as explained in Section 4.1.3. Core-drilling gave rise to hairline cracks or even the complete disintegration of samples, so they were initially sliced on a circular diamond saw, then shaped by grinding with grade 240 SiC paper into orthogonal slabs, free of surface cracks, and of no dimension greater than 15 mm. One side of these slabs was ground with SiC paper down to 1200 grade. They were then gold sputtered and affixed with silver epoxy resin to brass discs. Each of the resultant assemblies was then embedded with epoxy resin in moulded epoxy resin mounts and allowed to set. Excess epoxy resin was then ground away to reveal a fresh mineral

surface. In all cases the thickness of mineral in these detachable electrode mounts was less than 5 mm. **Figure 2.2.1** illustrates their design, together with a universal screw-fitting electrode arm. For experiments involving light, the angle subtending the screw and glass arm would be 90 degrees. The brass collar inside the screw just accommodated the copper wire to which it was soldered. It lay proud of the screw in order to make contact with the brass disc in the electrode mount. To the other end extended a length of copper sheathed flexible cable ending in a 4 mm plug.

Electrodes were checked for good electric conductivity by gold sputtering the exposed surface and coating it with silver loaded epoxy resin. A modified crocodile clip was attached to this face enabling the resistance to be measured. If it exceeded 20 Ω the electrode was refabricated or discarded.

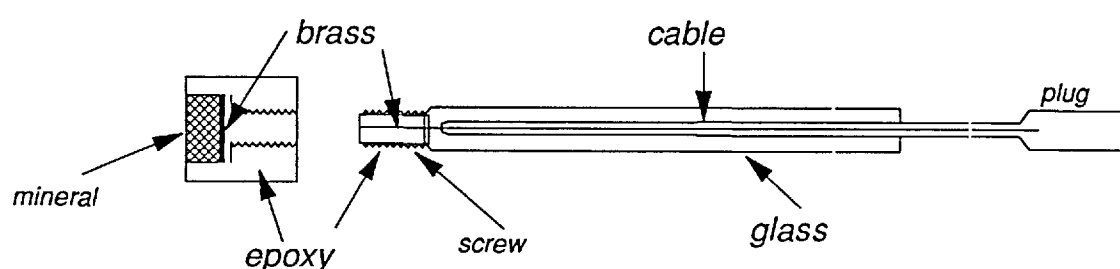


Figure 2.2.1. Mineral electrode arm and mount.

2.2.2. Surface preparation.

Before each experiment at least 0.5 mm layer of the working electrode surface was removed by grinding with SiC paper. Therefore exhaustion of working electrodes was commonplace, but it was assured that virgin cp was exposed at the start of each experiment, and not a cp surface for which ionic diffusion had lowered the metal:sulphur ratio. In acid solutions the electrode's destruction was much faster. The surface was then polished using a rotary polisher on polishing pads with alumina of mean particle size 0.3

micrometres. Prior to final polishing the electrode was inspected under a light microscope for any defects or cracks. Polishing with alumina of smaller particle size caused the mineral surface to bevel, as did excessive polishing.

No more than ten seconds was allowed to elapse between termination of polishing and immersion in solution. One minute has been established as a sufficiently short time for exposure to air not to reduce the size of the anodic prewave (described in Section 4.4) as a result of surface oxidation [5]. This will be explored more fully in the Section concerning rest potentials.

2.3. THE ELECTROCHEMICAL CELL

Photoelectrochemical experiments involved the cell shown in cross section in Figure 2.3.1. It had a capacity of 150 cm³. It is also illustrated in Appendix 2.

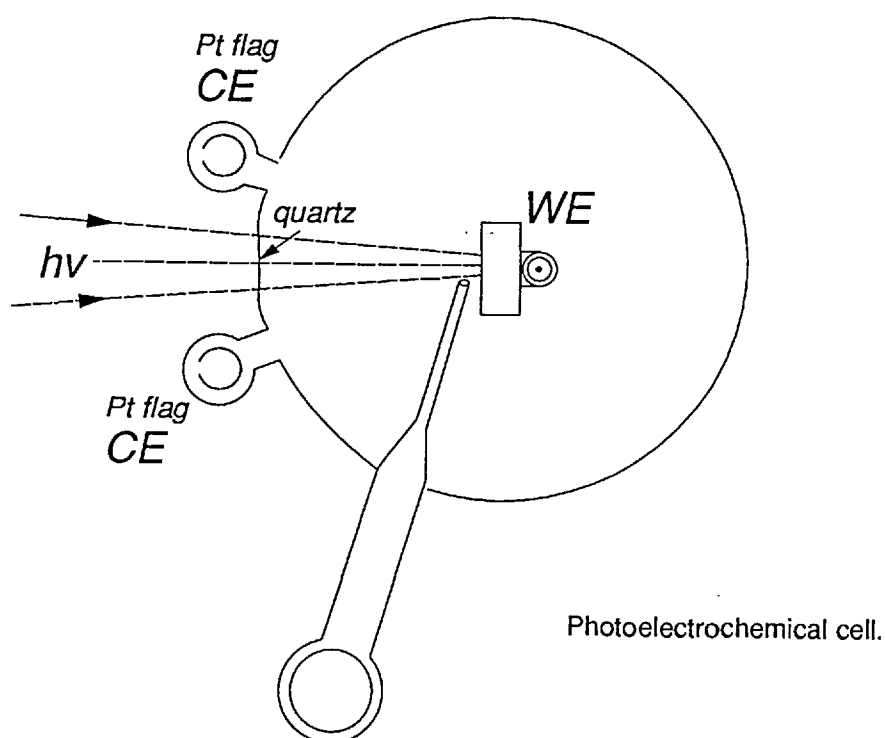


Figure 2.3.1. Photoelectrochemical cell.

The four ports were of 12 mm diameter and could be interchanged. Thus the positions of the glass frit gas inlet and 3 mm thick silica glass observation window were reversed without affecting the voltammetric behaviour of a working electrode (W.E.). The overall design ensured the most uniform potential and current distribution at the working electrode, and using two counter electrodes of high surface area should reduce the capacitance arising from the SC/EL interface too, an especially important consideration

in a.c. measurements at high frequency. These Pt counter electrodes consisted of flags, 10 x 10 x 0.5 mm spot welded to 30 mm of 0.5 mm Pt wire, sealed into a 7 mm glass arm and spot-welded to tin sheathed 1 mm copper wire. As with the illustrated W.E., a sufficient length of this cable extended out of the glass arm to connect directly with the potentiostat.

Above the illustrated cross section, the cell carried a wide-necked ground glass stopper, supporting the W.E. arm. Thus, between experiments the arm could be lifted out of the solution, the W.E. mount repolished and replaced, the solution discarded, the cell rinsed, the solution replaced, and the stopper refitted without altering the relative positions of the working and reference electrodes and incident light. However, the differing dimensions of various working electrodes resulted in there being a variable photon flux per unit area. Also the incident light was far from being of uniform intensity (see Section 2.4.1.). Therefore, where relative photocurrent efficiencies were of interest it was necessary to use the same W.E. and reposition it between experiments very carefully.

Throughout this project a Luggin probe was used containing a saturated calomel reference electrode (S.C.E.). All potentials applied to the W.E. will be quoted henceforth relative to this reference electrode (R.E.). The Luggin probe was always brought up against the W.E. so as to just not touch the centre of it. The intention behind this procedure was to minimise uncompensated ohmic potential losses whilst not shielding the electrode and distort the potential distribution.

2.4. INSTRUMENTATION

2.4.1. For photoelectrochemical experiments

Figure 2.4.1.1 is a schematic diagram of the photoelectrochemical cell and associated electronic instrumentation comprising: an Applied Photophysics 150 W xenon arc lamp, power supply, f/3.4 monochrometer and stepping motor control unit, a Rofin light chopper and chopper control unit, a Faraday cage, a Solartron 1286 Electrochemical Interface, an EG & G 5210 phase sensitive lock-in amplifier, and Elonex 286S-10 microcomputer. In preliminary light experiments described in Chapter 3, a Bentham 213 differential amplifier, 223 lock-in amplifier and 218 integrating ADC were used in place of the EG & G phase sensitive lock-in amplifier. The apparatus is also shown in Appendix 2.

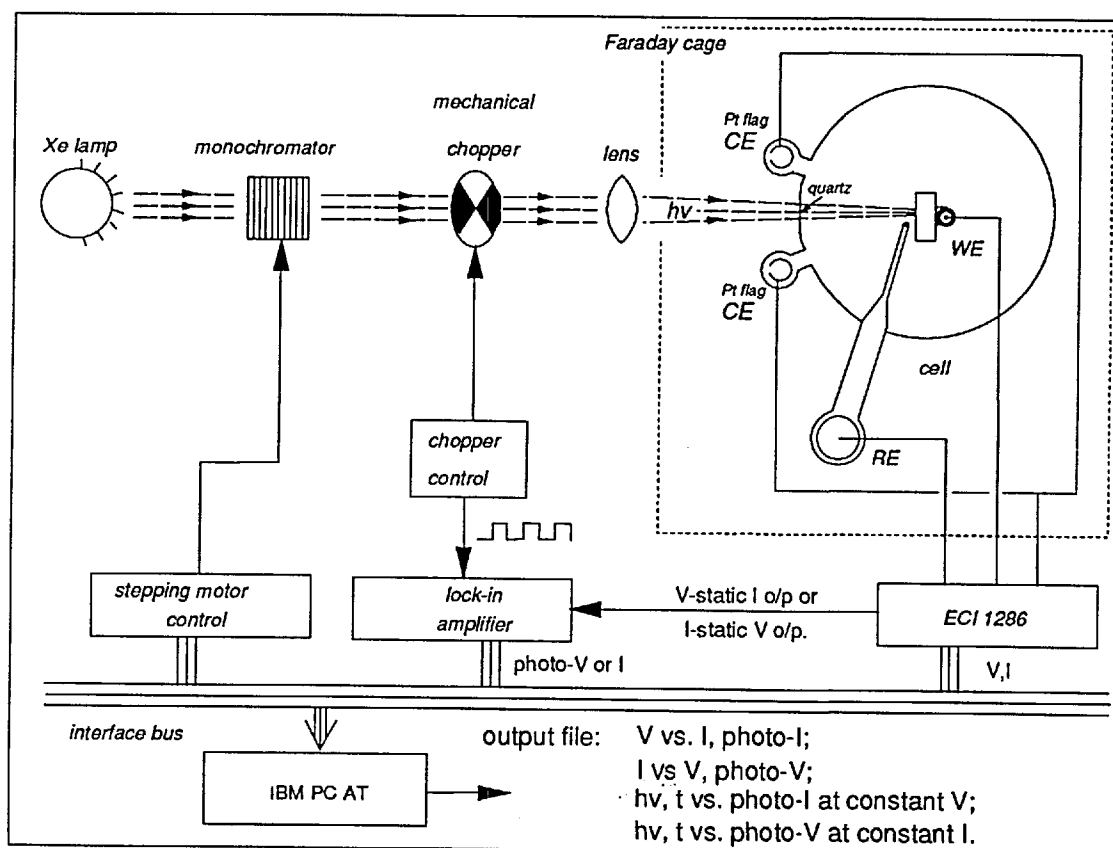


Figure 2.4.1.1. Photoelectrochemical apparatus.

The stepping motor and potentiostat were controlled via a PASCAL computer program written for this purpose [219]. Likewise values of applied potential, V , and total current, I , from the ECI, and values of photo-current, $I(\text{ph})$ from the integrating ADC were stored in a computer file via an IEEE interface by this programme. The programme was extended and modified to allow for more active rather than pre-ordained control of the Solartron 1286. It was thus possible to commence experiments under a galvanostatic zero current condition, effectively recording the open circuit or rest potential until it stabilised, whereupon the appropriate polarisation could be set and the 1286 switched to potentiostatic control. The programme was further modified to accommodate the EG & G amplifier, to allow for more variable data reading rates, and to output more details of experimental conditions. The output file was formatted so as to allow for the data to be processed by Lotus 123 worksheet macros designed for the respective types of experiment. The most important are shown in Appendix 3.

For preliminary light experiments involving the Bentham equipment, the analogue current output from the potentiostat was connected to the high pass input of the differential amplifier. The low pass input was earthed. Differential gain was set at 100

and high and low pass filters to remove noise > 100 Hz and < 50 Hz. The output from the differential amplifier was connected to the lock-in amplifier input, the square wave reference input (of 75 Hz) originating at the chopper control unit. By using the dummy cell shown in **Figure 2.4.1.2**, the sensitivity and gain of the lock-in amplifier could be maximised. Typically this resulted in setting a time constant of 1 s, and sensitivity of 0.15 mV. The output of the lock-in was connected to the integrating ADC, from which digital readings were taken via the IEEE-488 bus. The photocurrent voltammetry of **Chapter 3** and other experiments where maximum sensitivity was desirable, required the removal of the monochromator as this increased the photon flux about tenfold. The cell was positioned so as to focus the light beam on the W.E. surface.

The chopping frequency was chosen at 75 Hz, a compromise, for photo-responses may be too slow to respond to faster light modulation, and heating of the electrode at low chopping frequencies give rise to a thermal lock-in response. Notwithstanding the latter, photo-responses are reduced at low frequency of light modulation relative to the dark responses, as observed in intensity modulated photocurrent spectroscopy (IMPS) [220]. The photo-response is somewhat analogous to imaginary impedance frequency dependence described in **Section 1.5**.

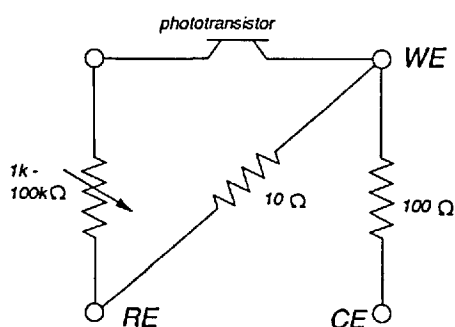


Figure 2.4.1.2. Dummy cell used before undertaking photoelectrochemical experiments.

When the phase sensitive lock-in amplifier was employed, the dummy cell served to tune the instrument and render $\pm 90^\circ$ signals for in-phase photo-anodic and cathodic responses (checked with an oscilloscope). Here the reference frequency was tracked using the 'bandpass' option, enabling the phase sensitive detector to respond only to the fundamental of the reference frequency of 75 Hz, established as a more stable and less noisy frequency at which to chop the light. The instrument was set to track this reference frequency and the phase sensitive detector driven at the same frequency. The sensitivity

was adjusted to give maximum resolution for each experiment. 'Normal' dynamic reserve of 110 dB was chosen. The time constant was adjusted to suit each experiment, but the roll off rate set at a maximum 12 dB per octave. The output from the amplifier to the computer file via the IEEE interface was subsequently 'normalised' in the worksheet macro to yield the phase angle θ ($\pm 180^\circ$) and magnitude I_{ph} (μVcm^{-2}) of the photo-response. In galvanostatic mode photo-voltages V_{ph} and θ could be measured simply by inputting the potential rather than current signal from the potentiostat.

The monochromator housed an assembly of mirrors conducting the light beam onto a 500 nm blaze 1200 lines per mm diffraction grating. A slice of the diffracted light was reflected by further mirrors to the monochromator exit slit of width adjusted to 3mm. The light output from the monochromator would be an envelope, at this exit slit width spanning 5 nm. To obtain spectral photocurrent responses, it was first necessary to measure the lamp output via the monochromator as a function of wavelength, using a thermopile and digital voltmeter. Readings were taken at 2 nm intervals. The output at the entire available range of photon energies is shown in Figure 2.4.1.3. A computer macro was designed to calibrate each photocurrent value according to the photon flux at the corresponding wavelength. Spikes in the xenon lamp output hampered the use of both wide and narrow monochromator output bandwidth settings. Moreover, the size of photocurrents often approached the maximum sensitivity of the amplifiers, so only small electrodes allowing for the use of a large current measuring resistor (1000 or 10000 ohms) and completely covered by the incident light could be employed. Indeed all sources of noise had to be avoided, the complete assembly including the Faraday cage with a common earth to mains.

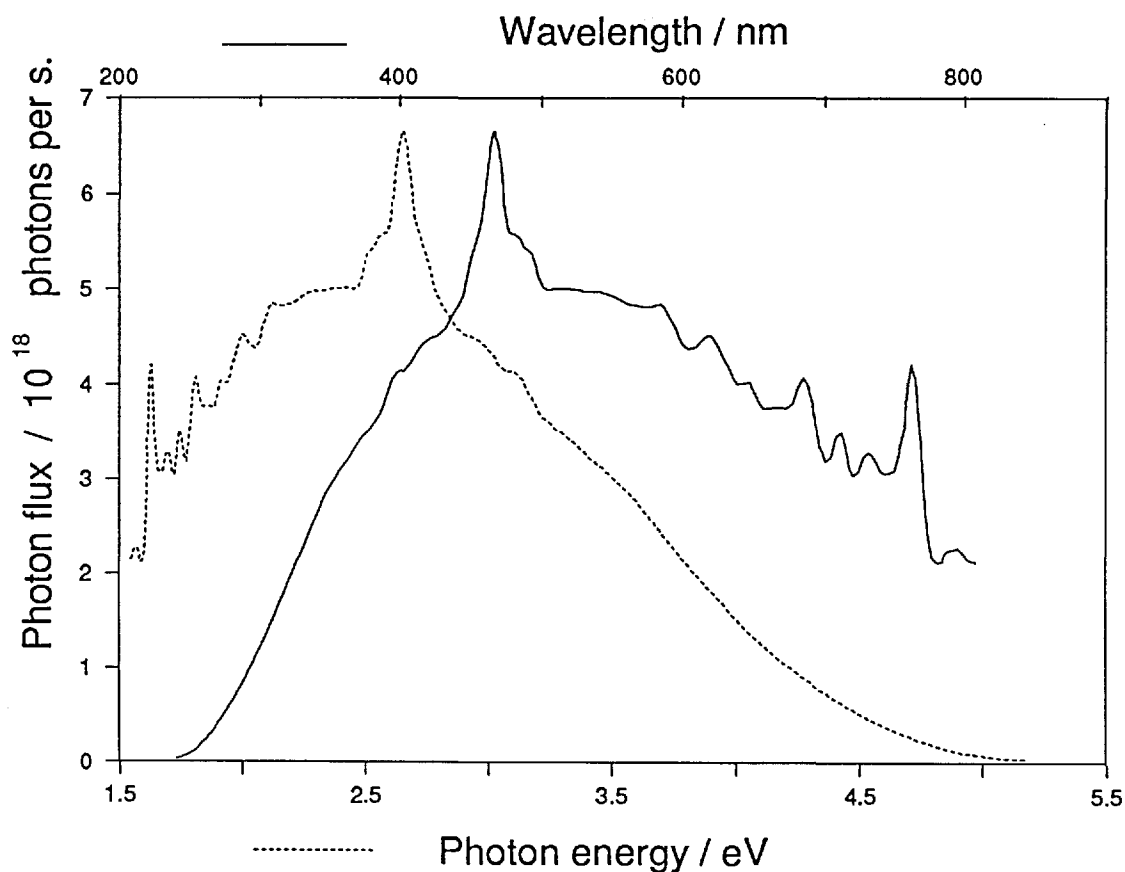


Figure 2.4.1.3. Output of 150 W xenon lamp vs photon energy and wavelength. Slit width 3mm.

2.4.2. For a.c. impedance spectroscopy

The apparatus used in impedance spectroscopy was much the same as above, a Solartron 1250 frequency response analyser (FRA) replacing all the photo-related equipment. The 350 mV output from the 1250 generator was input into the 1286, reduced a hundred fold to minimise noise. The analogue current and applied potential outputs from the 1286 were input into the 1250 analyser. Unless otherwise stated, twenty frequency responses were measured per decade decrease in frequency, each one by integration over 100 cycles. All a.c. measurements were made at constant potential.

2.4.3. For other experiments

As a means of determining the variation in electrochemical behaviour between different mineral specimens, all were subjected to 3 cycles of polarisation from 0 V to ± 1 V at pH 2 and from -0.2 V to between -1.2 and 0.8 V at pH 9.2 against a standard calomel electrode (S.C.E.), employing the cell illustrated in **Figure 2.4.3.1**.

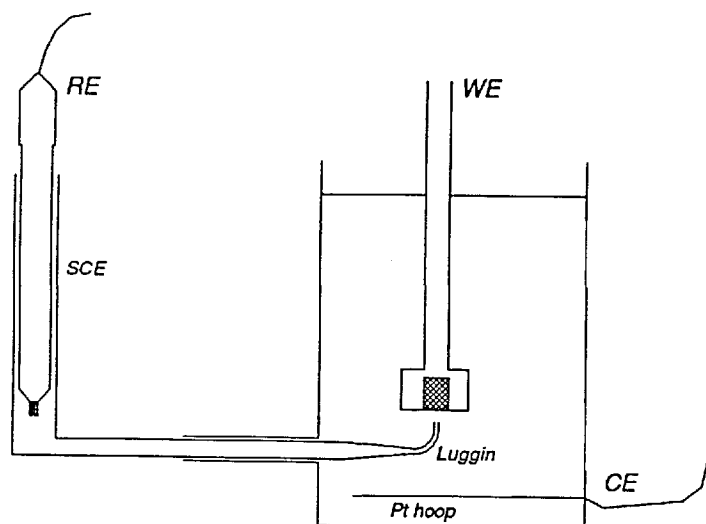


Figure 2.4.3.1. Electrochemical cell employed in certain voltammetric experiments.

Electrolysis was effected through a Solartron 1186 interface coupled to an Oxford Electrodes wave form generator. The sweep rate was set at 20 mV s^{-1} throughout. Voltammograms were recorded on graph paper with a Gould Series 60000 chart recorder.

The rest potential and air oxidation experiments were carried out in a similar cell. Equipment used in these studies comprised a Wenking ST 72 potentiostat, a Hi-Tek PP RI waveform generator, and a computer with suitable interface and software.

CHAPTER 3. RESULTS OF PRELIMINARY INVESTIGATIONS ON TWENTY CHALCOPYRITE SAMPLES

In the following chapters, electrode potentials are quoted with respect to the S.C.E., which has a potential +0.241 V vs S.H.E.. Reference will be made to the potential-pH diagram and electrochemical half-equations listed in **Appendix 1**.

3.1. The Hall Effect.

Attempts were made to determine the semiconductor type and carrier concentrations from Hall effect measurements using a magnet capable of generating a flux density of 0.75 Tesla and a Kiethley voltmeter. However, background noise smothered any inherent Hall voltage and this experiment was abandoned. There was also difficulty in preparing a cruciform sample of adequate size.

3.2. Resistivity measurements.

Initially, the van de Pauw [221] method was employed using a four point probe for resistivity measurements. In order to ensure 'suitably small ohmic contacts' four spring loaded metal pins were applied to the sides of a 0.85 x 0.85 cm cp orthogonal sample of 0.31 cm thickness. In the van de Pauw method two probes, A and B, are used to apply a voltage across the sample, V_{AB} , whilst from the other two, C and D, the current is measured, I_{CD} . $R_{AB,CD}$ is then V_{AB}/I_{CD} . The leads are exchanged to measure $R_{BC,DA}$, and van de Pauw's formula applied to determine the 'specific resistivity'. The method is valid regardless of the slab shape and relative positions of the four contacts. For cp the method's validity was repeated by measurement of $R_{AB,CD}$ and $R_{BC,DA}$. The same result were obtained, 31 k Ω cm. This is some one thousand times larger than the average resistivity obtained by the simpler method described below. Indeed, the resistance between any two probes exceeded 1 k Ω , and it was concluded that suitably small ohmic contacts could not be made.

When the same cp sample square faces were gold sputtered and coated with silver loaded epoxy resin, the measured resistance across them was 8.5 Ω . Therefore the resistivity of cp was calculated as 19.8 Ω cm, consistent with resistivity measurements on other samples.

3.3. Microprobe analysis.

Table 3.3.1 summarises data concerning the mineral specimens investigated, including chalcocite and bornite. Some samples were saved for crystal surface studies. Others proved too friable for use in electrochemical experiments. Cross-sectional areas were

determined by travelling microscope image analysis. **Table 3.3.1** quotes atomic ratios of copper and iron, correct to within 1 % as determined by a Cameca Camebax electron probe X-ray microanalyser. It was to prove that the mineral chalcopyrite 22 was representative of the naturally occurring specimens and so a further analysis was conducted on 22 by a Cambridge Instruments Microscan IX. A comparison of results is shown in **Table 3.3.2**. The Camebax analyser indicated a lower metal:sulphur ratio and the atomic ratios are more disparate. This may be due to the 'burning off' of surface sulphur by the incident electron beam. It is reasonable to accept the Cambridge Instruments results as being more accurate.

Under the electron microscope impurities were revealed with clear boundaries between adjoining phases. No such inclusions appeared to cover more than 0.5 % of the mineral surface. These were analysed quantitatively, and are indicated in the Table.

Ref.	Source	Origin and type (p)x = (poly)crystalline	Cu:Fe (S=2)		Impurities
			Cu	Fe	
1	ex-GBL	Sudbury, N. Ontario, px	0.934	0.990	PbS
2	ex-GBL	Peru; px	0.955	1.016	ZnS,(FeS)
3	ex-GBL	Norway; px	0.999	1.011	Fe,Al sil.
4	ex-GBL	Zambia; px	0.966	1.012	
5	N. Welham	Geevor Mine, Cornwall; px	0.913	0.971	
6	BM 31329	Monte Catini, Italy; px	0.976	1.027	
7	BM 1934,749	St Day, Cornwall; px			
8	BM 43309	Ballycumisk, Cork, Ire.; x			
9	BM 55608	Schapbach, Baden, Ger.; x on quartz	0.984 0.989	1.010 1.021	PbS
10	BM 82037	Zellerfeld, Harz, Ger.; x	0.929	0.997	
11	BM 1957,112	Levant St Just, Cornwall; x	0.980	1.023	Qz, PbS
12	BM 1920,136	Mt Lyall, Tasmania; x			
13	BM 1932,1334	Namaqualand, S.Africa; x			
14	BM 1906,80	Ani, Ugi, Japan; x			
15	BM 1917,222	Tilt Cove, Newfoundland; px			
16	BM 31672	Wheal Towan, Cornwall; xal	0.951	1.026	
17	BM 41072	Caradan, Cornwall; twin xal			
18	BM 31383	Carn Brae, Red Ruth; xals			
19	M. Smith	Arizona; xal	0.916	0.921	cubanite
20	BM 1924,1030	Sante Fe, Chiapas; x			
21		Norway; x	0.953	0.984	PbS,ZnS,qz, py
22	ex-Wards	Messina, Transvaal; x	0.993	0.967	
bn	BM 31324	Monte Catini, Tuscany; x	2.57	0.505	see [35]

Table 3.3.1. Mineral specifications. BM = British museum; GBL = Gregory, Botley and LLOYDs Ltd, London. py = pyrite, qz = quartz, bn = bornite

Microprobe.	Camebax.		Cambridge IX	
Atomic ratios (S=2)	Cu:Fe (S=2)		Cu:Fe (S=2)	
	Cu	Fe	Cu	Fe
	0.996	0.958	0.998	0.991
	0.990	0.964	0.993	0.992
	0.989	0.970	1.002	0.991
	1.001	0.967	0.997	0.980
	0.984	0.975	0.997	0.989
			0.994	0.985
			1.011	0.986
			1.003	0.990
			1.007	0.990
			0.999	0.991
Average	0.993	0.967	0.9998	0.9885

Table 3.3.2. Specifications of chalcopyrite 22.

3.4. X-ray crystallography.

In addition to the above microprobe analyses, corroborative evidence to identify the massive polycrystalline sample from Messina, Transvaal as α -chalcopyrite was gained as follows. XRD analysis on a powdered sample, using a PW1700 series Phillips X-ray diffractometer, revealed line spacings of 2.6, 2.64 and 3.03 Å of relative intensity 10 : 3 : 1, corresponding to the chalcopyrite mineral structure, as opposed to one of its close relatives, such as talnakite (β -chalcopyrite, $\text{Cu}_9\text{Fe}_5\text{S}_{16}$). With further evidence that a number of electrodes fabricated from this mineral behaved self-consistently, and that it exemplified the photoelectrochemical behaviour of chalcopyrite from other sources, it was adopted as the main subject for investigation presented in the following chapter.

3.5. Rest potentials and the atmospheric oxidation of chalcopyrite.

It is known that the rest potentials of chalcopyrite and covellite electrodes in aqueous electrolytes vary significantly with time upon contact with solution. In our experiments, it was found that the rest potentials of chalcopyrite and covellite electrodes depended not only on the pH, but also the length of time for which the electrode was exposed to the laboratory atmosphere - see Table 3.5.1. The results show conclusively that the rest potential was related to the interaction between the surface of electrode and the

electrolyte. In particular, in the case of chalcopyrite, rest potentials following short periods of exposure to the atmosphere lie within the region of stability predicted by the **Appendix 1** stability-pH diagram near the boundary for electrochemical oxidation, whereas exposures of a minute or more result in open circuit potentials exceeding this potential boundary at all pH. Covellite is clearly more resistant to atmospheric oxidation. The uncertainty in these results is likely to have arisen from effects of traces of dissolved oxygen in solution. A quantitative determination of the extent of surface oxidation by atmospheric oxygen is pursued in the next section.

Electrode	pH	Time exposed to atmosphere before immersion			
		0 s : predicted *	< 10 s	1 min	75 hr
CuFeS ₂ 22	2	-106		-149 to -102	-49 to -15
	7.2	-800 to -227	-220 to -190	-171 to -147	-135 to -107
	12.2	-914 to -540		-409 to -373	-198 to -162
CuS	2	-178 to 257		+28 to +54	+63 to +96
	7.2	-475 to 156	-142 to -127	-134 to -84	-69 to -32
	12.2	-623 to -140		-247 to -205	-236 to -192
Rest potentials of electrodes vs S.C.E. / mV.					

Table 3.5.1.

*: predicted range of stability according to metastability diagram in **Appendix 1**.

Variation in the rest potential with time from immersion is shown in **Figure 3.5.1** for bornite, chalcopyrite and covellite in solution of pH 9.2. It is seen that covellite achieves its rest potential much more quickly than chalcopyrite and bornite.

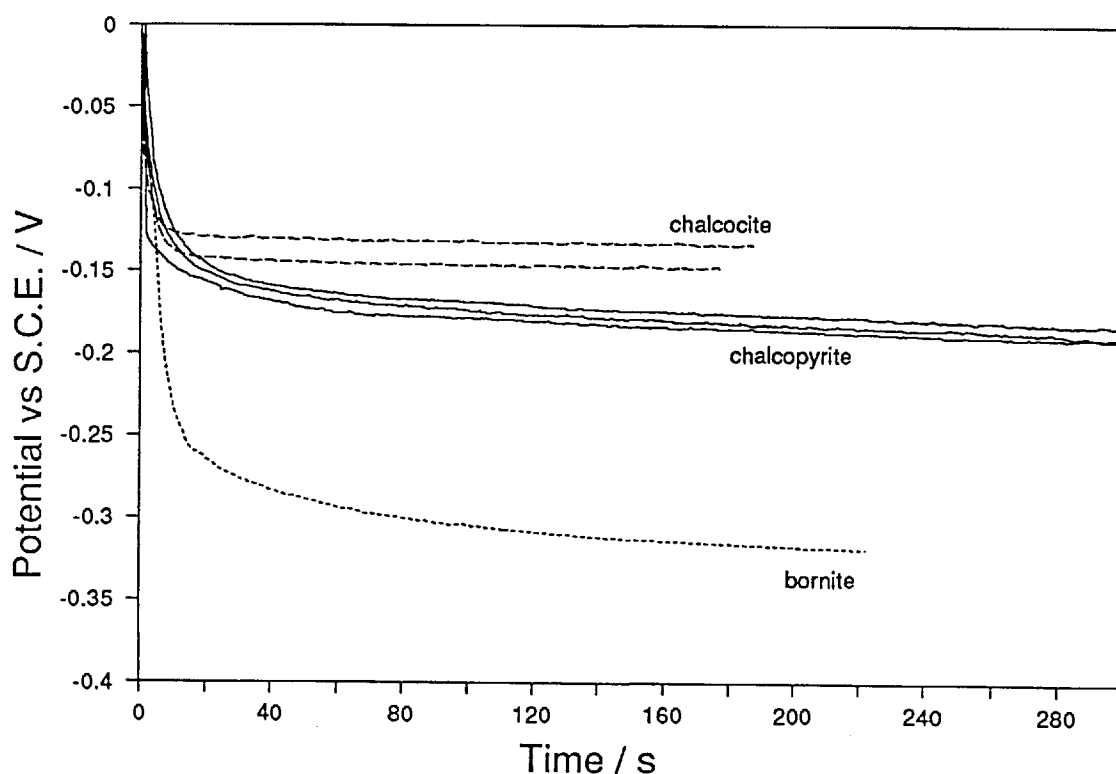


Figure 3.5.1. Time dependence of mineral open circuit potential in 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$. Prior exposure to the atmosphere was < 10 s. The several chalcopyrite plots give some idea of the variation of these plots between experiments.

The thickness of an oxidation layer on the electrode surface is expected to vary in some way with atmospheric exposure time, *e.g.* parabolically, if the film grows under solid state diffusion control. The charge associated with cathodic reduction currents in response to negative-going potential sweeps should then reflect the atmospheric oxidation kinetics. This was confirmed by the experimental results shown in Figures 3.5.2, 3 and 4, which were obtained in neutral, basic and acidic sodium sulphate solutions respectively. **Figure 3.5.2** demonstrates that even the chalcopyrite electrode exposed in atmosphere for 10 s oxidized significantly. With increased exposure time, the oxidation rate decreased, as expected for a topochemical reaction. In basic sulphate solution, as shown in **Figure 3.5.3**, the situation was similar, but in acidic sulphate solution, because of the large reduction current of chalcopyrite itself, the difference between the two curves was not so obvious. Therefore, in order to determine the extent of atmospheric oxidation, the results of the experiments pertaining to **Figure 3.5.2** were analysed. The charge associated with reduction of the oxide layer were obtained by considering the excess of cathodic current (integrated with respect to time) shown by curve b over that in curve a. For c, d and e, allowance was made for the suppression of cp reduction either by the oxide layer or a

reduction product, perhaps sulphur. In the case of c and d this is particularly noticeable. This charge was then tentatively equated with reduction of the cp oxidation products in air, which have been identified by XPS as $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and a copper sulphide of stoichiometry CuS_2 [222]. A comparison of standard potentials for FeOOH (goethite), $\text{Fe}(\text{OH})_3$ and Fe_2O_3 (hematite) reduction to Fe^{2+} ions, the thermodynamically favoured product:



$$E / \text{V} = 0.771 - 0.1772\text{pH} - 0.0591 \log(\text{Fe}^{2+})$$

At pH 7.2 and $\log(\text{Fe}^{2+}) = -4$, $E = -0.278 \text{ V}$



$$E / \text{V} = 0.545 - 0.1772\text{pH} - 0.0591 \log(\text{Fe}^{2+})$$

At pH 7.2 and $\log(\text{Fe}^{2+}) = -4$, $E = -0.500 \text{ V}$



$$E / \text{V} = 0.541 - 0.1772\text{pH} - 0.0591 \log(\text{Fe}^{2+})$$

At pH 7.2 and $\log(\text{Fe}^{2+}) = -4$, $E = -0.504 \text{ V}$,

suggest that the oxide reduction peak on Figure 3.4.2 can be identified with iron oxyhydroxide reduction. However, in addition:



$$E / \text{V} = -0.397 - 0.0296\text{pH} - 0.0296 \log(\text{HS}^-)$$

At pH 7.2 and $\log(\text{HS}^-) = -4$, $E = -0.485 \text{ V}$.

No thermodynamic data was available for CuS_2 . It can be reasonably expected to have a less negative Gibbs energy of formation than CuS and therefore be reduced to chalcocite at less negative potentials. Therefore it was assumed that both iron and copper oxide product reduction proceeded concurrently, and one mole of cp was oxidised per two moles of reduction charge passed. Assuming the radius of one CuFeS_2 formula unit in the mineral lattice to be 0.27 nm, the thickness of oxidized layer on the surface of chalcopyrite electrode was then calculated, as shown in Table 3.5.2.

Atmospheric exposure time	0 min	1 min	14hr	24hr	98hr
reduction charge / mC cm^{-2}	2.0	2.65	3.4	3.7	5.2
oxide thickness / nm	0	0.2	1.9	2.4	4.6

Table 3.5.2. Surface oxidation of chalcopyrite in atmosphere.

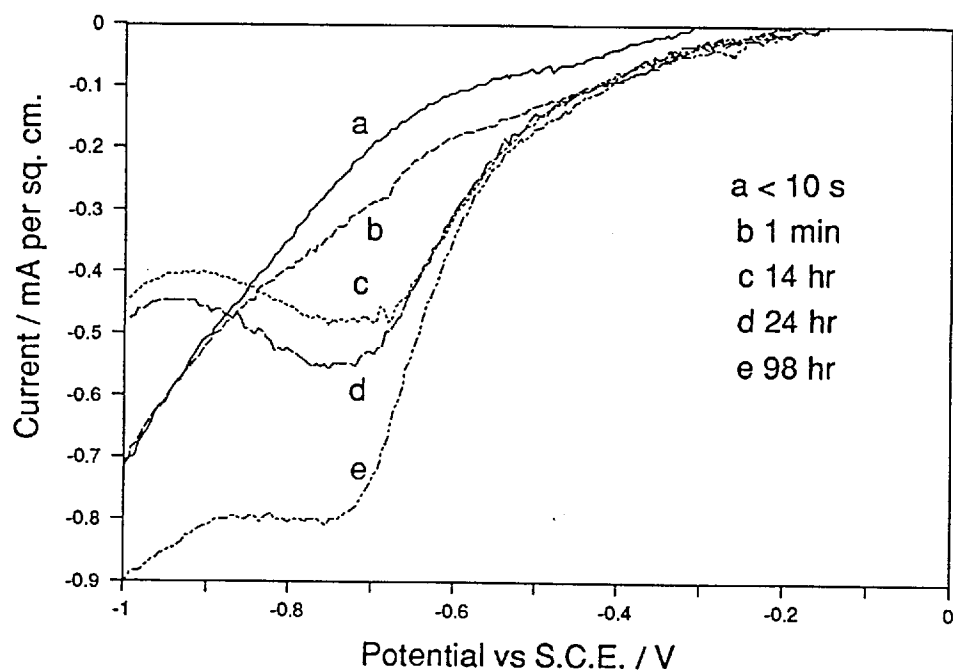


Figure 3.5.2 Cathodic reduction curve for chalcopyrite in 0.3 M Na_2SO_4 , pH 7.2.
Sweep rate 50 mV s^{-1} .

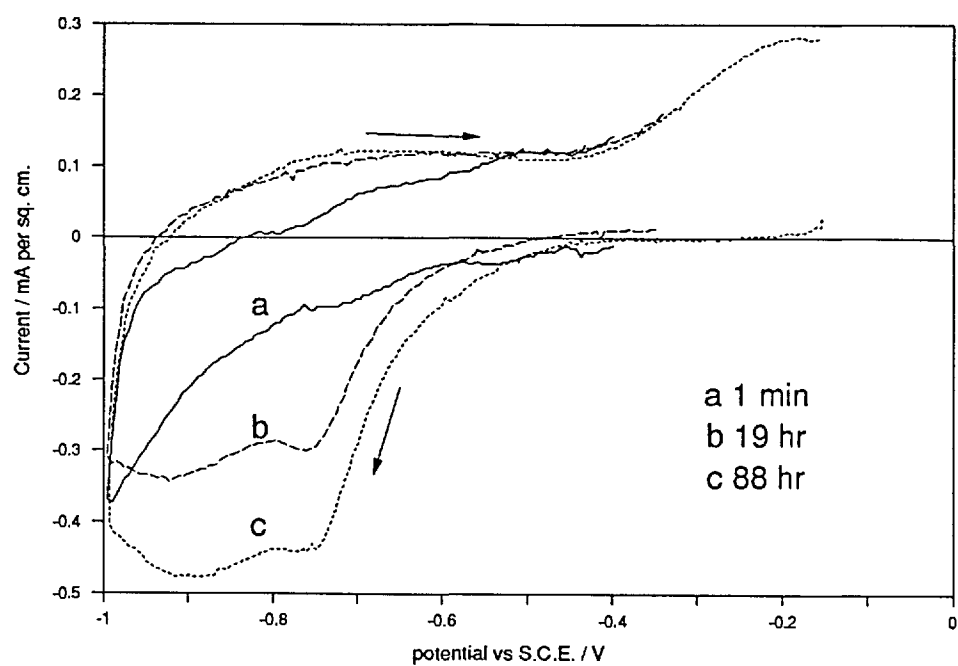


Figure 3.5.3. Voltammogram of chalcopyrite from the rest potential to -1.0 V in 0.3 M Na_2SO_4 pH 12.16 50 mV s^{-1} .

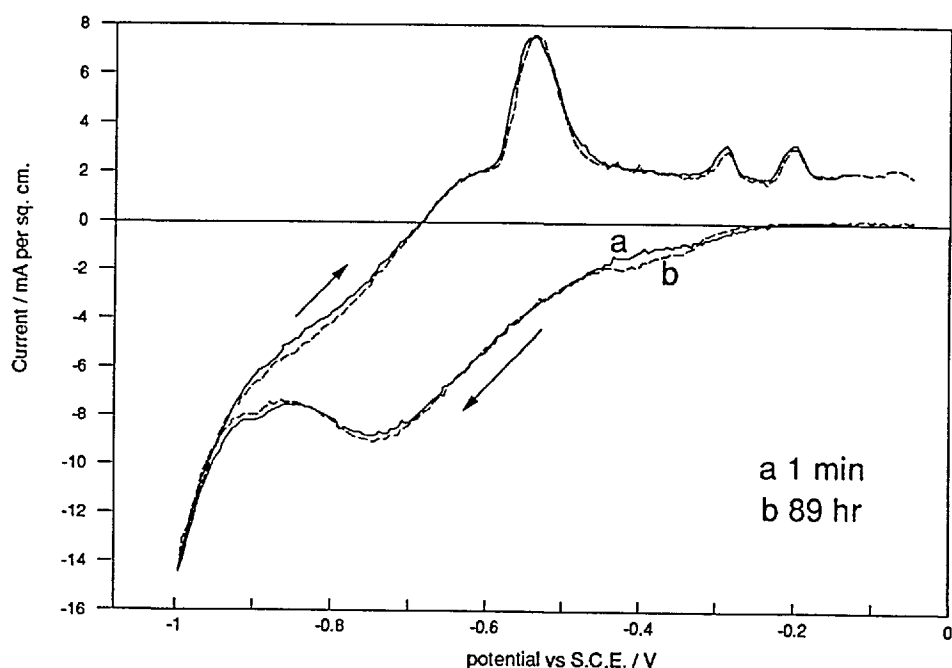


Figure 3.5.4. Voltammogram of chalcopyrite from the rest potential to -1.0 V in 0.3 M Na_2SO_4 pH 2 50 mV s^{-1} .

3.6. Photocurrent and dark current transients in acid solutions.

The upper graphs in Figures 3.6. 1 - 13 show current responses of the various fabricated mineral electrodes to applied potentials swept at a rate of 50 mV s^{-1} from 0.0 V in 0.1 M HClO_4 . The lower graphs are the corresponding photocurrent responses. In those on the left, the initial excursion was negative-going, and in the right it was positive-going. Characteristic peaks are annotated with Roman numerals, with particular reference to Figure 13, which will be discussed in detail in the next chapter. Cycle numbers are indicated with Arabic numerals.

It will be seen from the potential-pH diagram in the appendix that chalcopyrite is not thermodynamically stable below pH 2, and a number of phase changes are possible. Moreover, chalcopyrite's behaviour is largely determined by kinetic control, the formation of pyrite being totally inhibited by slow nucleation [12] and sulphur being the oxidation product preferred over sulphate [93]. Considering also the diverse origin and impurities present in the electrodes, their dark current responses showed surprisingly similar behaviour at low pH. In the first instance identical sweeps had been applied to the same electrodes but using the conventional equipment described in Section 2.4.3. The minerals in the main had behaved self-consistently. For instance Electrode 6 in Figure 7,

had passed especially high anodic currents between 0.4 and 0.6 V whilst the same relatively low currents predominated in voltammograms pertaining to electrode 7. All voltammograms had portrayed peaks annotated in Figure 13. It was remarkable that IX and X appeared in all the voltammograms with much the same profile and at invariant potentials whilst a much larger current preceding peak III was manifest in shoulders or peaks of extremely variable magnitude.

The two lower graphs in Figures 1-13 show photo-currents, i_{ph} , as a function of potential V. As they never exceeded 1 % of the overall current, they are not manifest in the cyclic voltammograms described above. Also, the relative magnitude of photo-currents shown in different figures are not strictly comparable because the photon fluxes varied between experiments as described in Section 2.4.1. Nonetheless, the figures illustrate fairly consistent behaviour between mineral samples. The limit of resolution is illustrated in Figure 3. The size of the response in Figure 12 would allow the apparatus to be used in studying the effect of monochromatic light as described in the next chapter. All graphs exhibit a rise in i_{ph} at positive potentials, although the current profiles of some electrodes were dissimilar. Figures 1-3 and 10-13 are consistent in showing a rise in i_{ph} at 0.6 V to a value at 1 V that gently rose then decayed to zero on the negative-going potential scan at 0.25 V. This behaviour conforms with the nucleation behaviour described later, and with the supply of holes to the surface of an n-type semiconducting film affecting the rate at which it is oxidised.

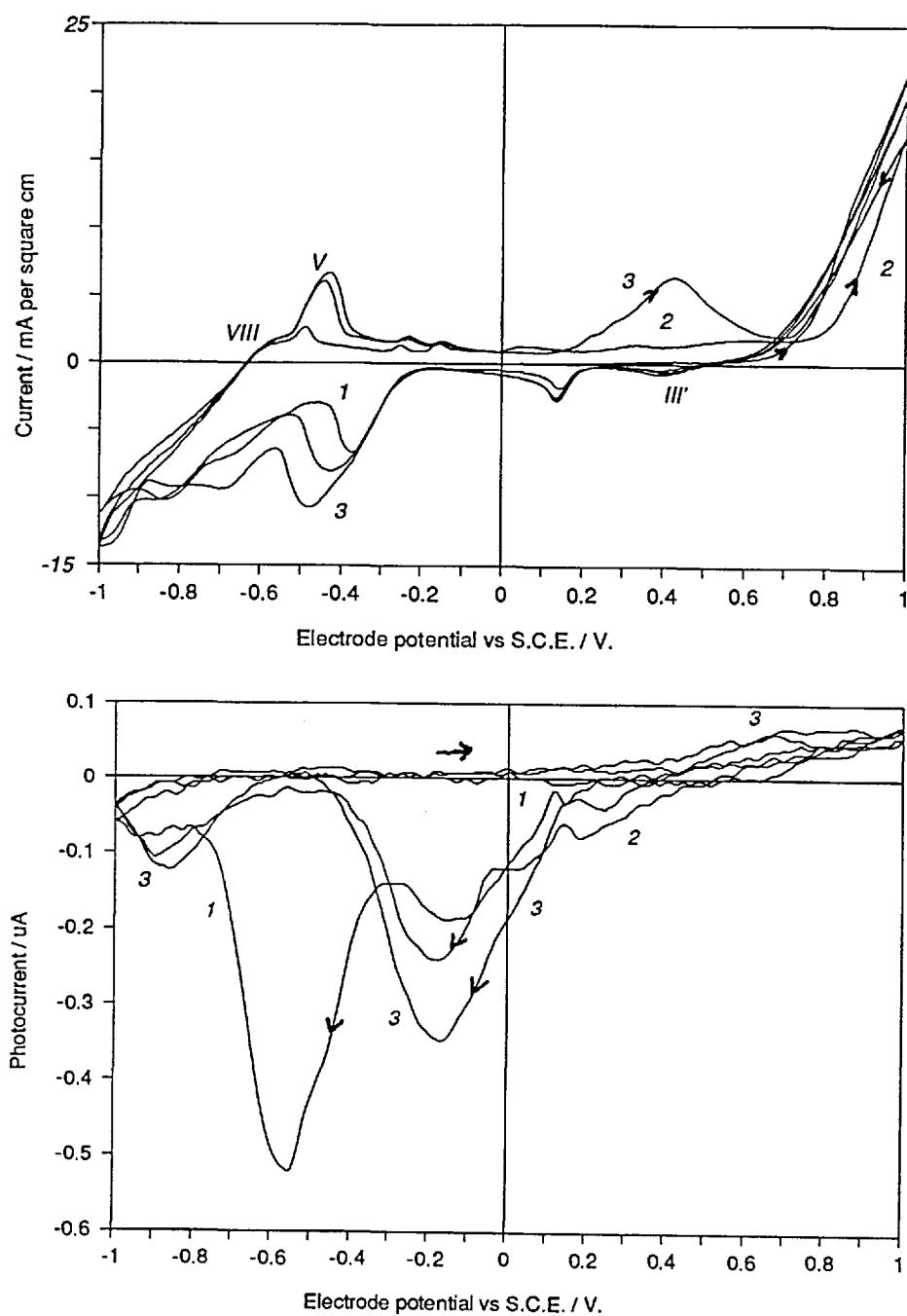


Figure 3.6.1a. Electrode 1a. Dark and photo- current responses to a positive potential excursion from 0 V vs. S.C.E at pH 1. Sweep rate = 50 mV s^{-1} .

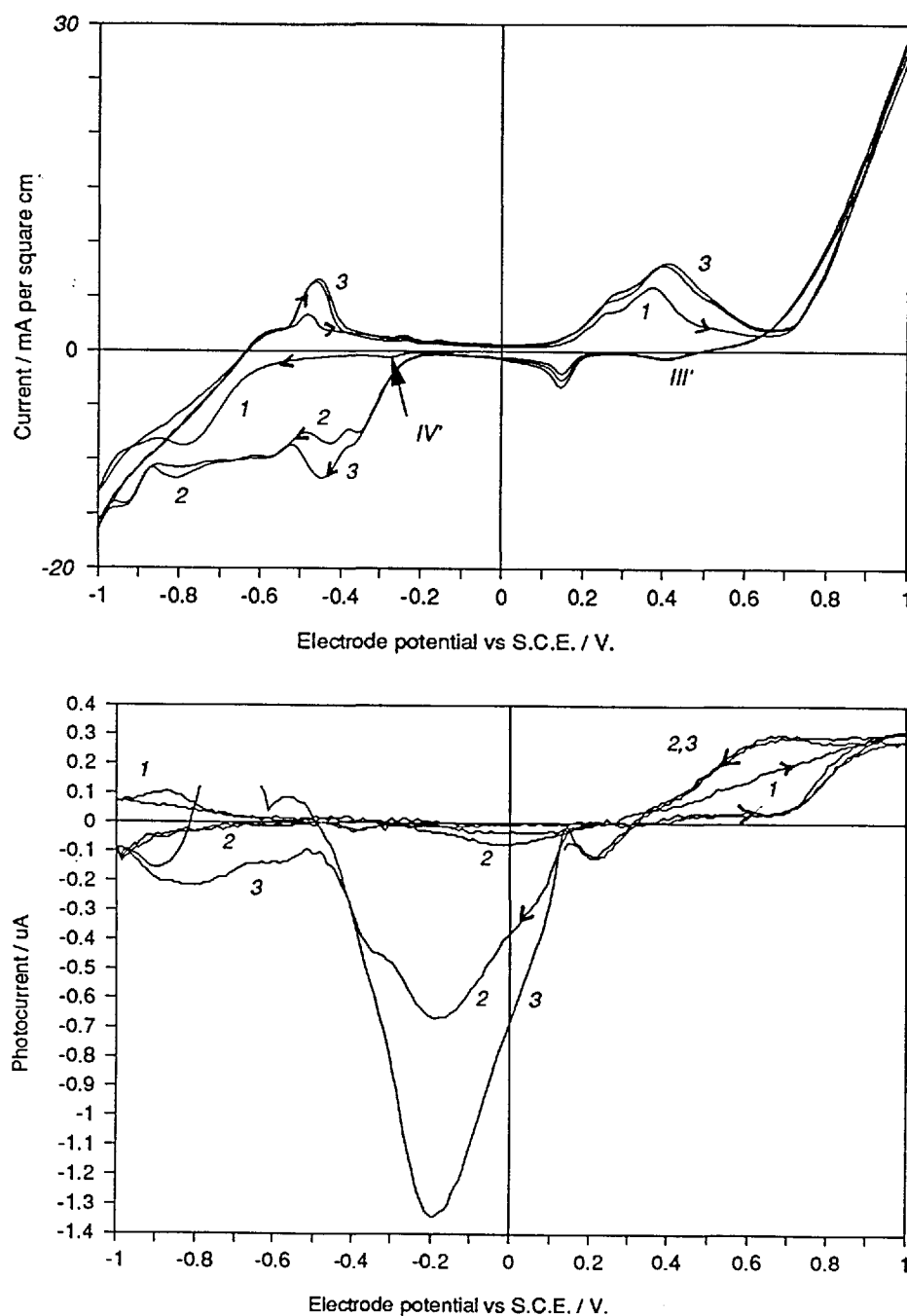


Figure 3.6.1b. Electrode 1a. Dark and photo-current responses to a negative potential excursion from 0 V vs. S.C.E at pH 1. Sweep rate = 50 mV s^{-1} .

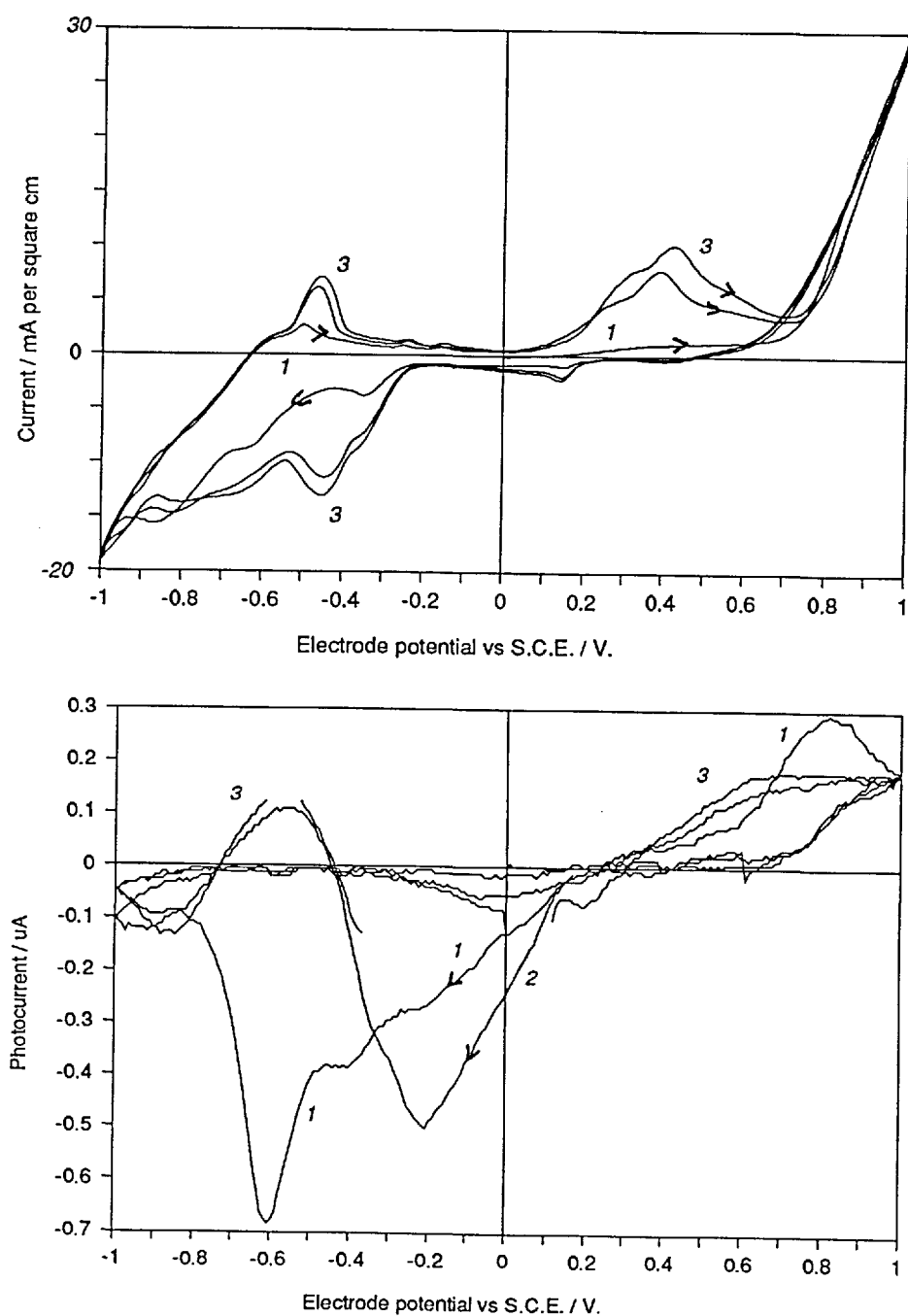


Figure 3.6.2a. Electrode 2a. Dark and photo- current responses to a positive potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

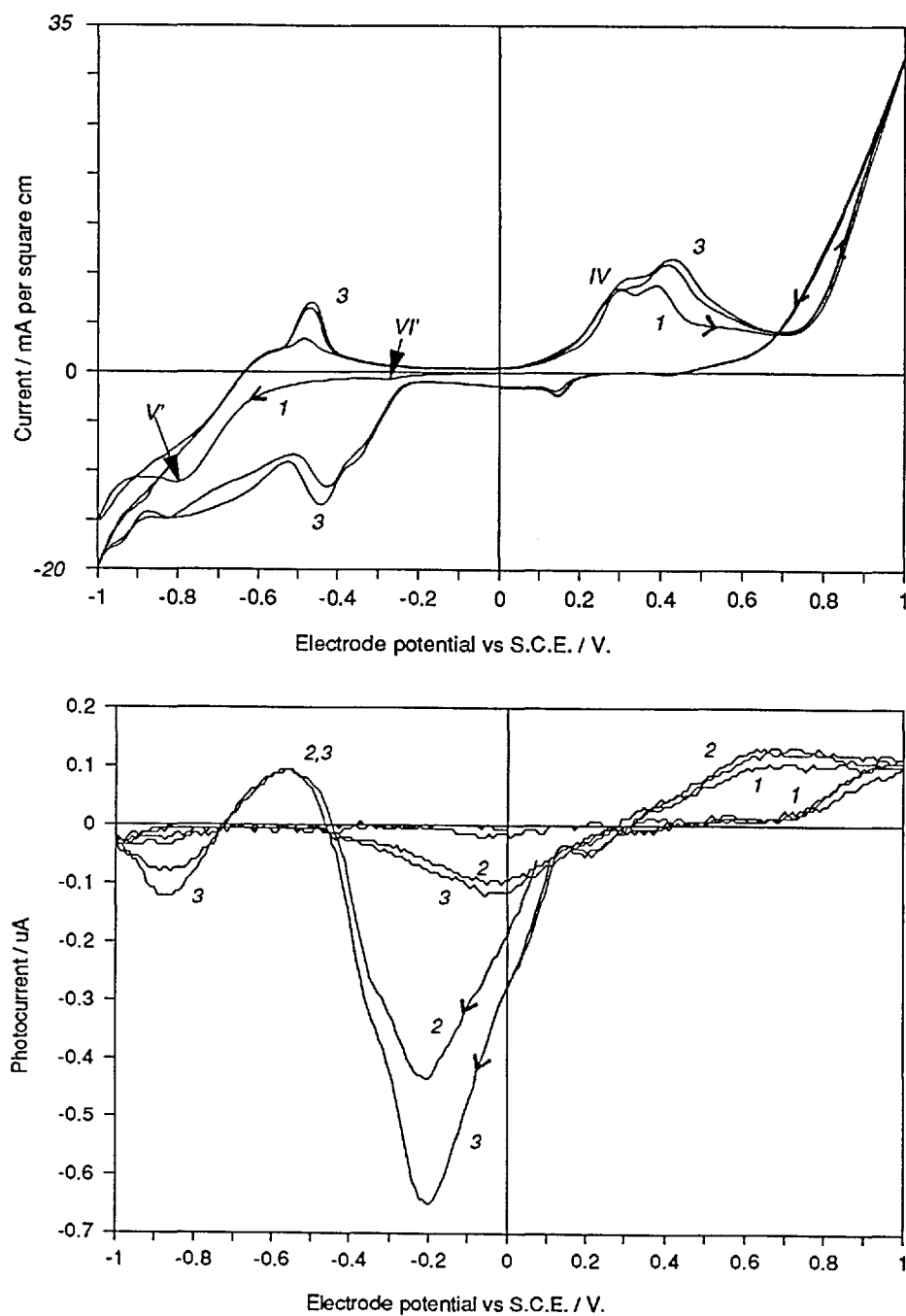


Figure 3.6.2b. Electrode 2a. Dark and photo- current responses to a negative potential excursions from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

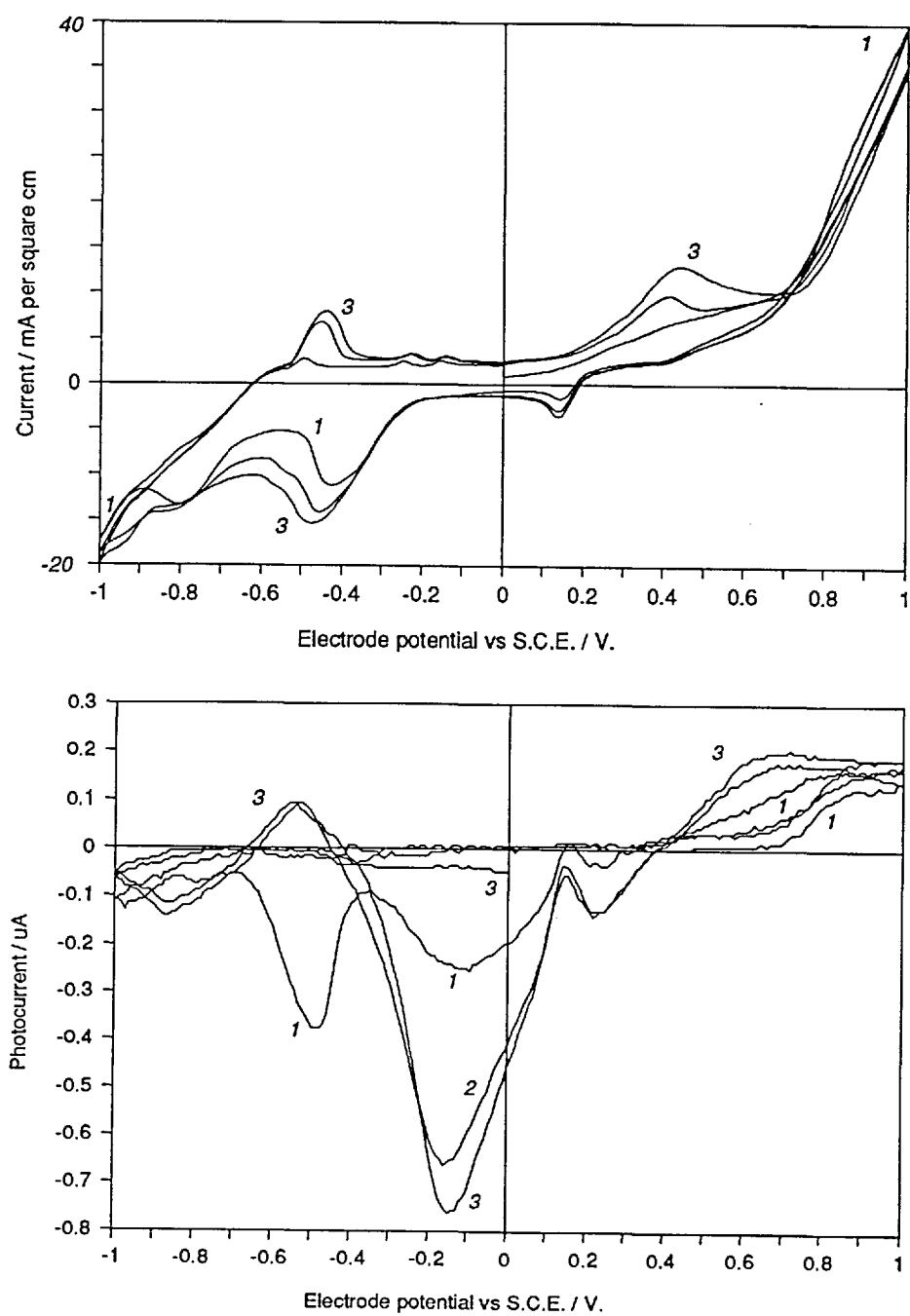


Figure 3.6.3a. Electrode 5. Dark and photo- current responses to a positive potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

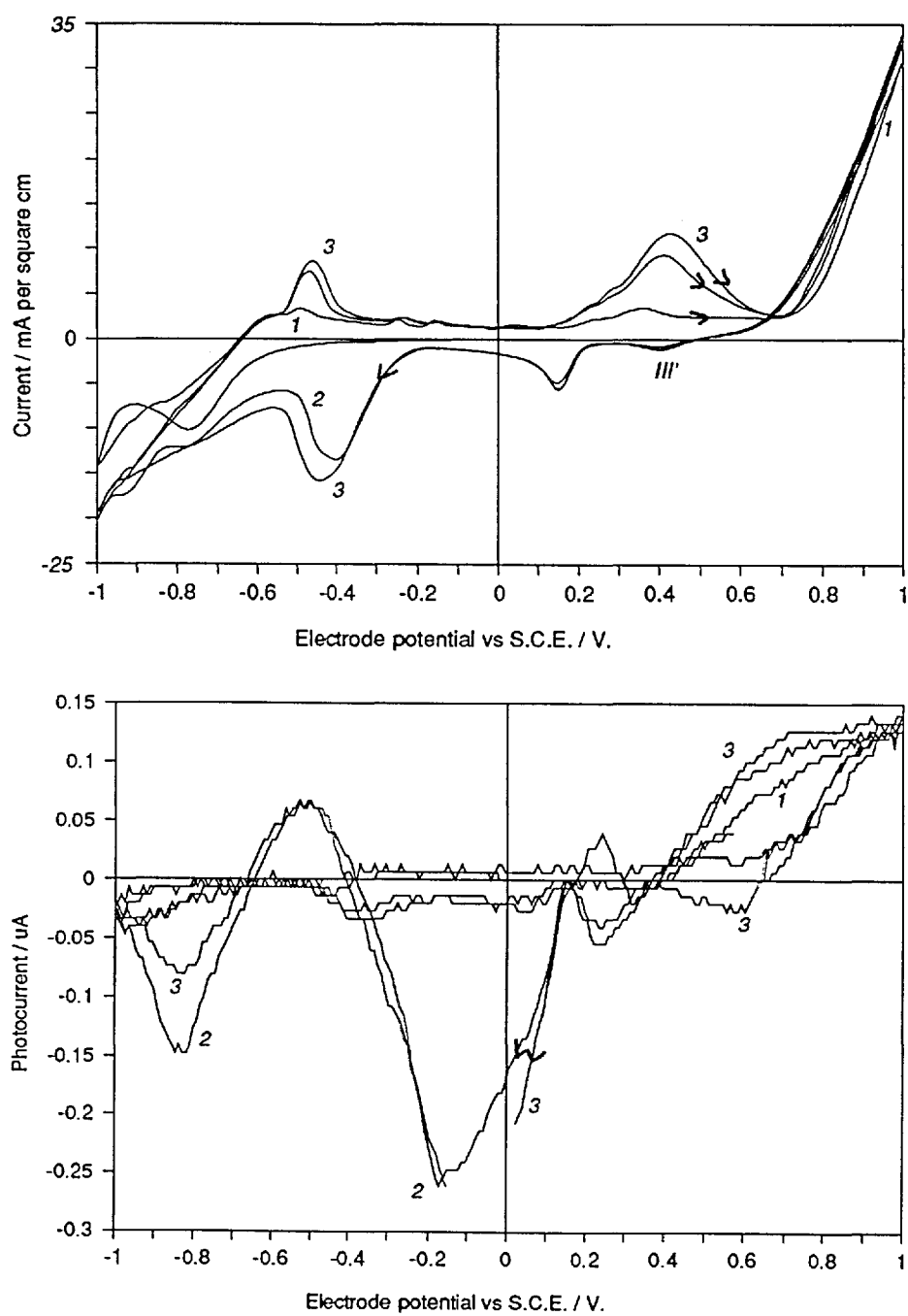


Figure 3.6.3b. Electrode 5. Dark and photo- current responses to a negative potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

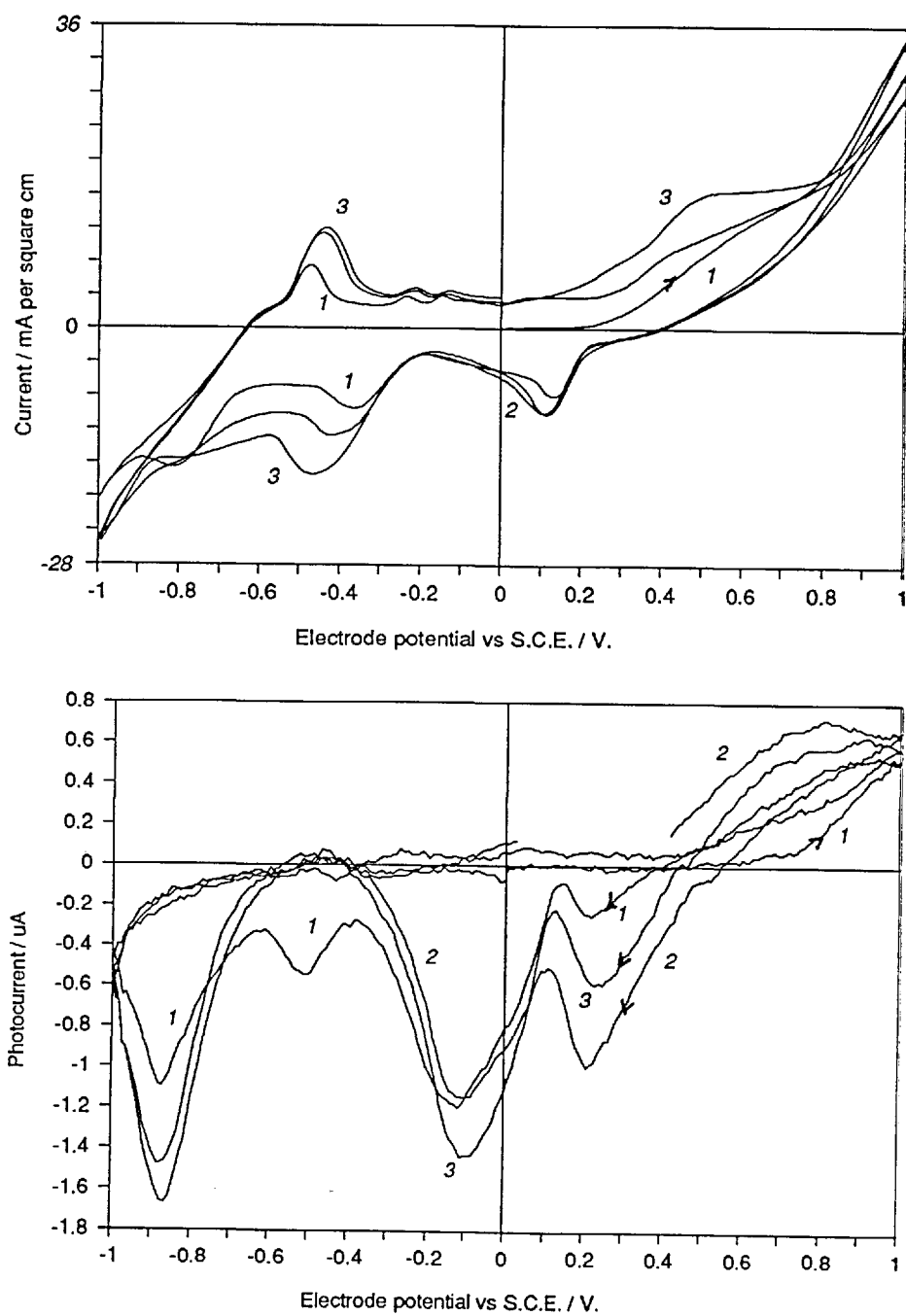


Figure 3.6.4a. Electrode 6. Dark and photo- current responses to a positive potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

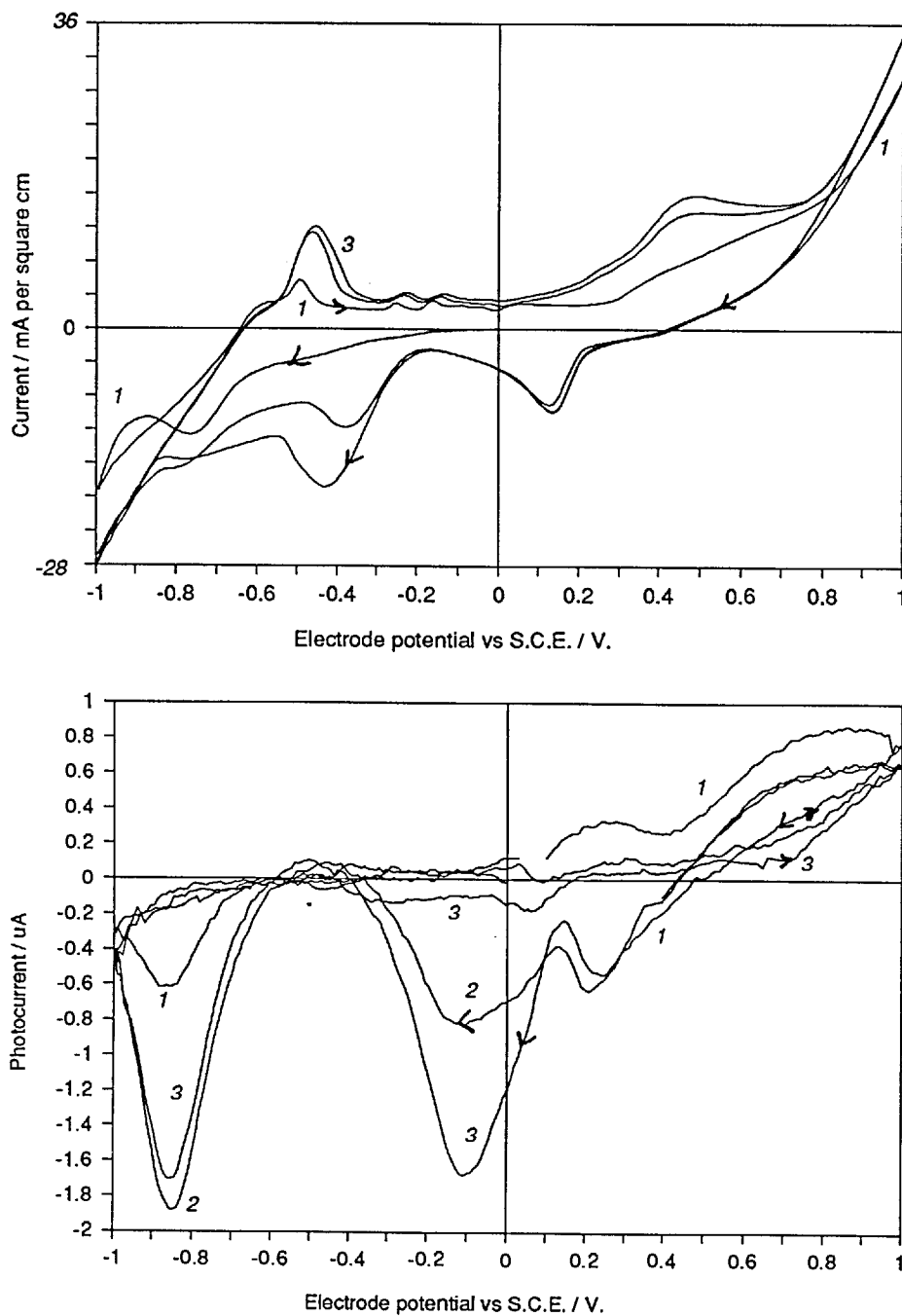


Figure 3.6.4b. Electrode 6. Dark and photo- current responses to a negative potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

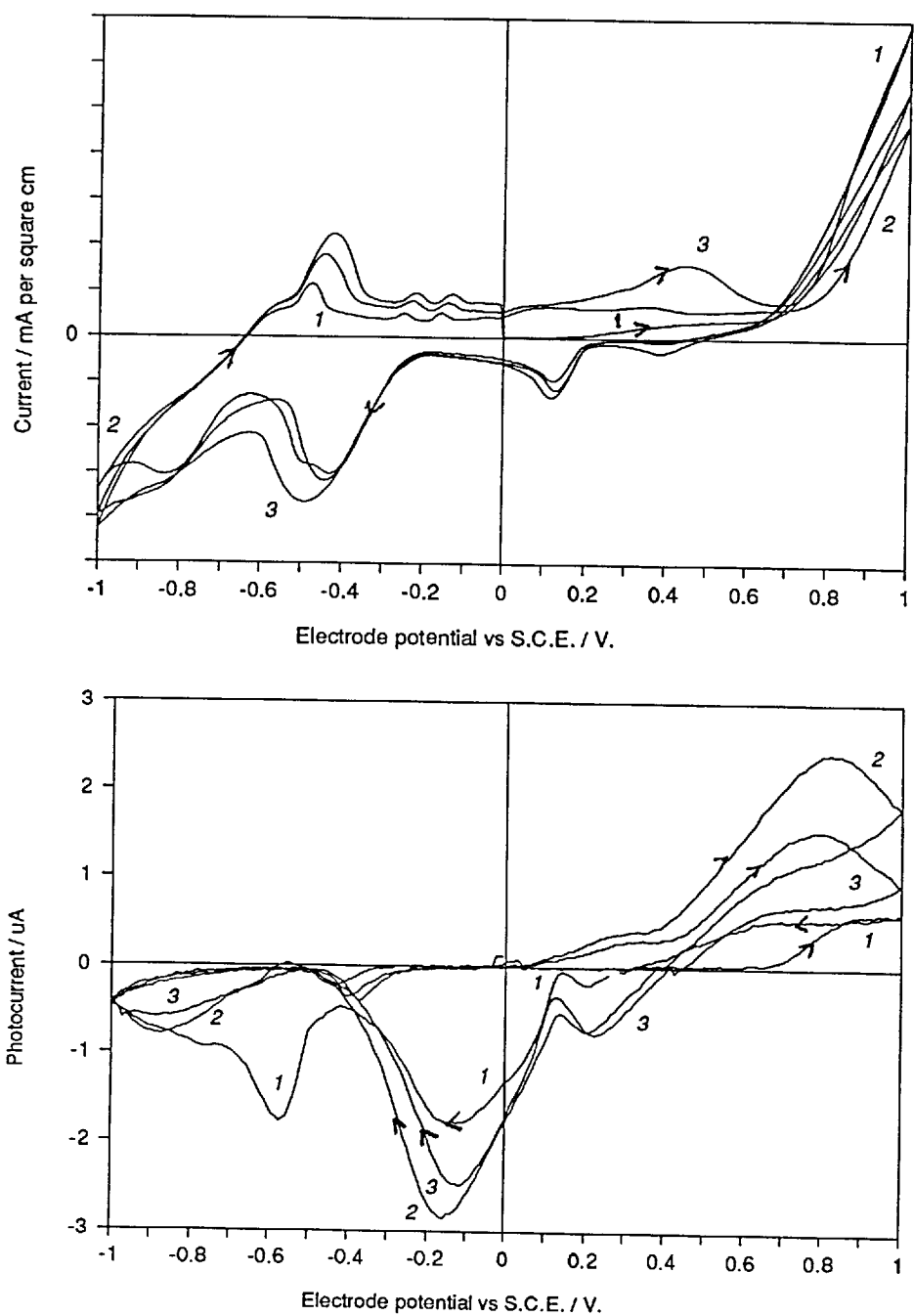


Figure 3.6.5a. Electrode 7. Dark and photo- current responses to a positive potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

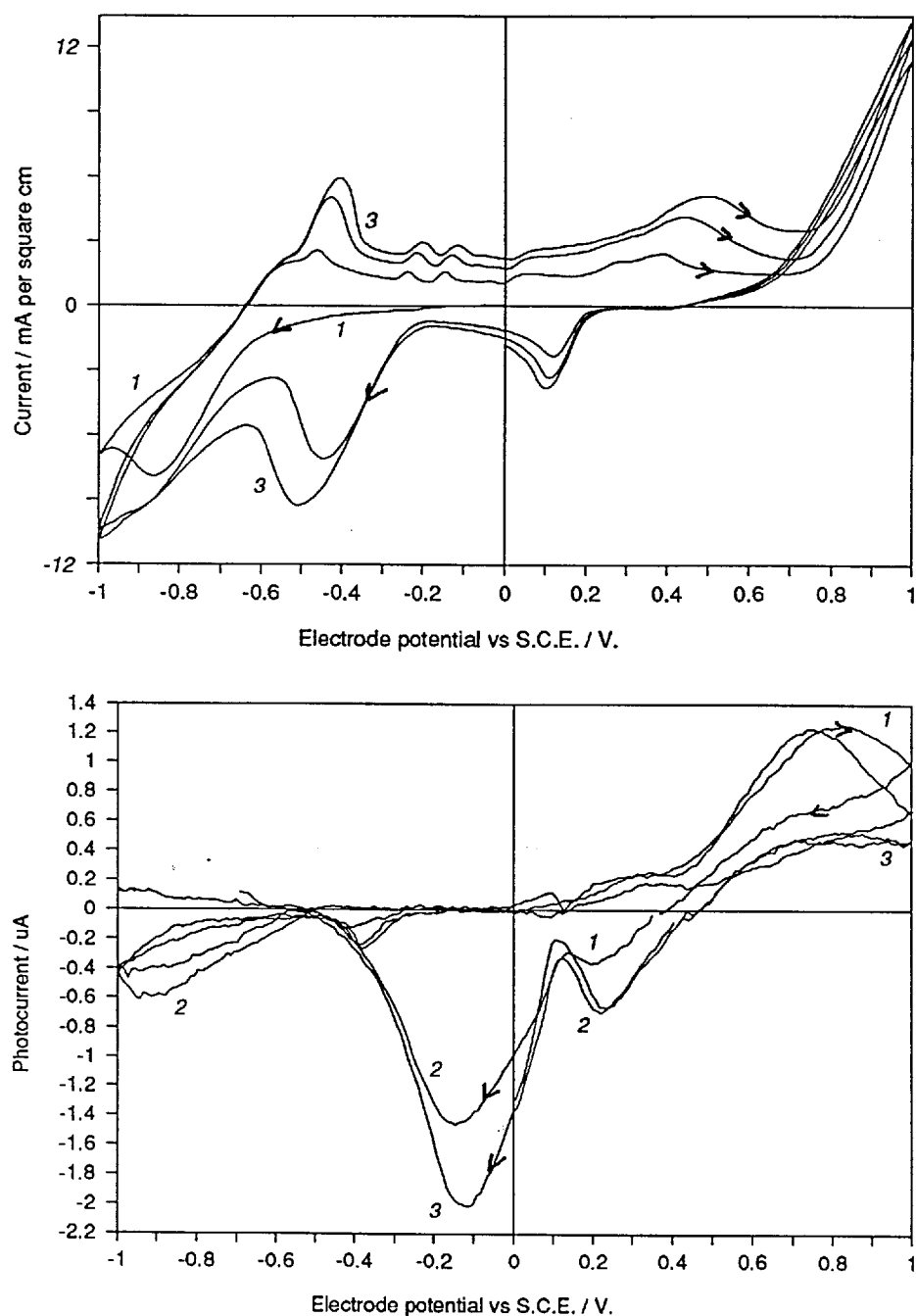


Figure 3.6.5b. Electrode 7. Dark and photo- current responses to a negative potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

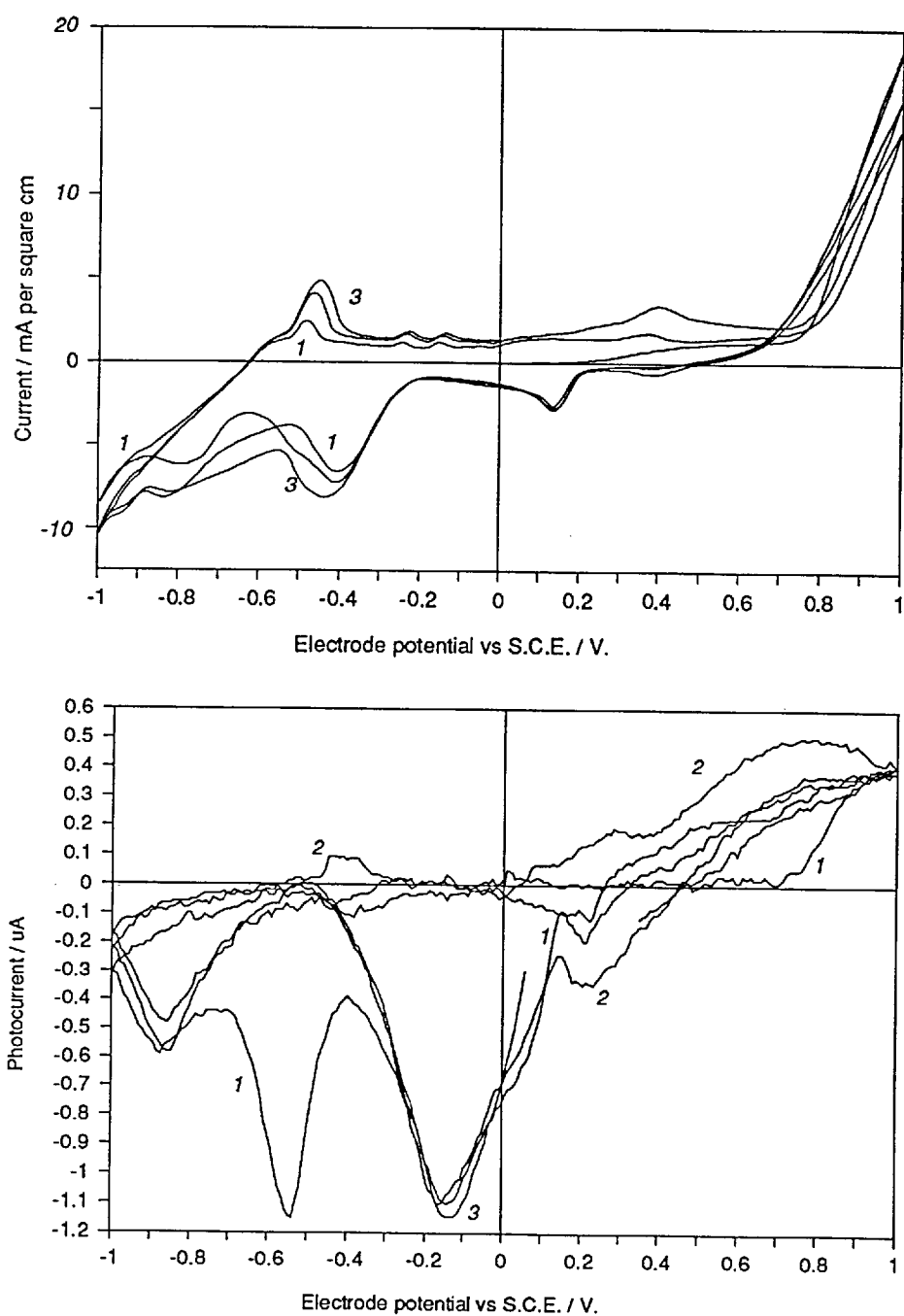


Figure 3.6.6a. Electrode 9. Dark and photo- current responses to a positive potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

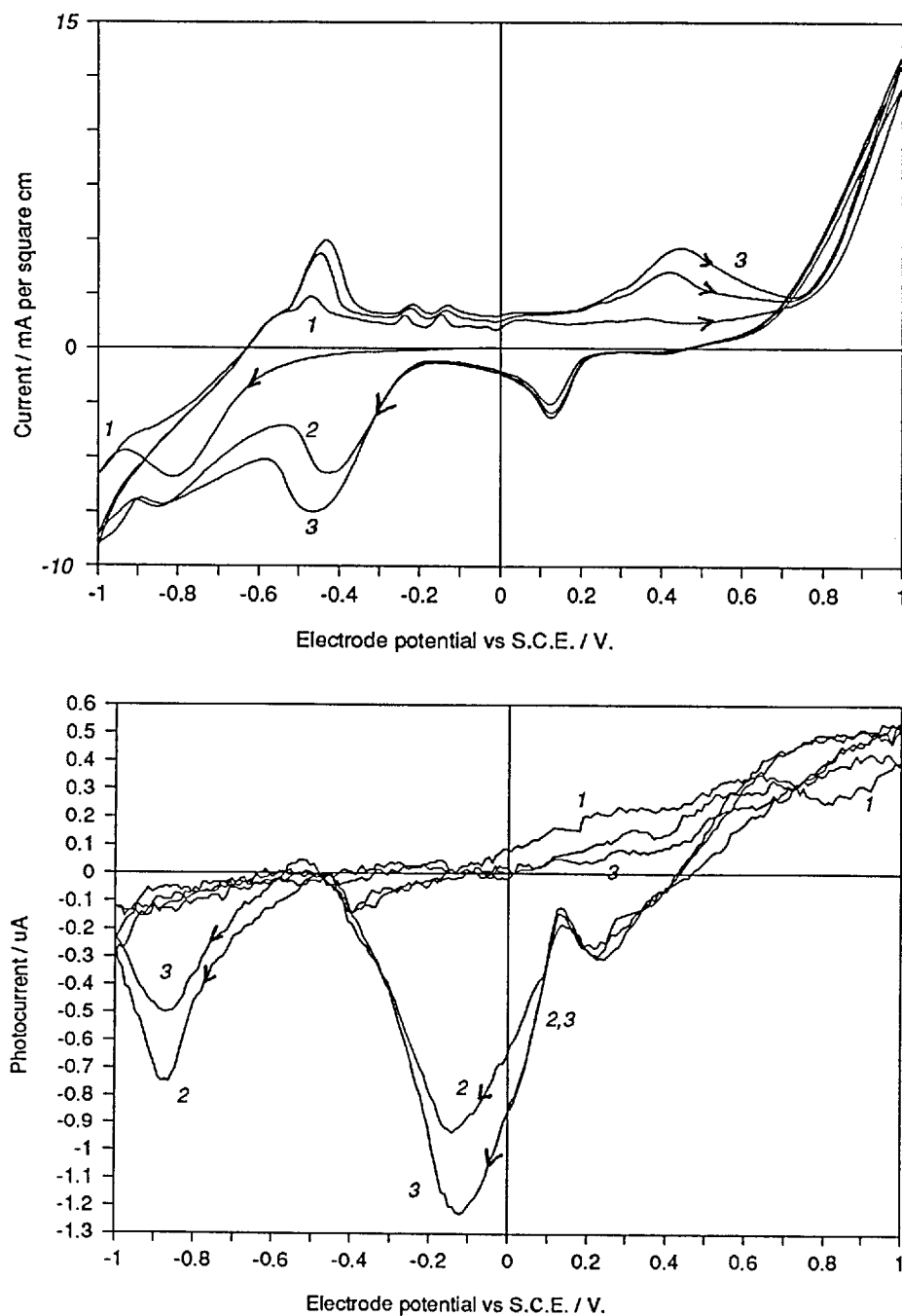


Figure 3.6.6b. Electrode 9. Dark and photo- current responses to a negative potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

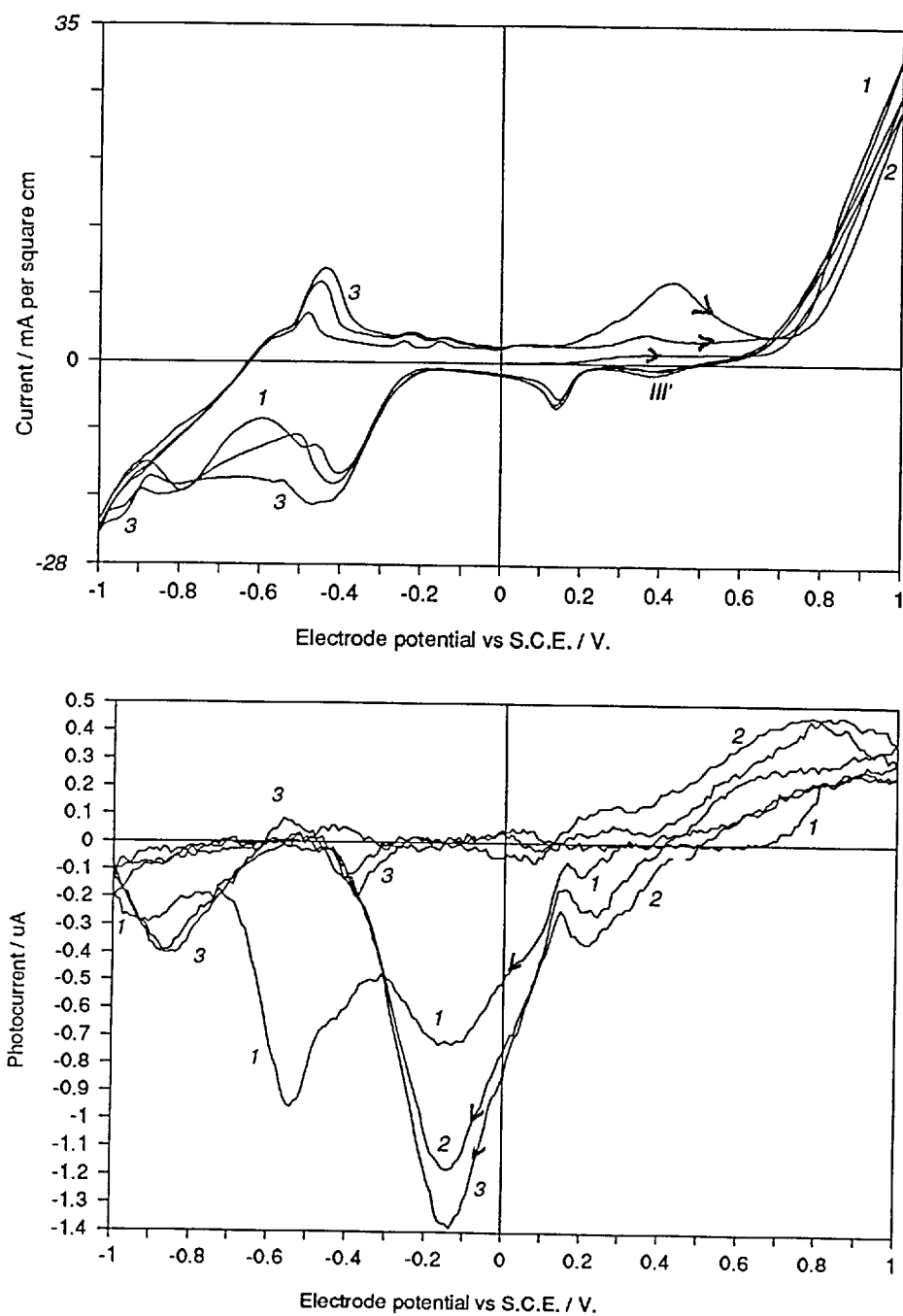


Figure 3.6.7a. Electrode 10. Dark and photo- current responses to a positive potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

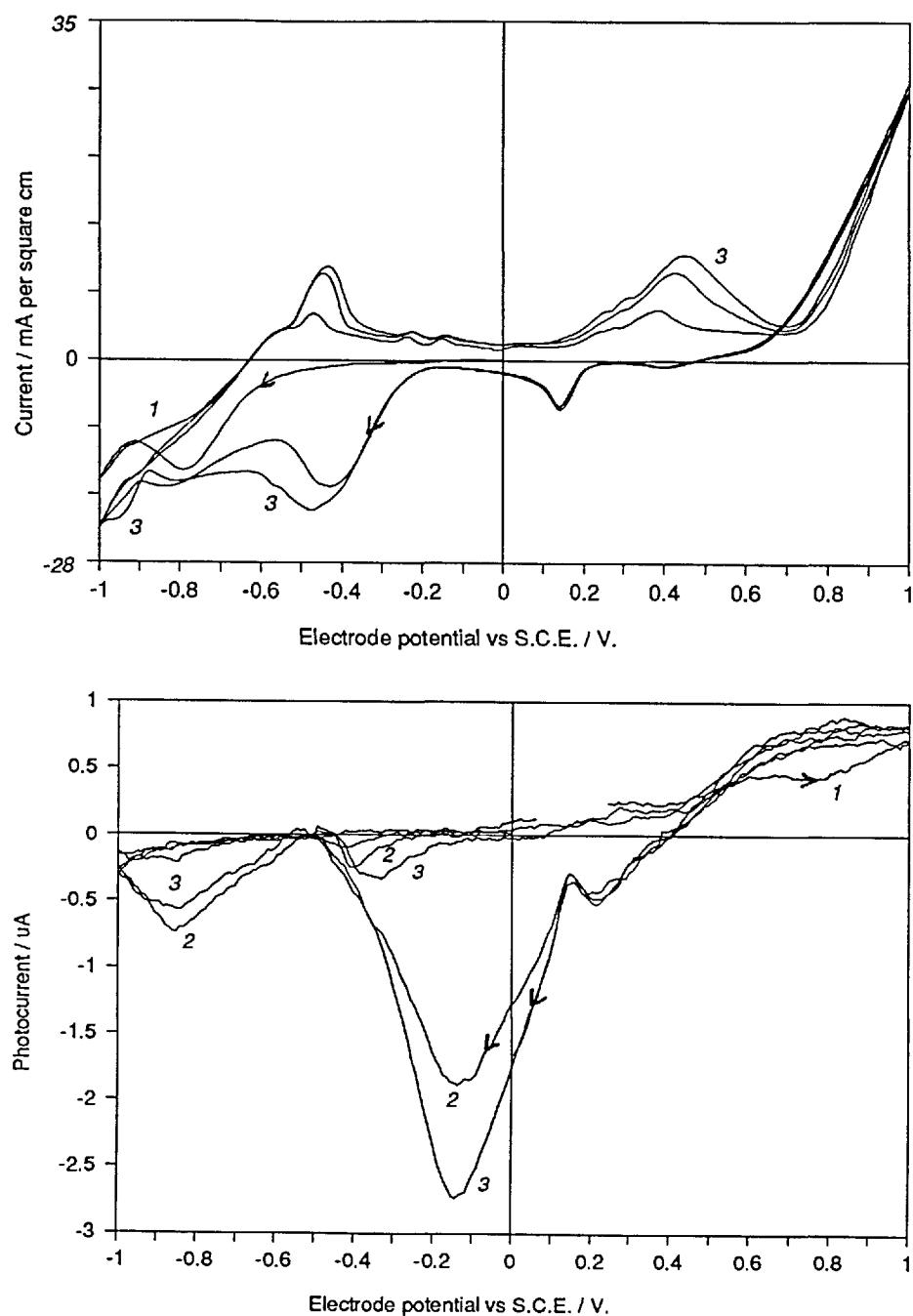


Figure 3.6.7b. Electrode 10. Dark and photo- current responses to a negative potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s⁻¹.

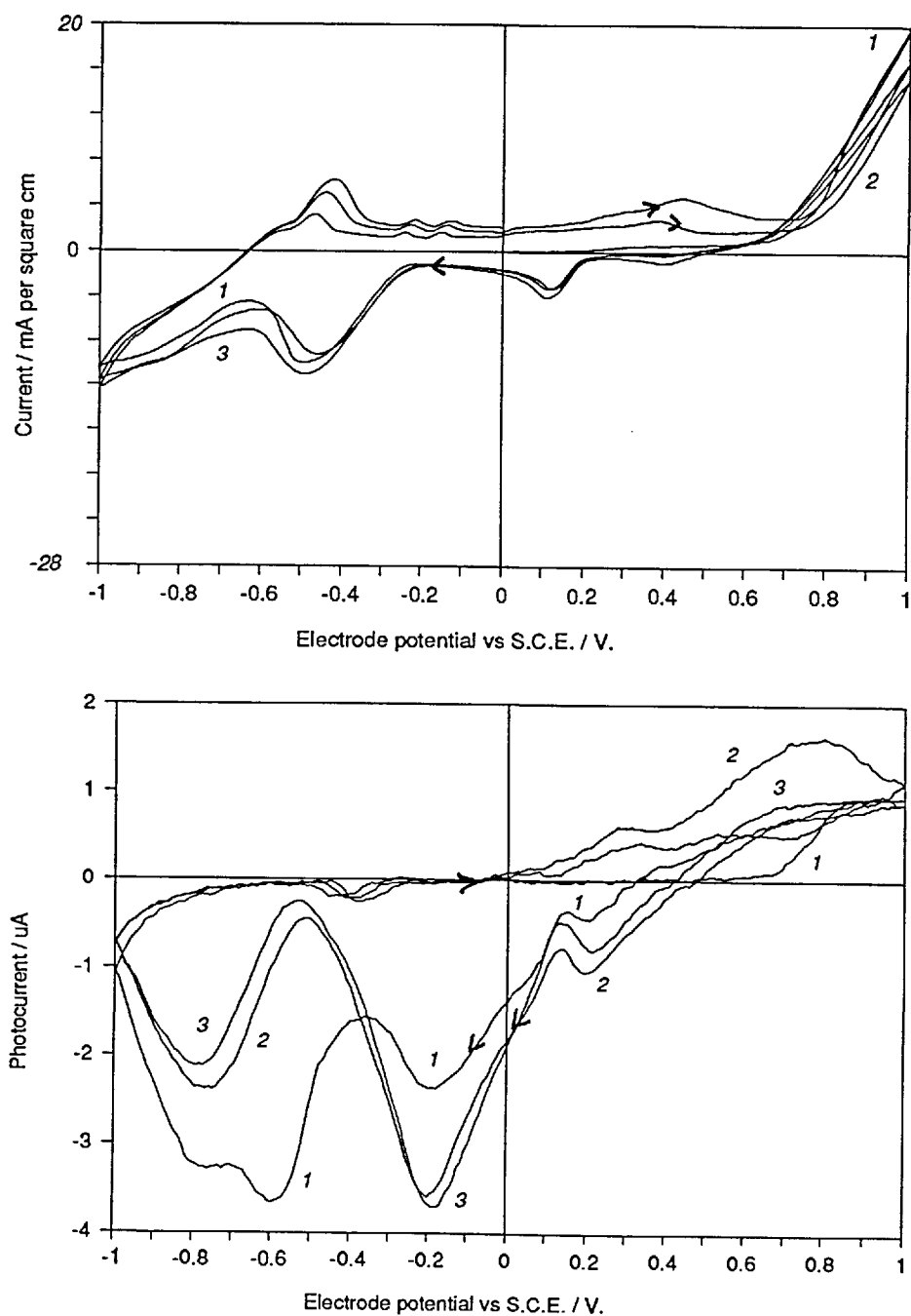


Figure 3.6.8a. Electrode 11. Dark and photo- current responses to a positive potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

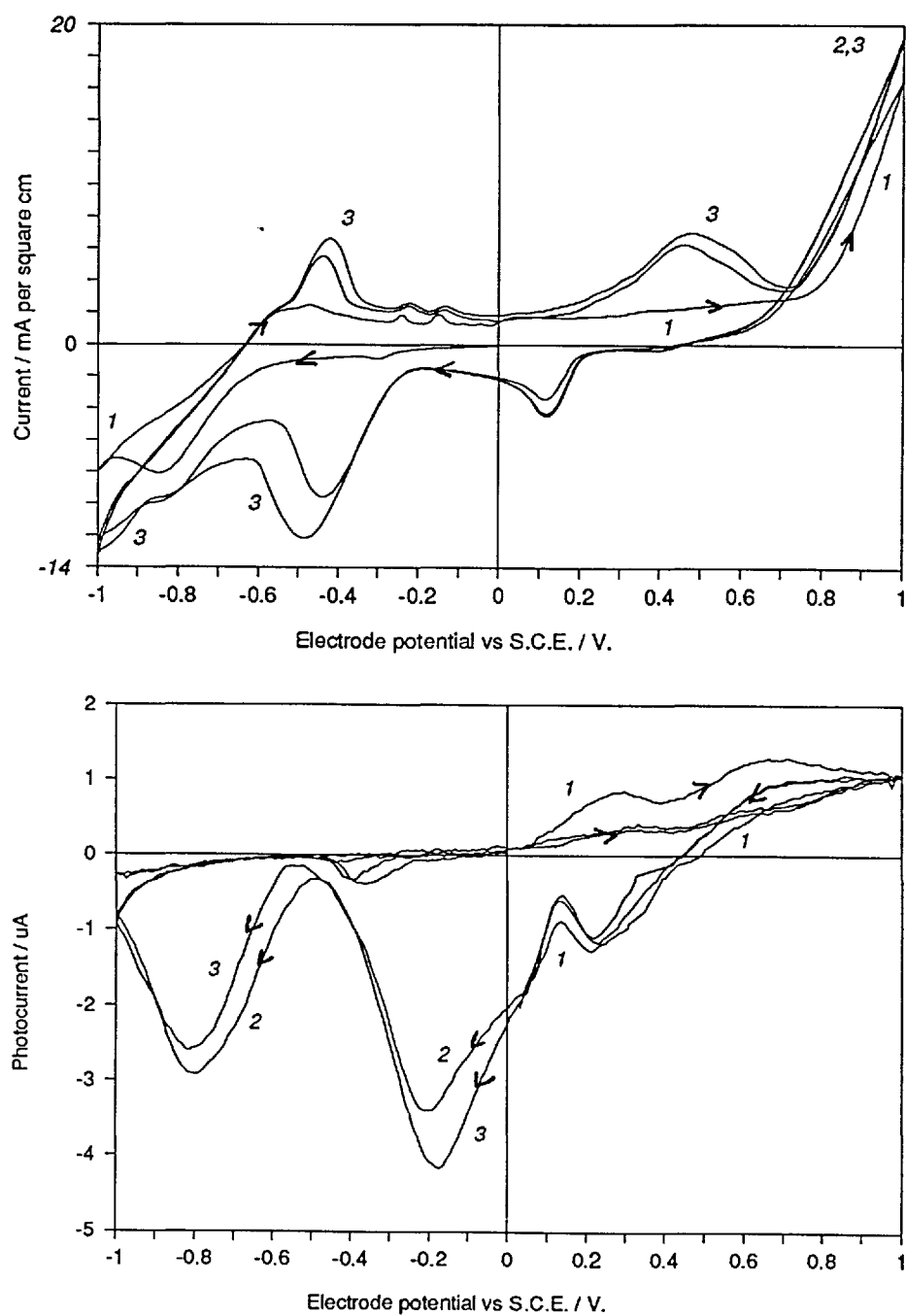


Figure 3.6.8b. Electrode 11. Dark and photo- current responses to a negative potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

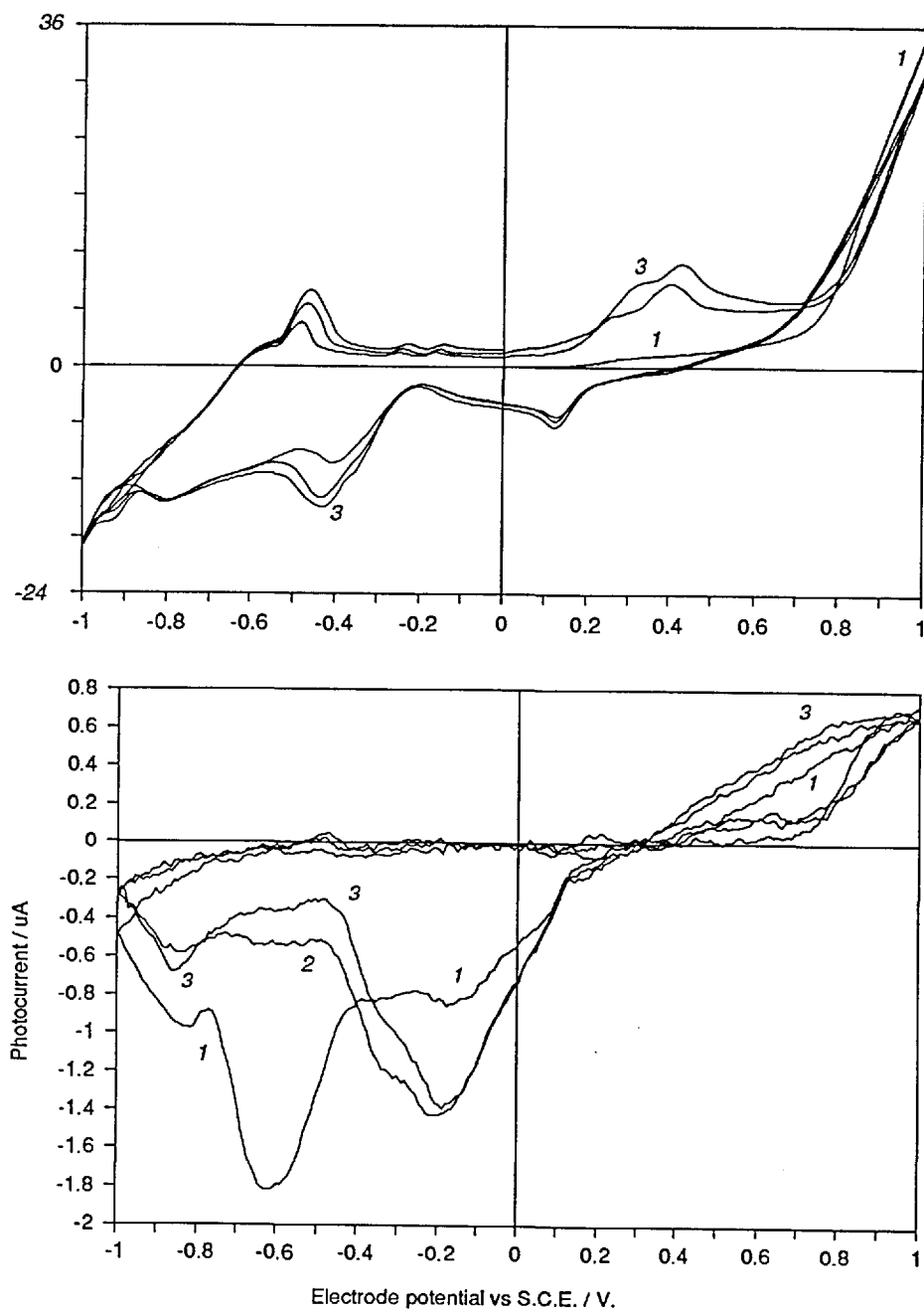


Figure 3.6.9a. Electrode 12. Dark and photo- current responses to a positive potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

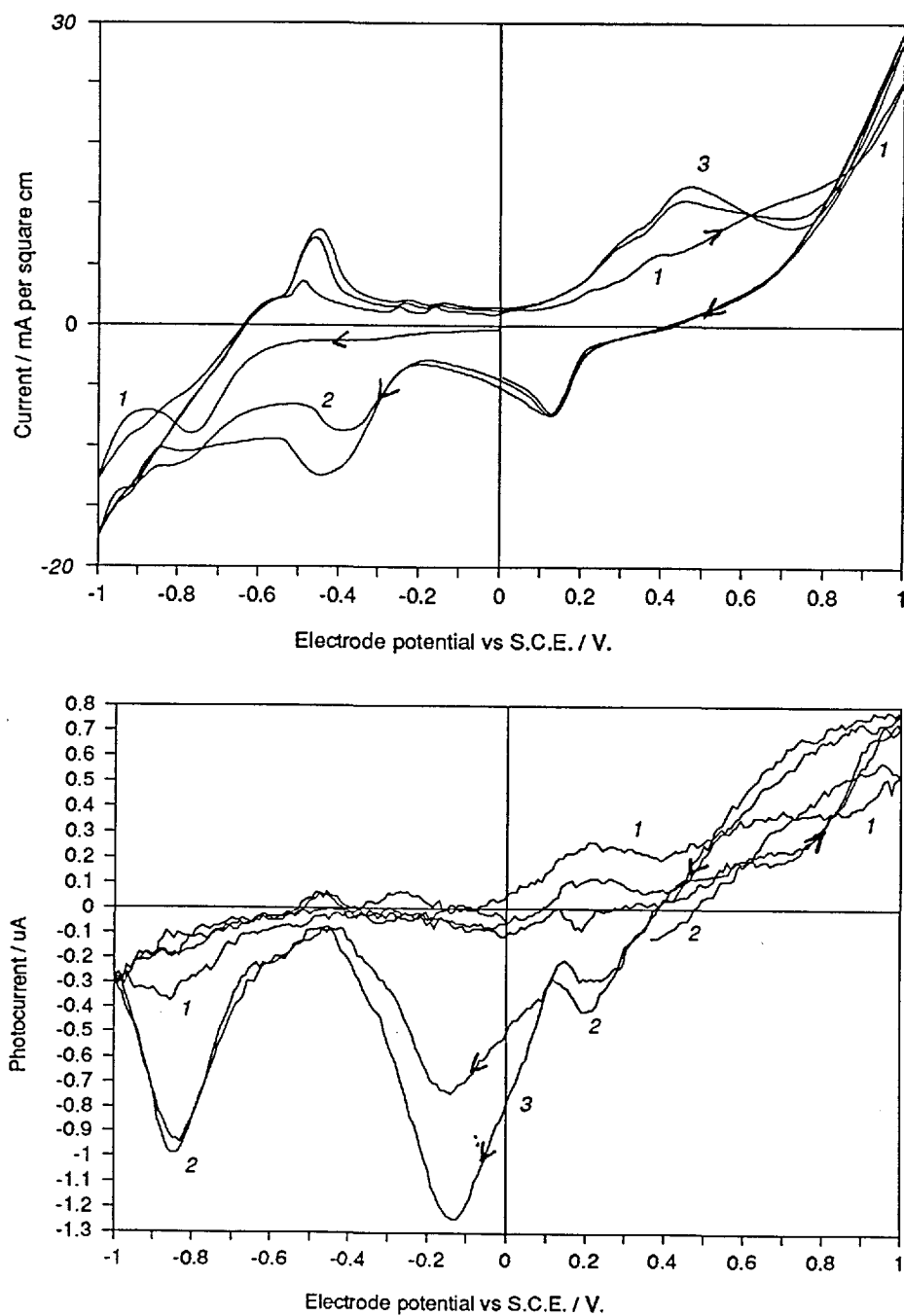


Figure 3.6.9b. Electrode 12. Dark and photo- current responses to a negative potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

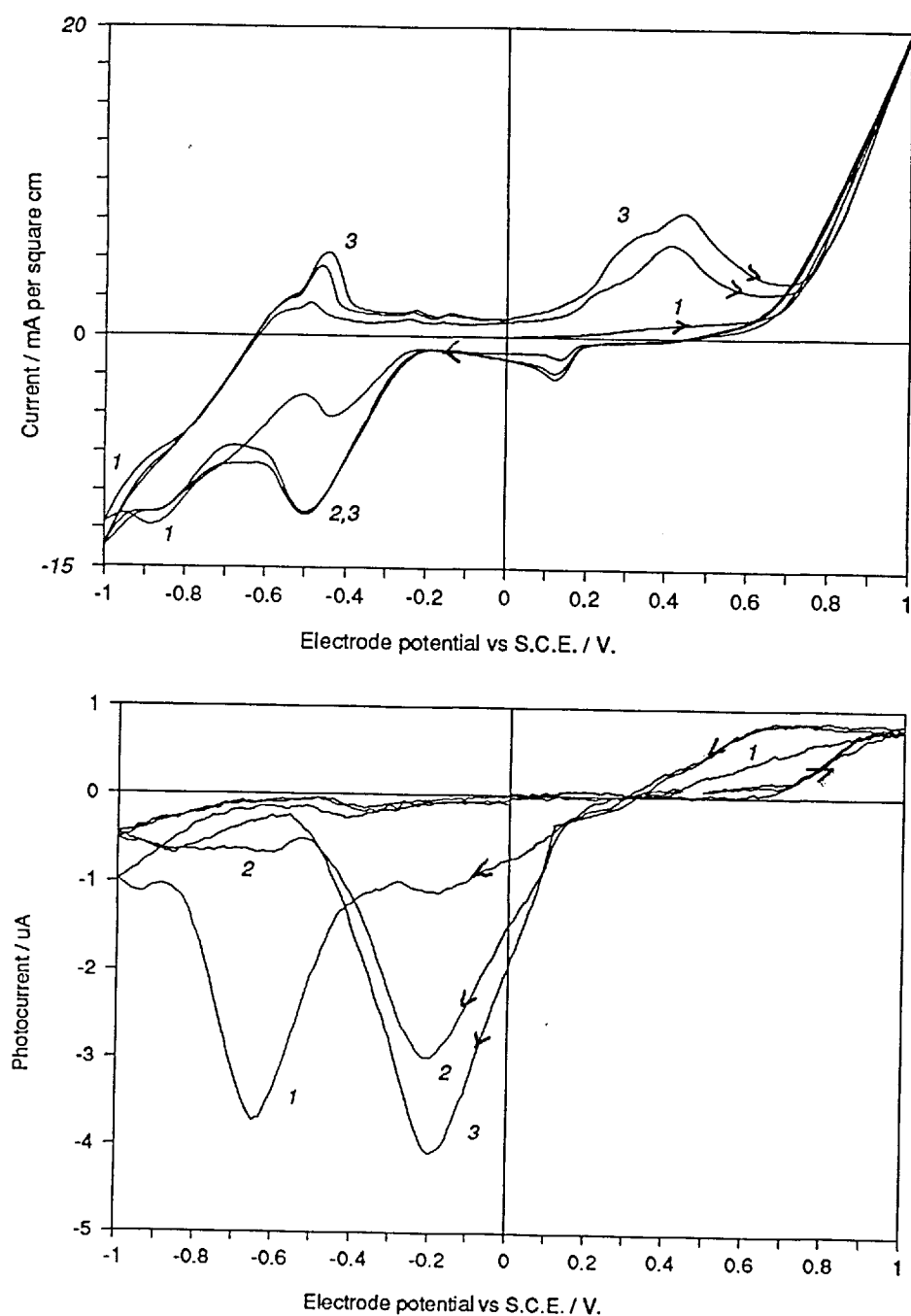


Figure 3.6.10a. Electrode 16. Dark and photo- current responses to a positive potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

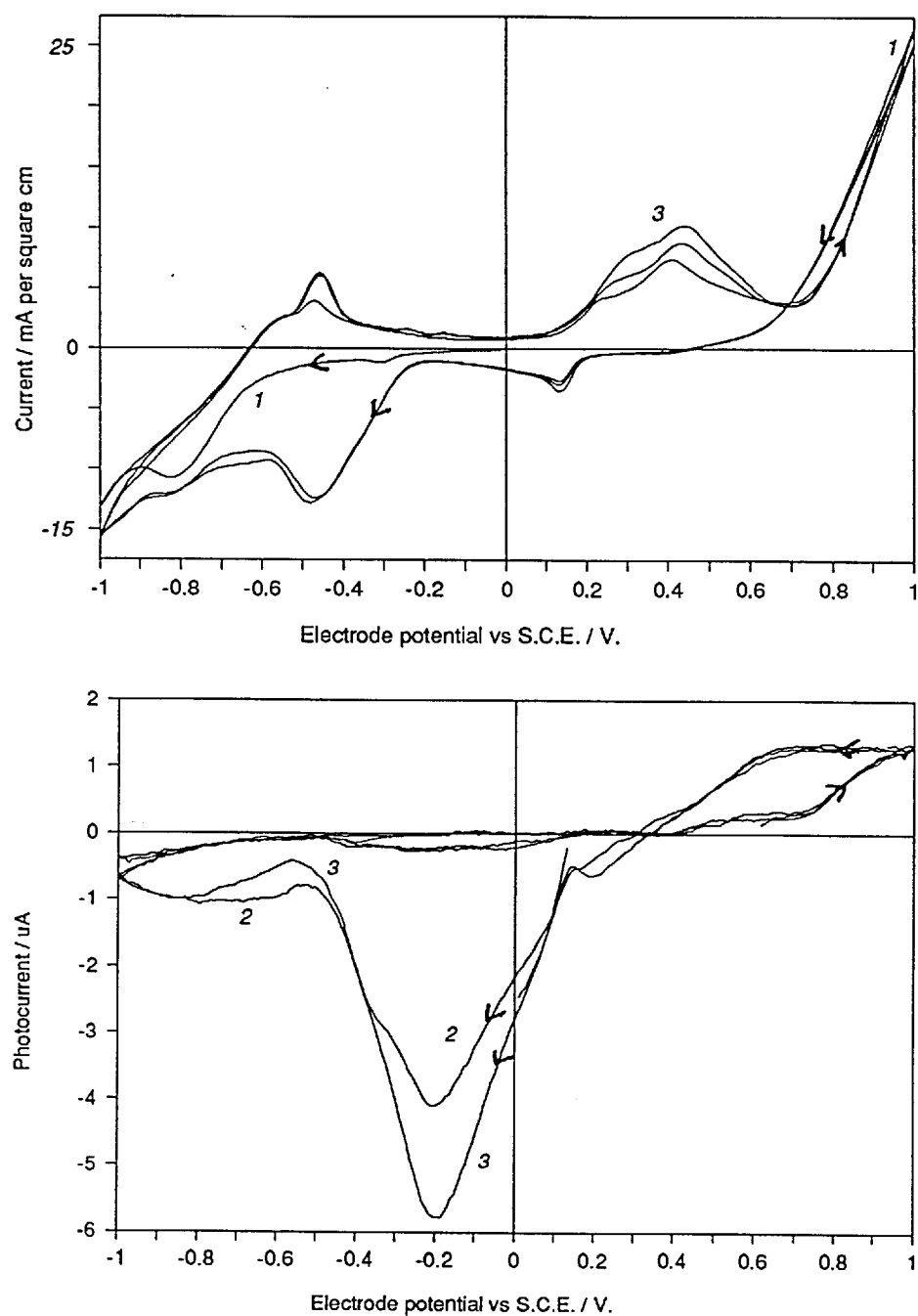


Figure 3.6.10b. Electrode 16. Dark and photo- current responses to a negative potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

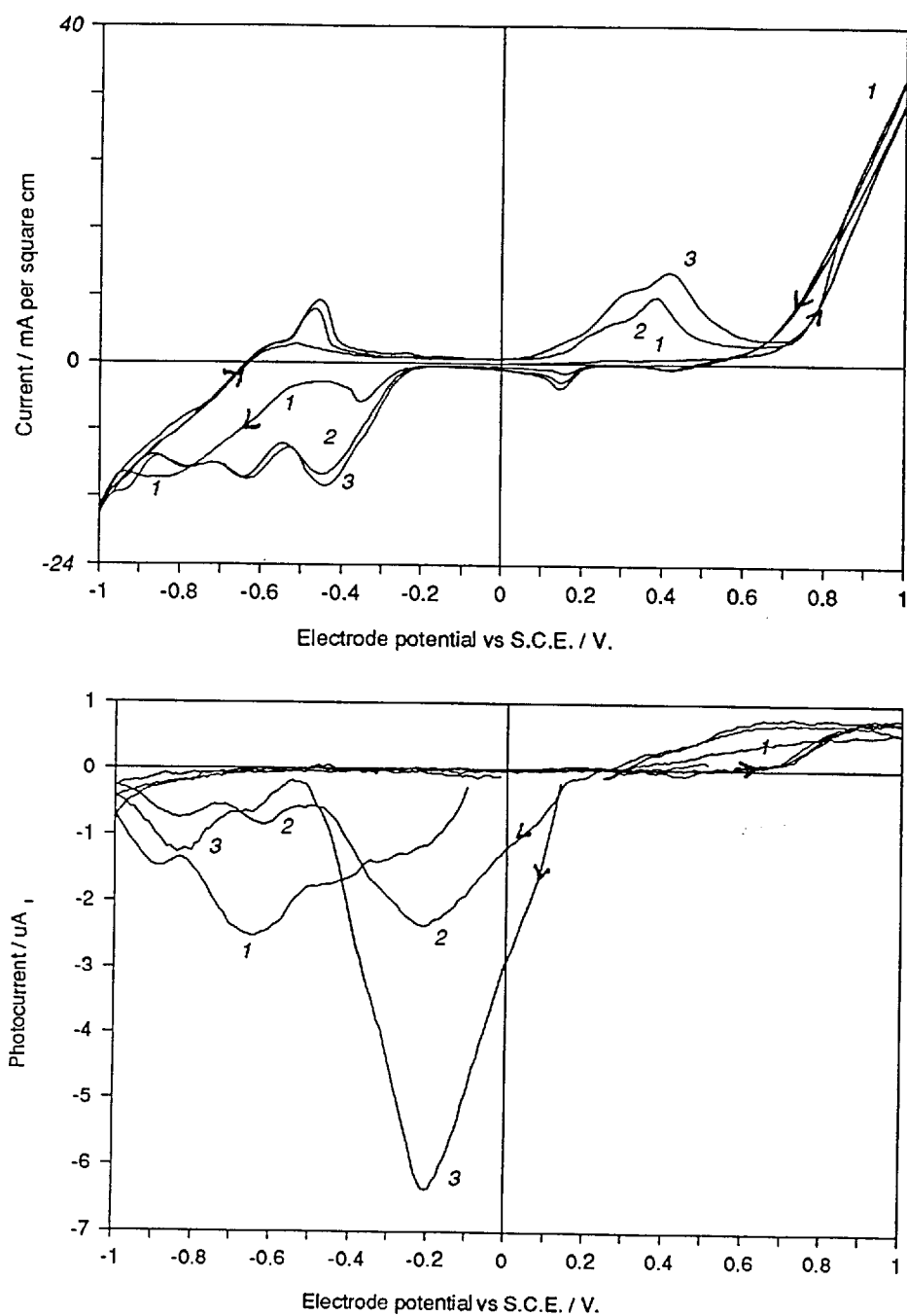


Figure 3.6.11a. Electrode 19. Dark and photo- current responses to a positive potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

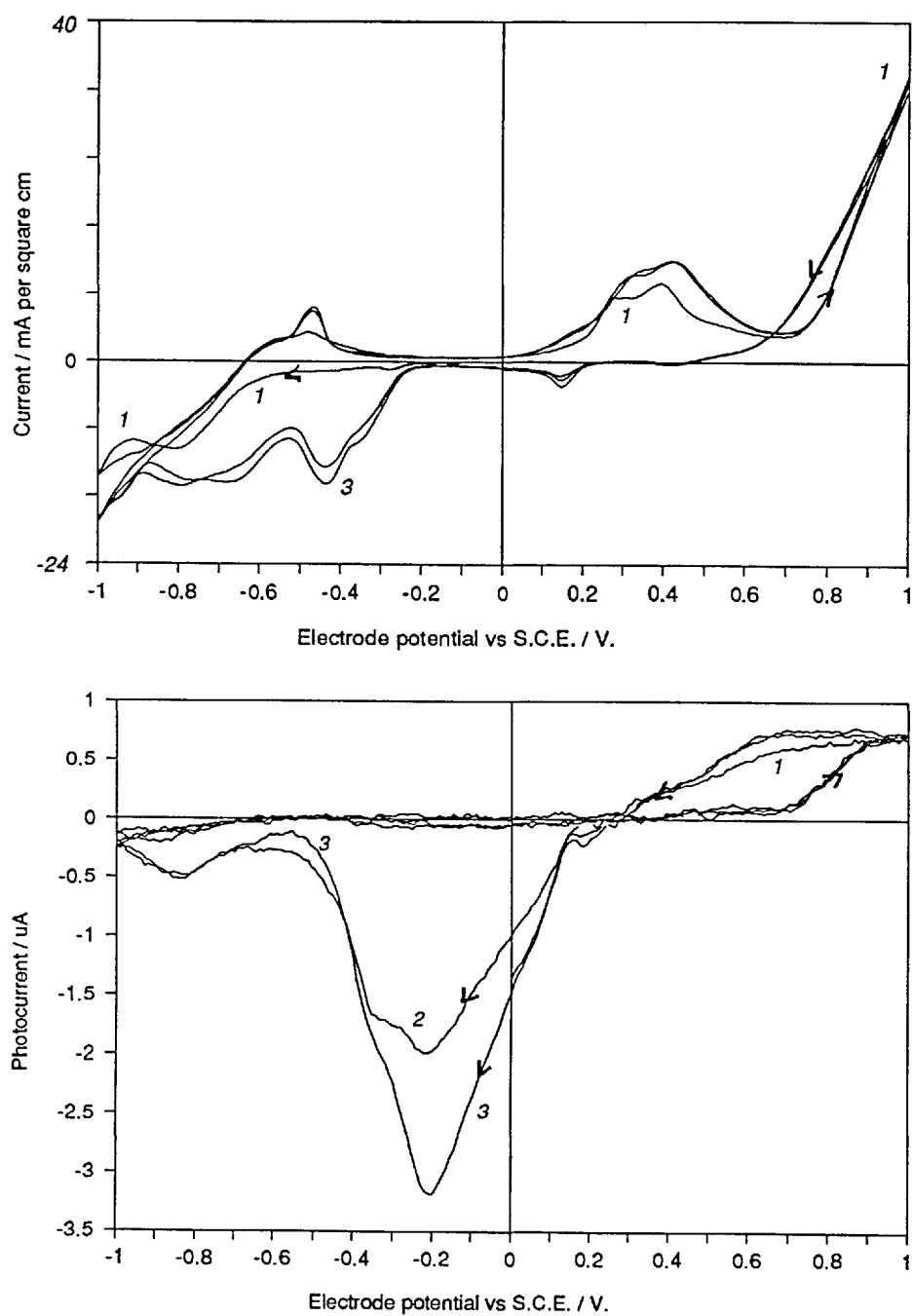


Figure 3.6.11b. Electrode 19. Dark and photo- current responses to a negative potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

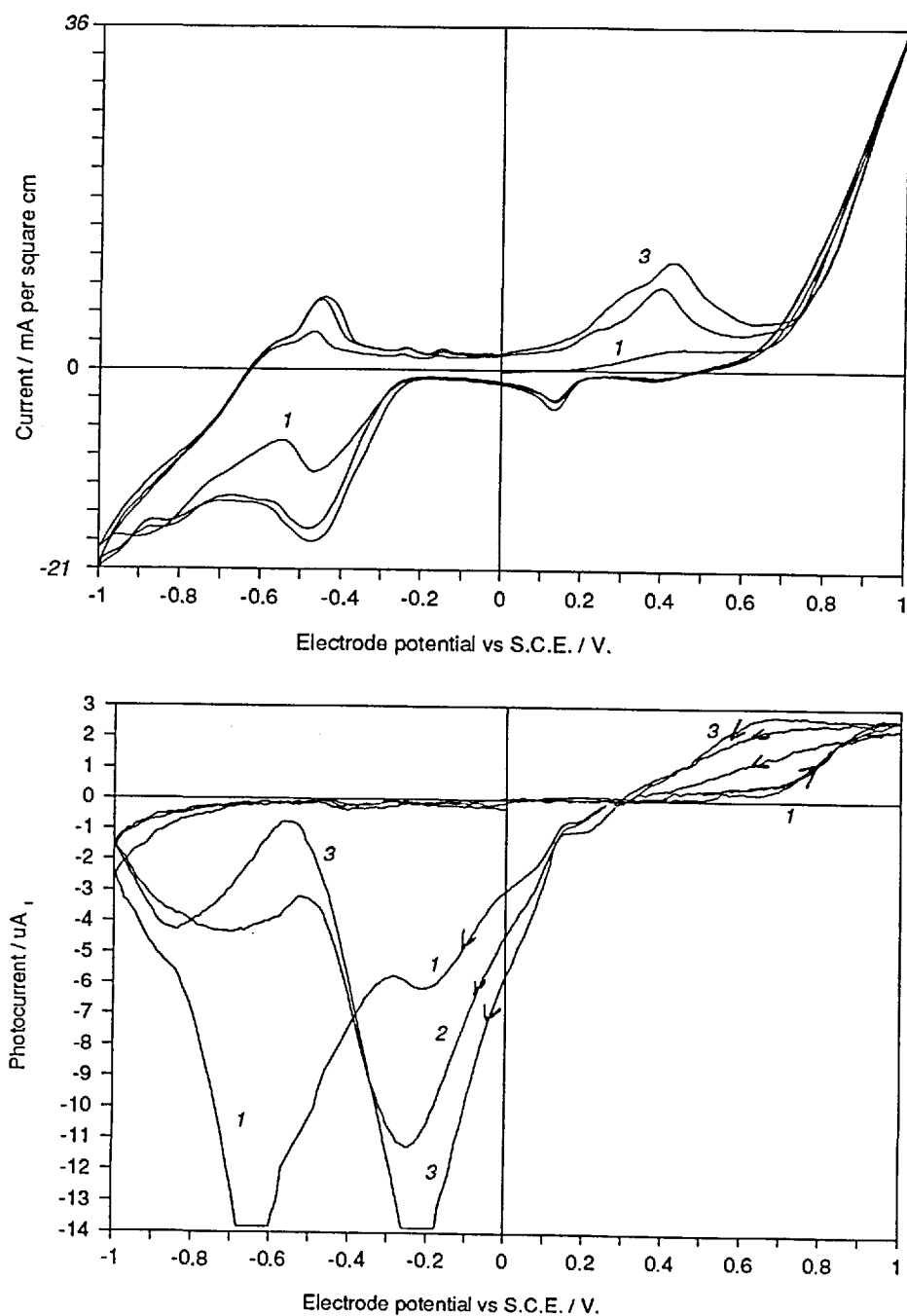


Figure 3.6.12a. Electrode 21. Dark and photo- current responses to a positive potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

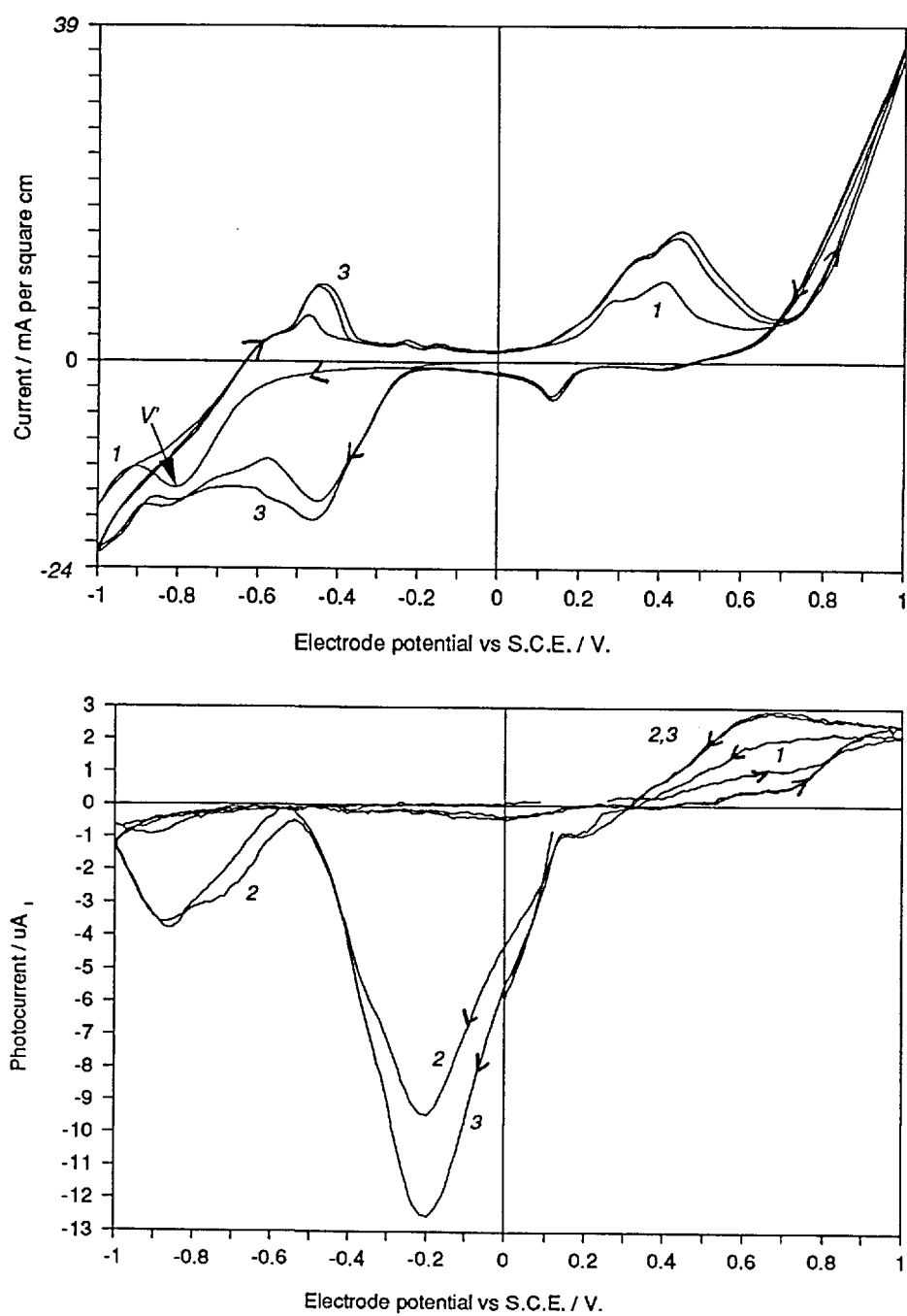


Figure 3.6.12b. Electrode 21. Dark and photo- current responses to a negative potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

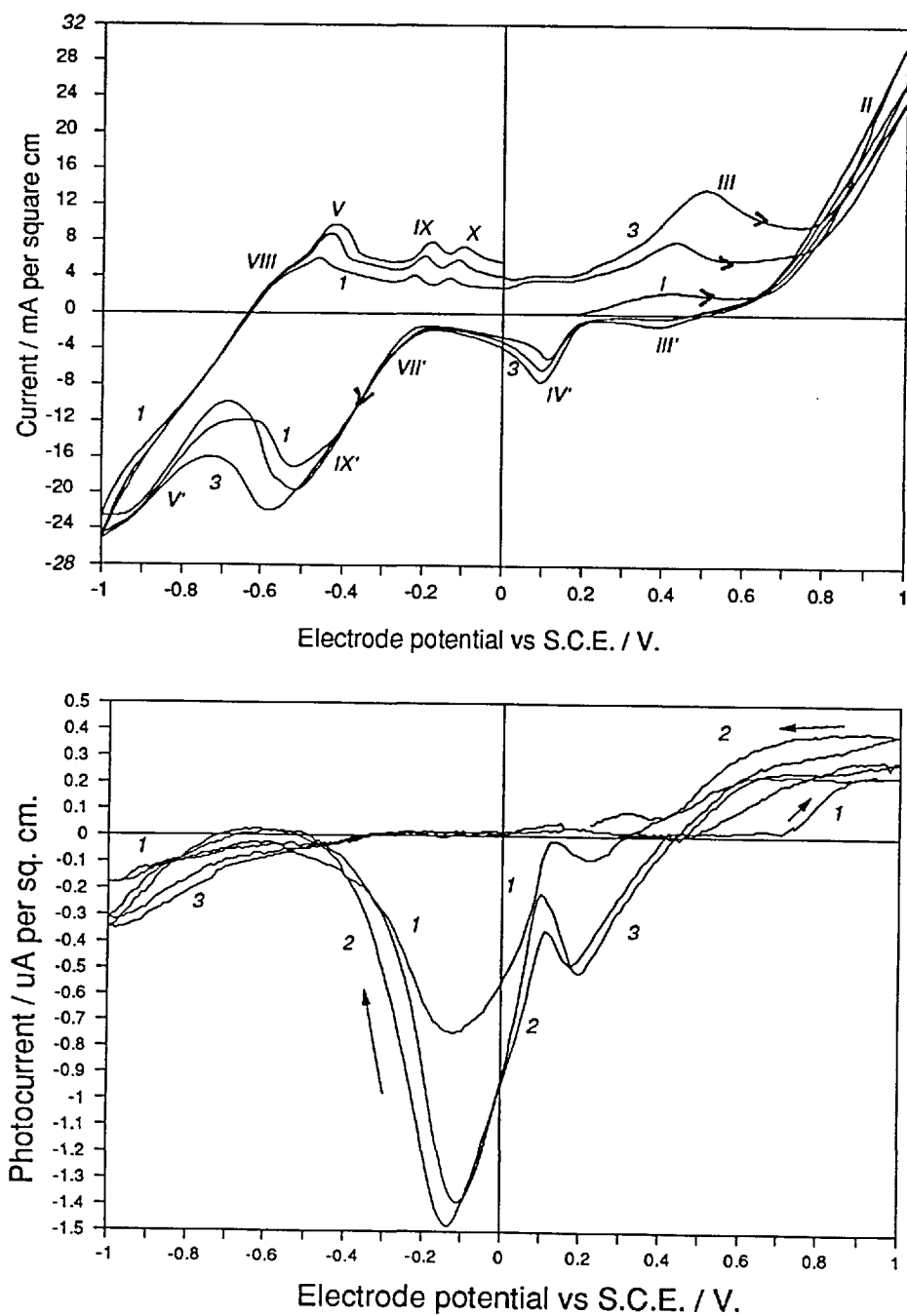


Figure 3.6.13a. Electrode 22. Dark and photo- current responses to a positive potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

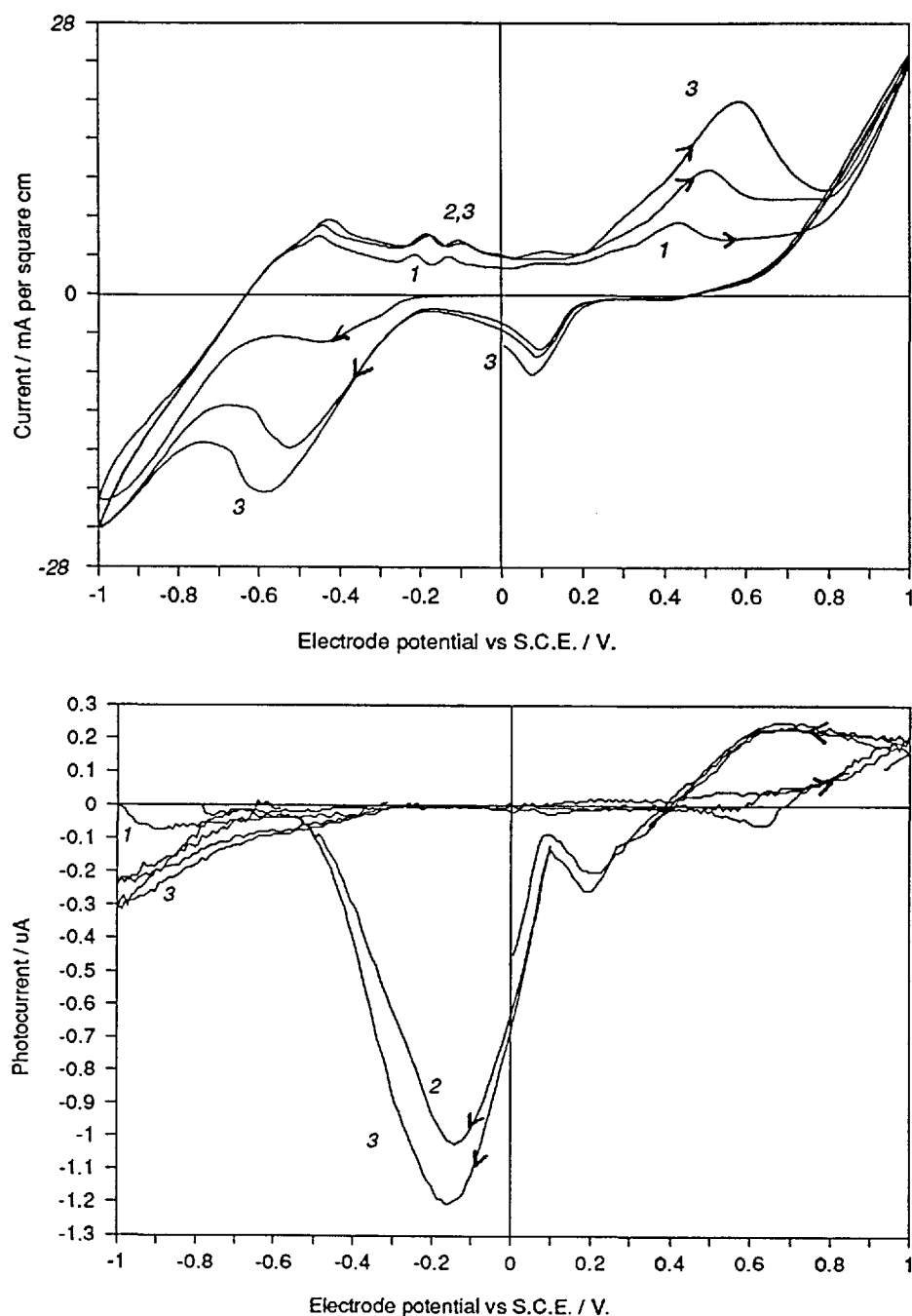


Figure 3.6.13b. Electrode 22. Dark and photo- current responses to a negative potential excursion from 0 V vs. S.C.E. at pH 1. Sweep rate = 50 mV s^{-1} .

3.7. Photocurrent and dark current transients in alkaline solutions.

Cyclic voltammograms recorded in buffer solutions of $0.05 \text{ mol Na}_2\text{B}_4\text{O}_7$ are depicted in the upper graphs of Figures 3.7.1 - 6. All the potential sweeps commenced at -0.2 V . Electrodes in alkali were subject to much less oxidative corrosion, enabling a much slower potential sweep rate of 5 mVs^{-1} to be used without the electrodes being destroyed.

Thus, kinetically limited currents and photocurrents appeared over a narrower potential range than in Figure 3.7.6 and peaks in Figure 3.7.7 are sharper. Again, identical experiments had been carried out using less sophisticated equipment, but voltammograms in alkali were to prove more reproducible: it may even be said that each mineral sample is fingerprinted by this voltammetry. Thus Electrode 9b showed exceptional but characteristic peaks on initial negative going potential scans (Figure 3.7.4). Trends dependent on pH and sweep rate are reported in the following chapter.

The photo-voltammograms shown in these figures illustrate quite a different response to those at pH 1, but they are equally consistent. Despite the slow sweep rate, there was a broad rise and decay in photoanodic current (at potentials > 0.25 V) that increased following a negative going potential excursion. On the second negative going excursion following a positive excursion from -0.2 V, (e.g. bottom left, Figure 3.7.3), the decrease in $i(\text{ph})$ continued unabated to negative values, which suggests that the surface phase responsible had a flat band potential, V_{fb} corresponding to the potential of zero current flow, i_e between 0.25 V and 0.38 V. It will be seen in Chapter 6 that the phase responsible was only reduced at potentials < 0 V.

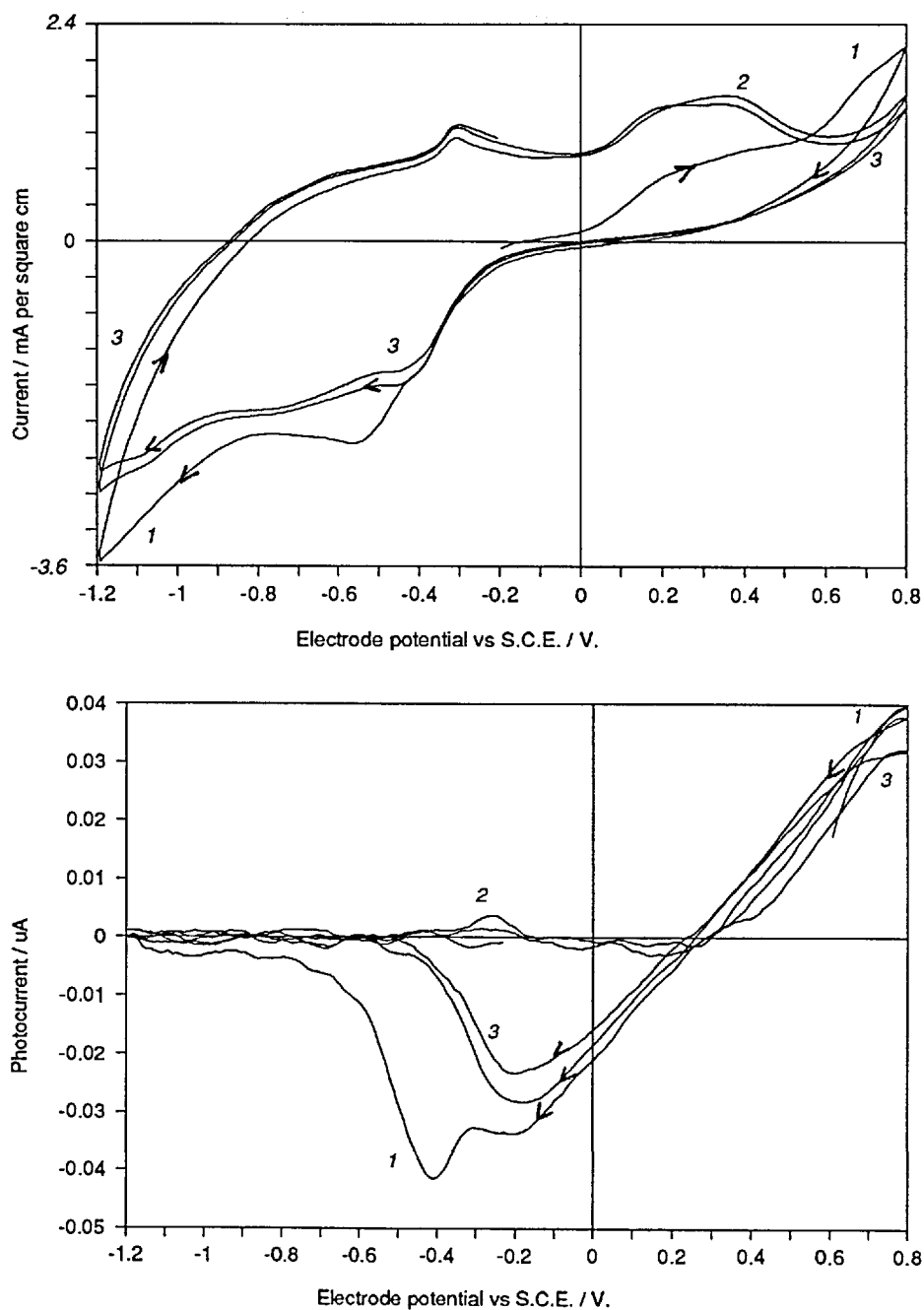


Figure 3.7.1a. Electrode 22. Dark and photo- current responses to a positive potential excursion from -0.2 V vs. S.C.E. at pH 9.2. Sweep rate = 50 mV s^{-1}

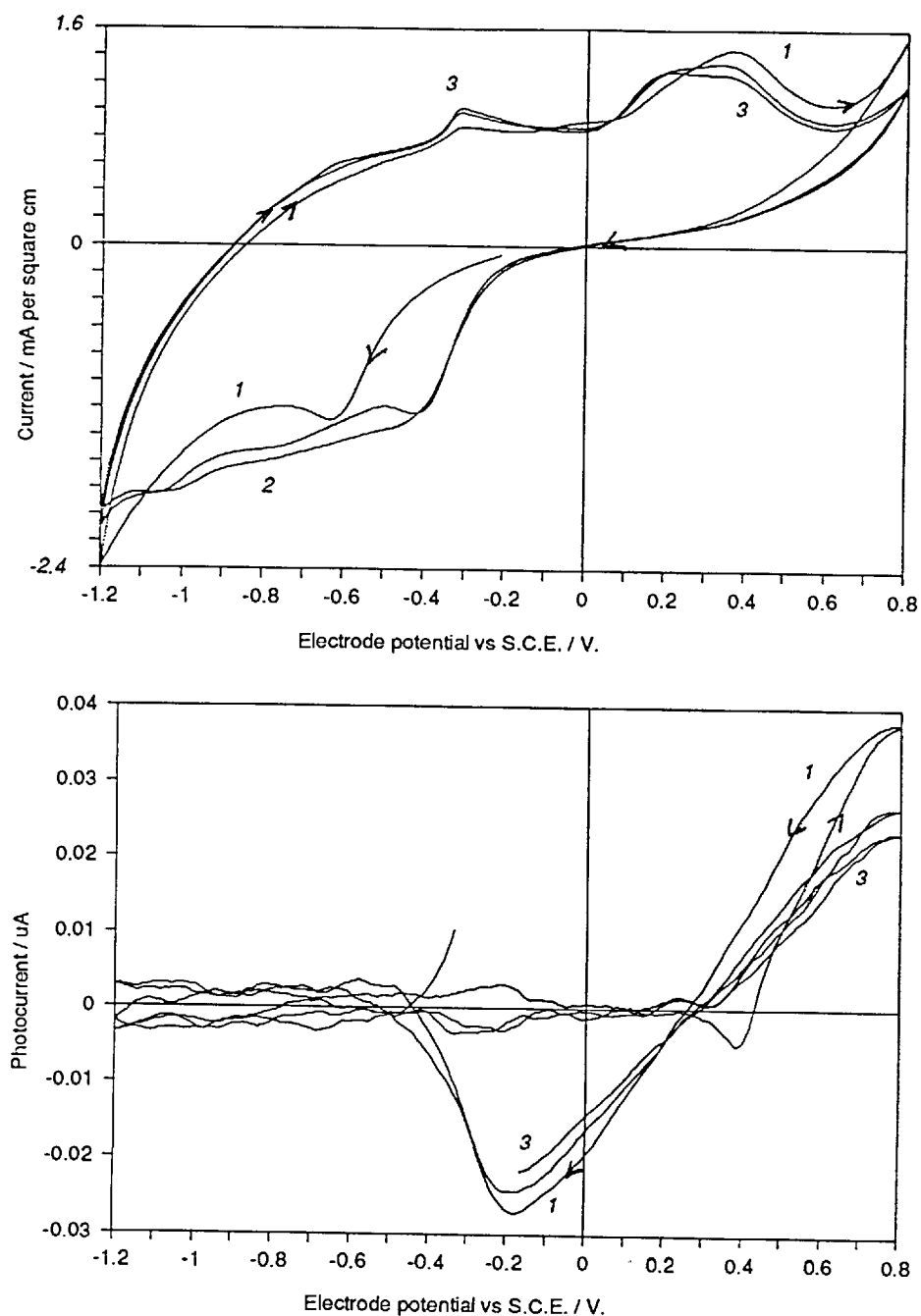


Figure 3.7.1b. Electrode 22. Dark and photo- current responses to a negative potential excursion from -0.2 V vs. S.C.E. at pH 9.2. Sweep rate = 50 mV s^{-1}

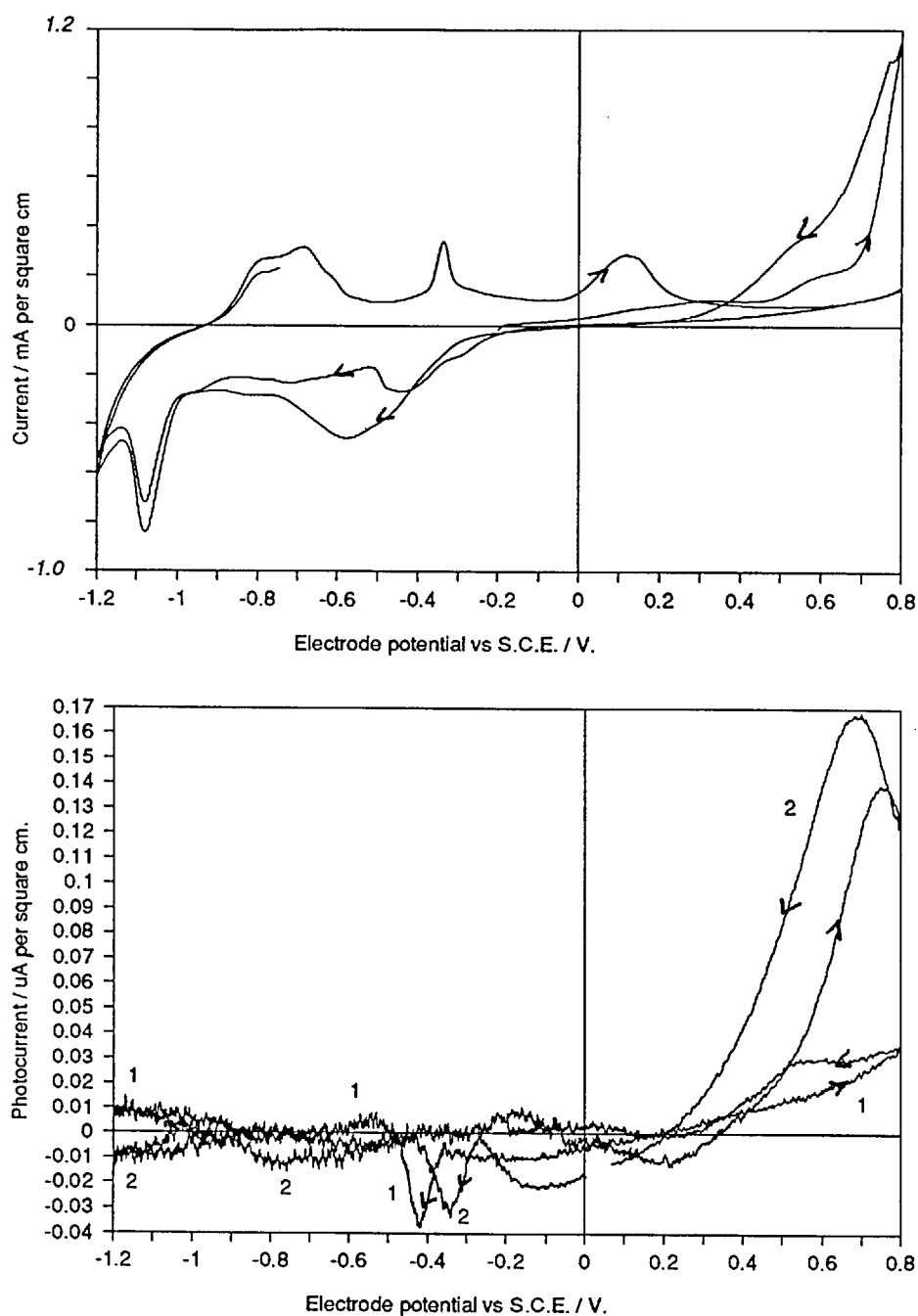


Figure 3.7.2a. Electrode 22. Dark and photo- current responses to a positive potential excursion from -0.2 V vs. S.C.E. at pH 9.2. Sweep rate = 5 mV s⁻¹.

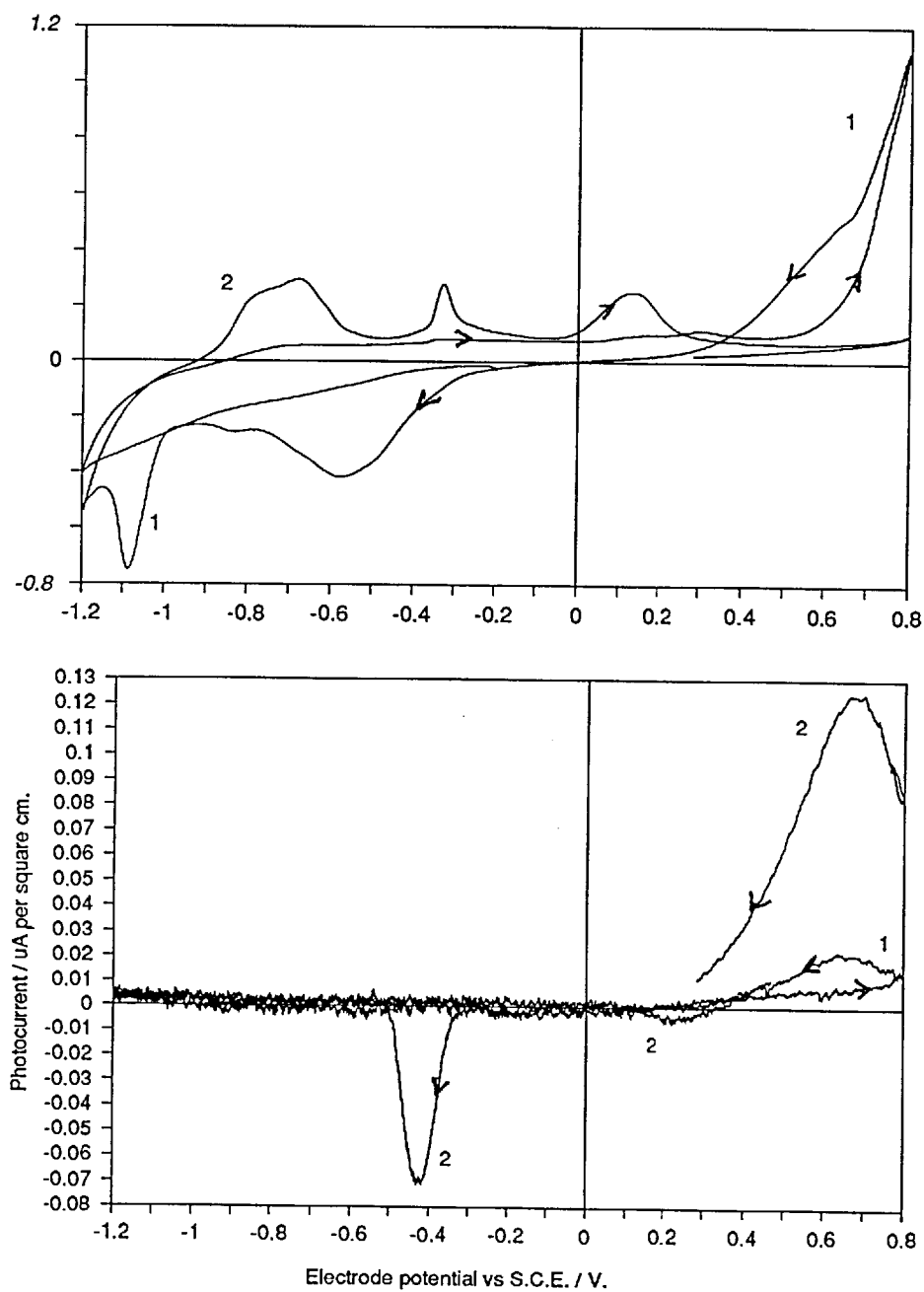


Figure 3.7.2b. Electrode 22. Dark and photo- current responses to a negative potential excursion from -0.2 V vs. S.C.E. at pH 9.2. Sweep rate = 5 mV s^{-1} .

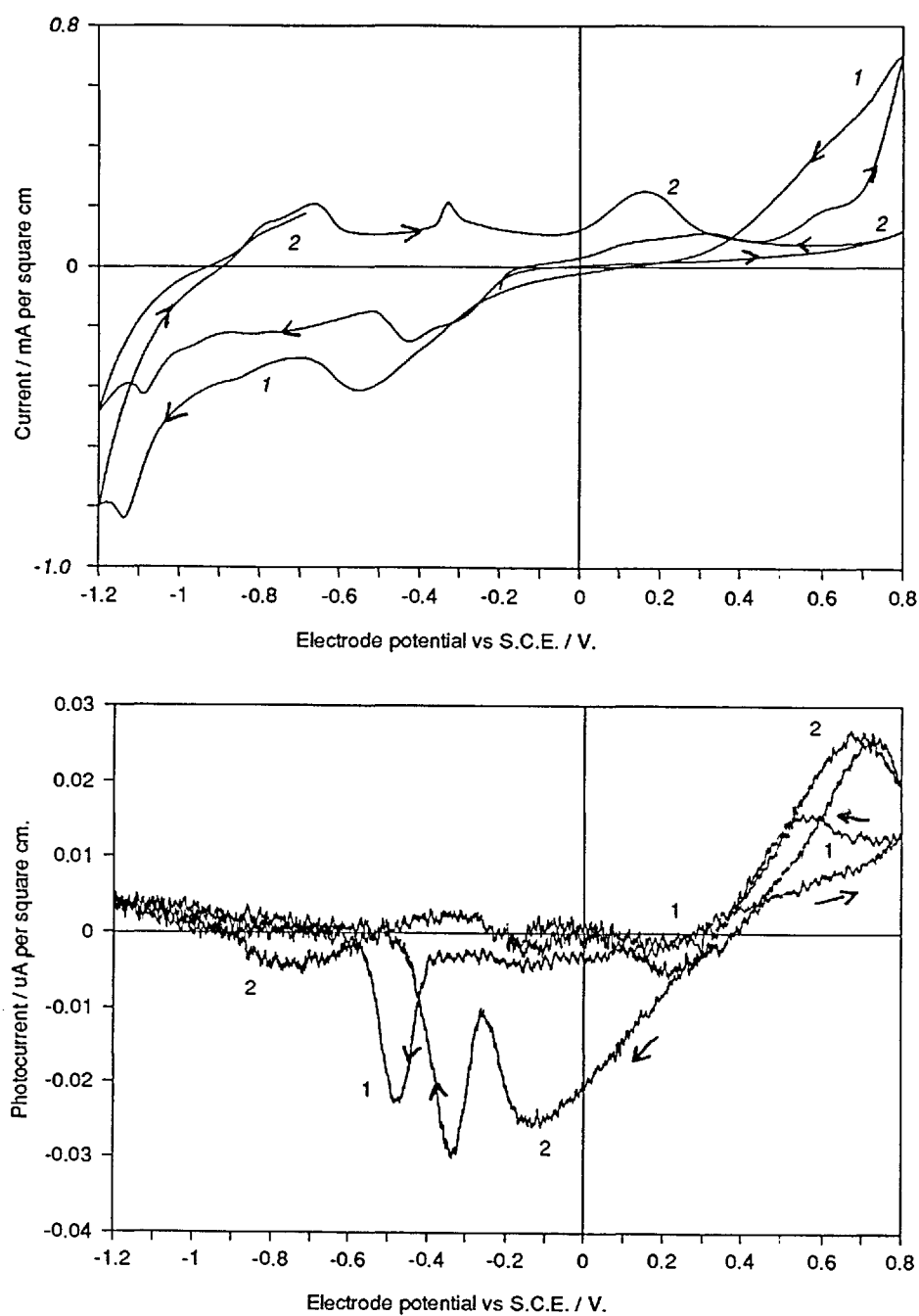


Figure 3.7.3a. Electrode 6. Dark and photo- current responses to a positive potential excursion from -0.2 V vs. S.C.E. at pH 9.2. Sweep rate = 5 mV s^{-1} .

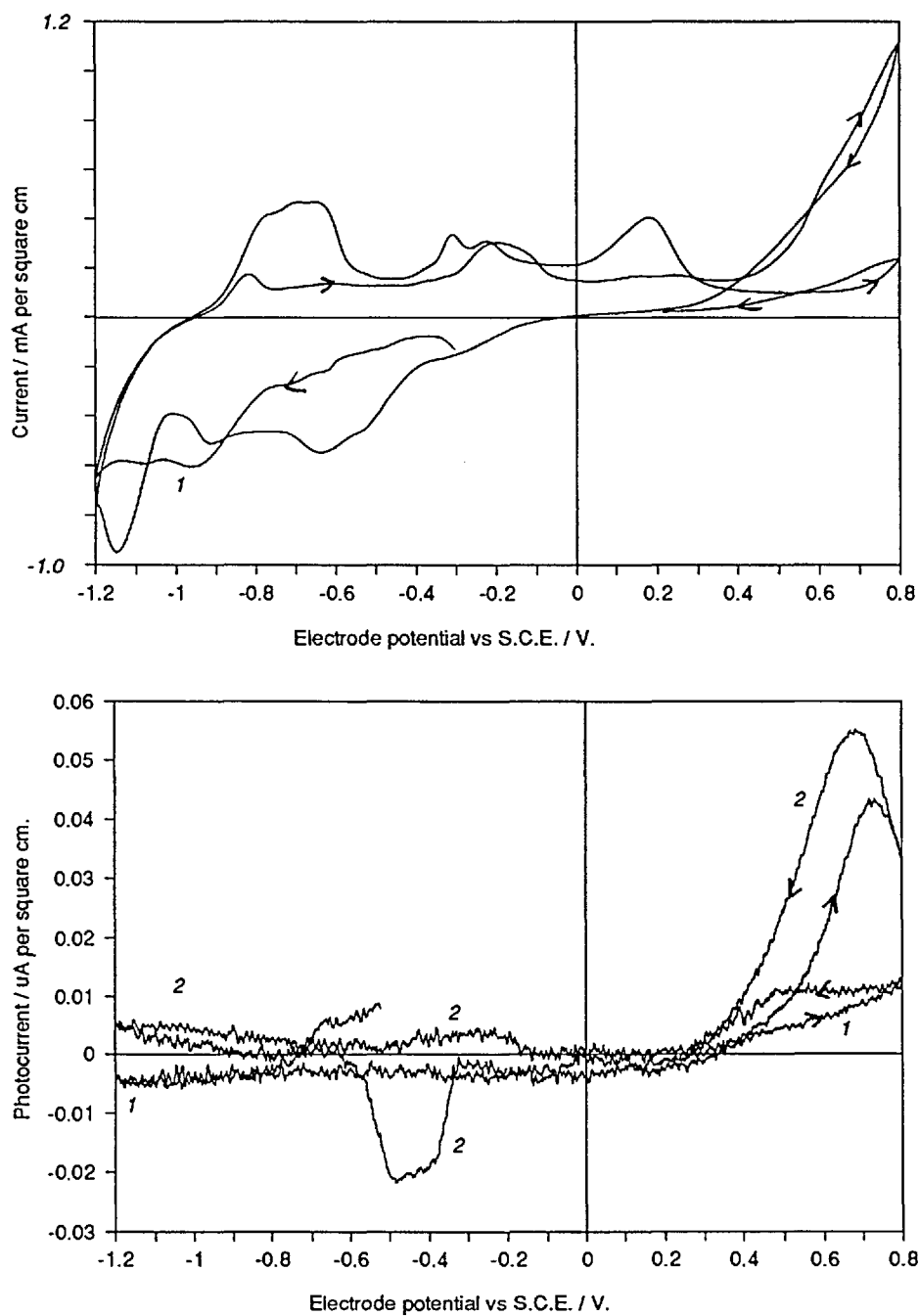


Figure 3.7.3b. Electrode 6. Dark and photo- current responses to a negative potential excursion from -0.2 V vs. S.C.E. at pH 9.2. Sweep rate = 5 mV s^{-1} .

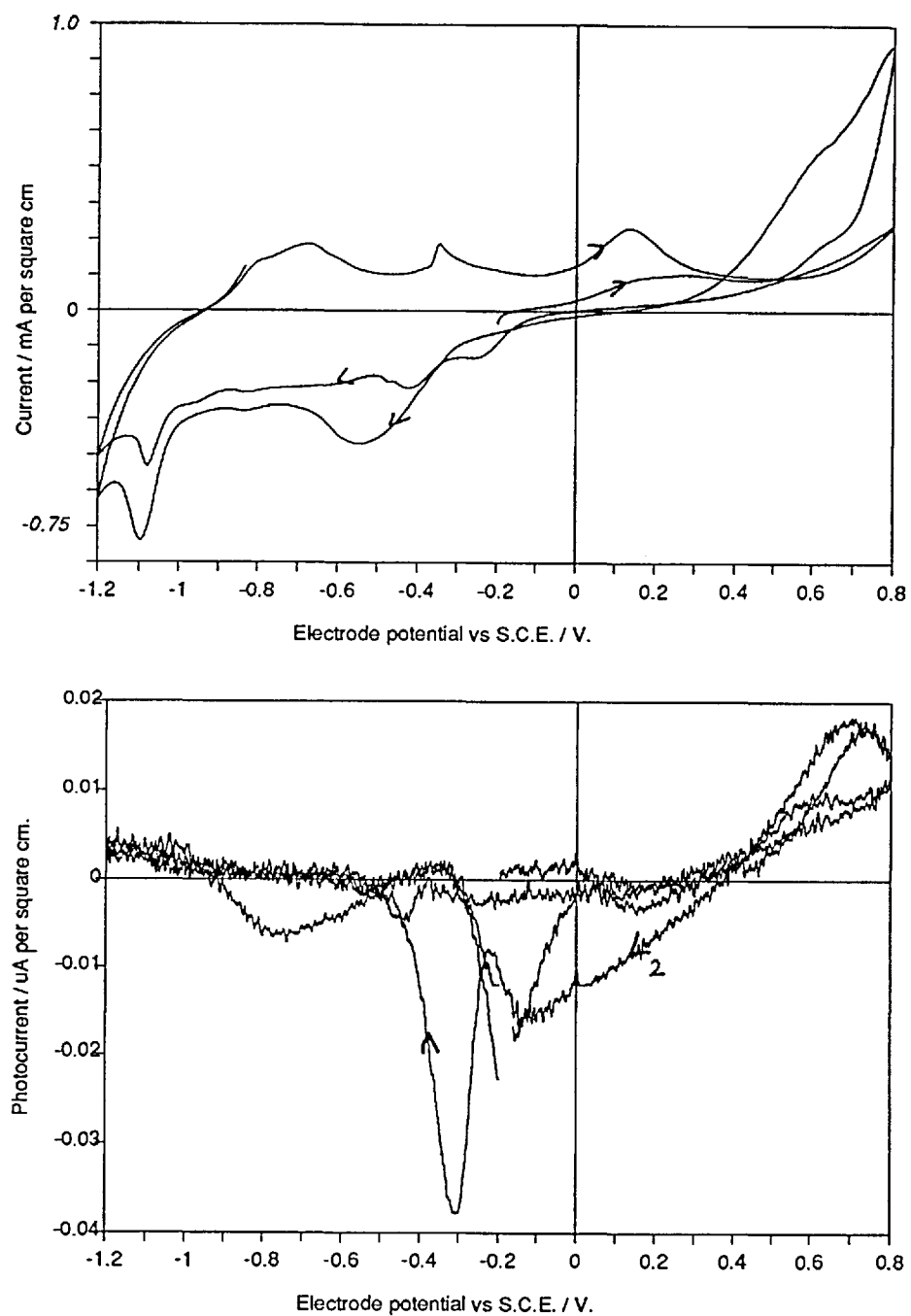


Figure 3.7.4a. Electrode 9b. Dark and photo- current responses to a positive potential excursion from -0.2 V vs. S.C.E. at pH 9.2. Sweep rate = 5 mV s^{-1} .

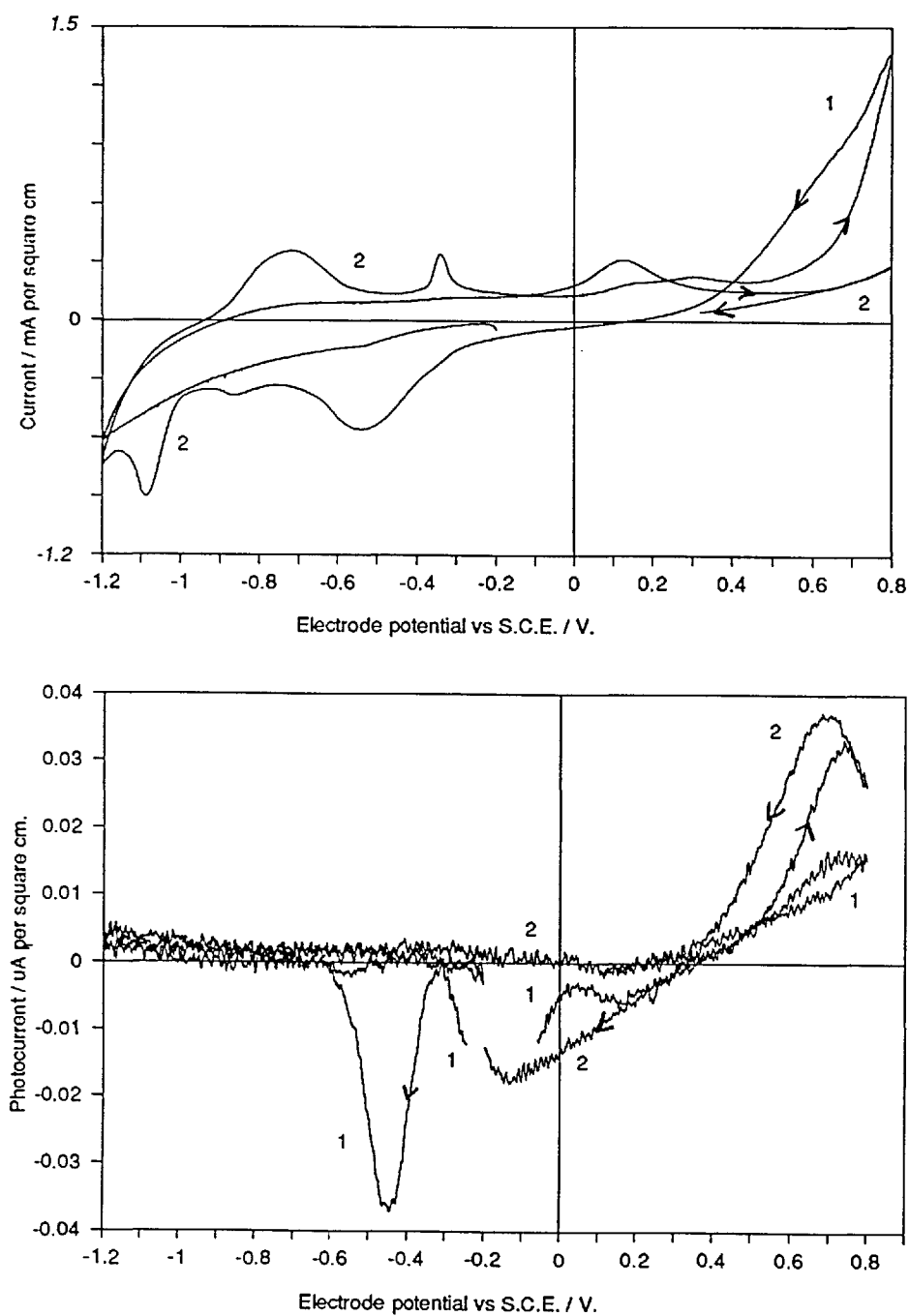


Figure 3.7.4b. Electrode 9b. Dark and photo- current responses to a negative potential excursion from -0.2 V vs. S.C.E. at pH 9.2. Sweep rate = 5 mV s^{-1} .

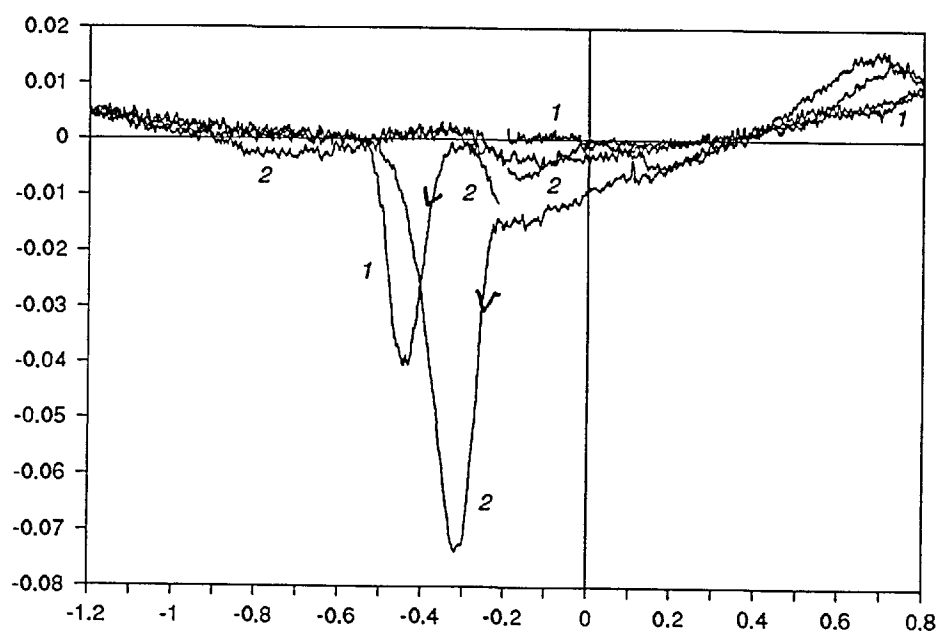
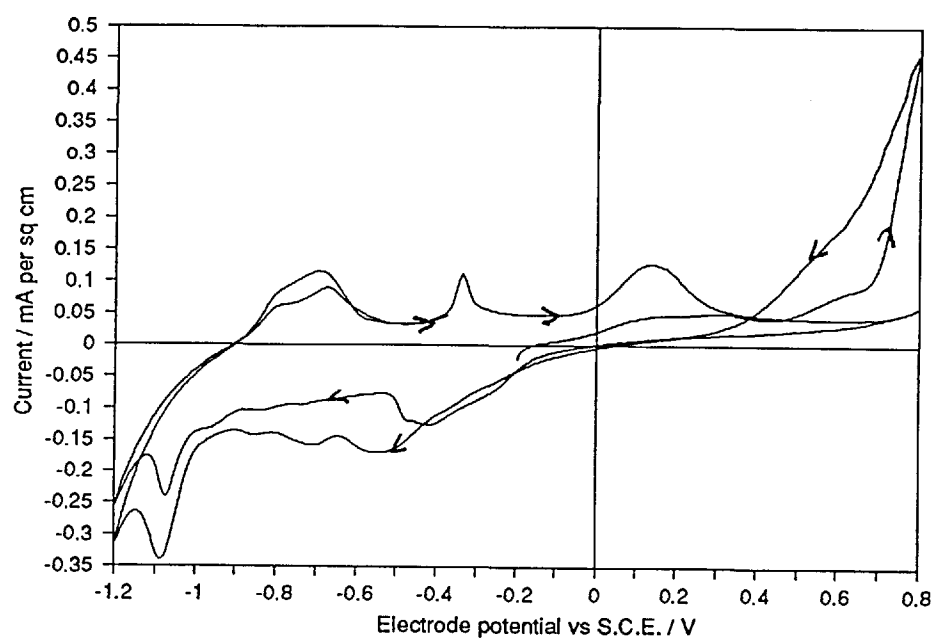


Figure 3.7.5a. Electrode 12. Dark and photo- current responses to a positive potential excursion from -0.2 V vs. S.C.E. at pH 9.2. Sweep rate = 5 mV s^{-1} .

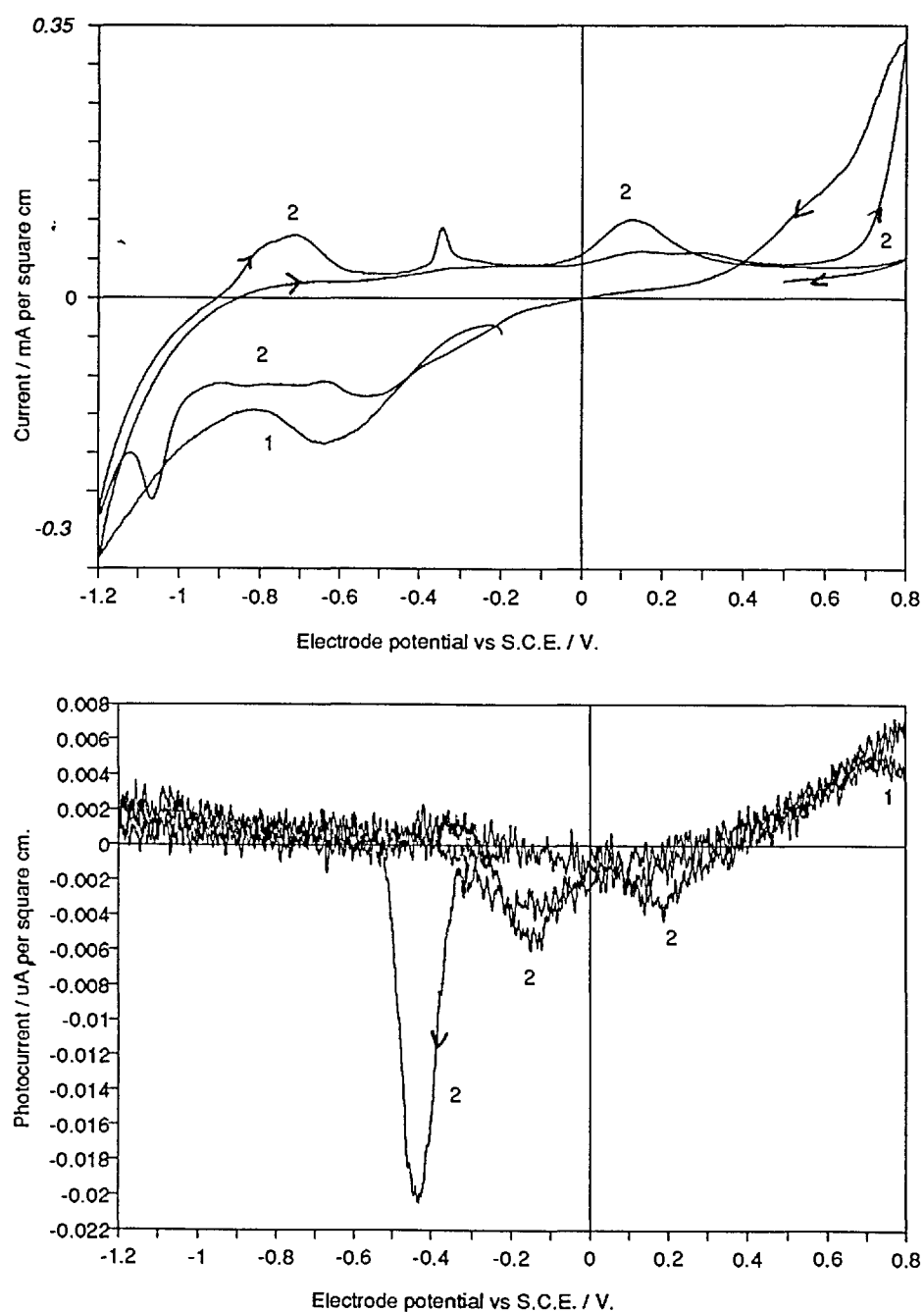


Figure 3.7.5b. Electrode 12. Dark and photo- current responses to a negative potential excursion from -0.2 V vs. S.C.E. at pH 9.2. Sweep rate = 5 mV s^{-1} .

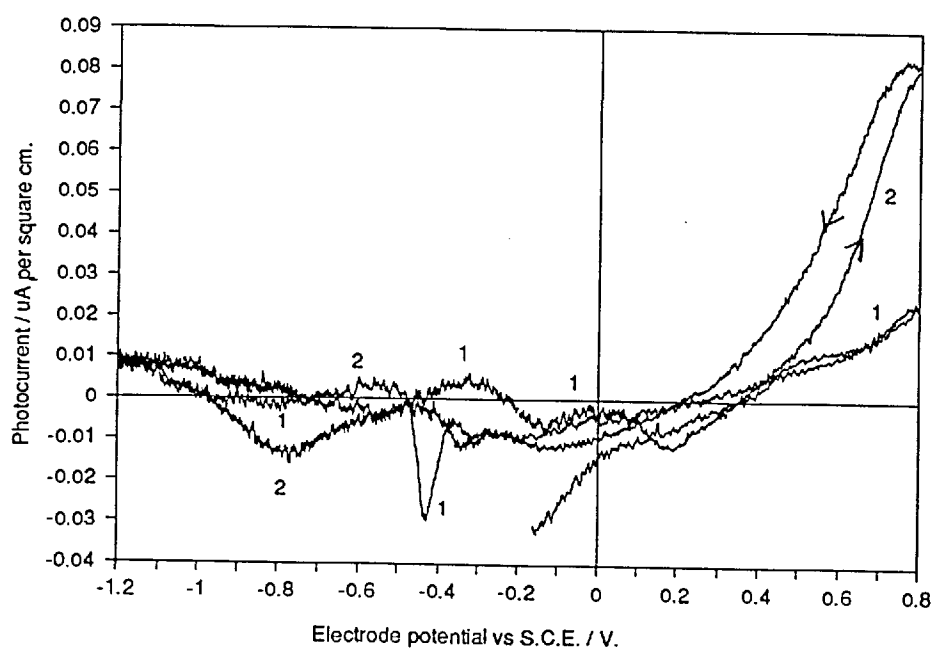
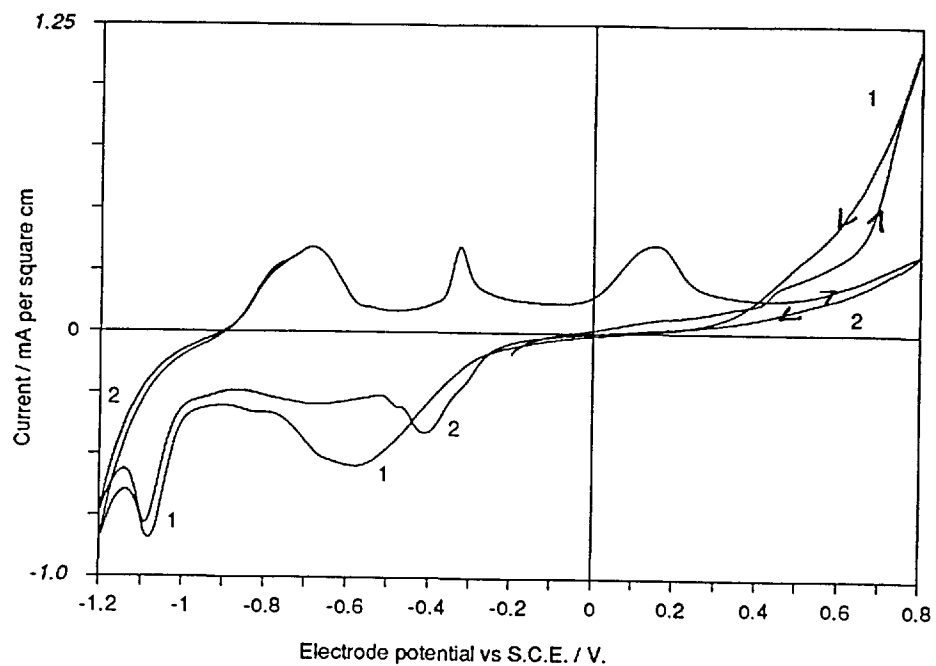


Figure 3.7.6a. Electrode 16. Dark and photo- current responses to a positive potential excursion from -0.2 V vs. S.C.E. at pH 9.2. Sweep rate = 5 mV s^{-1} .

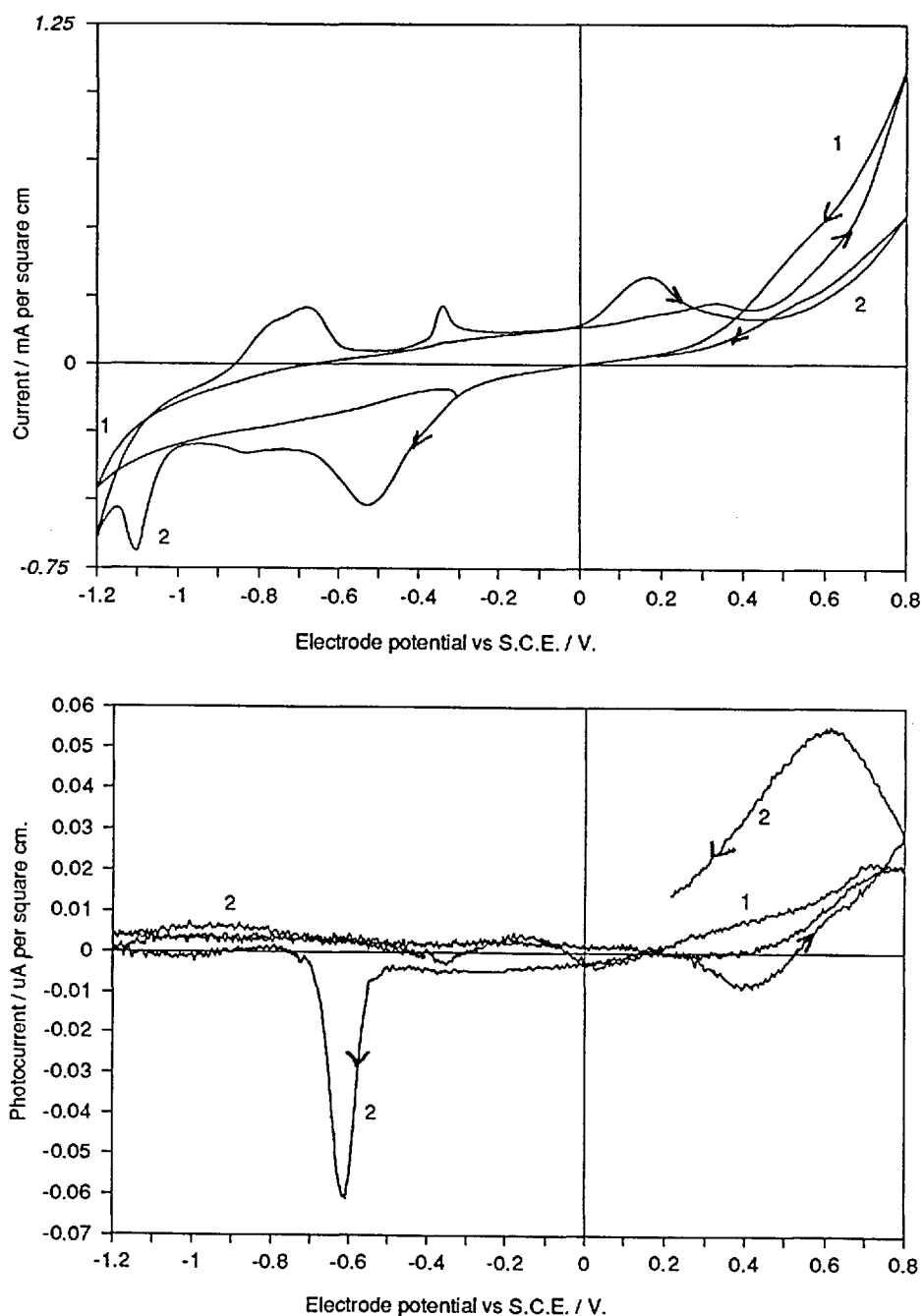


Figure 3.7.6b. Electrode 16. Dark and photo- current responses to a negative potential excursion from -0.2 V vs. S.C.E. at pH 9.2. Sweep rate = 5 mV s^{-1} .

CHAPTER 4. ELECTROCHEMICAL BEHAVIOUR OF CHALCOPYRITE IN ACID SOLUTIONS

The potential-pH diagram in **Appendix 1** suggests that cp's behaviour in acid and alkali could be considered separately, because the $\text{H}_2\text{S}/\text{HS}^-$, $\text{Cu}^{2+}/\text{CuO}$ and $\text{Fe}^{2+}/\text{FeS}$ boundaries broadly divide the diagram in two. This has been borne out in experiment, both previously and in the results reported here. Though the effect of pH over the range 0.67 - 7.0 was studied, the behaviour of cp was determined mainly at pH 2, since at lower values the larger decomposition currents resulted in less reproducible behaviour, both with time and between electrodes. Even so, any one electrode was prone to display inconsistent behaviour between experiments. Whether or not this was due to the nucleation and growth of pits or some other self-perpetuating phenomena is difficult to establish. Birth and growth processes could have been subject to very slight changes in initial surface inhomogeneity and electrolyte agitation. Also, oxidising potentials tended to result in deep cracks within the mineral surface so that the electrode would have to be discarded. The very fact that large currents flowed through cp in acid electrolyte precluded measurement of small photocurrents, because a current measuring resistor of 10Ω rather than 100 or 1000 Ω had to be employed to prevent current overload through the potentiostat; the current output signal fed into the lock-in amplifier was then correspondingly smaller. Many such photocurrents were found to be too transitory for detailed analysis. It is doubtful whether some of the lengthy experiments described in the following chapters would have been possible in acid, but several important conclusions are reached by the end of this chapter.

4.1. Oxidation.

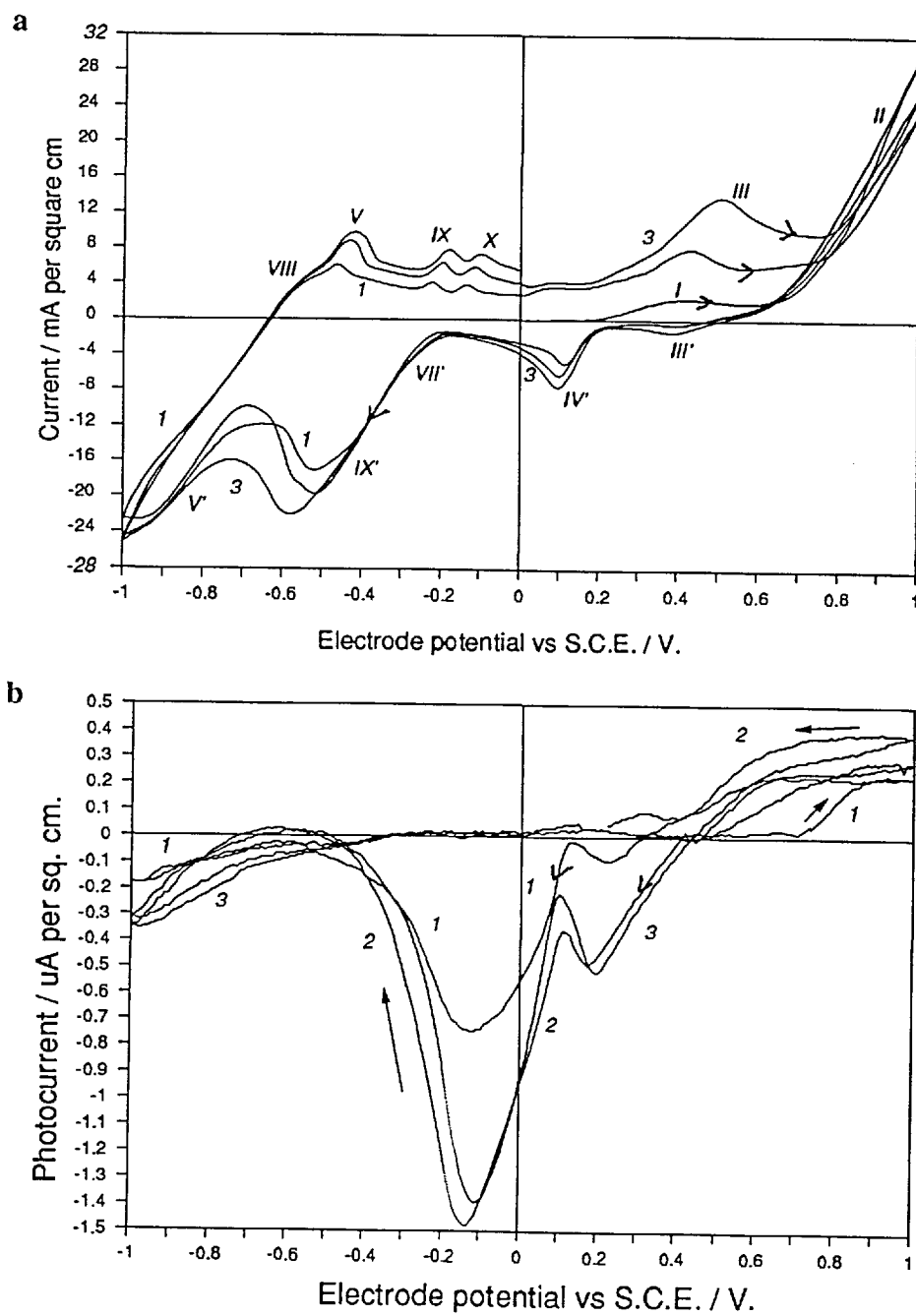


Figure 4.1.1. Electrode 22. Dark current, a, and photocurrent response, b, following a positive potential excursion from 0 V vs S.C.E. in 0.1 M HClO_4 . Sweep rate = 50 mV s^{-1} .

As discussed earlier, there are two types of phase change cited to explain the observed chalcopyrite electrochemical behaviour in acid, one of which is strongly supported by the present work. The first account requires catastrophic phase transformation from one discrete and well-known phase - of calculable metastability - to another. In **Figure 4.1.1** (and **Figures 3.6.1-13**, top left), Peak I is the prewave (see section 2.4.1), resulting from initial preferential iron dissolution from the chalcopyrite surface by reactions such as:



$$E / V = 0.019 + 0.0296 \log(\text{Fe}^{2+})$$

and:



$$E / V = 0.231 + 0.0296 \log(\text{Fe}^{2+})$$

and with increasing potential:



$$E / V = 0.278 + 0.0591 \log(\text{Cu}^{2+})$$

These reactions combined are consistent with the known final dissolved Fe:Cu ratio of 2:1 [62] at 0.4 V. The reverse of (4.1.3), by its enhancement upon copper sulphate addition [76] can be immediately identified with peak IV' at 0.12 V: it is found on all the voltammograms. That peak IV' emerged in **Figure 4.2.1** (next section) only after exceeding 0.3 V agrees well with this hypothesis. The shoulder (or even a peak, see **Figure 3.6.5**), in subsequent positive-going potential sweeps, at about 0.3 V can likewise be ascribed to reaction (4.1.3). Also, the results of coulometry at 50 mV s⁻¹ to 0.4 V show that when the electrolyte was quiescent, the net charge for one cycle was +0.065 C cm⁻², but when the electrolyte was stirred, the net charge for one cycle was +0.108 C cm⁻² because more ions formed anodically were dispersed from the electrode surface.

There is considerable evidence presented in Chapter 1 that the above interpretation is over-simplified. This became apparent even from the above experiments. Firstly, the total charge passed in sweeping the potential to 0.3 V at 50 mV s⁻¹ was 2 mC cm⁻². Assuming reaction by (4.1.1) and (4.1.2) this charge corresponds to 6.7 layers of reacted chalcopyrite forming about 3 layers of Cu₂S (high chalcocite), which entails a fundamental transformation in crystal symmetry concomitant with migration away from the surface of three moles of sulphur per mole of reacted cp. Low chalcocite has lower symmetry and so makes for an even less plausible oxidation product. Consideration of

charge passed per equivalent of chalcopyrite oxidised at sweep rates of 5 and 50 mV s⁻¹ are presented in **Table 4.1.1** below. It shows that for the slower sweep rate more substantial product layers of chalcocite would form at 0.3 V - but subsequent oxidation revealed them not to be chalcocite : a plot of ln(I) vs potential as in **Figure 4.1.2** bears out that whilst the reaction at 50 mV s⁻¹ proceeded and peaked at 0.4 V, at 5 mV s⁻¹ it had reached a limiting value by 0.3 V. This limited current is even more clear in **Figure 4.2.1**, and is uncharacteristic of chalcocite at this potential [219]. The table shows that approximately the same quantity of cp was oxidised in sweeping from 0.6 to 0.8 V as between 0.0 and 0.6 V, even assuming that Fe³⁺ rather than Fe²⁺ was the iron oxidation product. Between 0.8 V and 1.0 V the cp oxidised must have exceeded the total quantity oxidised at lower potentials. Now the standard electrode potential for the Fe³⁺/Fe²⁺ couple is 0.53 V_{vs} S.C.E.. Therefore the results concur with the view that the oxidation of cp in acid is limited below this potential, oxidation to Fe²⁺ being restricted by the oxidation state of iron in the cp lattice: III. Significantly Fe²⁺ has never been detected in these circumstances [11].

10 cp => :	20e + 5Cu ₂ S + 10Fe ²⁺ + 5S	30e + 5 CuS + 5 Cu ²⁺ + 10Fe ²⁺ + 5 S	40e + 5CuS + 5Cu ²⁺ + 10 Fe ³⁺ + 5 S	50e + 10 Cu ²⁺ + 10 Fe ³⁺ + 10 S	70e + Cu ²⁺ , Fe ³⁺ , S, HSO ₄ ⁻ *
50 mV s ⁻¹ :	[0.045 V]	[0.123 V]	[0.226 V]	[0.256 V]	1.00 V
0.0 to 0.3 V	6.7	4.5	3.3		
0.3 to 0.6 V	46	31	23	18	
0.6 to 0.8 V	67	46	34	27	
0.8 to 1.0 V					86
5 mVs ⁻¹ :					
0.0 to 0.3 V	44.5	29.7	22.2		
0.3 to 0.6 V	96	64	48	38	
0.6 to 0.8 V	86	57	43	34	
0.8 to 1.0 V					267

Table 4.1.1. Calculated layers of chalcopyrite required for oxidation to various end products over increasingly positive potential ranges to account for observed dark

currents at two different sweep rates. For the reaction $aX \rightleftharpoons ne + products$, the number of layers required is $V_m a / \{nF(V_e)^{1/3}\}$.

* At 1.00 V, S and SO_4^{2-} formed in ratio 6:1. See text.

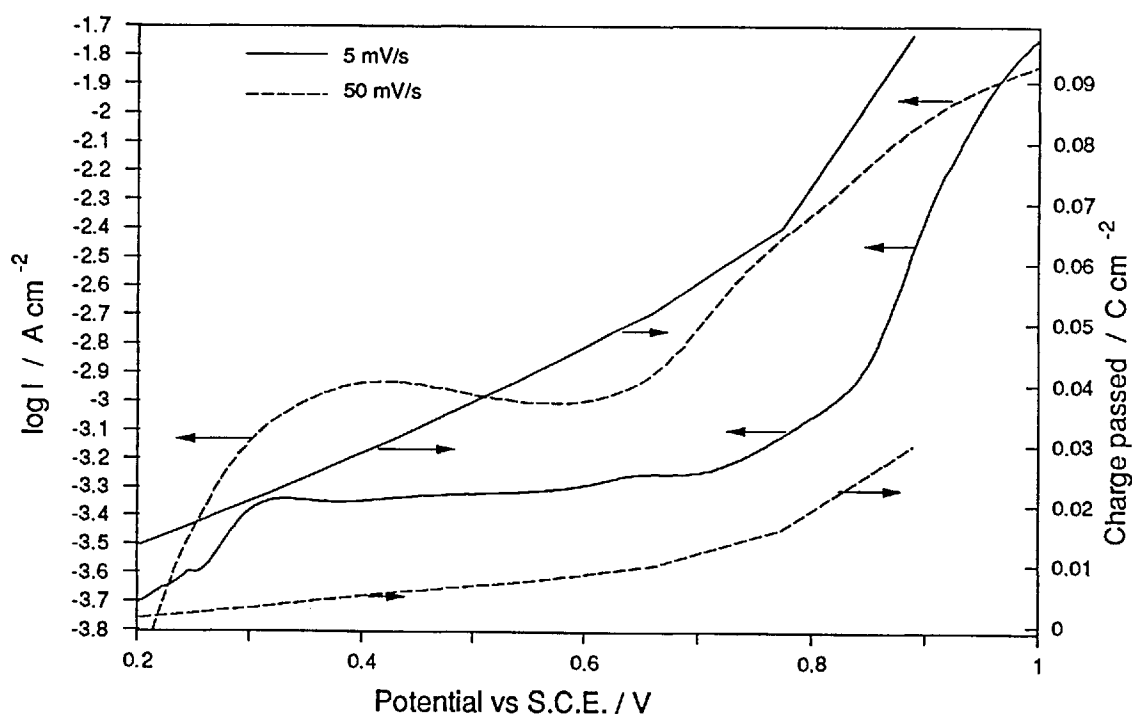


Figure 4.1.2. $\log(I)$ vs E for positive excursions from 0 V at 5 mV s^{-1} and 50 mV s^{-1} in $0.1 \text{ M HClO}_4 + 0.5 \text{ M NaClO}_4$, pH 1.

The photocurrents under oxidising conditions were too small or unstable to enable photocurrent spectroscopy to be performed. However, a.c. impedance measurements were made, and the results illustrated in the following graphs and diagrams in **Figure 4.1.3** were obtained from one such experiment where the potential was stepped positively by 0.1 V every 100 s. **Figure 4.1.3a** is typical of impedance plots in the complex plane for chalcopyrite at potentials just positive of the rest potential in acid solutions. The semicircular arc at low frequencies was modelled on an RC parallel network with R equal to $0.78 \text{ k}\Omega \text{ cm}^2$ and C equal to $1.45 \times 10^{-4} \text{ F cm}^2$. The high frequency response is equivalent to that of a similar network comprising a resistance of $0.013 \text{ }\Omega \text{ cm}$ and capacitance of $2.8 \times 10^{-4} \text{ F cm}^2$ in parallel, in series with the circuit above. This response is seen in **Figure 4.1.3b** to be independent of potential, extending to negative values of Z_{real} : to negative resistances. It is difficult to account for the high frequency response: it may well have been a function of cell design. It is unlikely to have arisen from an electrode process, being independent of the electrode potential. Negative resistances are

predicted to occur under certain conditions on metals in the passivating potential region according to the model of Armstrong and Edmondson [223], who considered the rates of positive and negative ion migration to a film-solution interphase from the electrolyte and a metal oxide passivating layer. When the rate constant for net charge flow towards the electrode interior is small relative to ω , a semicircular plot spanning the complex impedance axis can be obtained, unlike the high frequency response observed on cp in acid.

Returning to the response at low frequencies, the line inclined at about 15° from the vertical in Figure 4.1.3a pertains to a Faradaic charge transfer resistance R_{ct} at the surface in parallel with a double layer capacitance C_{dl} . In fact it comprises part of a semicircle, as shown in c. If this semicircle lay on the real axis, ideal capacitive impedance could be attributed to the electrode surface; as it is, a 'constant phase element' caused a frequency independent shift in imaginary impedances: a depression of the semi-circle. The latter has been explained in the review (Section 1.5) as being due to the fractal nature of the surface; it is expressed in terms of the fractal dimension D , and gives an indication of the surface roughness. Using the computer program described in Appendix 2 for curve fitting and modelling such results on the basis of a parallel RC circuit, Table 4.1.2 was drawn up. Theoretical values for real and imaginary impedance at the measured frequencies are plotted in Figure 4.1.3a using the table values for R_{ct} , C_{dl} , and R_{so} , and they show good agreement with the experimental results.

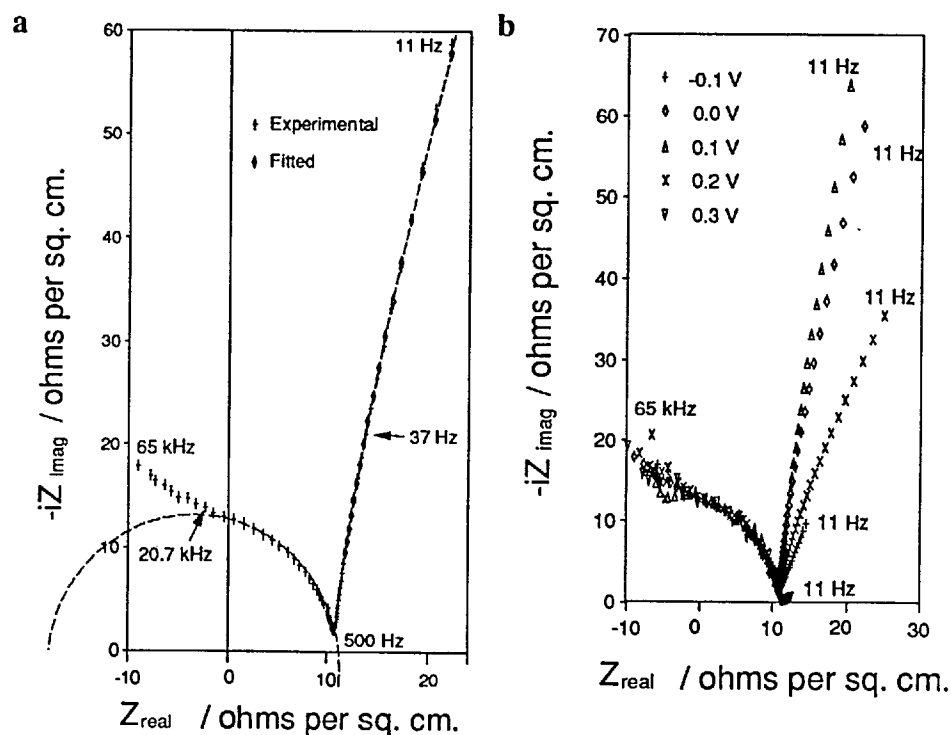


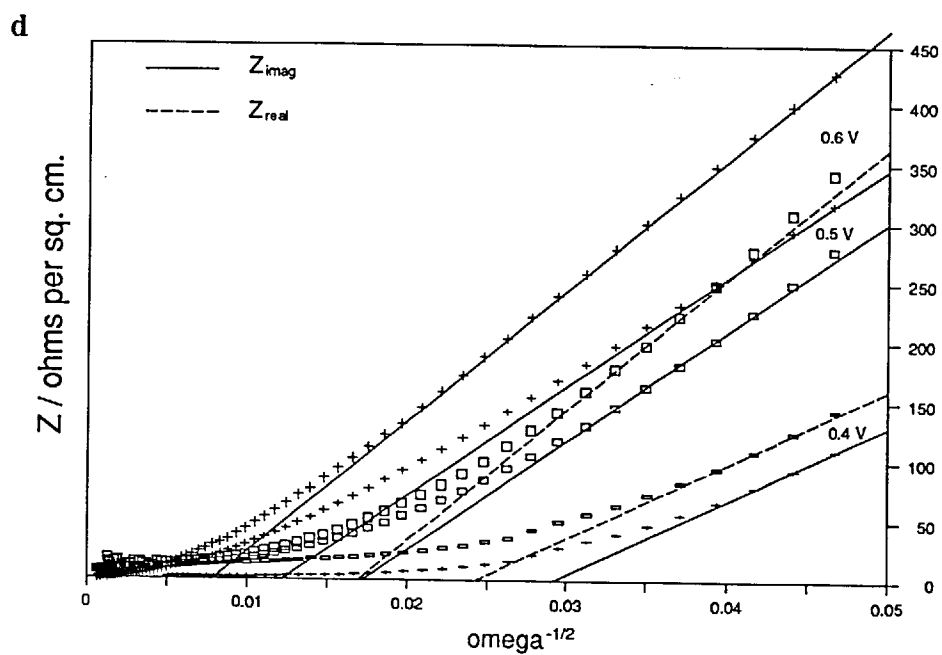
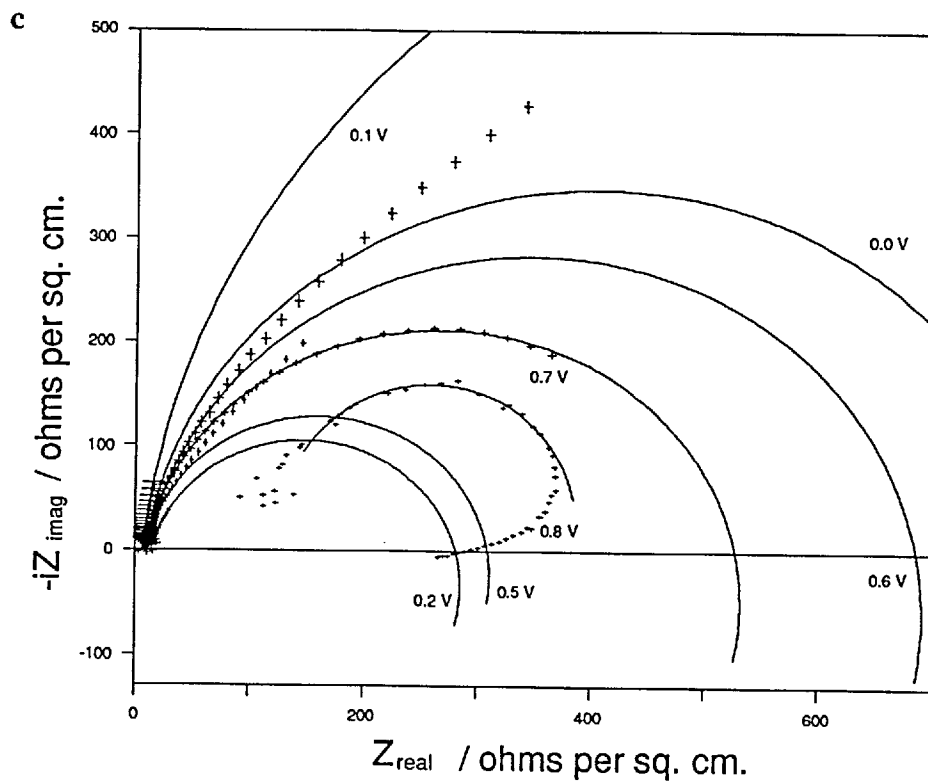
Figure 4.1.3. Impedance data obtained for chalcopyrite electrode 22K in 0.1 M HClO₄ and 0.5 M NaClO₄ at applied potentials between -0.1 V and 0.8 V stepped positively 100 mV. 20 data points per frequency decade, 10 to 65000 Hz. One minute lapse before measurements to allow the current to reach a steady state.

a: At 0.0 V, plotted in the complex plane showing theoretical values obtained using the parallel RC circuit described in the text.

b: Impedance data between -0.1 V and 0.3 V plotted in the complex plane,

Overleaf **c:** Similar plots for the entire range of potentials,

d: $Z(\text{real})$ and $Z(\text{imag})$ vs $\omega^{-1/2}$ indicative of the Warburg impedance operative at the low frequency limit for higher potentials.



Potential vs S.C.E. / V.	$R_{so} / \Omega\text{cm}^2$	Fractal D.	$f_{\max} / \text{Hz}$	$R_{ct} / \text{k}\Omega\text{cm}^2$	$C_{dl} / \mu\text{F cm}^{-2}$	$\lambda \times 10^3$
0.0	10.5	2.09	0.69	0.78	145	0.647 0.225
0.1	10.8	2.07	0.37	1.61	130	
0.2	10.3	2.20	1.21	0.20	320	
0.3	10.3					
0.4	10.2			(0.22)		
0.5	10.0	2.12	21.1	0.26	14.5	
0.6	9.9	2.12	12.1	0.64	10	
0.7	8.8	2.15	19.1	0.47	8.5	
0.8	(0.00013)		(512)	(0.30)	(0.5)	

Table 4.1.2. See text. Values for parameters in parentheses are ambiguous.

In Table 4.1.2 the resistance R_{ct} is seen to increase significantly at 0.1 V and then fall to lower values, consistent with the known passivation of cp at 0.1 V. The low frequency limit at 0.3 V (not shown) is an almost straight line of slope 20° . As mentioned above, following passivation at slow sweep rates, the current did not increase significantly until the potential exceeded 0.6 V (II in Figure 4.1.1). Figure 4.1.3e indicates that at 0.4, 0.5 and 0.6 V diffusion was critical to reaction kinetics. These plots of Z_{real} and Z_{imag} vs $\omega^{-1/2}$ become parallel at low frequencies as the Warburg diffusion impedance became dominant. The slope of these plots is equal to $\sqrt{2}/R_{ct}\lambda$ allowing λ , equal to $(k_b D_O^{1/2} + k_f D_R^{1/2})$ to be calculated, R_{ct} being known from high frequency behaviour. The coalescence of the Warburg and RC-type impedance is noticeable at 0.5 V and 0.6 V in Figure 4.1.3c, where impedances approaching low frequencies strayed from the semicircular fit to a 45° asymptote. The prevalence of the Warburg impedance means that the diffusion of some soluble oxide species away from the electrode surface was rate limiting at low frequency: no redox couple was initially present in solution to give rise to it, and the potentials were well below the standard potential of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and oxidation of water. It differs from a Warburg type impedance only in that the concentration of oxidant is zero everywhere; a boundary condition which makes no difference to the diffusion limited current frequency dependence. Taking into account a simultaneous increase in R_{ct} and decrease in C_{dl} , it would appear that between 0.4 and 0.6 V the passivating layer on the chalcopyrite surface increased in thickness, and it is this that restricts current flow at high frequency potential modulations. Significantly, n-type photocurrents increase in this range, providing corroborative evidence that a deepening depletion layer formed at the surface. All the above provides strong evidence for the interpretation of chalcopyrite

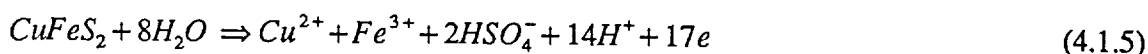
oxidative behaviour in acid put forward by Parker *et al.* [14], namely, a semiconducting surface phase forms on chalcopyrite which restricts further oxidation to the migration of minority carriers - holes - to the electrode surface. In subsequent sweeps, **Figure 3.6.1-13**, the photocurrent often reached a plateau on positive going scans at 0.5 V, as if it were saturated.

The values for C_{dl} in **Table 4.1.2** are far too high to be attributed to capacitance across the Helmholtz layer, and the corresponding extrapolated frequencies of maximum imaginary impedance are very low. It is proposed that the calculated capacitances pertain to a chemical charge storing capacity within the surface layers of oxidised cp. Noticeable in **Table 4.1.2**, and very apparent in **Table 4.1.3** are the large changes in f_{max} and R_{ct} over potential regions where C_{dl} changed continuously and less dramatically.

In the region of II in **Figure 4.1.1** the current rose sharply, and by 1.0 V the rates of reactions of overall stoichiometry:



and:



are known [93] to approach the ratio 6:1. **Table 4.1.1** indicates that unreacted chalcopyrite must have been oxidised at this and higher potentials. Upon the onset of the first negative-going potential sweep, all voltammograms exhibited a current cross-over, associated with the time dependent nucleation of pits by which bulk oxidation had occurred. The impedance plot for 0.8 V in **Figure 4.1.3c** clearly shows inductive behaviour at low frequencies, and it is remarkably similar to the plot for iron in acid at low oxidative overpotentials [224]. The latter is found to follow second order reaction kinetics with respect to OH^- , involving a $(FeOH)_{ads}$ intermediate. A similar mechanism is conceivable here.

On reverse scans following positive potential excursions a small but distinct peak was frequently observed, labelled III' in **Figure 4.1.1** and **Figures 3.6.5, 7 and 11 - 13**. Coincidentally there appeared constant photocurrents. The onset of peak III' was at potentials positive of the Cu^{2+}/Cu standard potential, but negative of that for Fe^{3+}/Fe^{2+} . Therefore it is assigned to the reduction of Fe^{3+} ions, iron oxides and hydroxides not being stable at pH 1. **Table 4.1.3** shows the results of impedance spectroscopy. Clearly a surface phase had formed on chalcopyrite during the positive-going potential sweep for which, in the region of III', while R_{ct} increased, there was no significant change in C_{dl} . Fe^{3+} ion reduction provides the only reasonable explanation. It is necessary that this initial

cathodic peak is not assigned to the reduction of the oxidised cp surface itself, since this was an invariant semiconducting surface phase in the region of III', responsible for the steady photocurrents and capacitances.

Potential vs S.C.E. / V.	R_{so} / Ω cm^2)	Fractal D.	$f_{\max}$ (Hz)	$R_{ct} / \text{k}\Omega$ cm^2	C_{dl} $/ \mu\text{F cm}^{-2}$
0.7	4	(2.32)	(25.8)	(0.18)	(16.9)
0.6	12.2	2.07	10.6	1.00	12.4
0.5	10.0	2.09	7.4	1.43	7.5
0.4	10.5	2.10	4.9	2.13	7.6
0.3	10.4	2.10	19.0	0.55	7.6
0.2	10.5	2.10	18.9	0.52	8.1
0.1	10.5	2.11	6.5	1.43	8.6
0.0	10.3	2.11	7.0	1.20	8.7
-0.1	10.3	2.11	8.4	1.06	8.9

Table 4.1.3. See text. Values for parameters in parenthesis are ambiguous.

On all negative-going potential scans from 0.8 V a further peak at 0.2 V appeared, labelled IV' in Figures 3.6. Cu^{2+} ions are known to be involved [49,62]. The peak could be assigned to the reduction of covellite with Cu^{2+} , or the reduction of cp itself by Cu^{2+} ions:



$$E / \text{V} = 0.25 + 0.0397 \log(\text{Cu}^{2+})$$

although this would require diffusion of the Cu^{2+} ions back through the anodic product layer or pores therein. At 0.3 V R_{ct} decreased sharply, whilst at lower potentials it increased again. The involvement of a solution species would account for this. The simultaneous rise in C_{dl} suggests modification of the semiconducting surface layer, and, as expected, was complemented by a decrease in photocurrents over the same potential range.

Subsequent negative-going potential sweeps indicated the formation of a semiconducting film with remarkably reproducible characteristics despite the emergence of the dark current peak III, arising from oxidation of reduction products discussed later. Thus not only did photocurrents retrace their potential dependent profiles from sweep to sweep as illustrated in Figures 3.6, but also impedance measurements showed C_{dl} of similar

magnitudes, even for chalcopyrite immersed in solutions of 2 M H₂SO₄. Table 4.1.4 presents typical impedance results following a stepped potential excursion to 0.6 V. Doubtless the decrease in surface molar volume - 77 % for the formation of Cu₂S from chalcopyrite - is important in exposing fresh chalcopyrite to electrolysis after reductive sweeps, whereby the same semiconducting metal-deficient underlying anodic product layer could be formed at positive potentials on freshly exposed cp once overlying copper-rich reduction products had oxidatively dissolved.

Potential vs S.C.E. / V	Fractal D.	f _{max} / Hz	R _{ct} / kΩ cm ²	C _{dl} / μF cm ⁻²
0.5	2.074	8.2	0.043	225
0.45	2.030	3.21	0.178	140
0.4	2.026	1.56	0.349	129
0.35	2.016	0.69	0.423	127
0.3	2.022	1.49	0.424	125
0.25	2.017	3.80	0.167	125
0.15	2.040	2.17	0.275	133
0.1	2.046	1.15	0.493	140
0.05	2.056	0.856	0.541	173
0.0	2.077	1.30	0.240	255
-0.05	2.128	3.45	0.0308	748
-0.1	(2.53)	(0.249)	(0.0097)	(32700)

Table 4.1.4. Values for R_{ct} and C_{dl} calculated from impedance data following stepped excursion from 0.0 V to -0.7 V to 0.65 V. 0.05 V per step, 2 minutes per step. cp in 2 M H₂SO₄.

The cathodic current increased sharply below -0.2 V. The reaction:



$$E / V = -0.102 - 0.0591 pH - 0.0241 \log(H_2S)$$

may have contributed at VII'; it is known that electrode rotation decreases the reverse reaction [50], not observed here. The odour of hydrogen sulphide was evident after each experiment.

Though any Fe^{3+} ions formed at anodic potentials has been excluded from consideration here, because of the high overpotential associated with Fe^{3+} ion reduction on cp [15], the reaction:



$$E / V = -0.681 + 0.0295 \log(Fe^{2+})$$

would have enhanced the cathodic current. Iron so deposited would cause the shoulder observed in subsequent anodic sweeps, VIII in **Figure 4.1.1**.

4.2. Reduction.

Chalcopyrite reduction in acidic electrolytes has not been studied extensively, and the current peaks on negative-going potential sweeps revealed the greatest disparity between electrodes, particularly after several potential sweep cycles. There are many possible reactions in this potential range. Clearly the surface and solvated products of each intimately affect the progress of others. However, helpful inferences can be made. Firstly, the ensuing positive-going potential scans show much more simple and reproducible behaviour. If these peaks are identified, one can know where to expect their cathodic counterparts given that the electrolysis is reversible. Secondly, initial negative-going excursions (top right, **Figures 3.6. 1 - 13**), have transients unencumbered by anodic product layer reduction peaks. Specifically, there was a peak, V', at around -0.80 V, whose enhancement of cathodic current on subsequent cycles, and on positive excursions can be clearly seen in **Figures 3.6. 1 - 10 and 25**. Peak V' on initial negative-going excursions was usually larger than on subsequent cycles. In studies of the cathodic behaviour of chalcopyrite in 2 M H_2SO_4 , Biegler and Swift [5] concluded that chalcocite formed at higher potentials is reduced to copper by the reaction:



$$E / V = -0.541 - 0.0591pH - 0.0296 \log(H_2S)$$

at a potential about 0.13 V below the standard potential at pH 0, *ie* at -0.73 V at pH 1. Chalcocite was also identified as the reduction product of cp in solutions containing Cr^{2+} and V^{2+} [225]. According to Biegler and Swift [53] on initial cathodic excursions the reaction:



$$E / V = -0.412 - 0.0886pH - 0.0295 \log(Fe^{2+}) - 0.443 \log(H_2S)$$

occurred with current efficiency approaching 100 % at low current densities. However, from experiments using a chalcopyrite rotating split cylinder bi-electrode under similar conditions, Page [11] suggested the major contribution to current on excursions extending below -0.4 V will come from:



$$E / V = -0.438 - 0.1183\text{pH} - 0.0295 \log(\text{Fe}^{2+}) - 0.0591 \log(\text{H}_2\text{S})$$

and that subject to hydrodynamic conditions, this reaction is reversible, contributing to the anodic current on return sweeps.

Beigler and Swift failed to detect thermodynamically predicted bornite but have investigated the prewave, VI', that can be seen in the top right voltammograms of Figures 3.6.5, 6, 11 and 13. They suggested that these may emerge from the formation of copper sulphides with Cu:S ratios between 1 and 2. From impedance measurements taken from the rest potential to increasingly negative potentials the parameters presented in Table 4.2.1 were calculated. For certain potentials no semicircular fit could be made, precluding their calculation. θ is the angle of depression of semicircular fits. Fractal dimensions are not quoted because it became clear from the straightness of Z_{real} vs $\omega^{-1/2}$ plots that the Warburg impedance prevailed at all frequencies, though not as to obscure the RC network at lower frequencies as was the case at anodic potentials. These large circular depressions certainly throw R_{ct} and C_{dl} values into doubt, but modelled values for Z_{real} and $Z_{\text{imaginary}}$ agreed well with the experimental values using the same algorithm used to obtain Tables 4.1.2-4. The genuine roughness of the electrode surface is revealed in constant values for θ of 3 to 10 ° on negative-going potential sweeps after polarisation to 0.8 V as already discussed. Very low values for R_{ct} at < -0.55 V bear out the high current efficiencies noted by Biegler and Swift [53].

Potential vs S.C.E. / V	θ	$f_{\max}$ / Hz	R_{ct} / $k\Omega$ cm^2	C_{dl} / $\mu F\ cm^{-2}$
0.00	63	0.58	5.49	25
-0.05	62	0.35	3.89	83
-0.15	59	0.16	2.77	175
-0.2	55	0.15	2.39	215
-0.25	53	0.039	6.72	310
-0.40	61	0.241	1.32	250
-0.50	54	7.8	0.0067	1510
-0.55	48	(6)	0.00035	(12000)
-0.65	53	(2.6)	0.000138	(220000)

Table 4.2.1. Values of parameters determined by impedance spectroscopy for chalcopyrite electrode in 2 M H_2SO_4 . Potentials stepped by -50 mV from 0 V vs S.C.E..

Following negative-going potential sweeps, small peaks (X and XI) usually appeared at -0.22 and -0.17 V, above which the current often behaved in an erratic fashion. It is likely that the oxidation of chalcocite occurred in this potential domain. Although the reaction:



$$E / V = -0.288 - 0.0591pH - 0.0296\log(H_2S)$$

has a standard potential at pH 1 below that of $Cu_2S/Cu_{1.75}S$ (analite), -0.235 V, and $Cu_2S/Cu_{1.4}S$ (blue-remaining covellite), -0.208 V, the above observations do suggest CuS is formed oxidatively via the intermediate sulphides.

In fact it is not certain whether chalcocite, Cu_2S , had been formed cathodically by reaction (4.2.2); djurlite ($Cu_{1.96}S$) is an alternative product [53]. The Gibbs energies of formation and thus reversible potentials of these two sulphides are too close to be distinguished from the current responses reported above. However, large cathodic photocurrents occur in the vicinity of their reversible potentials. Their emergence is evident in **Figure 4.2.1** and is further revealed in **Figure 4.2.2**. The figures show dark and photocurrent responses of chalcopyrite electrode in 2 M H_2SO_4 to potential excursions between ever-increasing potential sweep limits: **Figure 4.2.2** is a continuation of **Figure 4.2.1**.

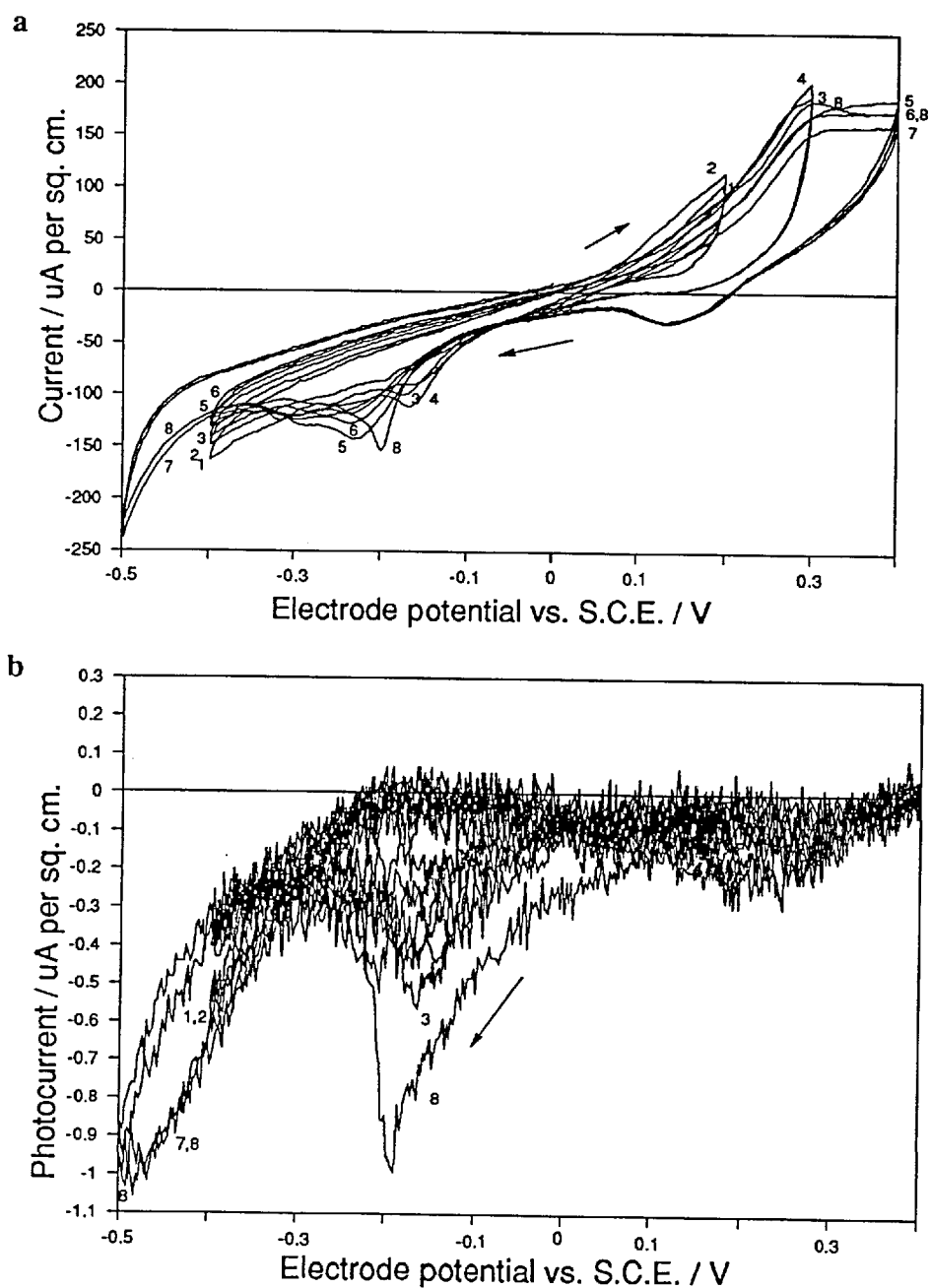


Figure 4.2.1. Electrode 22q. Dark current, a, and photocurrent, b, response to a positive potential excursion from 0 V to ever widening potential limits at pH 0.67. (2 M H_2SO_4). Sweep rate = 5 mV s^{-1} .

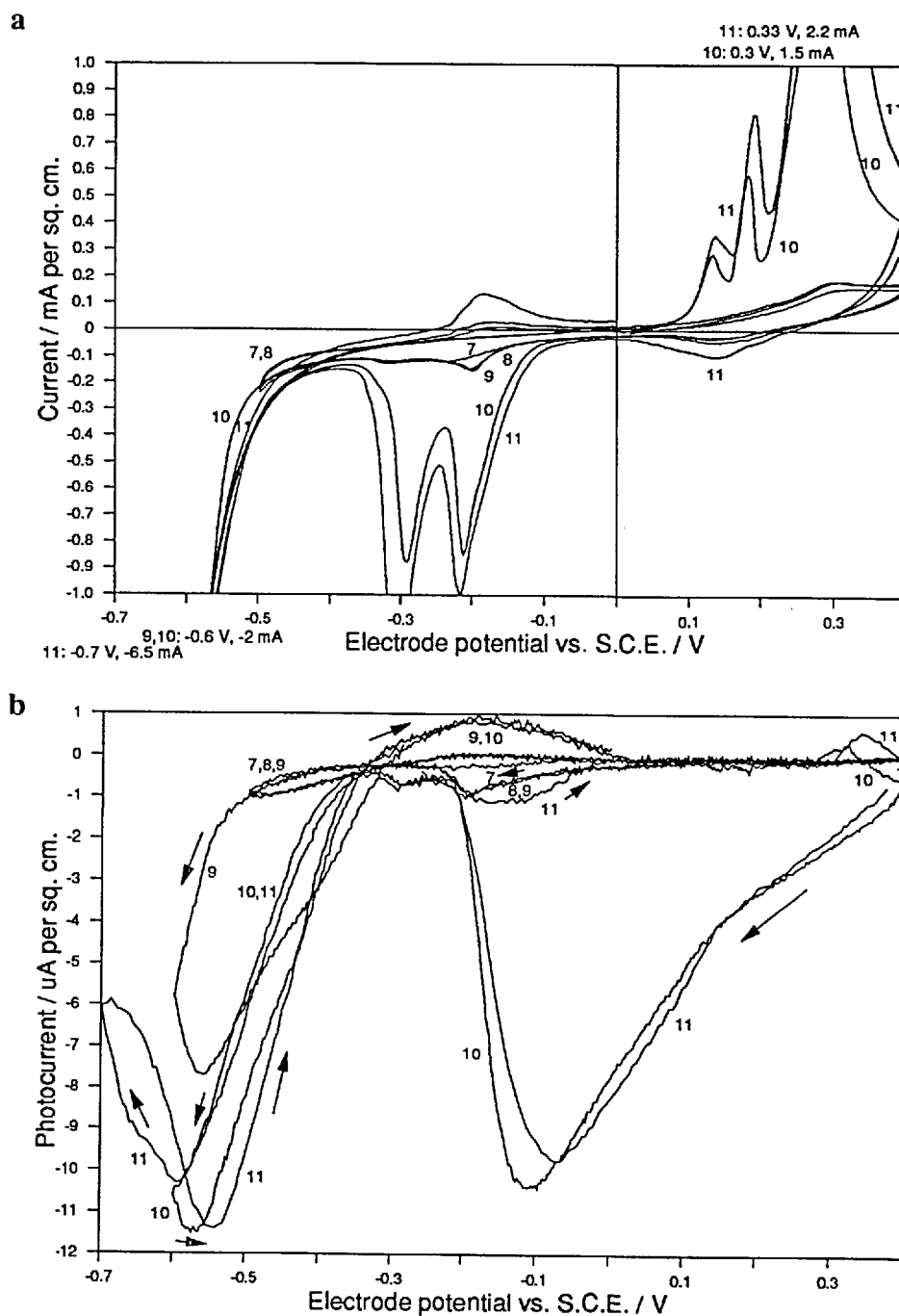


Figure 4.2.2. Continuation of experiment represented in **Figure 4.2.1**.

A photocurrent peak emerged at -0.1 V only after extending the cathodic potential limit to -0.5 V as shown in **Figure 4.2.2 b**. Neither photocurrent peak is likely to be due to copper (I) or (II) oxide reduction because apart from being unstable with respect to cation formation, no such activity was observed on a pure copper electrode under the same conditions, whereas peaks pertaining to these oxides were observed for copper electrodes

in alkali in both this and previous work (see Chapter 5). Nor is iron (III) oxide suspected, again being thermodynamically unstable, and also because it is an n-type semiconductor. Cu_2S , chalcocite, or a closely related sulphide such as $\text{Cu}_{1.96}\text{S}$ djurlite conforms closely with the observed behaviour though, and not only at -0.1 and -0.5 V, but even the -0.8 V peak frequently seen in Figures 3.6.

Now previous work showed no evidence of synthetic Cu_2S being photo-active using identical equipment [219], but for simplicity it is cited as the photo-active phase in the following argument, bearing in mind that djurlite's standard potentials lie very close to chalcocite's; the predominance of one over the other in stability-pH diagrams at low pH depends on which Gibbs energy values thermodynamic calculations are based upon (Section 1.3.1).

Firstly, the rise in photocurrent at -0.5 V coincides nicely with the reversible potential of reaction (4.1.2). Upon the reduction of chalcopyrite to chalcocite, a product layer of p-type chalcocite formed on the surface of chalcopyrite would limit the supply of electrons needed to effect further reduction. Light would increase the concentration of these minority carriers, which would be favourably conducted under the influence of the electric field towards the electrode surface. As the film thickened, the space charge layer - in which there was a depletion of majority carriers - became deeper, so separation of photo-generated electron hole pairs by a correspondingly more penetrating potential gradient is expected: the photocurrent increased.

Secondly, the absence of chalcocite from anodic reactions was discussed in the previous section, and the absence of the peak at -0.2 V as the positive potential sweep limit is raised to 0.4 V is entirely consistent with chalcocite not being formed. However, chalcocite was mentioned before with reference to reduction of covellite and chalcopyrite with Cu^{2+} ions associated with dark current peaks IV' and V'. Perhaps the photocurrent peak at -0.2 V would occur if, first, Cu^{2+} were generated at some potential beyond 0.4 V. This proved to be the case. It is evident in Figures 3.6 where the positive limit was 1.0 V, and from the photocurrent peaks following various positive potential excursions shown in Figure 4.2.3. These peaks were sensitive to electrolyte agitation and had quite a different profile from the peak at -0.5 V as they depended on the diffusion limited supply of Cu^{2+} ions. Figure 4.2.3 shows the photocurrent peaks at -0.5 V to be quite unaffected by the anodic potential preceding it and it had a similar profile to the peak at -0.5 V in Figure 4.2.2b. This observed photo-assisted reduction of cp to Cu_2S at -0.5 V required all overlying oxidation products to be reduced to Cu_2S and H_2S at less negative potentials, so as to generate a very reproducible surface at -0.5 V, which is consistent with the standard potentials of reactions such as (4.1.2), (3) and (6).

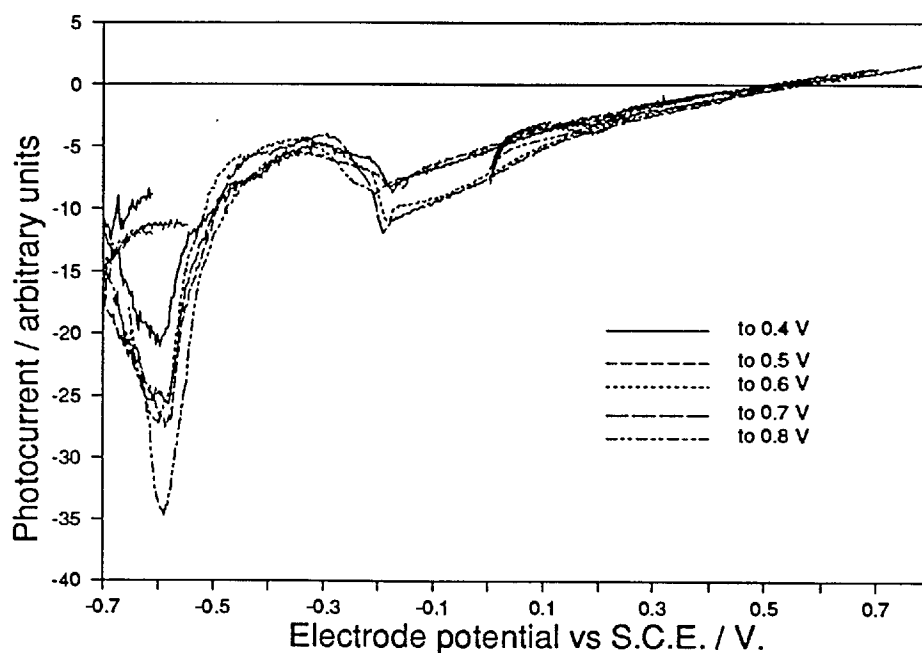


Figure 4.2.3. Photocurrent transients for chalcopyrite immersed in 1 M HClO_4 and swept to varying positive potential limits. Sweep rate 5 mV s^{-1} .

Thirdly, there was the peak at -0.8 V . Figures 3.6 show it to emerge following both positive and negative excursions from the rest potential. This is further evidence for the assured formation of chalcocite at less negative potentials and conforms with the established potential for chalcocite reduction to copper of -0.7 V (reaction 4.2.1 at pH 0.67). This photocurrent assists in the reduction of the photo-active chalcocite. The photo-effect at -0.8 V could be said to assist in its own destruction, but the relatively large total currents at -0.8 V imply that coincident photocurrents merely give some indication of the negative potential limit of stability of the chalcocite layer. The transience of photo-currents at -0.8 V was confirmed during attempts to perform photocurrent spectroscopy at this potential after positive potential excursions to $+1.0 \text{ V}$. They were found to decay rapidly.

Finally, if the photocurrent at -0.5 V in Figure 4.2.2b was indeed due to a phase closely resembling chalcocite, its formation thereafter at -0.1 V can be easily explained. The subsequent positive-going potential total current peaks (Figure 4.2.2a, sweeps 10 and 11) would be due to oxidation of chalcocite to Cu^{2+} ions. The latter, hitherto unavailable, could then participate in chalcopyrite reduction to chalcocite by reaction (4.1.6). Reduction of cp to Cu_2S by reaction (4.2.2) would yield 4 moles of electrons per mole of Cu_2S . The complete oxidation of one mole of Cu_2S to Cu^{2+} ions would produce 4 moles of

electrons. Table 4.2.2 shows that the excess charge generated on the negative-going potential sweep 9 to -0.6 V over the charge generated in the previous negative-going sweep to -0.5 V was almost exactly matched by the excess charge generated on the following positive-going potential sweep 10 to 0.4 V. This is further strong evidence of the importance of chalcocite formation by reactions such as (4.1.6) and (4.2.2). The balance in charge passed anodically and cathodically during potential sweeps 5 and 6 confirms that Cu^{2+} ions do not form oxidatively from chalcopyrite below 0.4 V.

Sweep no.	V +ve limit	Charge / mC cm^{-1}	V -ve limit	Charge / mC cm^{-1}
1	0.2	2.66	-0.4	-11.99
2	0.2	2.72	-0.4	-10.99
3	0.3	5.59	-0.4	-11.31
4	0.3	5.75	-0.4	-10.46
5	0.4	9.83	-0.4	-11.64
6	0.4	9.76	-0.4	-10.92
7	0.4	8.64	-0.5	-15.71
8	0.4	10.29	-0.5	-15.54
9	0.4	10.64	-0.6	-50.8
10	0.4	42.2	-0.6	-70.82
11	0.4	61.65	-0.7	-243.22

Table 4.2.2. Total cathodic and anodic charge passed in experiment pertaining to Figures 4.2.1 and 2. pH 0.67. 5 mV s^{-1} .

Anodic photocurrents were discussed in the previous section as being too unstable to provide reliable photocurrent spectra. This was not the case for the photocathodic peak at -0.2 V. A buffer solution of pH 2.1 was used in order to minimise the deleterious effect of acid electrolysis on chalcopyrite electrodes. The potential was swept to +0.8 V then to -0.2 V, at which it was maintained. It was allowed to stabilise for 20 minutes. The response is shown in Figure 4.2.4. In accordance with equations (1.4.2.1) and (2), in Figure 4.2.5 $(i_{\text{ph}}h\nu)^n$ vs $h\nu$ is plotted to distinguish between direct and indirect photo-excitation, assuming the i_{ph} to be proportional to the absorption coefficient, α . The straight line for $n = 1/2$ in Figure 4.2.5 implies indirect electron transition, and extrapolation indicates a bandgap for the film of 2.45 eV.

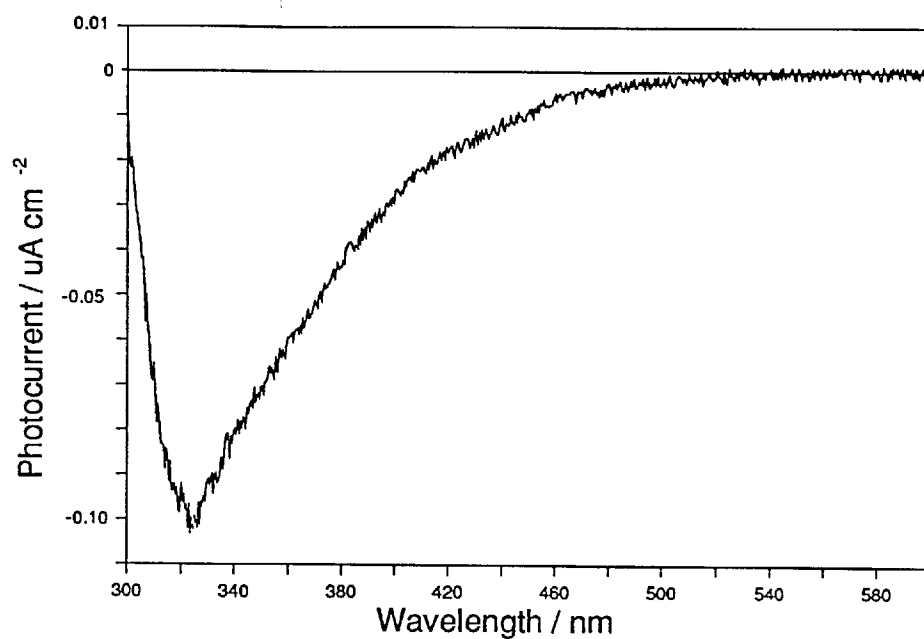


Figure 4.2.4. Spectral photocurrent response of chalcopyrite electrode 22, following the same regime used to obtain Figure 4.2.1, only at pH 2.1.

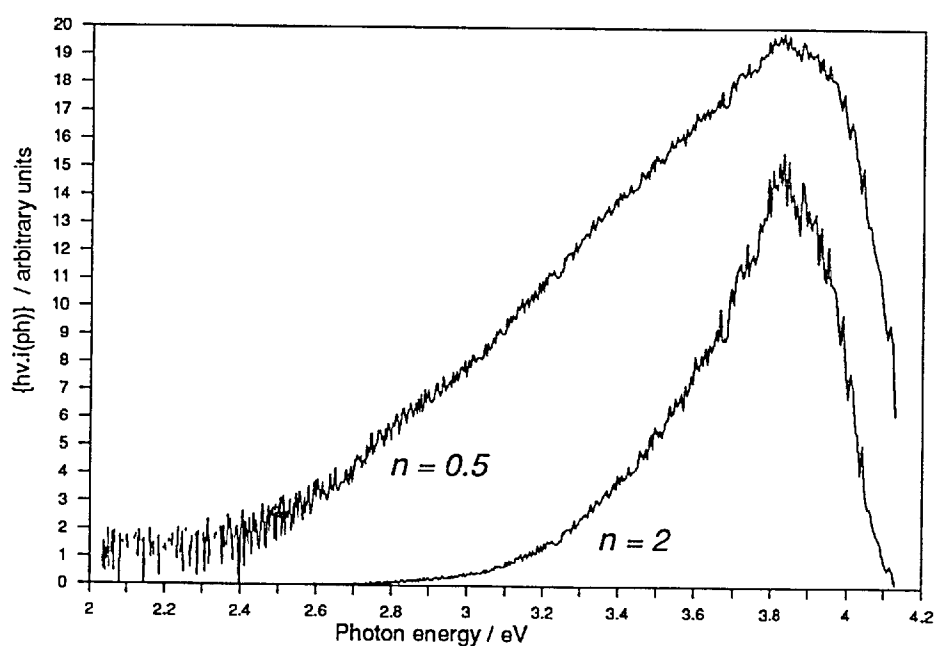


Figure 4.2.5. See above. Plots of photon energy vs $(i_{ph} \cdot hv)^n$ where $n = 0.5$ and 2 .

CHAPTER 5. THE REDUCTION OF CHALCOPYRITE IN ALKALINE SOLUTIONS

Most attention in the present study was given to chalcopyrite electrochemistry in alkaline solutions, providing a new insight into phase changes that occur on cp during its froth flotation. The chalcopyrite surface was found to be photo-active over a wide potential range, but the photocurrents were more stable at high pH, giving wider scope for spectroscopic measurements. Considering also the chrono-amperometric and impedance spectroscopy results, there is a great deal of diverse evidence discussed in the following two chapters, which are separated more for clarity than for content.

5.1. Chalcopyrite at potentials negative of the rest potential

Thermodynamic considerations predict stability of cp over a potential range of about 0.5 V (see **Appendix 1** figure). In practice, not far negative of its anodic potential limit of stability cp exhibited modified Cottrell type behaviour shown in **Figure 5.1.1**, in which the current approached some negative value at increasing time. It was never seen to decay to zero. It is possible that the transient reduction current at -0.15 V was due to the reduction of an oxide layer which had formed prior to the immersion of the electrode in solution. The underlying cp was then exposed and oxidised at this potential. However, the experimental procedure did not allow for so thick an oxide layer to form as to account for the negative charge densities at lower potentials. As discussed in **Chapter 3**, rest potentials at pH 9 ranged between 0.0 V and -0.2 V, indicating at least partial oxidation of the electrode surface had taken place, despite all efforts to exclude oxygen from the cell; aerial oxidation during polishing and transfer of the electrode to the cell is most likely the cause for this behaviour.

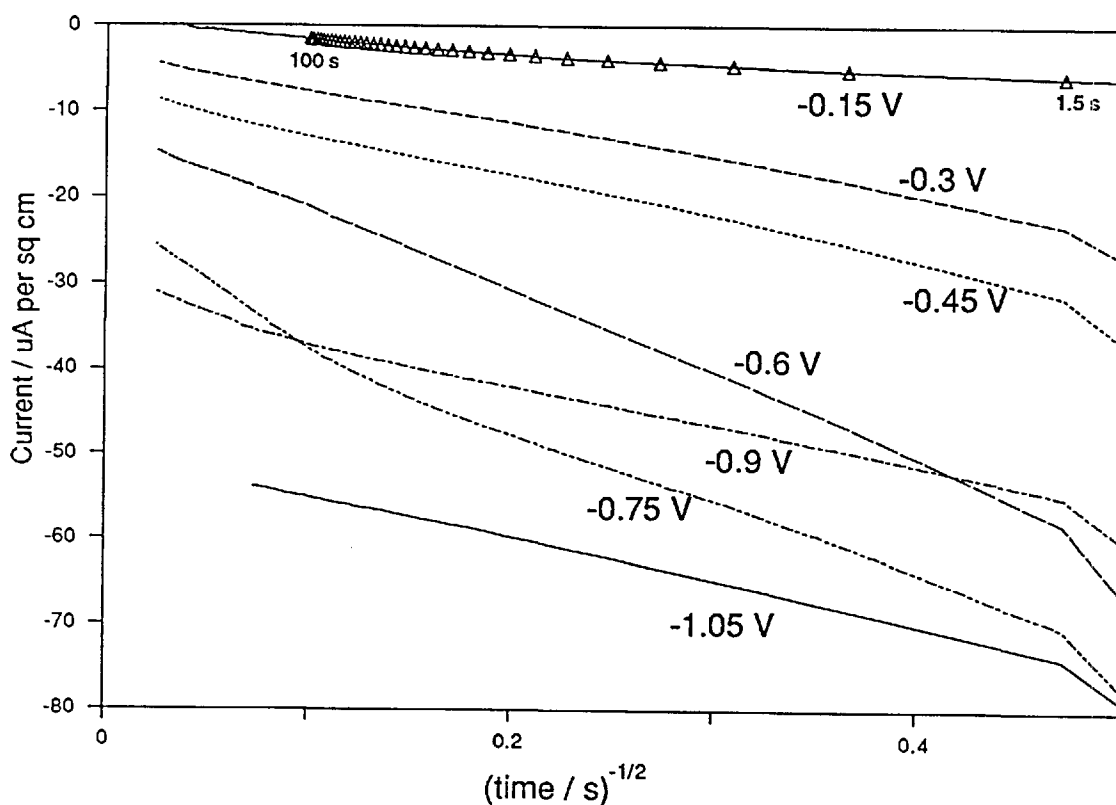


Figure 5.1.1. Cottrell plot of dark current transients for cp at increasingly negative stepped potentials.

In one experiment the steady cathodic dark current, I_{dk} at -0.3 V stabilised at about $1 \mu\text{A cm}^{-2}$ after 1 hour, remaining unchanged even after 20 hours. There are two explanations that present themselves for this behaviour. Firstly, the current could have been due to adventitious oxygen:



$$\log(O_2(aq)) = -2.85 + \log P_{O_2}$$



$$E / V = 0.453 - 0.0591pH - 0.0296 \log(H_2O_2) + 0.0296 \log P_{O_2}$$



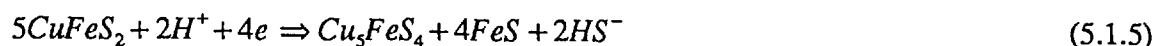
$$E / V = 0.537 - 0.0591pH - 0.0296 \log(H_2O_2) + 0.0296 \log(O_2(aq))$$



$$E / V = 1.521 - 0.0591pH + 0.0296 \log(H_2O_2)$$

The $t^{1/2}$ dependence of current on time would then arise from diffusion limited oxygen reduction (probably to peroxide) over a Nernst diffusion layer of finite thickness, δ , say 0.1 mm. Considering the oxygen concentration, $[O_2]$, could not exceed one part per billion - the concentration of oxygen in the purging gas, the contribution of oxygen reduction to the reduction current given by $i_c = zFD[O_2]/\delta$, where D is the diffusion coefficient for O_2 equal to $2.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, was very small, if not negligible, and does not account for the observed behaviour. Besides, the reduction currents increase steadily with decreasing potential. The question is what alternative reduction at the mineral surface can occur?

Gibbs energy data in **Appendix 1** is not available for a wide range of sulphides of stoichiometry between that of cp and bornite, yet Cu-Fe-S thermochemistry would suggest no dominant stability of one of these sulphides over the others. True, chalcopyrite is by far the most abundant copper iron mineral on the earth's crust, but it should be considered that of an entire structural family of copper iron sulphides - which excludes cubanite, CuFe_2S_3 - it is cp that is most 'saturated' with iron. Therefore it is entirely plausible that the electrochemically preferred reduction of iron in the cp lattice over copper in forming bornite is representative of a trend borne out by several intermediate sulphides, and the actual region of thermodynamic stability of cp is probably much smaller than it is shown to be in the **Appendix 1** diagram. The non-stoichiometric behaviour upon cp oxidation in acid has already been noted, and a whole range of copper sulphides themselves are predicted to form in alkali [93]. Notwithstanding, even for the representative reaction:



there are different possible reaction pathways, and currents limited by diffusion of protons or HS^- ions could give rise to the transients in **Figure 5.1.1**. In this respect the photoelectrochemical behaviour of cp was informative.

Initial cathodic current transients for various mineral samples in 0.1 M borax solution were presented in the top right of **Figures 3.7.1-6**. They showed several peaks associated with cp reduction. Below them, corresponding photocurrents were too small to discern, but using more the more sensitive EG&G lock-in amplifier (see **Section 2.4.1.**), both photocurrent and photo-voltage spectroscopy proved possible. Indeed, stable photocurrents at constant potentials between -0.2 V and -1.1 V under white light were discovered which, though small, stabilised within minutes, remaining constant over a period of days, thereby permitting long lock-in integration times over which to detect photocurrents and photo-voltages generated under monochromatic light.

The procedure adopted was as follows: at each constant applied potential, after the 'white light' photocurrent transient had stabilised, the light shutter was closed before adjusting the monochromator to 250 nm. The monochromatic response was then measured from 250 nm (4.89 eV) to at least 500 nm (2.48 eV) at which most responses were negligible. The monochromator slit width was 3 nm, corresponding to an output bandwidth of some 5 nm. In every sweep the sweep rate was 0.1 nm s^{-1} , and the lock-in time constant 30 s. The lock-in sensitivity was $30 \text{ } \mu\text{V}$ at $\geq -0.575 \text{ V}$ and $100 \text{ } \mu\text{V}$ at $\leq -0.65 \text{ V}$. At the end of each sweep the light shutter was closed, the monochromator was re-aligned to reflect the lamp 'white light' output as before, the lock-in sensitivity re-set to $100 \text{ } \mu\text{V}$ and the time constant re-set to 1 second: then the light shutter was re-opened. When the photocurrent stabilised again, the potential was stepped down 75 mV, and the procedure repeated.

The results of these measurements are presented in the following figures. **Figure 5.1.2** shows the photocurrent conversion efficiency Φ plotted against photon energy at potentials between -0.275 V and -0.95 V . The plot is remarkable in showing such similarity between profiles over so wide a potential range. In **Figure 5.1.3**, the photocurrent phase angle at all photon energies above 3.4 eV is shown to have been stable and in the third quadrant (-90 to -180°). The phase angle moved to the second quadrant below about 3 eV. Below 2.8 eV the phase angle returned to its original value (see **Figure 5.1.10a**), though corresponding photocurrent magnitudes were too small to give rise to a discernible potential dependent trend. Plots of $\{h\nu \cdot \Phi\}^{1/2}$ vs $h\nu$ in **Figure 5.1.4** show a linear dependence between about 3.2 and 4 eV. Intercepts with the photon energy axis and their correlation uncertainty to within one standard deviation between these limits are shown in **Figure 5.1.5**. They provide preliminary evidence that the threshold energies for photocurrent transients arise from indirect light transitions. Also, the linear dependence of $(\Phi h\nu)^{1/2}$ vs $h\nu$ in **Figure 5.1.4** indicates that the implicit assumptions in equations (1.4.2.28) and (46) hold: Φ was proportional to the absorption coefficient, α . The proportionality is borne out in the close resemblance of **Figure 5.1.2** to the absorption spectrum of cp obtained by Sato and Teranishi [36].

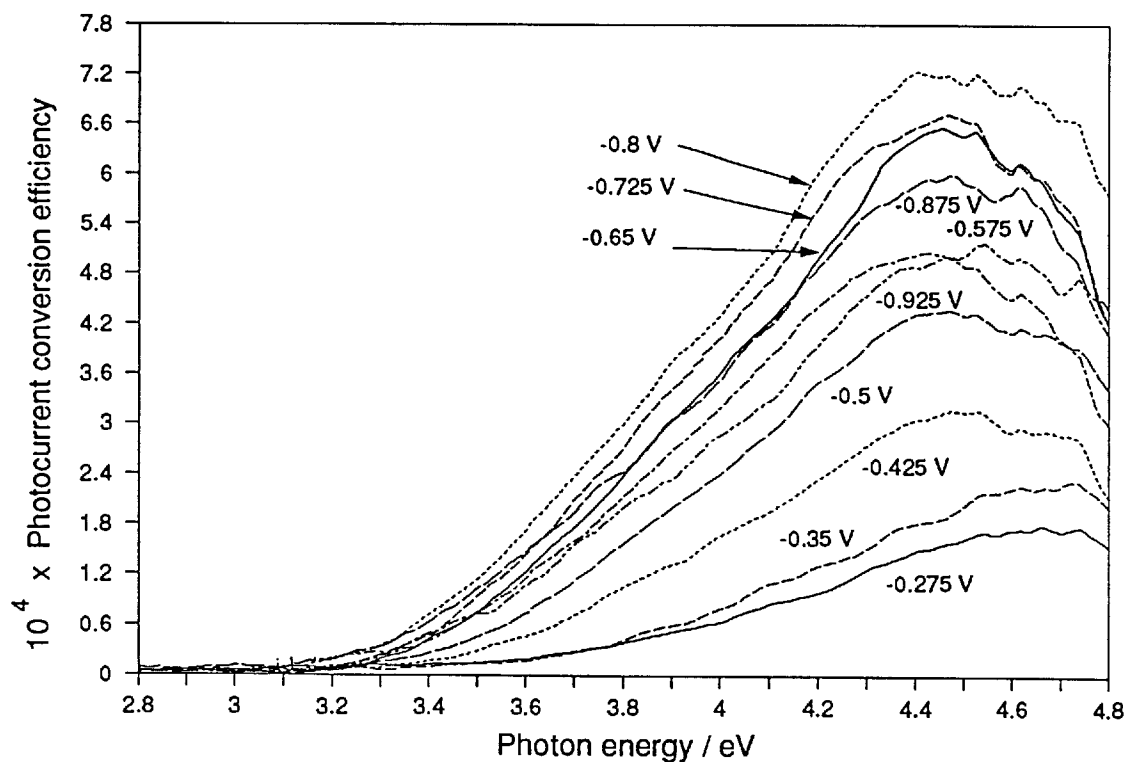


Figure 5.1.2. Photocurrent magnitude vs photon energy for cp in 0.1 M borax solution, pH 9.2, at increasingly negative stepped potentials. See text.

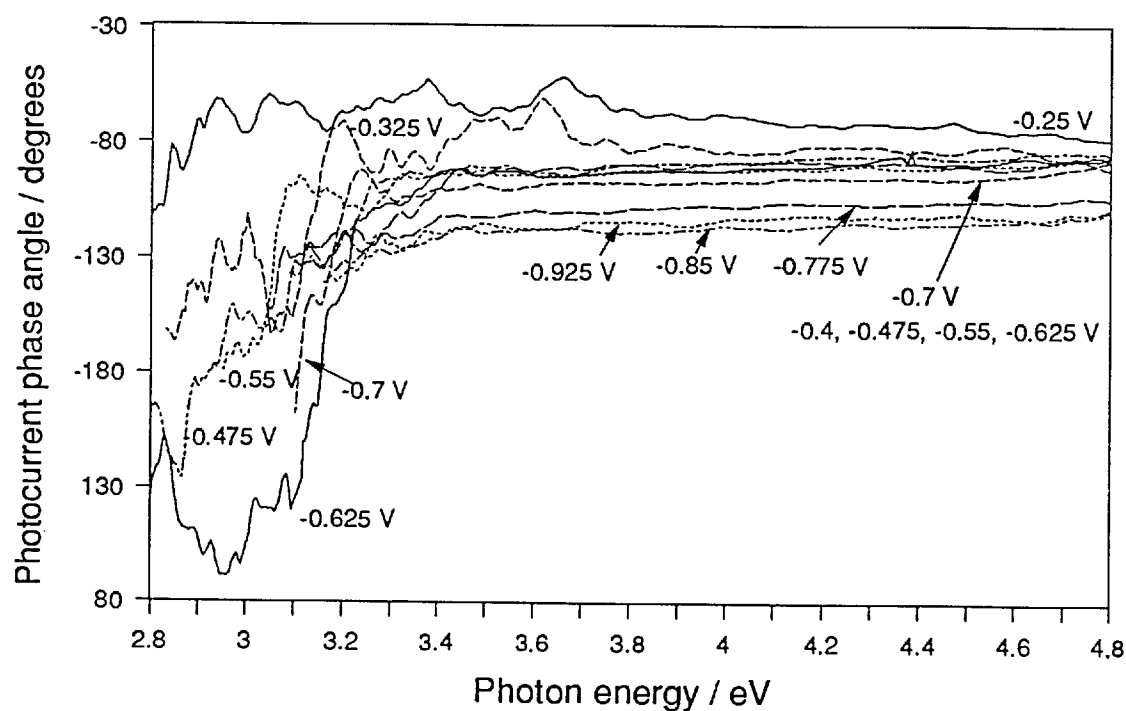


Figure 5.1.3. Photocurrent phase angle vs photon energy for cp as above. See text.

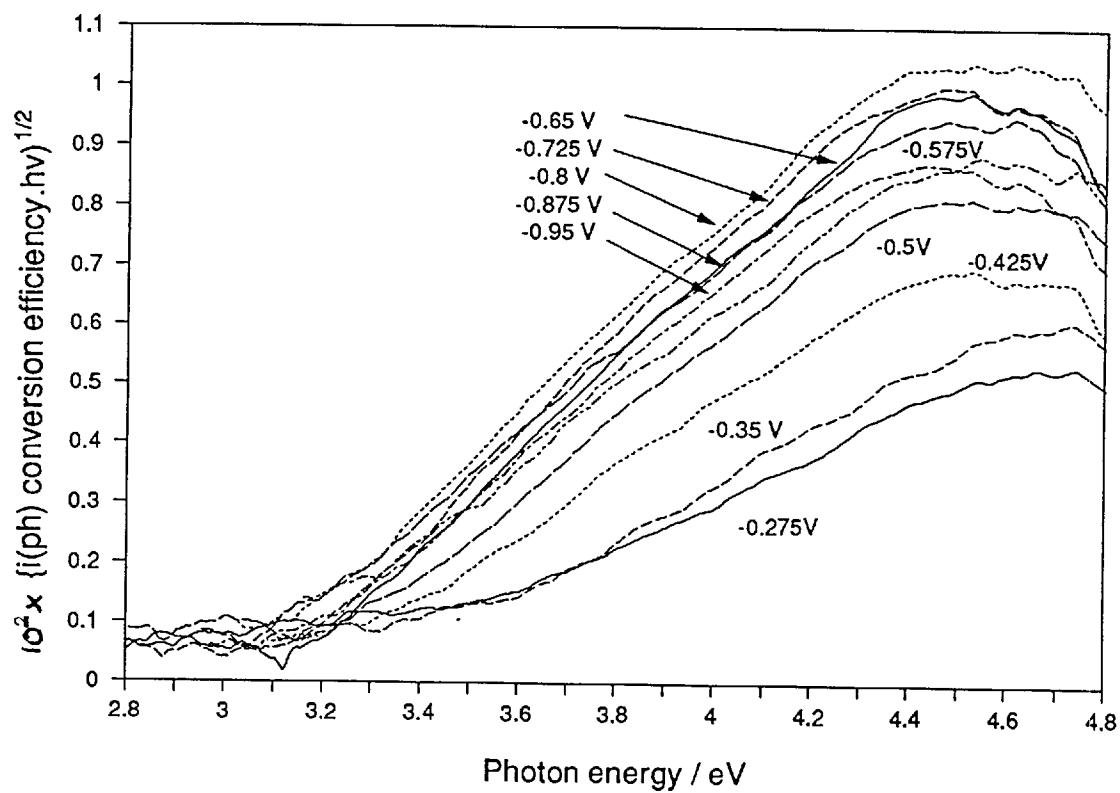


Figure 5.1.4. $(h\nu \cdot \Phi)^{1/2}$ vs photon energy, $h\nu$, for cp as above. See text.

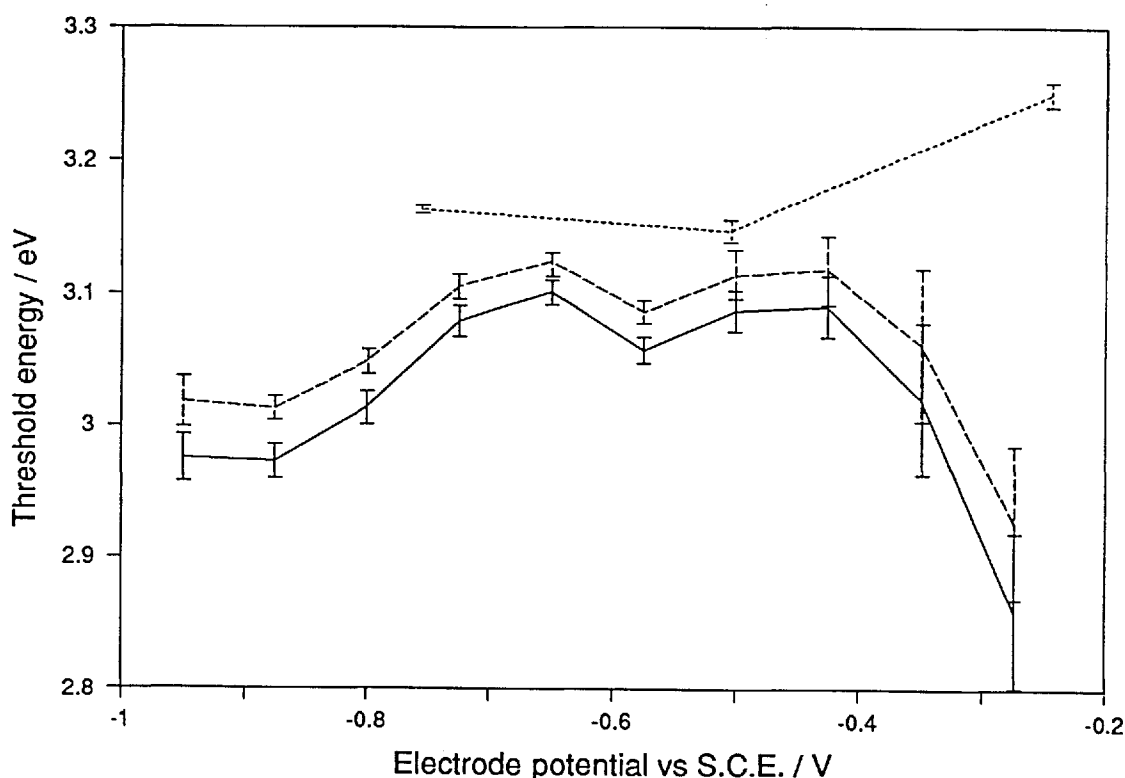


Figure 5.1.5. Photocurrent threshold energies for cp vs potential, calculated from plots of $\{V_{ph} \cdot hv/P\}^{1/2}$ vs $h\nu$ under galvanostatic control (....), and $\{h\nu \cdot \Phi\}^{1/2}$ vs $h\nu$ (____) and $\Phi^{1/2}$ vs $h\nu$ (----) under potentiostatic control.

From **Figure 5.1.5** it can be seen that there was no discernible trend between the threshold energy and applied electrode potential. This was confirmed in equivalent experiments conducted under galvanostatic control. Thus in one such experiment photo-voltage spectra were recorded consecutively at -0.6 , -2.4 , and $+4.8 \mu A cm^{-2}$. Again, each 'white light' photo-voltage was allowed to stabilise before and after monochromatic measurements. The results of this experiment, presented in **Figures 5.1.6-8**, are comparable with **Figures 5.1.2-4**. They indicate that both the photo-voltage magnitude normalised for the lamp power output, V_{ph}/P and its phase angle θ showed a very similar photon energy dependence as Φ ($= I_{ph} \cdot h\nu/P$) and θ at constant applied potentials.

Because photo-voltages were better resolved than photocurrents, they were measurable at lower photon energies, and afforded longer lock-in time constants and spectral sweep rates to be employed in this experiment: $100 s$ and $4.8 nm s^{-1}$ respectively. Even so, the "white light" photo-voltages before and after spectroscopy varied less than 3 % whereas corresponding photocurrents varied some 5 % as shown in **Figure 5.1.9**. The photo-voltage spectra give extremely linear plots of $\{V_{ph} \cdot h\nu/P\}^{1/2}$ vs $h\nu$ (see **Figures 5.1.5** and 8). From the spectrum at $-2.4 \mu A cm^{-2}$ a threshold energy of $3.1630 \pm 0.0003 eV$,

and a correlation coefficient of 0.99984 was obtained. At $+4.8 \mu\text{A cm}^{-2}$ these values were $3.147 \pm 0.001 \text{ eV}$ and 0.99940. As will be seen in **Figure 5.1.11** the potential varied during the course of these photo-voltage measurements. Therefore it is certain that the threshold energy did not decrease significantly with increasing potential, and photo-emission was not the phenomenon giving rise to these photocurrents [226-228]. On the other hand plots of $(\Phi)^{1/2}$ vs $h\nu$ at the less negative potentials showed greater linearity than corresponding plots of $(h\nu.\Phi)^{1/2}$ vs $h\nu$.

On the basis of the above results alone, it is reasonable to say that the cp electrode surface had an electronic structure essentially unaltered between its rest potential and -0.95 V despite the charge passed. That charge was considerable. At the onset of applying -0.575 V , it was equivalent to 430 layers of cp being reduced to bornite according to reaction (16). At -0.8 V it was 1900 layers and at -0.95 V equivalent to 4000 layers. To assign the photo-excitation responsible for the observed photo-effect, reference is made to **Figure 1.1.1.3**. Optical absorption of thin films of cp show peaks at 1.1 and 2.0 eV with an absorption edge at 3.2 eV [36]. The absorption edge has been assigned to the onset of the band to band transition between the S 3p valence band and the empty metal 4s and 4p conduction band, and therefore is in good agreement with the present work. The lower energy transitions are purported to arise from a charge transfer type mechanism from the same S 3p valence band to empty Fe 3d orbitals [36]. The latter are of $2e$ and $4t_2$ symmetry, crystal field orbitals effected by the prevailing ligand field, *i.e.* there is considerable mixing between them and the S 3p orbitals. From the evidence of **Figures 5.1.2** and **6** alone, these are delocalised orbitals, assuming that is, that the cp is p-type with respect to its photo-activity in reducing conditions.

First, it is desirable to obtain the flat-band potential of cp in these conditions. Then at least the direction of the field gradient on the electrode surface can be known. Photocurrent phase angles by no means made it clear whether the photocurrent opposed or reinforced the dark current. It should be noted that while the spectral photo-effects were detectable only by virtue of their longevity, the total currents I_{tot} or voltages V_{tot} as measured by the potentiostat were dramatically affected by the presence or absence of incident radiation. **Figures 5.1.10** and **11** illustrate the variation in measured parameters during typical potentiostatic and galvanostatic steps. **Figure 5.1.10** suggests that "white light" has an enhancing effect on the current, because shortly after the shutter was closed ("light off"), the total current rose. However, the detail (b) confirms that this increase was not instantaneous. It is, after all, the short term differential response to light over one chopping cycle (0.0133 s) that the lock-in amplifier measured, whereas the total current shown in **Figure 5.1.10** is time averaged (over 3 s intervals). The photocurrent phase

angle of 88° may be consistent with the preceding photo-activity being anodic. During the sweep of short wavelength radiation I_{tot} had a negative gradient roughly proportional to the magnitude of I_{ph} , suggesting that the negative phase angle θ again conveys the "sign" of photo-activity, in this case cathodic. After the spectral sweep to wavelengths at which there was no photo-effect, the shutter was closed without perturbation of the total current (as expected). Upon re-exposure to the "white light", the current at first rose and then recovered once more to its more negative value, suggesting a photo-anodic effect. Meanwhile I_{ph} and θ as measured by the lock-in amplifier returned to their pre-spectral values within the few seconds required for lock-in integration of the photo-response.

Now a photo-anodic effect that diminished the total cathodic current at constant potential would in galvanostatic conditions require the applied potential to move to more negative potentials in order to maintain a constant current. So it did, as shown in **Figure 5.1.11** when the shutter was re-opened. However, the values for V_{ph} and θ in no wise accord with the variation in V_{tot} .

In other respects **Figure 10** and **11** agree. Most significantly the photo-effects under "white light" were of only up to twice the magnitude of maximum monochromatic responses (see **Figure 5.1.9**). Conservatively estimating the monochromatic photocurrent responses to emerge from all the light available over a waveband of 8 nm, the combined spectral responses could render "white light" photocurrents at least 20 times those observed. Therefore it is likely that photocurrents reached saturation under "white light" conditions. On the other hand, the linearity displayed in **Figures 5.1.4** and **8** suggest that the spectral photo-effects were never saturated.

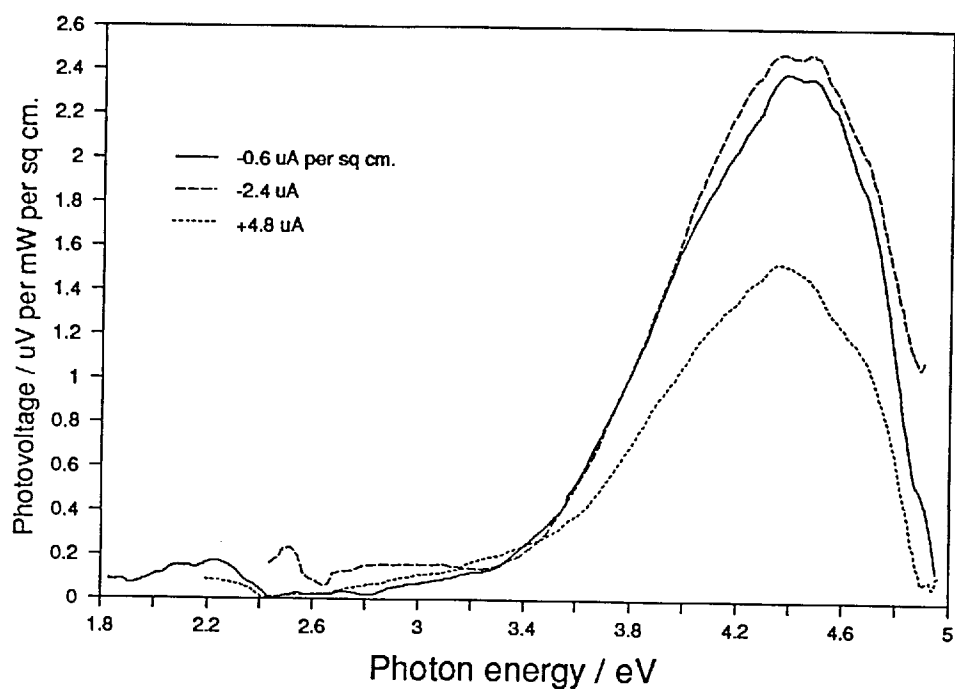


Figure 5.1.6. Photo-voltage magnitude normalised for the lamp power output V_{ph}/P vs photon energy $h\nu$ for cp in 0.1 M borax solution, pH 9.2, under cathodic followed by anodic constant currents. See text.

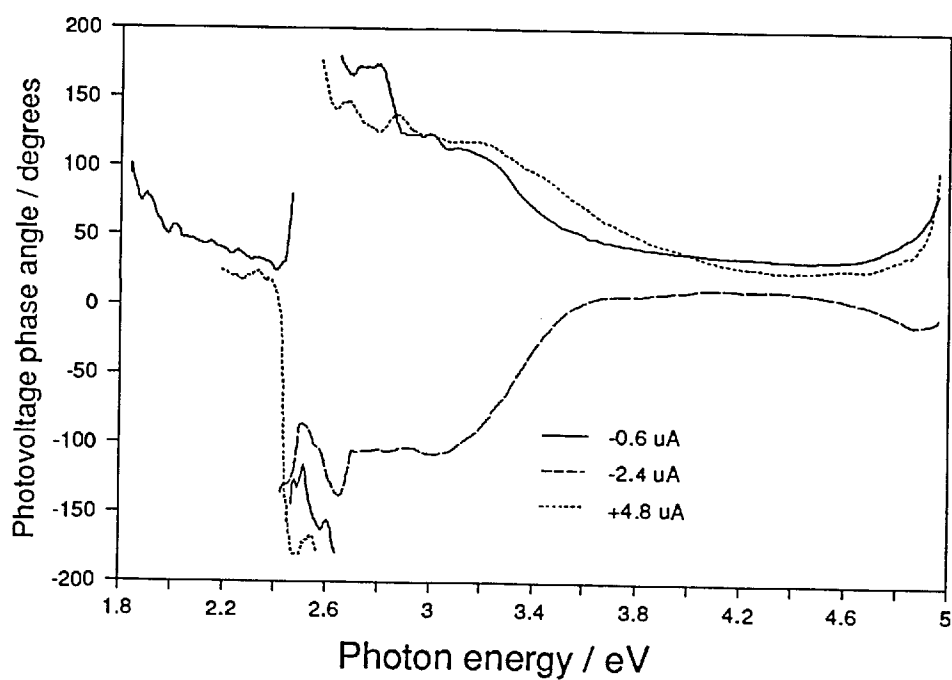


Figure 5.1.7. Photo-voltage phase angle vs photon energy for cp as above. See text.

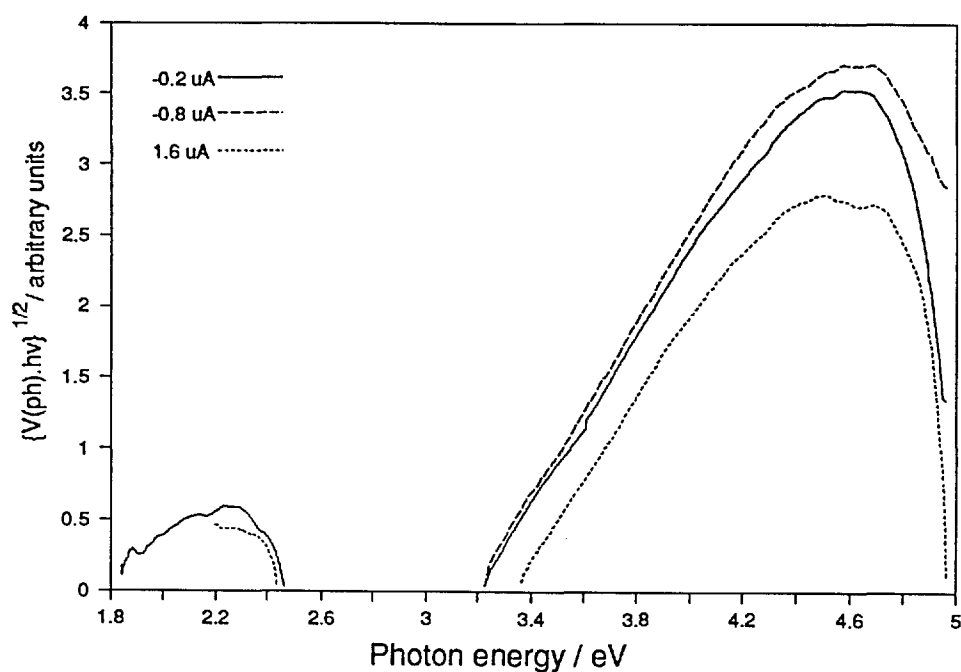


Figure 5.1.8. $(V_{ph}h\nu/P)^{1/2}$ vs photon energy, $h\nu$, for cp as above. See text.

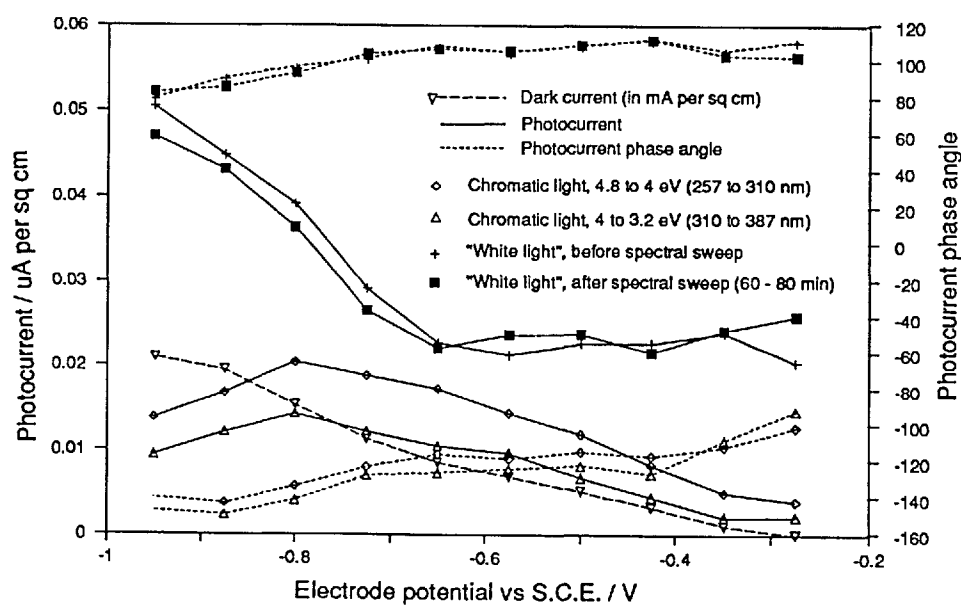


Figure 5.1.9. Averaged magnitudes and phase angles of photocurrents as a function of potential. The averaged spectral values have not been normalised for the flux output of the xenon lamp, to indicate their size relative to 'white light' photocurrents.

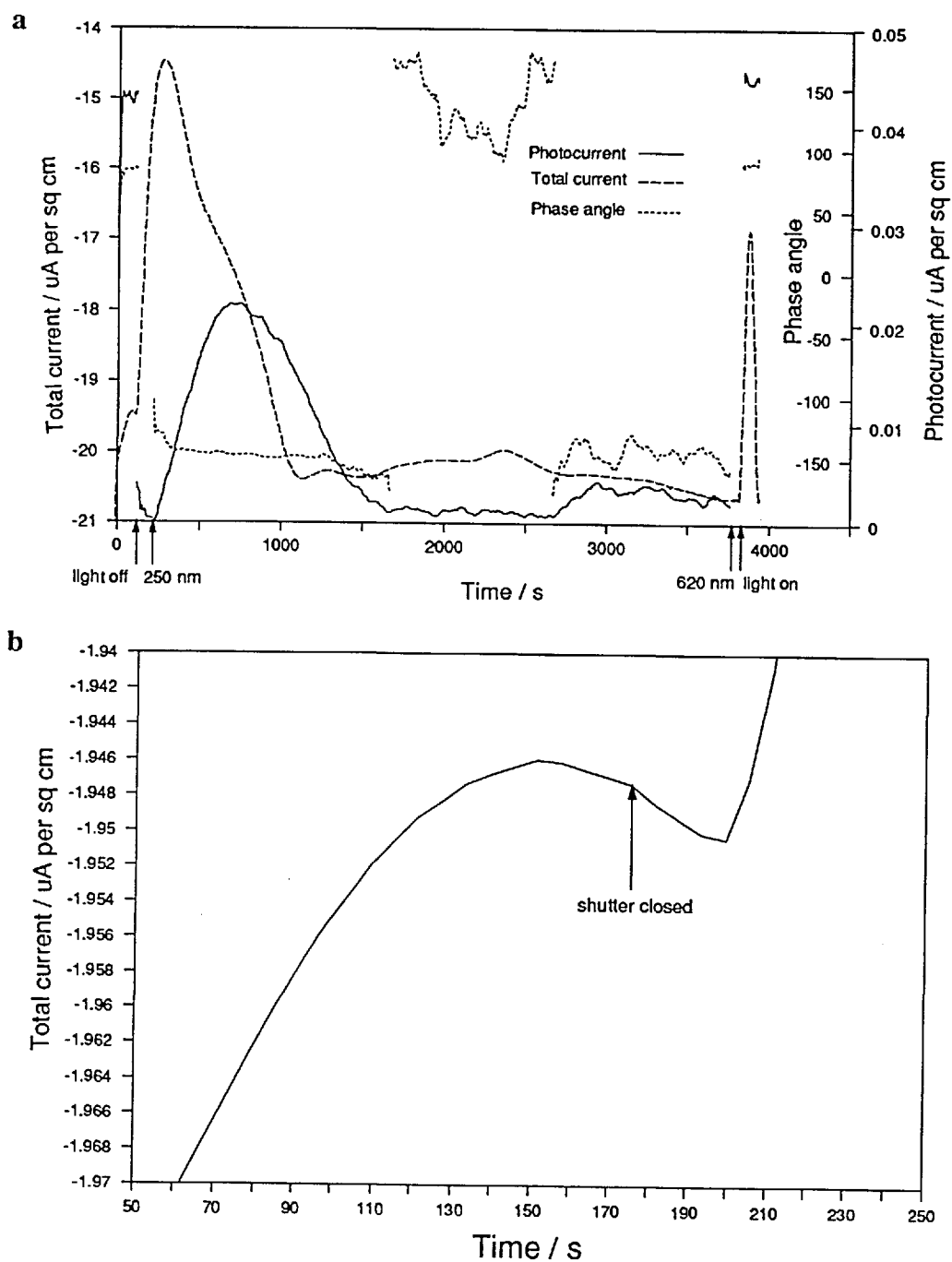


Figure 5.1.10a. Variation with time I_{tot} , I_{ph} and θ after stepping the potential from -0.8 to -0.875 V vs S.C.E. as described in the text.
b, detail of I_{tot} vs t , upon closing the shutter.

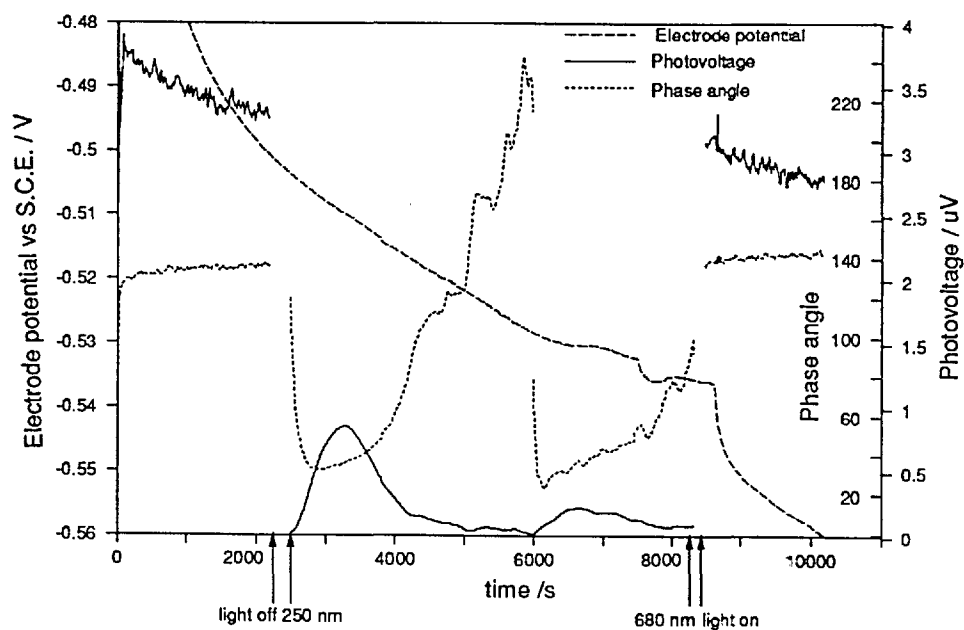


Figure 5.1.11. Variation with time V_{tot} , V_{ph} and θ from the onset of applying $-2.4 \mu\text{Acm}^{-2}$ as described in the text.

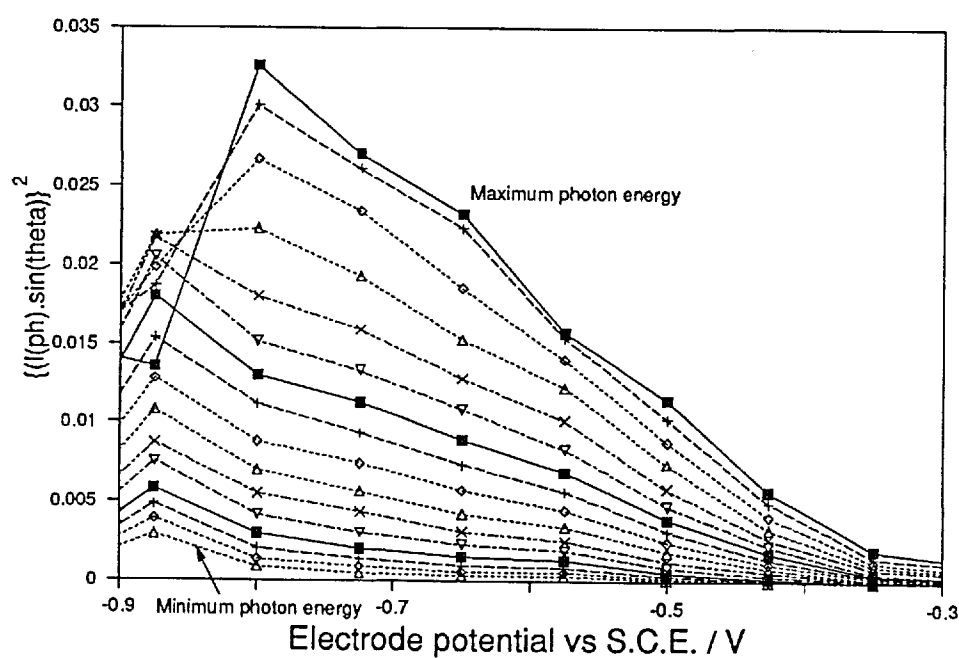


Figure 5.1.12. $(I_{\text{ph}} \cdot \sin \theta / P)^2$ vs potential. See text.

The similarity between spectra over the range of conditions described, together with the linearity of plots for indirect electron transitions which render invariant threshold energies, strongly suggests that one photo-active surface phase prevails on cp between -0.275 V and -0.95 V in 0.1 M borax solution. The evidence for this would be reinforced

by plots of I_{ph}^2 vs potential which are linear providing $\alpha d_{sc}(e/kT)^{1/2}(U-U_{fb}) \ll 1$. (See Section 1.4.2). Figure 5.1.12 shows that this linear dependence held for the experiment described above over a wide range of wavelengths, and between -0.3 V and at least -0.8 V. A flatband potential of -0.375 +/- 0.2 V for the photo-active phase is obtained.

The chalcopyrite, commonly an n-type semiconductor, would be expected to display photo-activity under the depletion conditions which prevail anodic of V_{fb} , whereupon the field is amenable to drawing the minority charge - holes - to the SC/El interface (Figure 1.4.2.2a). Negative of V_{fb} there would be no Schottky barrier but rather a field acting on electrons - the majority carrier charge - at the surface to accumulate them at the surface, and effect reduction. It is proposed that this very reduction modifies the surface phase as follows: the mineral reduction does not lead to a significant change in the relative position of energy levels at the electrode surface. It may be supposed that ions could have migrated from within the electrode interior to the surface, and were reduced to a solution species which then diffused away from the electrode rather than forming an entirely different solid surface phase. The migration of iron or copper to form their respective binary sulphides is not feasible because they would inevitably result in the formation of a metal depleted and thus more oxidised interior. It is possible that iron and sulphur could migrate to the surface, forming FeS and H₂S as exemplified by reaction (16), but FeS is structurally and electronically entirely different from cp having an optically observed absorption edge and band gap well under 3.15 eV. Also, the observed photocathodic activity indicates a field in the electrode which opposes positive ion migration towards the surface. Sulphide migration has not been observed and can be discounted in view of the ion's well known polarisability and large size.

This leaves iron or copper ion migration in the opposite direction, from the electrode surface to the interior, as the only viable alternative. Copper (I) ion diffusion is known to occur in the acidic anodic dissolution of chalcocite and digenite [34]. Furthermore the structure of a range of more metal-rich copper iron sulphides can be viewed as deriving from the filling of cp lattice octahedral vacancies [66]. Moreover, if preceded by surface sulphide reduction to H₂S, the favourable field would be reinforced by a metal ion concentration gradient. In that case the cathodic current could be limited by the supply of electrons of sufficiently high energy to occupy the low spin iron Fe3d-S3p crystal field antibonding orbitals 4t₂ and 2e which have been estimated to comprise 70-80 % Fe character [24]. An electron so placed at the surface would weaken the Fe-S bond whilst favouring electrophilic proton attack. This hypothesis agrees well with the observed photocurrents insofar as this very orbital has been identified with the optical absorption energy and photocurrent threshold energy at 3.2 eV. The photo-cathodic currents and

voltages under monochromatic light can now be understood to arise from the facilitated reduction of reducible surface sulphide. Under "white light" absorption the limited availability of this sulphide induces an accumulation of minority charge so as to diminish the surface electric field to the extent that the current is now limited by the rate of metal ion diffusion into the electrode interior. A saturated photoanodic effect is then observed.

5.2. Chalcopyrite under mildly oxidising conditions

Photocurrents which stabilised within minutes were also observed just above the rest potential of cp in 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$ between -0.2 V and 0.0 V. Again it was possible to measure the potentiostatic photocurrent as a function of wavelength of light. Typical results are shown in Figure 5.2.1, obtained at 0.036 V after 10 hours at that potential, during which some 0.018 C per cm^2 had been passed, the current having decayed from 3 to 0.5 $\mu\text{A cm}^{-2}$. The spectral sweep rate was set to 12 nm min^{-1} , and the lock-in time constant 3 s. The profile is similar to those obtained above, but shows an enhanced effect at the lower end of the spectrum, where θ , significantly, was $+90^\circ$, equal to the phase angle under "white light" illumination. It is possible that "white light" photocurrents were equal to the sum of photocurrents under monochromatic light across the entire spectrum of the lamp. Because the phase angles at most wavelengths were close to $+90^\circ$ or -90° , it is suggested that the timescale for this photo-response was much shorter than it was under reducing conditions. The presence of a thin oxide layer may account for this behaviour.

Another significant difference is to be seen in the photo-emission plots shown in Figure 5.2.2. After 10 hr at -0.036 V the photocurrent data clearly suggests two threshold energies above 3.2 eV and one below 1.5 eV. Table 5.2.1 shows the correlation for both indirect electron transition and photoemission plots over the two upper linear regions. Clearly it is difficult to discriminate between the two phenomena under these mildly oxidising conditions, but the uppermost threshold energies could be indicative of higher energies of antibonding orbitals involving oxygen rather than sulphur.

hv range / eV	$(\Phi \cdot \sin \theta \cdot hv)^{1/2}$ vs hv		$(\Phi \cdot \sin^2 \theta)^{1/2}$ vs hv	
	4.4 to 3.7	3.7 to 3.33	4.4 to 3.7	3.7 to 3.33
Threshold energy / eV	3.414	3.366	3.266	3.259
Correlation coef.	0.9994	0.9996	0.9954	0.9943
Standard error	0.0196	0.0173	0.0414	0.0444

Table 5.2.1.

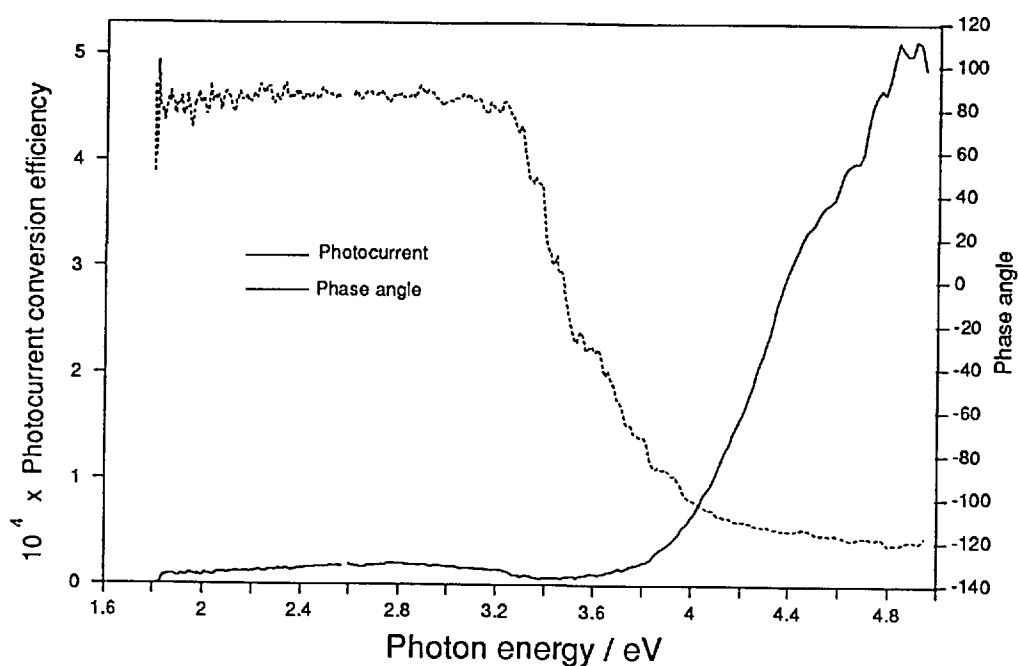


Figure 5.2.1. Photocurrent spectrum for chalcopyrite electrode just anodic of its rest potential, -0.036 V in 0.1 M borax, pH 9.2 .

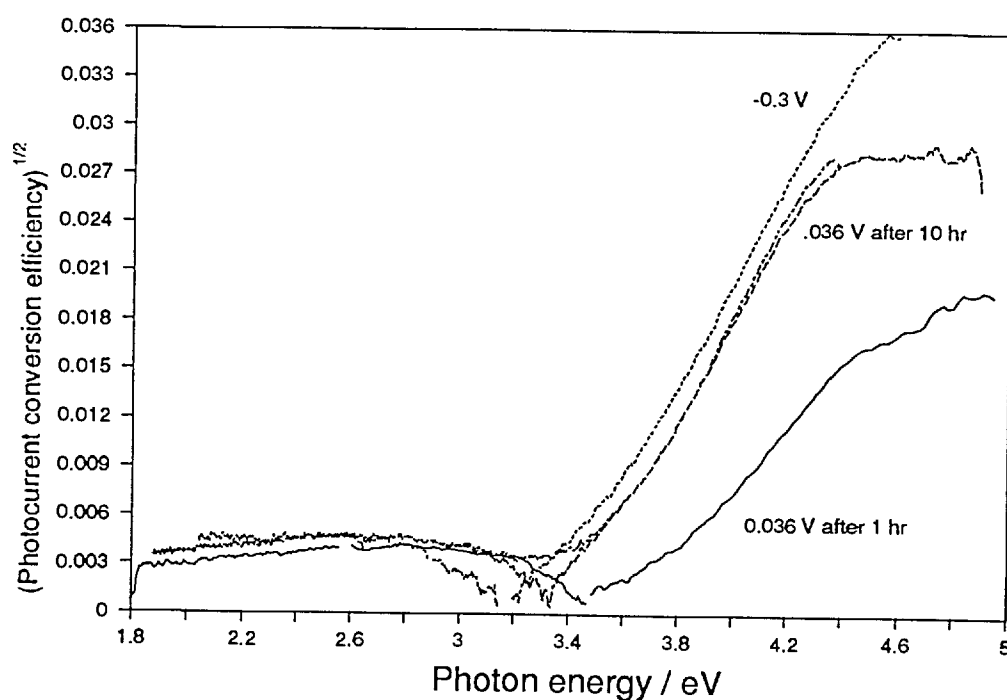


Figure 5.2.2. Indirect electron transition plot for cp as above and then shortly after reducing the potential to -0.3 V. The dot-dashed line is for values of $\Phi^{1/2}$ whilst the others pertain to $\{\Phi.(+/-)\sin\theta\}^{1/2}$

5.3. Bornite under reducing conditions

It would be interesting to compare the photocurrent data obtained for cp with those for bornite under similar conditions. Unfortunately, bornite photocurrents were considerably smaller than those for cp, and the most successful spectral results presented in Figure 5.3.1 did not allow for accurate determination of threshold energies and their potential dependence. However Figure 5.3.1 does indicate an electron transition of approximately 3.2 eV, and is strong evidence for the notion that cp, upon reduction in alkali, forms sulphides of composition intermediate between itself and bornite. Figure 5.1.1 also shows that the total current at -0.3 V was much smaller for bornite than cp, and that there is no simple correlation between I_{tot} and θ . The small current at -0.3 V supports the thermodynamic predictions considered in the introduction, namely that bornite is stable over greater potential range than cp at any given pH (see Appendix 1 Figure).

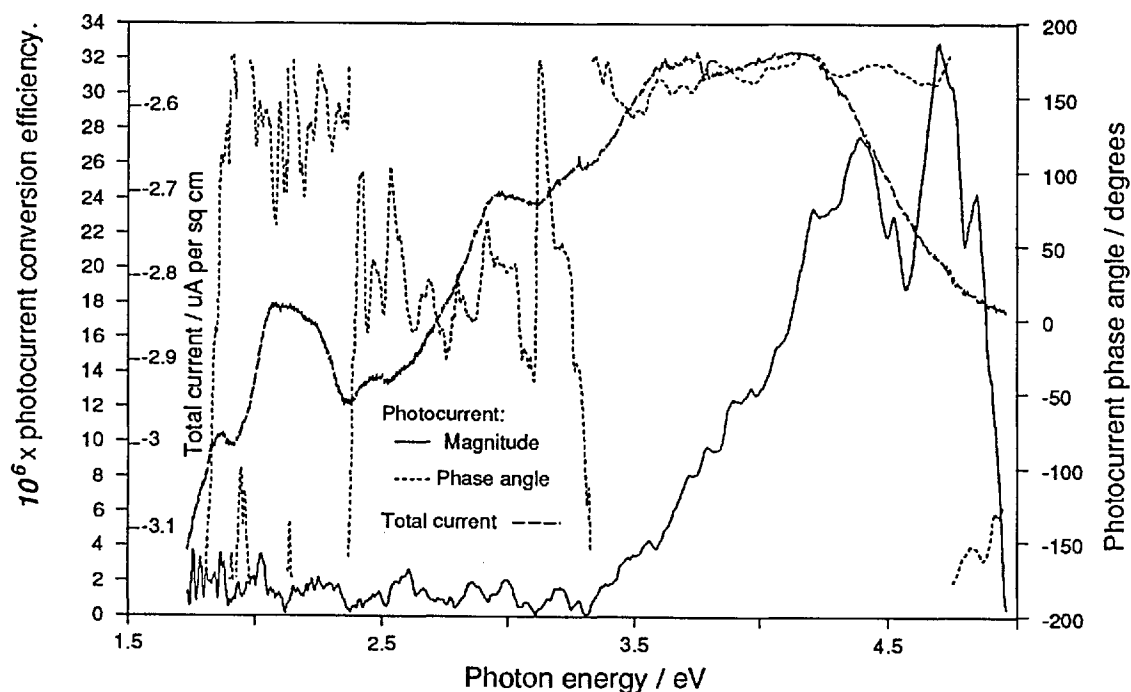


Figure 5.3.1. Photocurrent spectrum parameters i_{tot} , Φ , and θ vs $h\nu$ for bornite electrode in 0.1 M borax solution at an applied potential of -0.3 V.

5.4. Chalcocite at its rest potential

The formation of chalcocite, Cu_2S , from cp at moderately reducing potentials and pH 9 can be dismissed on thermodynamic grounds. However, to find out if there are similar electronic transitions involving the CuS_4^{7-} cluster in the two cases, photocurrent spectra were determined just above the rest potential of chalcocite, resulting in a plot of $\{\Phi \cdot h\nu\}^{1/2}$ vs $h\nu$ shown in Figure 5.4.1. The phase angle was $88^\circ \pm 1^\circ$ throughout the spectrum and

under "white light" irradiation. As discussed in the next chapter, the oxide formed on chalcocite at more anodic potentials gave rise to a similar response. It may be inferred from Figure 5.4.1 that photocurrents arose from an indirect electron transition for which the threshold energy was some 1.8 eV. Figure 5.4.1 bears very little resemblance to the equivalent plot for cp shown in Figure 5.2.2, suggesting that the photo-active surface phases were quite different on the two minerals.

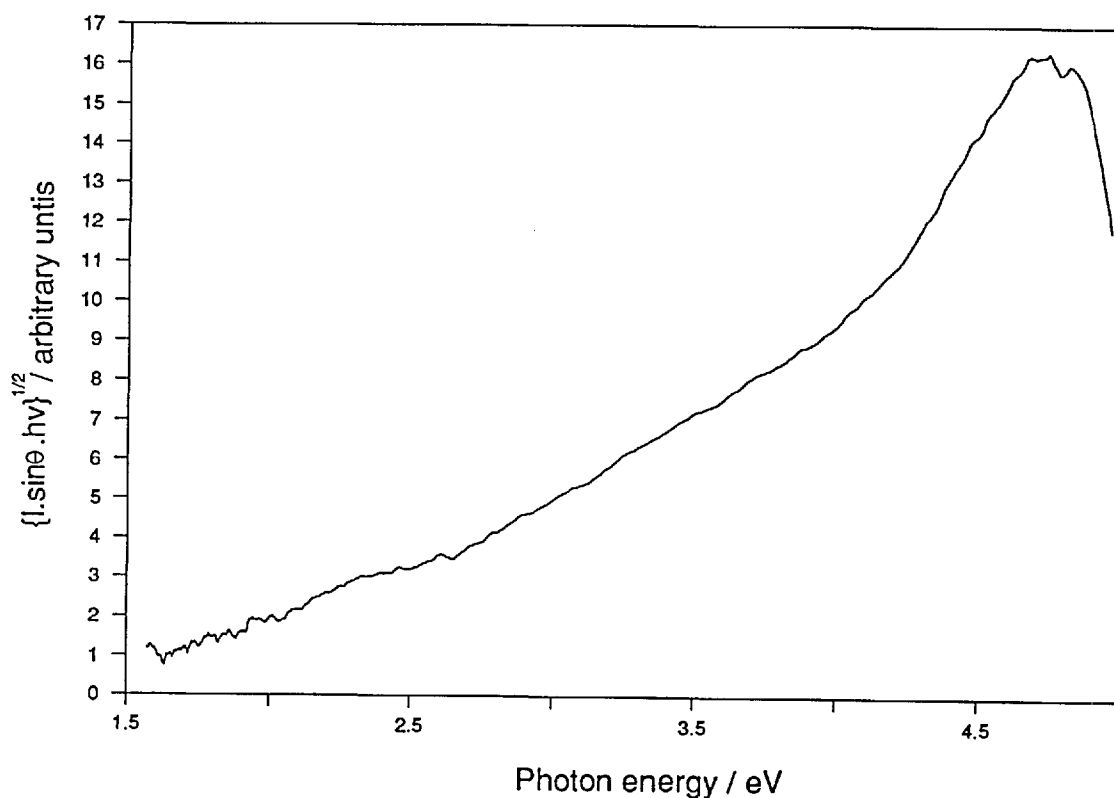


Figure 5.4.1. Indirect electron transition plot for Cu_2S at its rest potential of -0.07 V in 0.1 M borax.

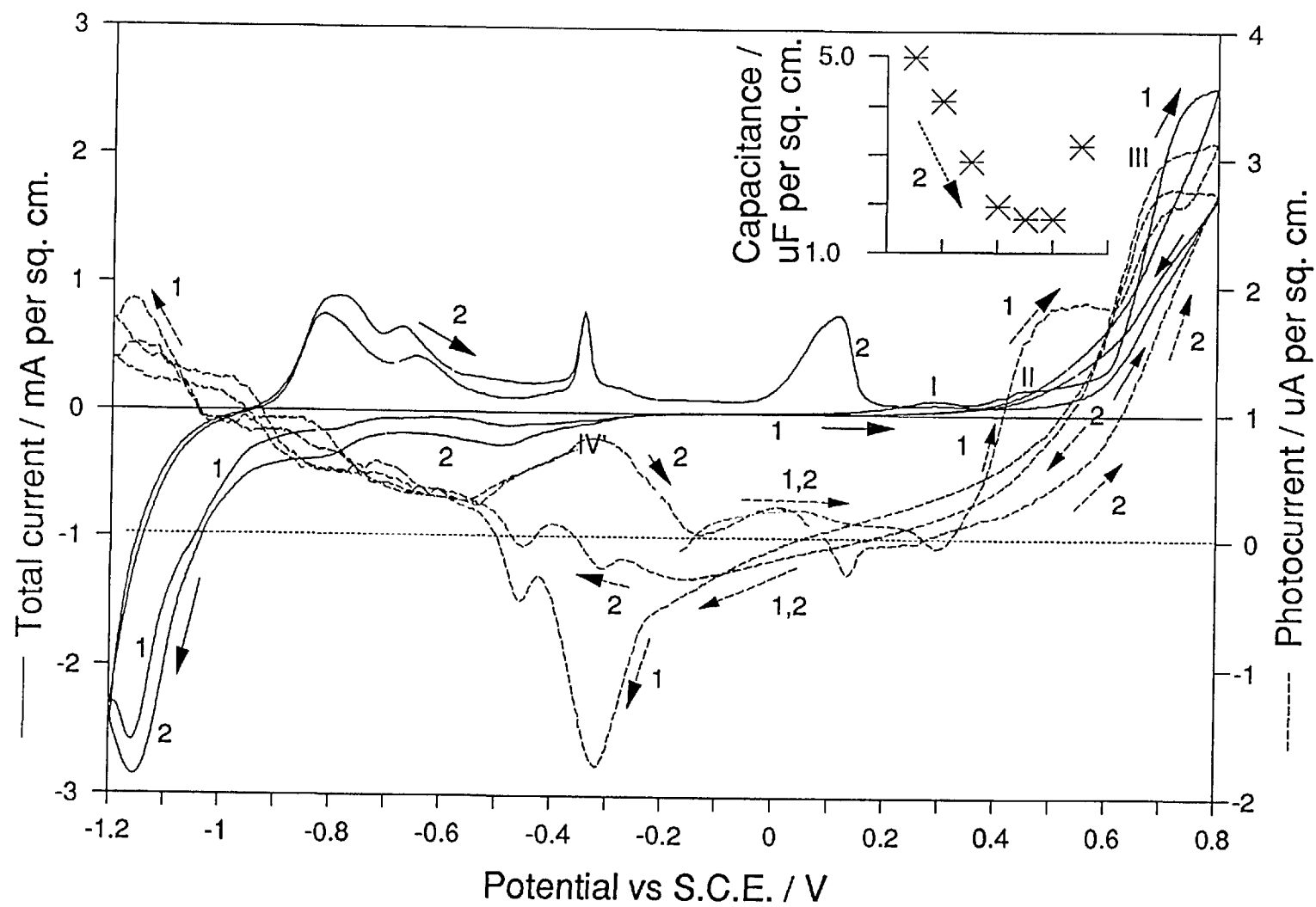
CHAPTER 6. OXIDATION OF CHALCOPYRITE IN ALKALINE SOLUTIONS

6.1. Introduction

Figure 3.7. 1 - 6 show that multifarious electron transfer processes occurred at the surface of a cp electrode during linear sweep voltammetry. Their deconvolution would seem to require a retrograde strategy, such as was successfully applied to identify the formation of chalcocite from cp in acid, Chapter 4. To identify the nature of the surface of cp under the mildly oxidising and alkaline conditions employed during froth flotation of cp from its ore, it is reasonable to begin with a consistent feature in Figures 3.7 1 - 6, even though it was apparent only after one full potential sweep cycle between -1.2 and 0.8 V. Such a feature is the broad photocurrent signal above 0.2 V. Chalcopyrite 22 was adopted for the remainder of the experiments, and a comprehensive illustration of its potential dependent behaviour is provided in Figure 6.1.1, which will be referred to in the following sections. That Figure 6.1.1 shows more complex photo-activity than the earlier figures is due to the phase sensitivity of the EG & G 5210 as opposed to the Bentham 213 lock-in amplifier, whereupon signals with phase angles near 0 or 180 ° were recorded. The experimental procedure remained unchanged.

Overleaf:

Figure 6.1.1. $i_{ph} \sin \theta$ and i_{tot} vs V , for cp electrode in 0.1 M $Na_2B_4O_7$ linearly swept between potential limits of +0.8 and -1.2 V, two cycles, 5 mV s^{-1} . Also depicted is the variation in capacitance under stepped potentiostatic control obtained from impedance spectra following one stepped sweep to -1.2 V and +0.8 V.



6.2. *n*-type hematite; α -Fe₂O₃

Figure 6.2.1 shows the variation of i_{tot} and i_{ph} with linearly swept potential, for a 5 mm diameter 99.99 % purity iron electrode in 0.1 M Na₂B₄O₇. Identical conditions prevailed, and the same apparatus was used to obtain this figure as in Figures 3.7. 1 - 6. Comparison between them shows that photo-anodic behaviour of both the iron and cp electrodes occurred above 0.2 V, although the resemblance of i_{ph} vs E profiles was closer for cp following potential excursions to -1.2 V, and closest following one full sweep cycle. α -Fe₂O₃ may be suspected, since the formation of iron by reduction of cp at -1.2 V is thermodynamically feasible, and all the more so by reduction of cp oxidation products, as shown in Appendix Figure 1. Now α -Fe₂O₃ is well identified as the photo-active and passivating film which can be grown on iron electrochemically, often overlaid with γ -Fe₂O₃ [229]. The photo-effects are smaller than those observed from bulk α -Fe₂O₃ electrodes, but bandgaps can and have been obtained from both, by optical and photocurrent spectra [28]. Table 6.2.1 includes typical bandgaps obtained from photo-active hematite prepared by a range of different methods.

Surface	Dopants, method of preparation.	Bandgap / eV	Ref.
α -Fe ₂ O ₃	TiO ₂ , sintered	1.9	[230,231]
α -Fe ₂ O ₃	TiO ₂ , sintered	2.1	[232]
α -Fe ₂ O ₃	SiO ₂ , sintered	2.2	[233]
α -Fe ₂ O ₃	GeO ₂ , SnO ₂ , PbO ₂ , sintered	2.2	[234]
α -Fe ₂ O ₃	Ti, sintered	2.2	[235]
Fe ₂ O ₃ film	CVD on Ti and Pt	2.2	[236,237]
Fe ₂ O ₃ film	Fe to 1273 K in O ₂	2.1	[181,238]
Fe ₂ O ₃ film	Fe electrode at 800 mV vs S.C.E.	1.9	[165]
<i>n</i> -type CuFeO ₂	from elements, sintered, pH 9.2	2.03	[117]
Film on cp	Natural cp at pH 9.8 at 0.7 V.	1.88	This work

Table 6.1.1. Threshold energies for various photoactive phases that could form oxidatively on cp.

In contrast to the situation near the rest potential, the decay in photocurrent at +0.7 V was too rapid for a clean spectral profile to be obtained unless preceded by one cyclic potential sweep to 0.8 and -1.2 V from the rest potential. Then the spectral response closely resembled that of passivated iron at the same pH obtained in both this work, **Figure 6.2.2**, and the work of Stimming [165]. The plot of $\{\Phi \cdot hv\}^{1/2}$ vs hv , is linear for photon energies above 2.2 eV. The threshold energy derived is 1.884 ± 0.015 eV, in agreement with Stimming's value for passivated iron of 1.9 eV. The latter is interpreted to arise from *non-direct* electron transition in a passive amorphous semiconducting film [225]. Moreover, as shown in **Figure 6.2.2**, the plot of $\{\Phi \cdot hv\}^2$ vs hv is also linear for higher photon energies, indicating a threshold energy of 2.45 ± 0.03 eV. This agrees favourably with Wilhelm and Hackerman's value of 2.5 eV for α -Fe₂O₃ on iron [141]. Indeed, it was by using their data that Stimming [165] derived the value of 1.9 eV. The photocurrent spectrum following one excursion to -1.2 V was only measurable at a positive potential limit of 0.6 V, and then only using a 900 W xenon lamp and the more sensitive EG & G 5210 lock-in amplifier. The profiles of Φ vs hv in **Figure 6.2.3** were therefore quite different from that in **Figure 6.2.2** and the magnitude of Φ in the two cases is not strictly comparable.

Figure 6.2.3 shows that the effect of a slower negative-going potential sweep rate (**b** vs **a**), was to lead to an oxide film forming at +0.6 V for which the plot $\{\Phi \cdot hv\}^{0.5}$ vs hv was linear over a wider range of photon energies. θ In both cases was 90° at all wavelengths and under white light. The band edge in case **a** was near 1.9 eV suggesting α -Fe₂O₃ as one likely surface phase. In case **b** entirely different photo-activity is suggested. On the basis of conclusions reached in **Chapter 5**, it is possible that the preferential migration of iron from the cp lattice at negative potentials led to a relatively iron rich surface at fast potential sweep rates. The scan at 0.1 mV s⁻¹ enabled copper metallisation to, as it were, 'catch up'. Indeed, enrichment in the more electro-positive copper is thermodynamically slightly preferred over iron at potentials below -1.0 V, as the **Appendix 1** figure shows. It follows that copper matallisation under kinetic control is favoured by slower negative-going potential sweep rates. Consequently, quite different photo-active oxide surfaces grew on the electrode surface at +0.6 V in the two cases. The extent of linearity of $\{\Phi \cdot hv\}^{0.5}$ vs hv for case **b** in **Figure 6.2.3** suggests the formation of a uniform semiconducting n-type oxide film for which non-direct electron transitions gave rise to photocurrents across a forbidden energy gap of some 2.6 eV. This result will be discussed in **Section 6.4** with reference to direct cp oxidation.

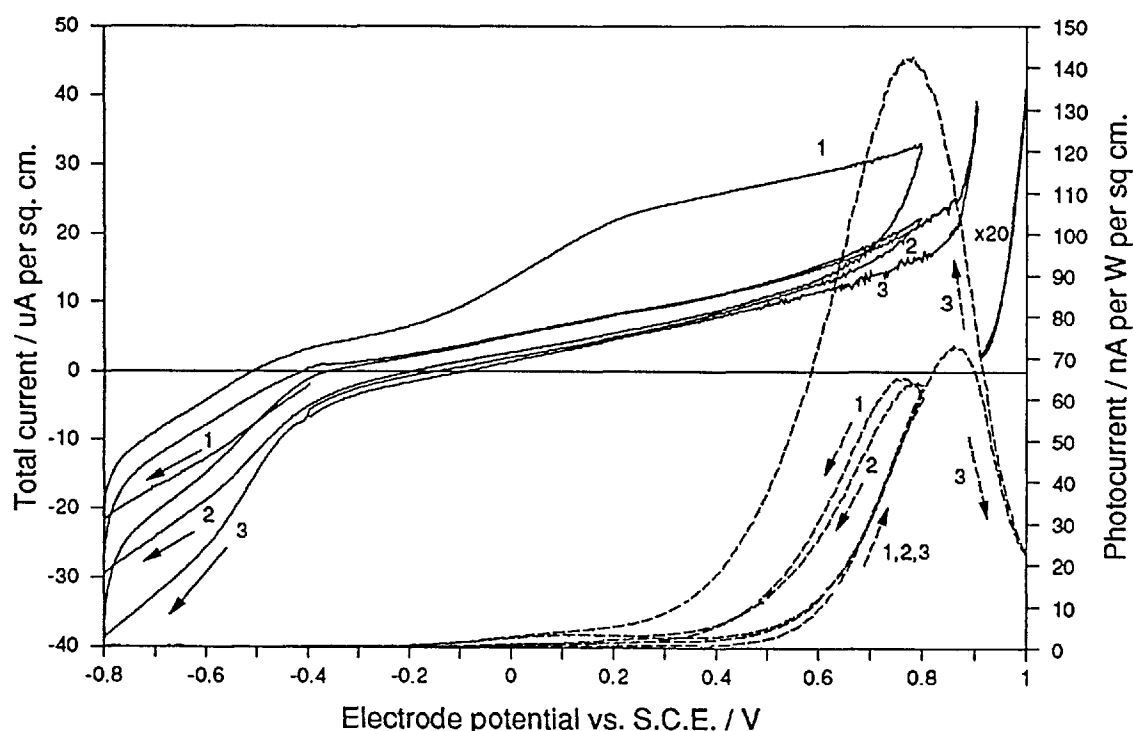


Figure 6.2.1. i_{ph} and i_{tot} vs V , for iron electrode in 0.1 M sodium tetraborate linearly swept between potential limits of +0.8 and -1.0 V, two cycles, and +1.0 and -1.0 V, 1 cycle.

For $\alpha\text{-Fe}_2\text{O}_3$ Anderman and Kennedy [28] gave a value for the flatband potential, U_{fb} , drawn from various reports, of -0.8 ± 0.25 V at pH 13.6. A Nernstian shift in U_{fb} with potential has been confirmed [239], so at pH 9.2, U_{fb} would be -0.56 ± 0.25 V. Values determined from the onset of photocurrents as opposed to Mott-Schottky plots to infinite capacity are higher, and in this work Stimming's value at pH 9.2 is adopted, namely -0.3 V. $\alpha\text{-Fe}_2\text{O}_3$ is reduced at potentials well negative of -0.1 V, yet positive of this potential the cp total current and photocurrent became cathodic. Therefore it is not surprising that the chalcopyrite electrode's capacitance variation with potential following a potential excursion to -1.2 V did not coincide with oxidised iron capacitance data presented by Stimming, which were consistent with Mott-Schottky type behaviour. The data for cp are shown in Figure 6.1.1. A plot of $1/C^2$ vs V gave no region of linearity, but at potentials > 0.2 V the capacitance varied inversely with anodic photocurrents, indicating that the capacitances, whilst genuinely indicative of the semiconducting phase, are governed not so much by a flatband potential as by its the potential dependent formation, and perhaps by other phases that do not give rise to a photo-anodic response. In particular it is unlikely that the photo-anodic response arose from copper (II) oxide, a p-type semiconductor both in the bulk and as a photo-electrode [240,241], but this product

could easily have affected the capacitance if present on the electrode surface in localised or layered zones. In the next section evidence is presented supporting this possibility. Hematite can exhibit p-type behaviour, but if the photo-anodic behaviour has been correctly attributed, it is unlikely that hematite was responsible for any photocathodic behaviour.

Certainly the preponderance of photo-anodic currents at pH 9.2 is firm evidence for the presence of oxides, notably hematite, and is contrary to previous understanding that chalcopyrite forms exclusively hydroxides under these conditions (see for example [6]). It could be argued that the harsh cathodic regime imposed prior to eliciting photocurrent spectra at > 0.5 V means they provide very little information about the chemistry of the mineral itself. At this stage, the important conclusion is that the fate of nearest neighbours sulphur and copper in the cp lattice under certain applied potential pre-treatment did not prevent the iron from eventually forming a discrete phase not unlike hematite in its photo-anodic behaviour.

As with ferric oxide on iron electrodes, the anodic photocurrent increased markedly upon addition of KI, which acts as an efficient hole scavenger:



Such effects were enhanced if the electrode was first subjected to potentials < -0.8 V.

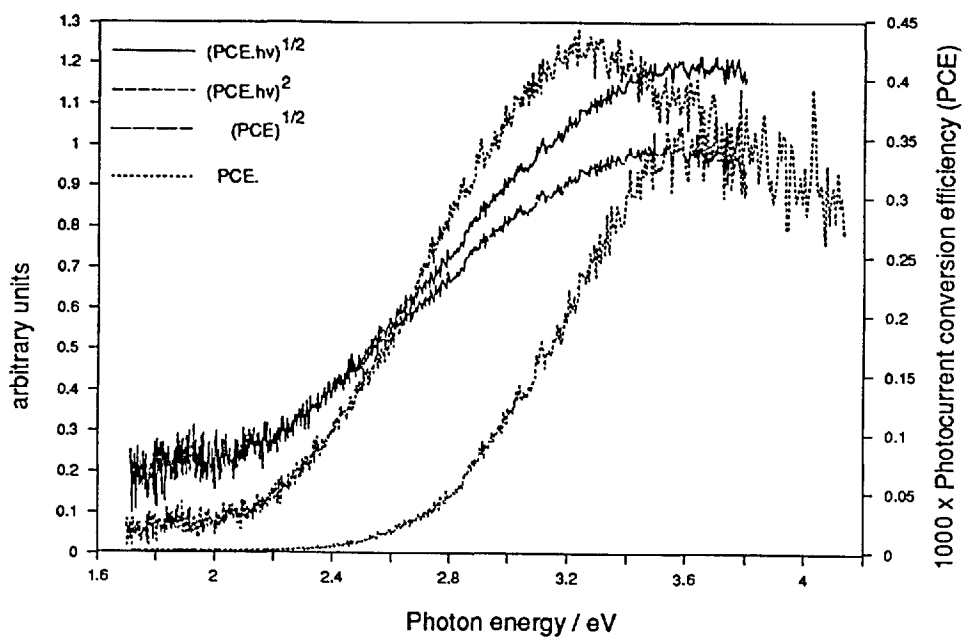


Figure 6.2.2. Plots of Φ and $\{\Phi.hv\}^n$ vs $h\nu$ for cp electrode in 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$ maintained at 0.7 V following a potential excursion from -0.2 V to and from -1.2 V at 5 mV s^{-1} . 60 nm s^{-1} monochromator sweep rate.

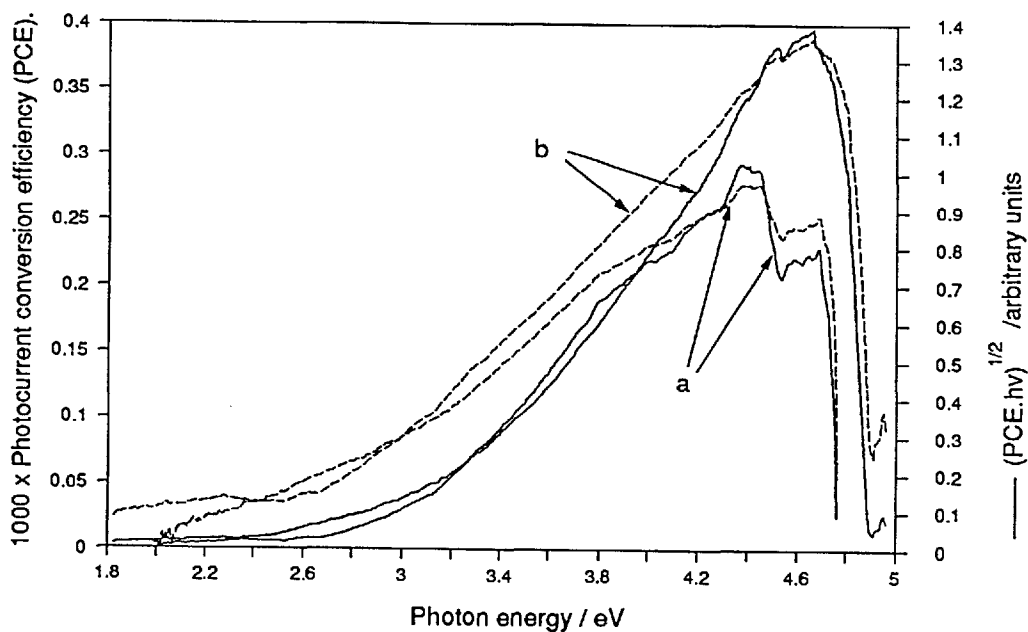


Figure 6.2.3. Plots of Φ and $\{\Phi.hv\}^n$ vs $h\nu$ for cp electrode in 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$ maintained at 0.6 V following excursions from -0.2 V: a, to and from -1.2 V at 5 mV s^{-1} ; b, to -1.2 V at 0.1 mV s^{-1} and from -1.2 V at 5 mV s^{-1} . 60 nm s^{-1} monochromator sweep rate.

6.3. *p*-type Cu_2O

The other outstanding feature evident from photocurrent-potential profiles for cp in 0.1 M sodium tetraborate was the sharp photo-cathodic peak near -0.3 V following potential excursions from the rest potential to 0.8 V. If oxidation of cp to delafossite (CuFeO_2) is not considered, then CuO is the thermodynamically predicted product at pH 9.2 and applied potentials of 0.8 V. In the first instance, it is reasonable to suppose copper oxidation products form on cp in a manner which may resemble the oxidation of copper when it is subjected the same positive potentials in the same solutions. Abrantes *et al.* [242] concluded that the metal surface at pH 9.2 and 0.8 V can be expected to consist of $\text{Cu}(\text{OH})_2$ overlying a thin layer of Cu_2O . Reduction of $\text{Cu}(\text{OH})_2$ to Cu_2O was observed on the reverse scan below the standard potential for this couple, -0.1 V at pH 9.8. The flat band potential of Cu_2O is 0.26 V at pH 7 [243], and assuming a Nernstian shift in U_{fb} with pH, U_{fb} at pH 9.8 would be 0.09 V. Therefore its reductive formation would occur under depletion conditions, giving rise to photo-cathodic currents. The Cu electrode on reverse scans following positive potential excursions to 0.8 V was found to do so, as shown in **Figure 6.3.2**, which is presented for comparison with **Figure 6.3.1**. It shows that in 0.1 M sodium tetraborate solution the photocathodic response to swept potential of the copper electrode closely resembled that of cp. **Figure 6.3.1** is contrary to the results presented by Abrantes *et al.* [242] in showing a photo-cathodic effect at potentials approaching 0.4 V on both forward and reverse scans. Likewise the reverse scan photocurrents in **Figure 6.3.2** were seen to decay by -0.7 V, not -0.9 V, as observed by Abrantes *et al.*. This is consistent with the slower sweep rate employed in the present work, 5 vs 10 mV s^{-1} . **Figure 6.3.2** shows an additional total cathodic current peak at -0.6 V associated with a photocurrent shoulder which Abrantes *et al.* attributed to photo-assisted Cu_2O reduction. This is well negative of the standard potential of the $\text{Cu}/\text{Cu}_2\text{O}$ couple of -0.274 V at pH 9.8, precisely the potential at which photo-activity shown in **Figure 6.3.2** was at its maximum.

It will be explored in the following section that a similar phase did indeed affect the observed cp spectral photocurrents, although "white" light photocurrents were too transient at all potentials approaching -0.3 V for photocurrent spectroscopy to be performed following potential excursions to 0.8 V. As regards the photo-active copper oxide phase on copper, it was readily grown and reduced by subjecting the electrode to 0.0 and -0.3 V respectively. At each constant potential the photocurrent was allowed to stabilise, and the spectral response measured. As with iron, a linear relationship is found

between $\{\Phi \cdot h\nu\}^{1/2}$ and $h\nu$ at photon energies above 2.4 eV, especially at 0.0 V as shown in **Figure 6.3.3**. Analysis of the 0.0 V spectral data regression indicated a threshold energy of 2.39 ± 0.04 eV.

An extraordinary possibility emerges from the photo-active nature of Cu_2O described above and $\alpha\text{-Fe}_2\text{O}_3$ described in **Section 6.2**. If they both formed anodically as discrete phases of a heterogeneous product layer on the cp electrode surface as shown in **Figure 6.3.4a**, illumination could give rise to opposing photocurrents from different surface zones. Above the flat band potential of n-type hematite, near -0.5 V, and below that of p-type Cu_2O , near +0.1 V, there could be a potential at which the net photocurrent is zero, but where the two phases were far from being photo-inactive. A similar situation would prevail if exposed p-type cp at potentials in excess of its flatband potential contributed to the total photocurrent, **Figure 6.3.4b**. These eventualities would be revealed in photocurrent spectra, where the photocurrent contributed by each of the two phases at any particular light wavelength is unlikely to be the same, and where indeed both photo-cathodic and anodic currents would be observed on varying the wavelength of incident radiation. What actually prevailed was the more subtle situation already exhibited in **Figure 6.3.1**. Only soon after the commencement of the potential sweep did "white" light photocurrent phase angles θ approach zero. On the reverse scan from 0.8 V, θ changed gradually from +85 to -130 ° *via* 180 - not 0 ° - whilst Φ moved through a minimum value, indicating that the p-type phase, when present on the electrode surface at all, was not entirely segregated from the n-type phase. One possibility is that one photo-active phase, say p-type Cu_2O , overlay another, say n-type $\alpha\text{-Fe}_2\text{O}_3$, their relative thickness determined by the applied potential regime. This is shown in **Figure 6.3.4c**. Alternatively, a complex photo-active phase prevailed on the electrode, homogeneous in the electrode surface plane, whose photocathodic vs photoanodic proclivity depended either on the potentially determined copper, iron and oxygen (or sulphur) atomic ratios within it, or on a modification of the band structure of the substrate directly beneath it. These possibilities are represented in **Figure 6.3.4d**. At the outset, in **Figure 6.3.4**, 'metal-depleted chalcopyrite' is understood to cover a wide range of sulphur-bound products of cp oxidation, from CuS plus S, to truly metal-depleted cp in which the cp structural integrity is maintained.

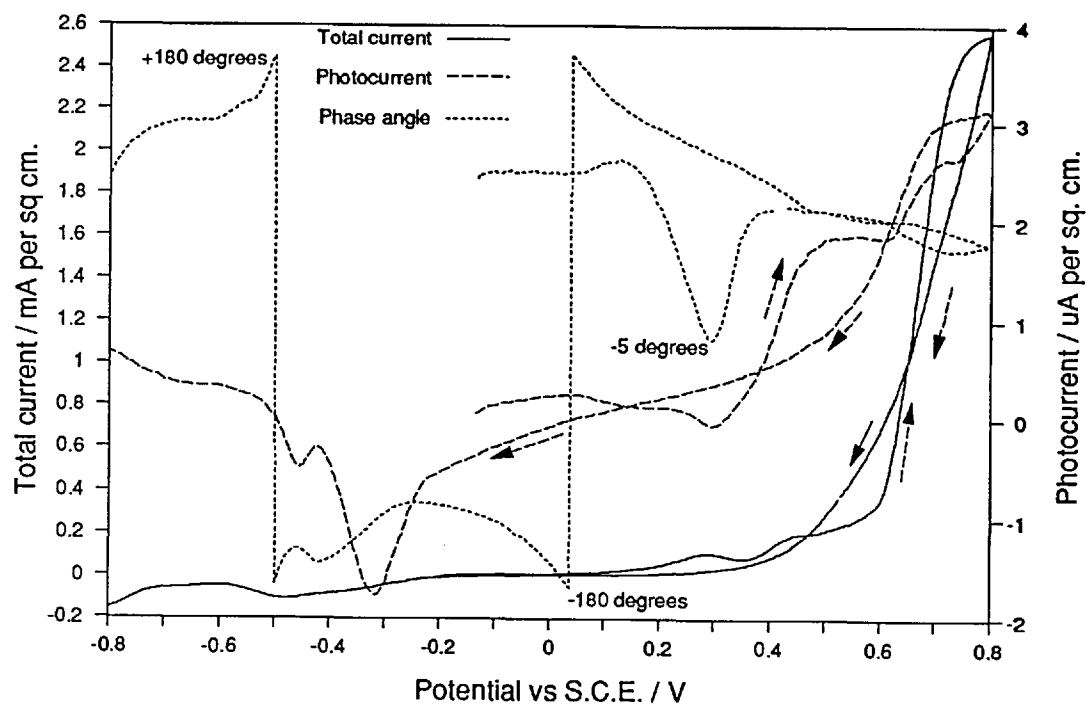


Figure 6.3.1. Detail of Figure 6.1.1, for cp at pH 9.2, showing initial response of i_{tot} , i_{ph} and θ to the swept potential.

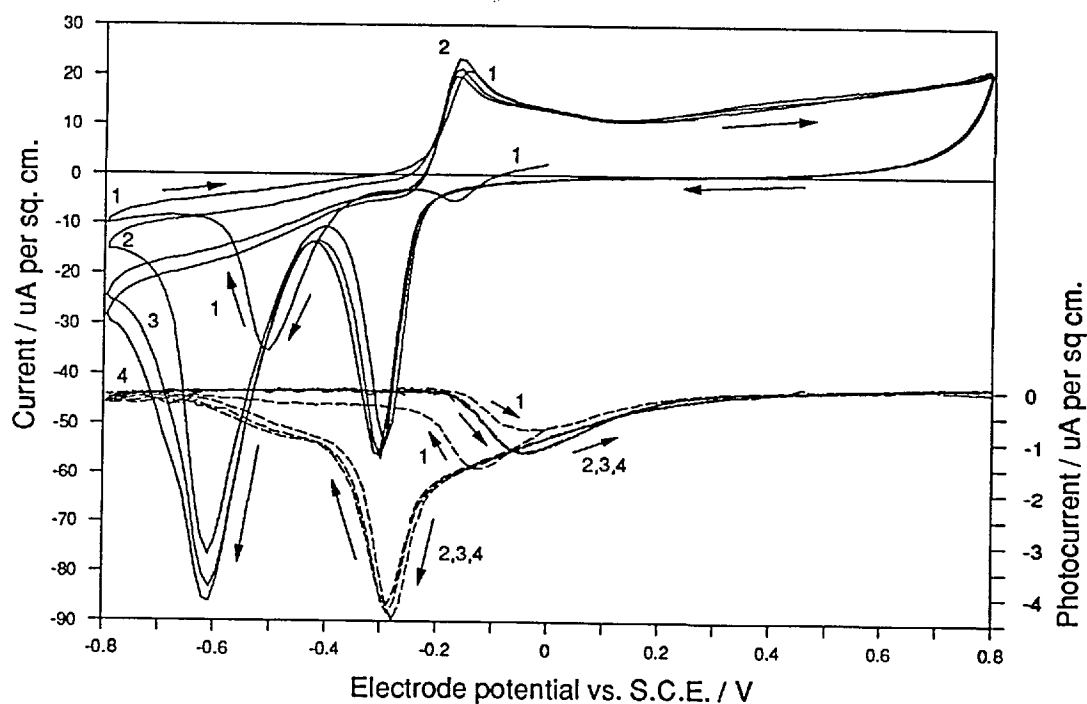


Figure 6.3.2. Total current and photocurrent response of a Cu electrode to potential excursions between -0.8 and 0.8 V at pH 9.2. Sweep rate 5 mV s^{-1} .

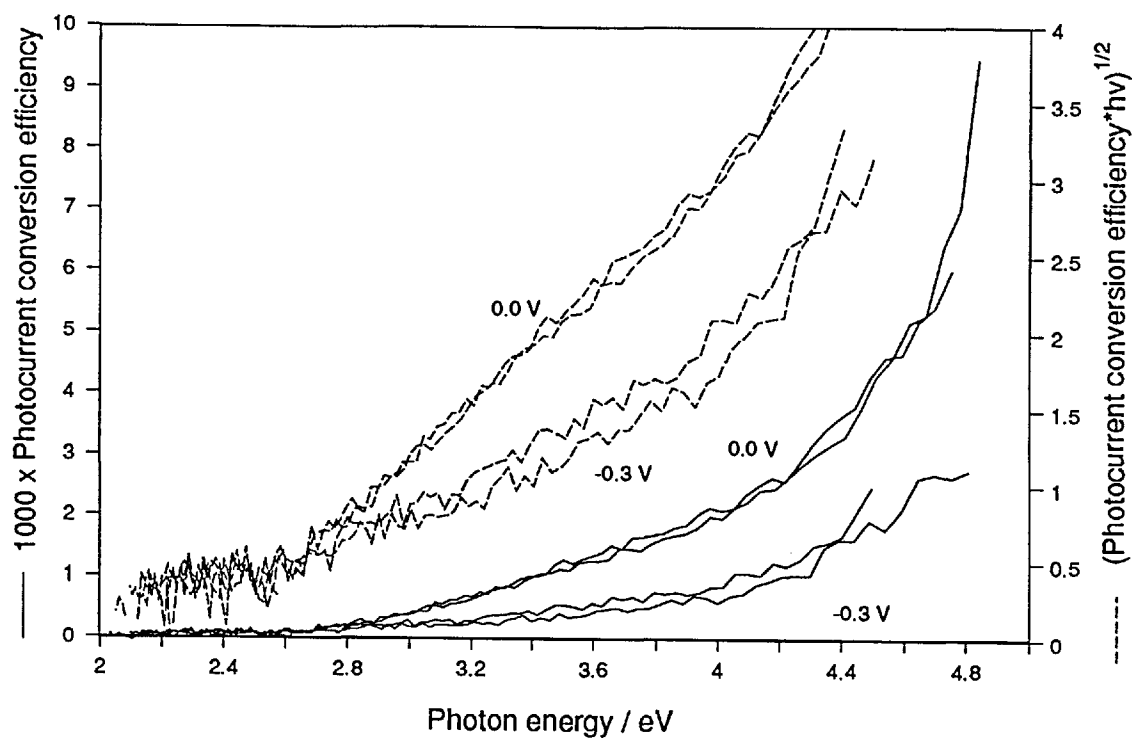


Figure 6.3.3. Plots of Φ and $\{\Phi \cdot hv\}^{1/2}$ vs $h\nu$ for a copper electrode in 0.1 M sodium tetraborate alternately maintained at 0.0 and -0.3 V after 8 minutes at each potential. Two spectra are presented at each potential to illustrate the consistency of the results. 1 nm s⁻¹ sweep rate.

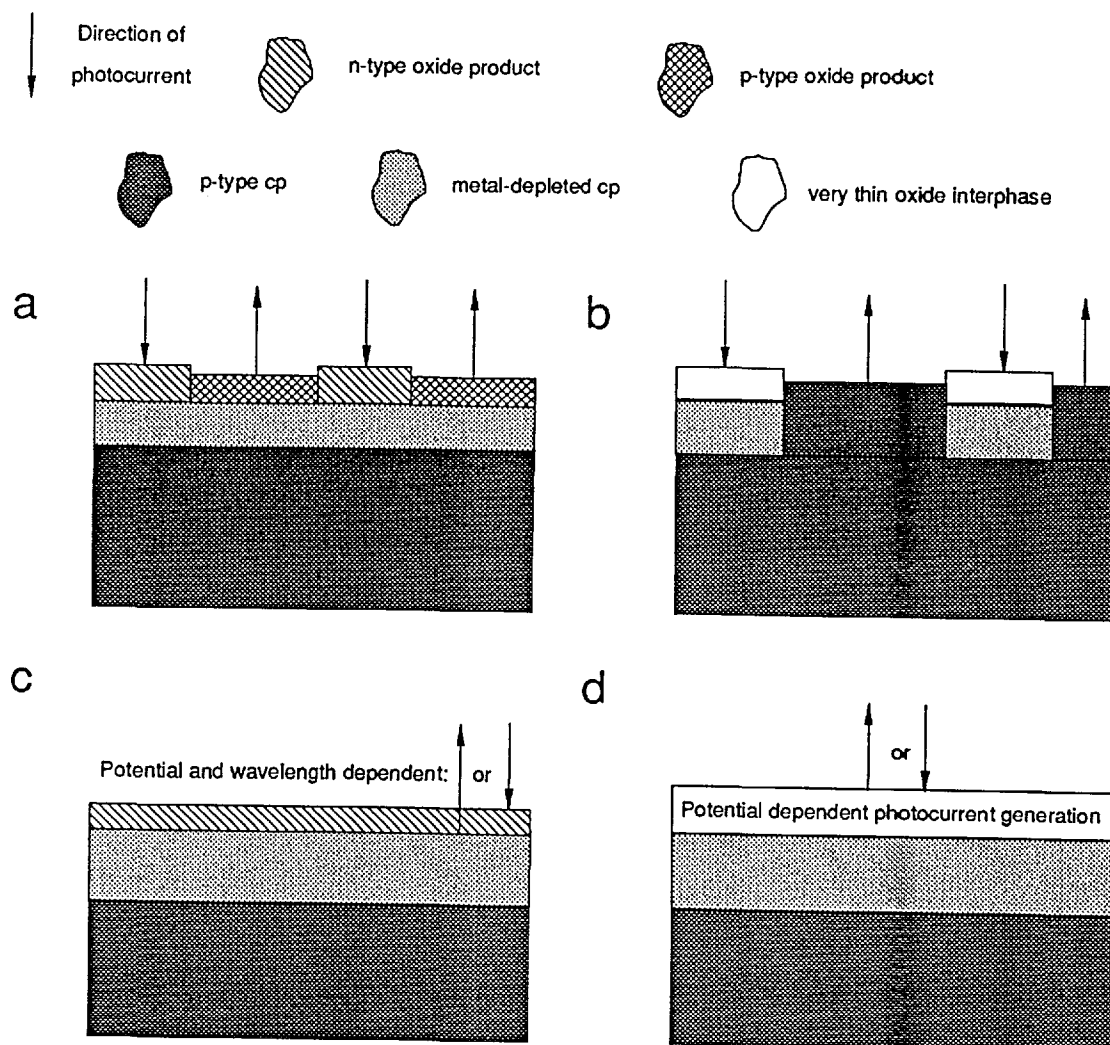


Figure 6.3.4. a and b, heterogeneous vs c and d, homogeneous oxide product formation on a cp electrode shown in cross section, in alkaline solutions. The direction of photocurrent indicated is for photo-generated electrons. Photo-generated holes will move in the opposite direction. b and d conform to the experimental evidence.

6.4. Photocurrent spectra of chalcopyrite at oxidising potentials

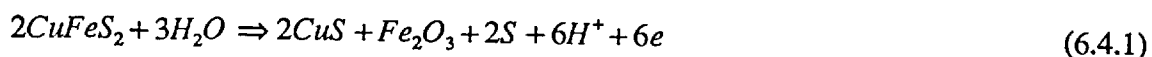
In Section 5.2 photocurrent spectra for cp at 0.03 V in 0.1 M sodium tetraborate were compared with spectra under reducing conditions. On the strength of the above observations the photocurrent spectra of cp at pH 9.2 under oxidising potentials can now be presented with a certain foresight about what may be expected if Cu_2O and $\alpha\text{-Fe}_2\text{O}_3$ are involved. The same procedure was adopted to obtain the following spectra as in Chapter 5. Indeed, the electrode used to obtain the results shown in Figure 5.1.2 was subsequently used to obtain those in Figure 6.4.1a. The plot for -0.275 V in Figure 6.4.1a has a similar profile to the plot for -0.25 V in Figure 5.1.2, but indicates

higher photocurrent efficiencies. This may be as much due to the history of the electrode as to different incident photon flux at the electrode surface. Between the two experiments, several attempts to measure photocurrent spectra were abandoned at the outset because the electrode's rest potential had been as low as -0.4 V. Only after at least 1 mm of the approximately 5 mm thick electrode had been ground away was the experiment described below conducted. This behaviour bears out one of the conclusions in the previous chapter. Metal enrichment had clearly extended deep into the cp lattice as a result of the cathodic conditions applied.

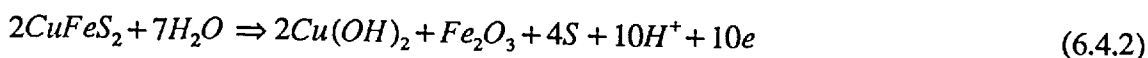
Figure 6.4.1a and **b** indicate the emergence of photo-anodic behaviour as the electrode potential was stepped positively. θ became increasingly positive, most markedly so in the photon energy range $2 \text{ eV} < h\nu < 3 \text{ eV}$, although the effect of increasing potential was diminished photocurrents over the entire spectral range. Now this might be explained in terms of two contributory but opposing photo-effects at any given photon energy if they are assumed to be combined by vector addition. For instance, if an n-type iron-rich oxide phase, $\text{Cu}_x\text{Fe}_y\text{O}_2$, ($x \ll y$), had grown from nucleation centres and prevented the generation of photocurrents by photo-generated carriers in the underlying cp, the two effects, $i_{\text{ph}}(\text{Cu}_x\text{Fe}_y\text{O}_2)$ at phase angle $\theta(\text{Cu}_x\text{Fe}_y\text{O}_2)$, and $i_{\text{ph}}(\text{cp})$ at $\theta(\text{cp})$, would combine by their simple vector addition.

The vectorial change in i_{ph} and θ at successive potentials relative to their values at -0.275 V, of magnitude $I(D)$ and angle $\theta(D)$, is illustrated in **Figure 6.4.2**. It does offer striking clues about what was occurring at the cp surface. Below 3.6 eV, it shows that the photocurrents at potentials $\geq -0.125 \text{ V}$ were effectively shifted by $I(D)$ equal to the entire magnitude of i_{ph} at -0.275 V, with a phase angle near 0° . This is in contrast to the photocurrents below 3.6 eV at -0.275 V, for which θ was approximately -110° , as shown in **Figure 6.4.2b**. Even at the rest potential of -0.275 V, some oxidation must have been inevitable, bearing in mind the predicted upper limit of cp stability at pH 9.2 is -0.385 V. At $> 3.6 \text{ eV}$, **Figure 6.4.2a** shows that the effect of increasing the potential was to progressively erode the photo-cathodic current signal due to the emergence of a photoanodic effect. It is postulated that the growth of an n-type oxide phase was instrumental at these higher photon energies in preventing the underlying cp photo-generated minority carriers, electrons, from reaching the electrolyte interface and effecting reduction. The low positive values of $\theta(D)$, **Figure 6.4.2b** also suggest the increasing contribution a *thin* film may have made to the observed spectral photocurrents. Because the availability of minority carriers from such a film on exposure to light would be quickly exhausted, it gave rise to very transient photocurrents, *i.e.* at the outset of each light chopping cycle, and so $\theta = 0^\circ$.

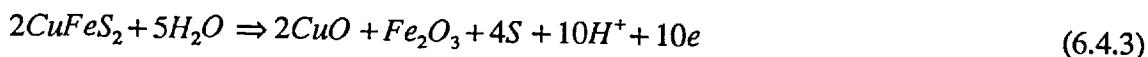
There are several reasons for thinking an iron-rich oxide phase formed on the cp surface. An oxide is reasonable on thermodynamic grounds. For the idealised reactions at pH 9.2:



$$E = -0.385 \text{ V},$$

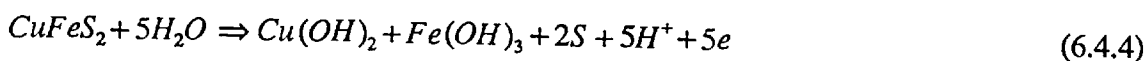


$$E = -0.197 \text{ V},$$



$$E = -0.211 \text{ V}.$$

Therefore any of these reactions are feasible at 0.025 V. The more likely initial formation of the oxides *via* hydroxides does not significantly alter these standard potentials. Nor does it change the predicted preferential formation of iron oxide depicted in the metastability potential-pH diagram in the **Appendix**. For instance, at pH 9.2:



$$E = -0.151 \text{ V}.$$

Reaction (6.4.1) has the lowest standard potential of all possible oxidative reactions between the species tabulated in the **Appendix**, and is a manifestation of the exceptional affinity between copper and sulphur.

The experimental evidence supported thermodynamic considerations. A copper oxide, rather than an iron oxide, is unlikely to have initially formed on the electrode surface, giving rise as it does to exclusively photo-cathodic currents at 0.025 V, whereas both **Figures 6.4.1 and 2** clearly indicate emergent n-type behaviour. This is supported by investigations into the oxidation of cp in air. Buckley and Woods [222], using X-ray photoelectron spectroscopy, concluded that an iron-rich oxide or hydroxide formed on the mineral surface after a few seconds exposure to air. From the results of electron spectroscopy and micro-reflectometry Holloway *et al.* [244] proposed that FeOOH or Fe₃O₄ formed on the cp surface during polishing, which grew 20 to 40 nm thick upon prolonged exposure to air.

Furthermore, Fe³⁺ ion diffusion at oxidising potentials away from the mineral bulk could determine the relative rates of oxide formation; an effect likely to arise from the relative charge to size ratios of Cu⁺ and Fe³⁺. On this basis iron oxide formation is kinetically preferred to copper oxide formation. As the formation of a complete surface layer of n-type iron oxide proceeded at 0.025 V, the larger Cu⁺ ions could be expected to begin to migrate directly underneath the zones of iron oxide formation - which is just where cp was

depleted in iron - to the cp / $\text{Cu}_x\text{Fe}_y\text{O}_2$ interface, where a favourable electric field and concentration gradient would further cause them to move to the $\text{Cu}_x\text{Fe}_y\text{O}_2$ / solution interface, thereupon reacting with hydroxide ions.

At potentials exceeding 0.1 V, previous experiments had provided unstable photocurrents and therefore unreliable spectral information, so in the experiment described above, the cp was maintained for 10 hours at 0.025 V. The resultant photocurrent spectrum at 0.025 V is also shown in Figure 6.4.1, in which it is evident that the spectral n-type photo-effect had almost completely disappeared. This is consistent with a modification in $\text{Cu}_x\text{Fe}_y\text{O}_2$ during the elapsed time, possibly the formation of a copper-rich phase similar to p-type Cu_2O at the oxide / solution interface.

From the data presented in Figure 6.4.1, plots of $\Phi^{1/2}$ vs $h\nu$ and $\{\Phi \cdot h\nu\}^{1/2}$ vs $h\nu$ at increasing potentials showed remarkable linearity considering the probable complexity of the growing oxide product on the cp surface. These plots were treated both as a function of θ and independent of it. For illustration, Figure 6.4.3 shows plots of $\{\Phi\}^{1/2}$ vs $h\nu$ and $\{\Phi \cdot \sin\theta\}^{1/2}$ vs $h\nu$. The threshold energies derived from these and non-direct transition plots and their degree of linear correlation is given in Figure 6.4.7 together with the results from other experiments. The slightly better correlation for spectra including the $\sin\theta$ term complements the evidence from Figure 6.4.2 that an n-type oxide phase grew on the cp surface, such that there would be a photocurrent contribution from cp of efficiency $I_{ph}(cp) \cdot \sin\{\theta(\text{Cu}_x\text{Fe}_y\text{O}_2) - \theta(cp)\}$ - approximately $I_{ph} \cdot \sin\theta$ - which was independent of $I_{ph}(\text{Cu}_x\text{Fe}_y\text{O}_2)$. It is apparent that Figure 6.3.4b aptly describes photo-active product formation on cp under mildly oxidising potentials and in alkaline solutions.

The further spectra recorded at potentials ≥ 0.025 V, after 10 hours at 0.025 V and 20 hours after the start of the experiment convey quite different photoelectrochemical behaviour, as is clearly illustrated in Figure 6.4.6. Firstly, at 0.025 V "white" light photocurrents had increased in the intervening period at this potential, and the phase angle shifted had from its value of $90 \pm 5^\circ$ characteristic of the cp surface at all the more negative potentials considered so far. The oxidised surface was now altogether more photo-active, giving rise to larger spectral photocurrents and modified "white" light responses following the sixty minutes required for spectral sweeps. Threshold energies at potentials ≥ 0.025 V are plotted in Figure 6.4.7 (D). They were obtained by linear extrapolation of the plots in Figure 6.4.5 between 3.2 eV and 4.5 eV. These threshold energies were now close to the value of 2.6 eV obtained at 0.6 V after the slow negative-going potential sweep, as shown in Figure 6.4.7 (B). Figure 6.4.7, especially considered together with Figure 5.1.5, suggests the dominance of a single photoactive

interphase at potentials between 0.025 V and 0.4 V, consistent with the picture of homogeneous product layer formation presented in **Figure 6.3.4d**. Moreover, between the upper thermodynamic stability of cp, namely -0.385 V, and 0.025 V the emergence of this phase can be identified with **Figure 6.4.7 (C*)**, where similar threshold energies were obtained from linear regression analyses of $h\nu$ vs $\Phi^{1/2}$ plots of the I(D) data shown in **Figure 6.4.2**. Thus **Figure 6.3.4b** accords with the initial stages of oxidation of cp.

The total charge passed on commencing the spectral photocurrent sweep at 0.1 V was 98 mC cm⁻². Conservatively estimating a surface roughness factor of 2, this is equivalent to the formation of Fe₂O₃ by reaction (6.4.1) of thickness 2.6 nm, or 40 unit cells. The absorption coefficient of polycrystalline Fe₂O₃ is approximately 2×10^5 cm⁻¹ between 2 eV and 3.6 eV [28], so if this were the oxide product, some 95 % of the incident radiation flux in this range could be expected to penetrate the oxide product layer. The corresponding absorption coefficient of cp is 10^6 cm⁻¹ [36]. However, it was very unlikely photocurrents were generated from metal-depleted cp underlying oxide product layers for reasons discussed later. In addition, the distinct shift in threshold energies from 3.2 eV to 2.7 eV at potentials positive of the rest potential would not be expected from electron excitations within increasingly metal-deficient cp.

Cu₅FeS₄ or Cu₂S have been proposed as products of cp oxidation, underlying an iron (hydr)-oxide product (see **Section 1.3** and **6.7**). These sulphides are unlikely to account for the observed behaviour. Chalcocite appeared to be photo-active only under oxidising conditions, giving rise to a spectrum indicative of p-type Cu₂O, as shown in **Figure 5.3.1**, whilst the bornite photocurrent spectrum in **Figure 5.4.1**, is entirely different from those presented in **Figure 6.4.5**. The slow reductive sweep employed prior to obtaining a threshold energy of 2.6 eV at 0.6 V, (B) in **Figure 6.4.7**, further supports the notion that the sulphide product of cp oxidation did not give rise to the observed photocurrent spectra in alkaline solutions.

The case for heterogeneous product formation depicted in **Figure 6.3.4a** was further discredited at these high potentials. It is conceivable that as the potential was increased, photo-anodic currents could emerge from an n-type phase in which increasing band bending took place, quite isolated from a p-type phase similar to Cu₂O whose photo-cathodic currents would be decreasing, and active over a different photon energy range. The formation of this heterogeneous oxide product layer would render plots in **Figure 6.4.5** non-linear or the threshold energies deduced from the linear plots at 0.175 V and 0.25 V to be significantly different. They are not.

Moving to more positive potentials, **Figure 6.4.4** shows a complete transformation from p- to n-type spectral response occurred between 0.175 and 0.25 V without a significant change in the profile of Φ vs $h\nu$. Indeed, the potential dependent trend of extrapolated threshold energies shown in **Figure 6.4.7** suffers no abrupt change to suggest a fundamental phase transformation had taken place when the potential was stepped from 0.175 to 0.25 V. The monochromatic and "white" light photocurrent efficiencies decreased sharply at 0.25 V, as shown in **Figure 6.4.6**. In **Section 6.5**, 0.2 V will be established, under conditions of "white" light cyclic photo-voltammetry, as the critical potential for "white" light photocurrents changing from anodic to cathodic on positive-going potential sweeps. Therefore 0.2 V is not simply a characteristic flatband potential of a p-type layer between the oxide substrate and solution interface. The thinness of the film estimated as above was about 2.35 nm at 0.025 V (after 12 hr), 2.6 nm at 0.1 V and 2.85 nm at 0.175 V, which would seem to preclude effective electron-hole pair separation solely by an electric field normal to the surface, E_z , in a photoactive oxide layer. Yet the evidence suggests that the applied potential determined the direction of movement of photo-generated carriers normal to the electrode surface.

A tentative and schematic electronic energy band diagram is presented in **Figure 6.4.8** to explain the photocurrent spectra. It is proposed that at 0.025 V, an oxide layer had formed over the entire electrode surface with the characteristic threshold energy of 2.7 eV. Underlying cp was metal-depleted, giving rise to an enhanced hole donor concentration in this sulphide layer near the cp / oxide interface in the form of metal lattice site vacancies. These hole donors could prevent photocurrent generation from within the metal-depleted layer insofar as photo-generated minority carriers (electrons) in this layer would be liable to rapid recombination. Also, the space charge layer would be thinner in metal-depleted cp as compared with un-oxidised cp, resulting in electron-hole separation in a narrow slice of this metal-depleted region. Thirdly, any photo-generated electrons from the sulphide substrate that were able to migrate to the metal-depleted cp / oxide interface would be subject to trapping at interfacial states, and possible migration into the oxide layer could have been prevented by a low density of energy states in the oxide conduction band of the oxide of appropriate energy. Therefore the photoactivity emergent from even a thin oxide interphase could effectively prevent photocurrent generation from the semiconducting sulphide layers directly beneath it.

Metal-depletion could have been so extensive as to 'unpin' surface band levels relative to the Fermi level near the cp / oxide interface. In this respect the outermost sulphide layers may have been quasi-metallic. Certainly a substantial portion of the electric potential drop between the electrolyte solution and electrode interior could be expected across the

oxide, *i.e.*, E_z within the oxide would be far in excess of E_z within the bulk of the metal-depleted sulphide layer. This would explain the rapid separation of photo-generated electron-hole pairs within the oxide film. Also, photo-generated holes within the oxide would be rapidly accelerated towards the sulphide interface. The transmission coefficient for 'hot' hole injection from the oxide valence band to the metal-depleted sulphide valence band would be subject to the density of states therein; as discussed with reference to Figure 1.1.1.3, there is a broad continuum of states within the valence band of cp, chiefly on account of the polarisability of the sulphur 3p orbitals that give rise to them. In this context, the slightly greater linearity of Fowler-type photo-emission plots as compared with plots pertaining to non-direct electron transition from an amorphous films - $\Phi^{1/2}$ vs $h\nu$ as compared with $(\Phi \cdot h\nu)^{1/2}$ vs $h\nu$ - in the range 3.2 to 4.5 eV, as conveyed by correlation coefficients in Figure 6.4.7a, is partially explained. Electron photoemission into electrolyte solution has been observed for a number of semiconductors [245]. However the 180 ° phase shift in spectra recorded at applied potentials > 0.2 V and the near potential independence of threshold energies deduced above rules out the possibility that a similar phenomenon gave rise to the observed photo-effect.

The spectrum recorded at 0.175 V conveyed larger cathodic photocurrents than at 0.025 V, as shown in Figure 6.4.4. Now if a p-type surface layer had given rise to the cathodic photocurrents at 0.025 V, decreasing band-bending within this layer would lead to less effective electron-hole pair separation and diminished photocurrents. Also the formation and growth of such a p-type phase would not account for the photocurrent reversal at 0.25 V. Figure 6.4.8b depicts all the possible changes in the proposed band model presented in a upon increasing the potential by 0.15 V. The Fermi level shift is emphasised, and all the effects of metal depletion discussed above are exaggerated in Figure 6.4.8b vs a.

On the basis of the excess charge passed, the oxide layer was some 25 % thicker at 0.175 V than at 0.025 V. Thus increased spectral photocurrents at 0.175 V shown in Figure 6.4.6, particularly in the range 3.2 eV to 4.0 eV, could be simply accounted for in terms of increased photon adsorption within the growing oxide film. An 'elastic' cp stoichiometry would result in Fermi level unpinning at the cp / oxide interface, and the steep metal ion concentration gradient within this layer would be expected to give rise to larger metal ion migrations than were commensurate with the observed currents; on stepping the potential positively from 0.175 V, the total charge passed previously amounted to only 112 mC cm⁻². Therefore, it transpired that the change in stoichiometry sustained in metal depletion of cp was very small and this depletion extended deep into

the electrode interior. Fermi level unpinning at the metal-depleted cp / oxide interface did not increase to any significant extent between 0.025 V and 0.175 V. This conclusion is supported on at least one account: identified metastable sulphides structurally related to cp are metal-rich, and can be viewed as having metal atoms in cp's octahedral interstices. Therefore **Figure 6.4.8a** is a possible band model appropriate to the electrode surface / solution interface at 0.025 V, except in showing band bending in the cp substrate far in excess of 0.175 eV. At 0.175 V the bands therein were virtually flat. The situation at potentials above 0.2 V is depicted in **Figure 6.4.8c**.

At 0.2 V the underlying metal-deficient cp had surpassed a characteristic flat band potential. Majority carriers, holes, were now in accumulation at the metal-depleted cp / oxide interface, and the field E_z in the oxide interphase reversed. Accordingly, photo-generated electron-hole pair migration in the oxide proceeded in reversed directions, as shown. If the spectral photocurrents had arisen from the metal-deficient cp layer, and the oxide layer were present only in the form of a porous hydroxide product layer, it would be reasonable to expect a large increase in dark current at the point where photocurrents reversed direction, as a result of increased metal ion migration to the electrolyte interface. This did not occur. There was a small enhancement in (anodic) total current at the point of photocurrent change, consistent with the migration of holes to the metal-depleted cp / oxide interface. Rapidly, this migration was abated by the discontinuity of the cp valence band energy levels at that interface, as would be expected from the band model presented in **Figure 6.4.8c**. The relationship between total current and the photocurrent is considered in more detail in **Sections 6.5 and 6.6**.

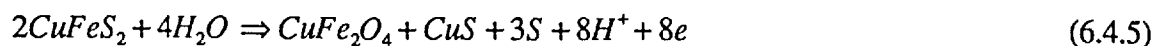
The increase in spectral photocurrent magnitudes on stepping the potential to 0.325 V, shown in **Figure 6.4.6**, is also consistent with the proposed model. Inexorably, the photo-active film had increased in thickness over the thirty four hours during which the cp surface had been subject to oxidising potentials. The charge passed at the outset of spectral photocurrent measurement at 0.25 V was 135 mC cm^{-2} , and the corresponding charge at 0.325 V was 150 mC cm^{-2} ; an increase of some 12 %. Spectral photocurrents had increased by a similar proportion suggesting that the enhanced photo-activity was chiefly due to increased photon adsorption within the growing oxide film.

In **Section 6.5** evidence is presented regarding the formation and destruction of the oxide interphase at 0.4 V. It will be shown that, as the potential was raised above this critical potential, the dark current increased dramatically, consistent with the view that the oxide layer hitherto envisaged was passivating, essentially non-porous, and unchanged at all potentials between -0.3 V and 0.4 V. One possibility presents itself. This potential was associated with fields at the sulphide / oxide interface that could not be sustained. The

Fermi level at this interface was unpinning; the Schottky barrier formed at 0.2 V began to break down, so that accumulated holes, *i.e.* metal ions, at the sulphide side of the interface were able to migrate to the oxide side. Once again, the field E_z in the oxide layer reversed, photocurrents would begin to flow in the opposite direction (cathodically). However the destruction of the interface allowed rapid field assisted migration of metal atoms to the oxide / electrolyte interface that had hitherto been restricted to defects and delocalised states therein.

From the foregoing discussion it has become evident that the photo-activity of cp in 0.1 M sodium tetraborate subjected to mildly oxidising potentials is not at all what is expected from the literature reviewed in Section 1.3.3. The previously understood consensus is certainly mistaken in its citation of oxidation products: they are photo-inactive. Moreover the gradual transformation of the surface as defined by its spectral photo-activity casts severe doubts that several discrete oxide products formed on the cp surface. In particular, the Φ vs $h\nu$ shoulder below 3.6 eV at -0.275 V shown in Figure 6.4.1 was still evident at +0.325 V shown in Figure 6.4.4, though by then, considering the linearity of $\{\Phi\}^{1/2}$ vs $h\nu$ plots had extended over the range 3.2 to 4.3 eV, as shown in Figure 6.4.5, and was the dominating photoactive phase. At potentials between 0.1 V and 0.25 V these plots were so straight, and indicative of a threshold energy so high, as to provide conclusive evidence against n-type Fe_2O_3 or p-type Cu_2O having given rise to the observed photocurrents. On the basis of this spectral evidence alone, it has been argued that one homogeneous oxide interphase at potentials ≥ 0.025 V developed between metal-depleted cp and the borax electrolyte, and that it was the field gradient within this layer that dominated cp's oxidation, whether light were incident or not.

Photocurrent spectroscopy has indicated characteristic threshold energies for p-type Cu_2O (Section 6.3), n-type Fe_2O_3 (Table 6.1.1) and n-type CuFeO_2 [117] of 2.4, 1.9 and 2.2 eV respectively. Thus CuFe_2O_4 is a possible oxide phase to account for the observations above. In comparison with CuFeO_2 , the formal oxidation state of copper is raised from I to II, so the bandgap between the conduction band of predominantly copper 3d character and valence band of predominantly oxygen character will be larger in CuFe_2O_4 . This could be expected to cause a smaller, but significant increase in the energy gap between the valence band and the conduction band of predominantly iron character. The formation of CuFe_2O_4 accords with the relative affinities of copper and iron for oxygen vs sulphur. From the data presented in the Appendix 1 Table, the standard potential at pH 9.2 for the idealised equation:



is -0.243 V *vs* S.C.E.. Therefore this reaction is thermodynamically allowed at all potentials at which the oxide phase was detected, and has a standard potential only 0.15 V positive of reaction (6.4.1).

Another aspect of the evolving picture of oxidation of cp in alkali is that the cp lattice was not destroyed, merely depleted in metal ions. This is consistent with recent XPS investigations in which no elemental sulphur could be detected on the surface of air oxidised cp [244]. The known reversibility of cp oxidation in alkali is more understandable in terms of the formation of a single oxide interphase and metal-depleted cp, as opposed to the formation of heterogeneously distributed products such as sulphur, Fe(OH)₃ and Cu(OH)₂. This will be further explored in Section 6.6.

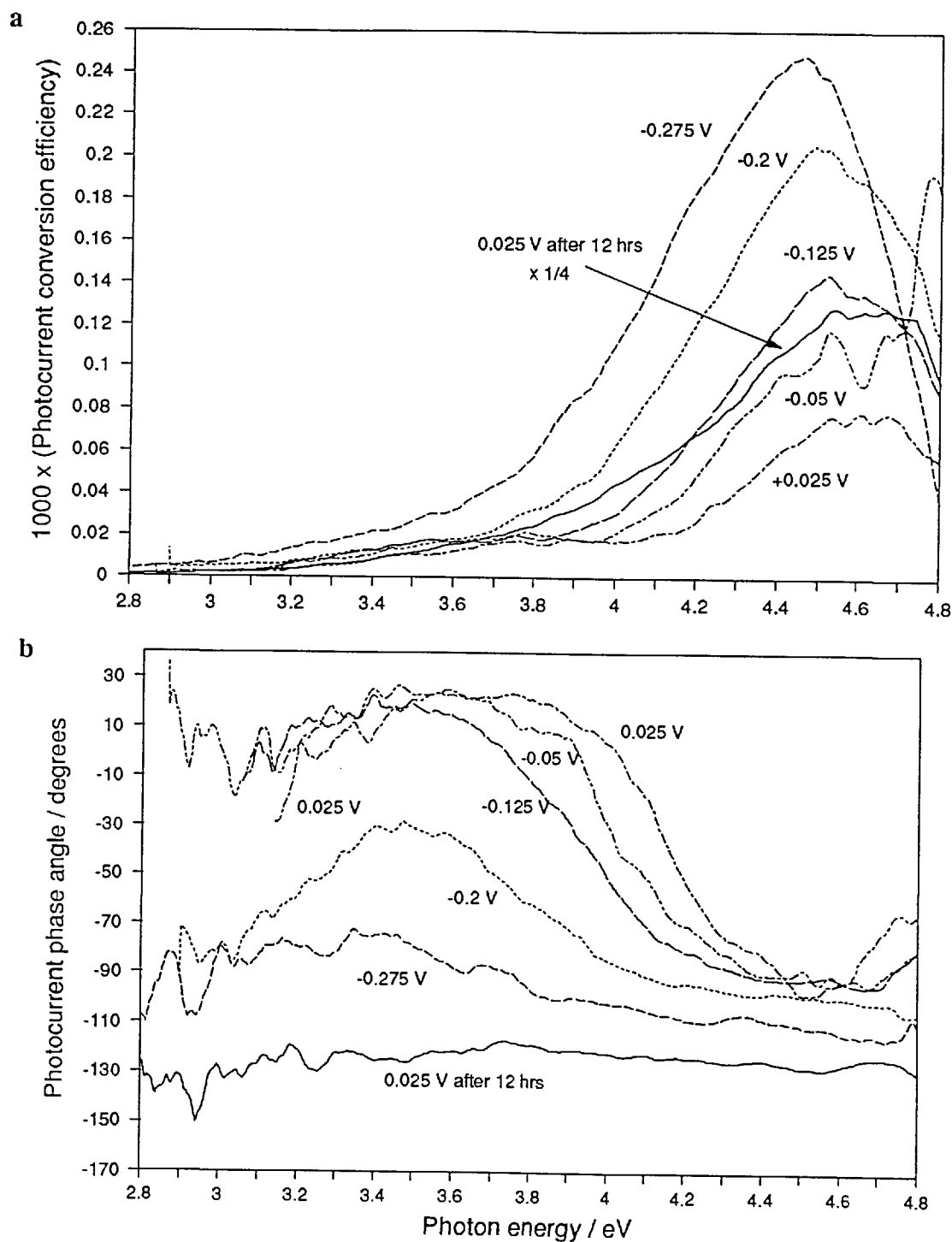


Figure 6.4.1a, photocurrent conversion efficiency, Φ , and **b**, phase angle θ vs photon energy $h\nu$, for cp in 0.1 M sodium tetraborate at constant applied potentials stepped positively from the rest potential. 60-90 minutes per step. 0.1 nm s^{-1} monochromator sweep rate. 30 s lock-in time constant. $0.3 \mu\text{V}$ lock-in sensitivity.

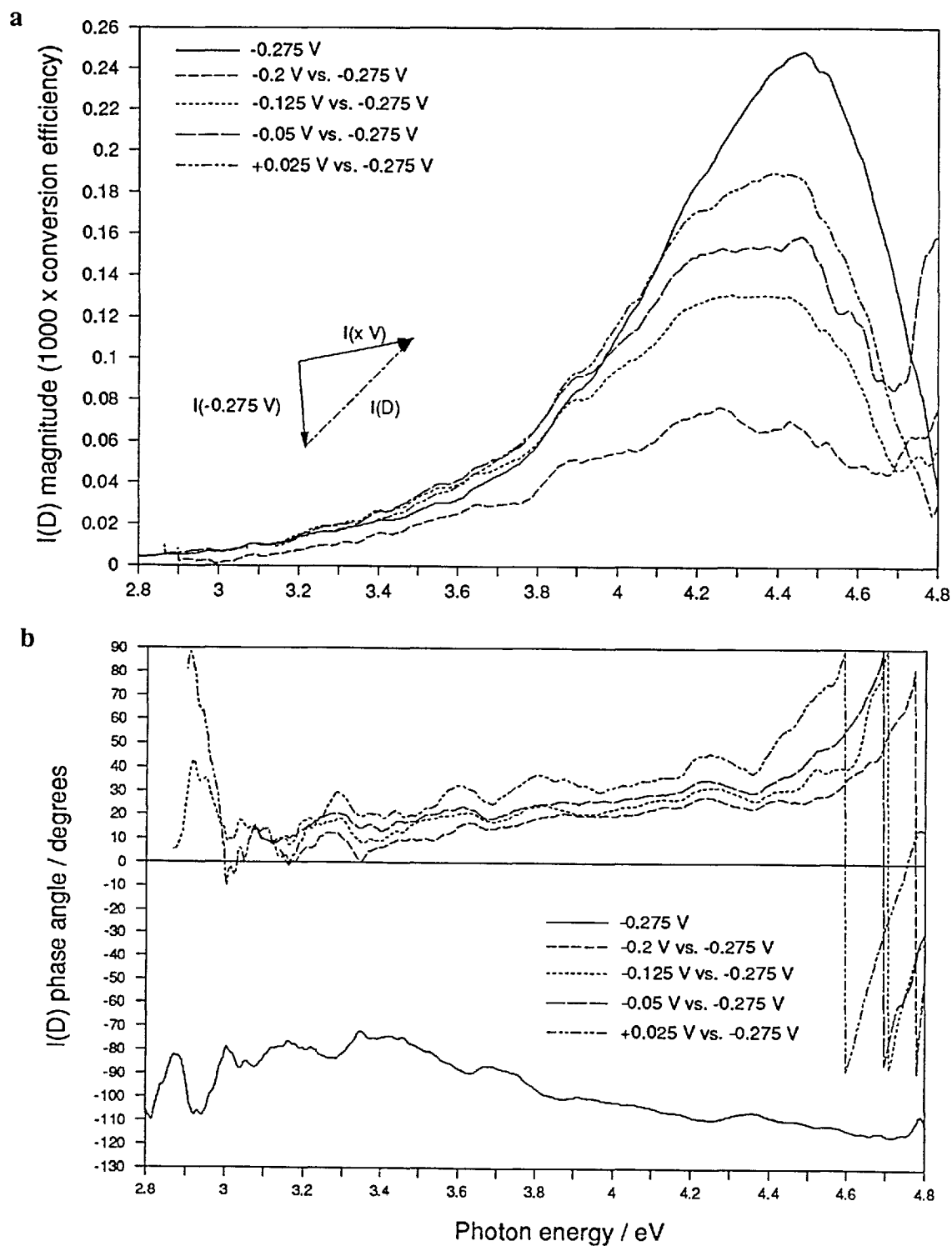


Figure 6.4.2 the vectorial modification of a , Φ , and b , θ vs photon energy $h\nu$, between spectra recorded at -0.275 V and subsequent more positive potentials for cp in 0.1 M sodium tetraborate as shown in **Figure 6.4.1**.

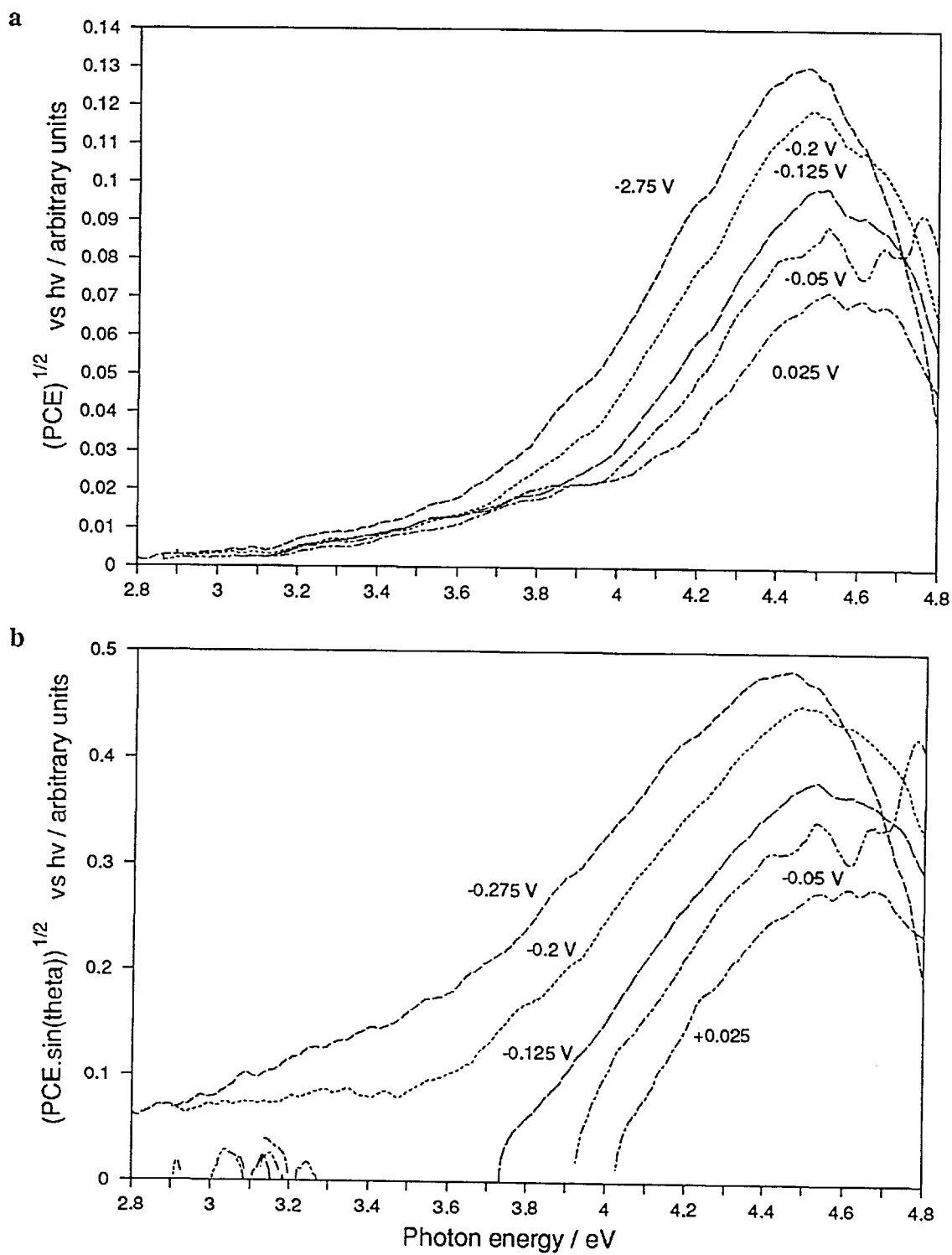


Figure 6.4.3, plots of **a**, $\{\Phi\}^{1/2}$ vs $h\nu$ and **b**, $\{\Phi \cdot \sin\theta\}^{1/2}$ vs $h\nu$ for spectra presented in Figure 6.4.1.

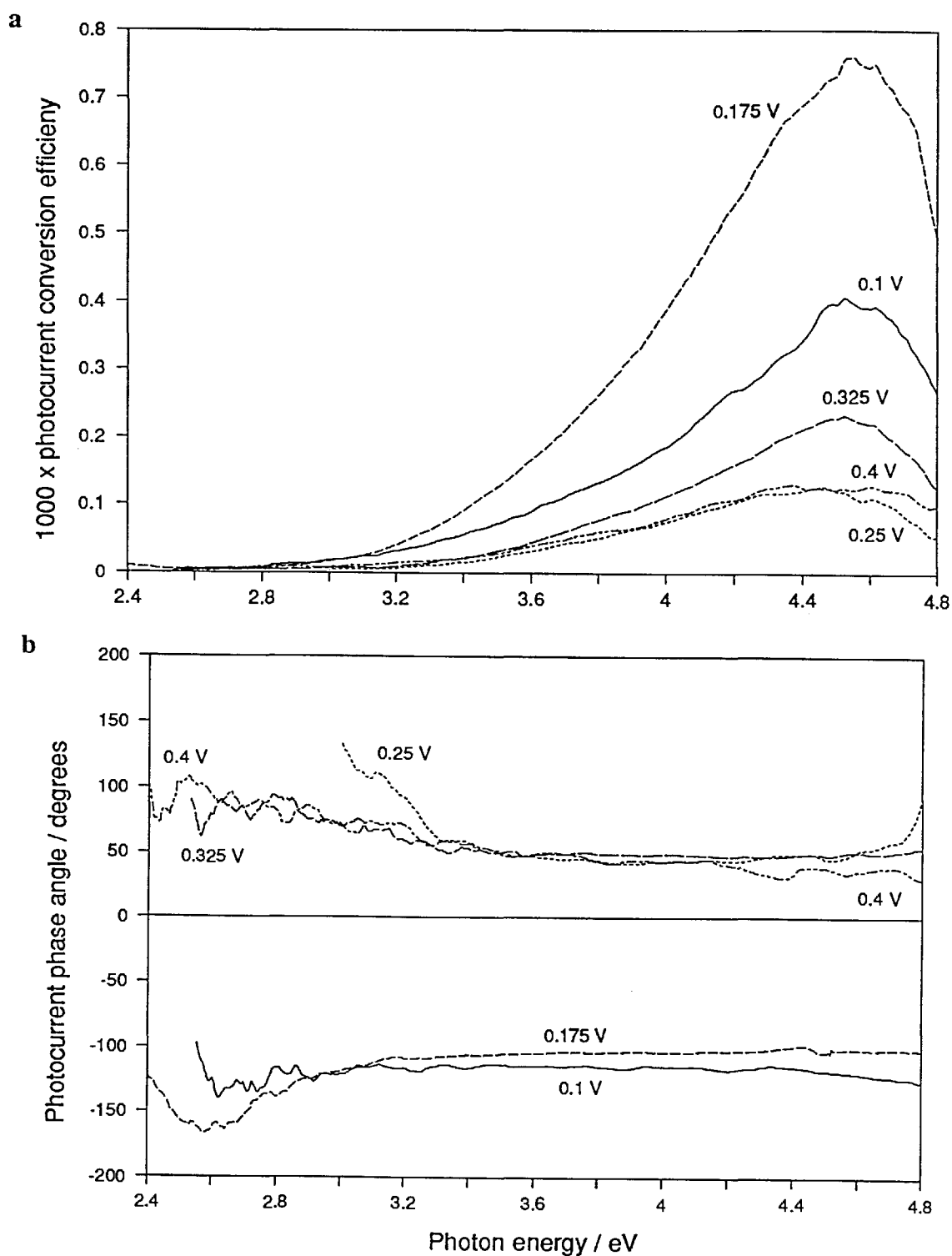


Figure 6.4.4a, photocurrent conversion efficiency, Φ , and **b**, phase angle θ vs photon energy $h\nu$, for cp in 0.1 M sodium tetraborate at constant applied potentials stepped positively from 0.1 V in continuation of experiment described in **Figure 6.4.1**. Same parameters.

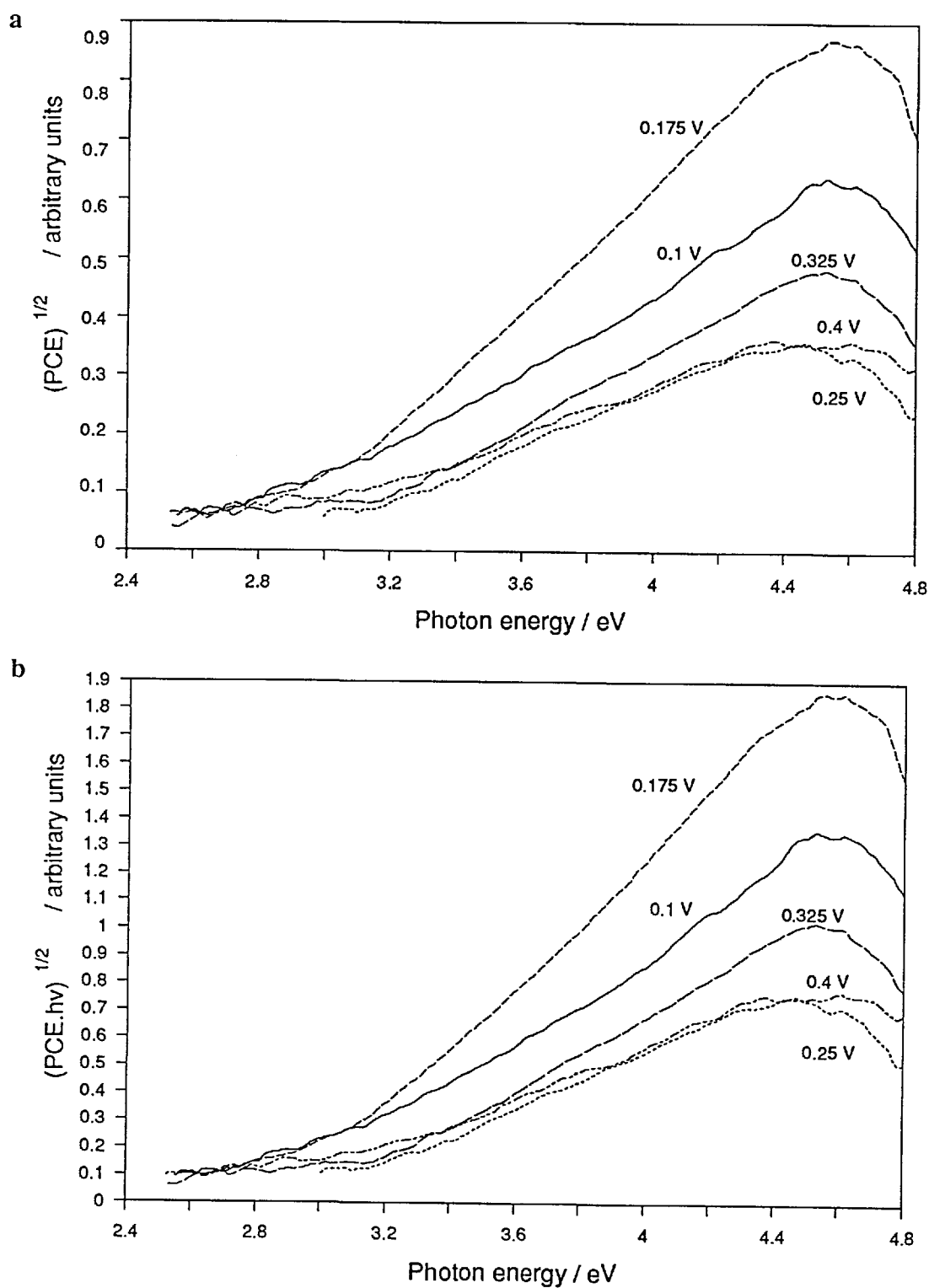


Figure 6.4.5, plots of a, $\{\Phi\}^{1/2}$ vs $h\nu$ and b, $\{\Phi \cdot h\nu\}^{1/2}$ vs $h\nu$ for spectra presented in Figure 6.4.4.

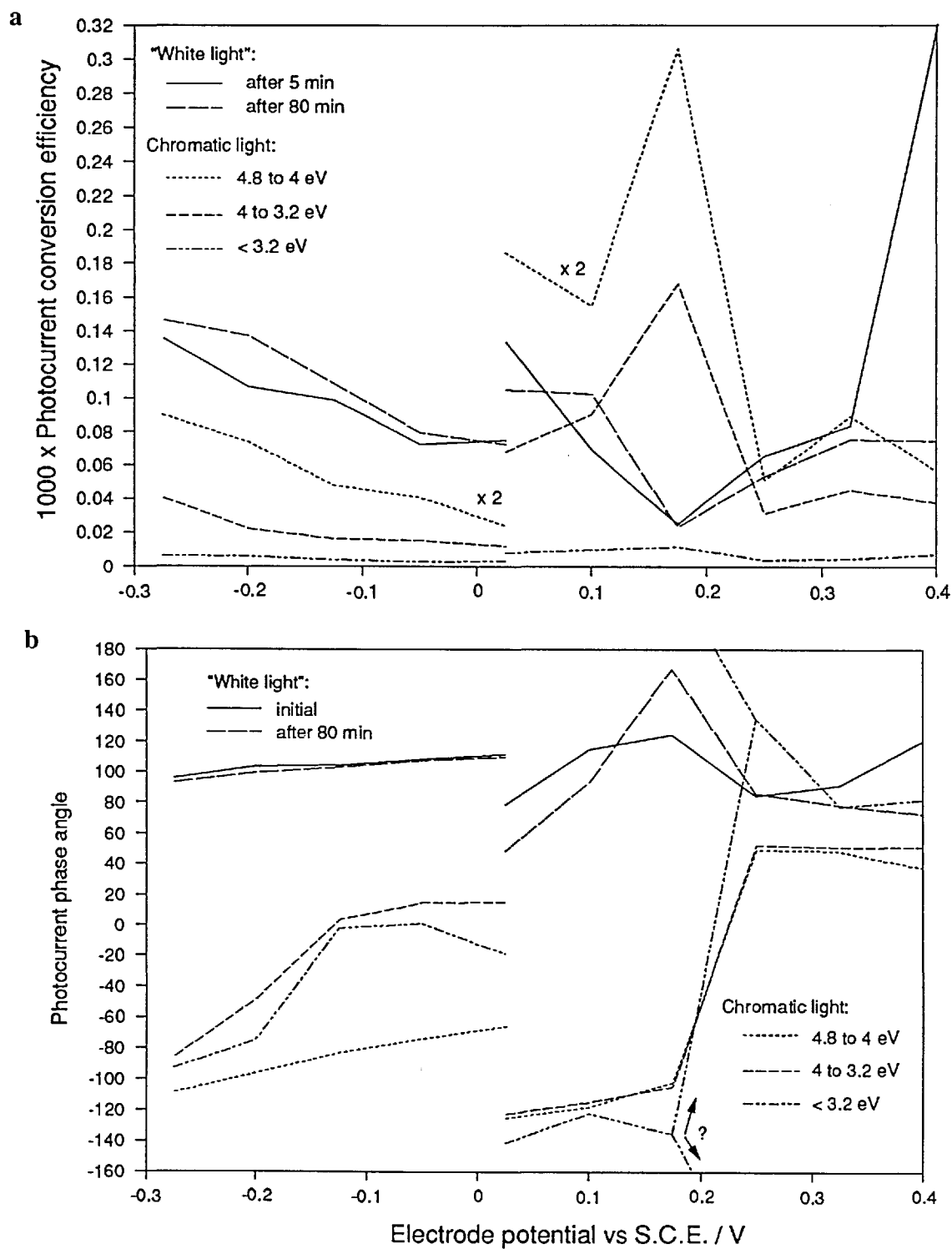


Figure 6.4.6. Comparison of "white" light and chromatic light.

a, photocurrent magnitude, and **b**, phase angle θ vs applied potential for cp in 0.1 M sodium tetraborate at constant applied potentials stepped positively from -0.275 V as described under Figures 6.4.1-4.

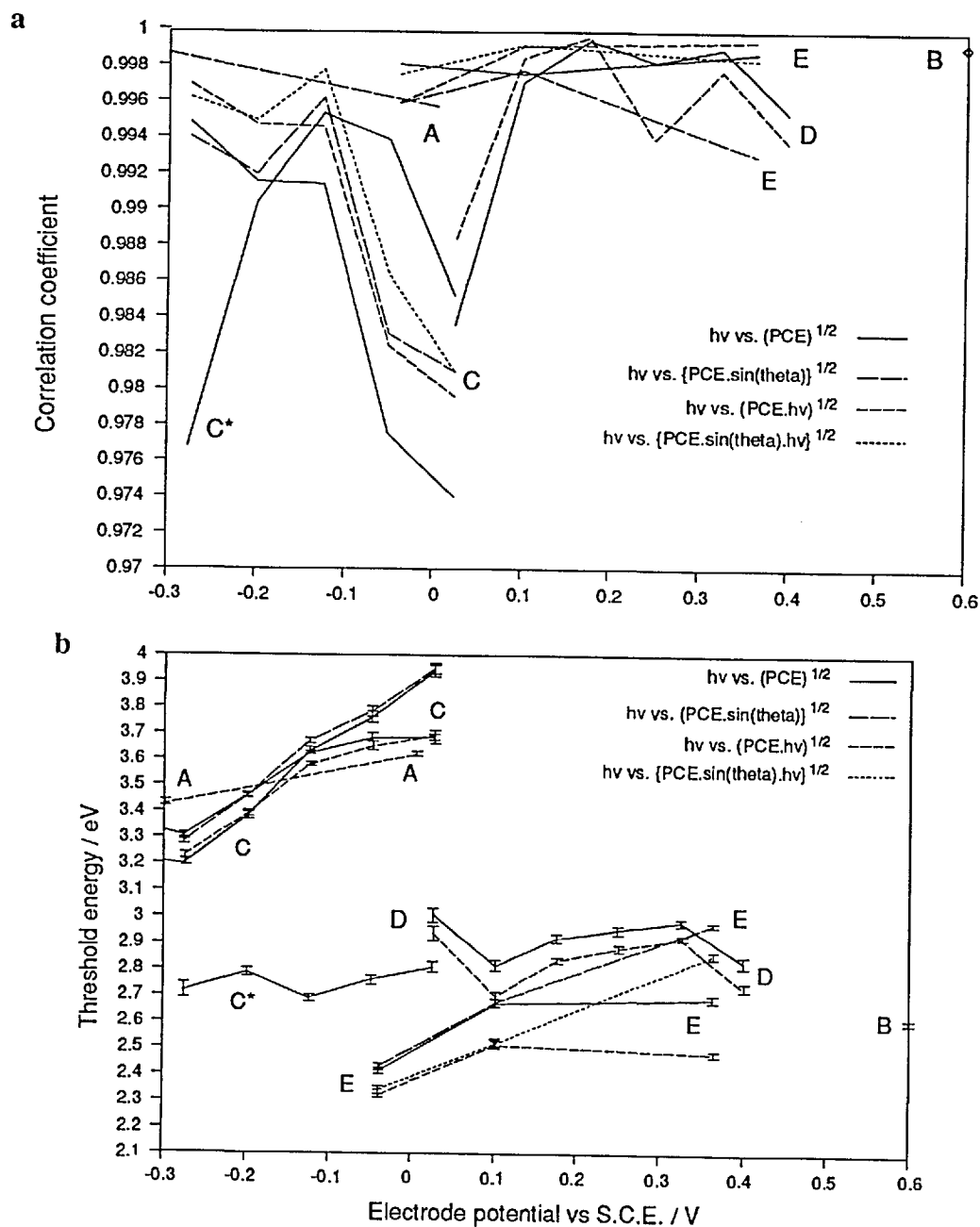


Figure 6.4.7a, correlation coefficients and **b**, threshold energies vs applied potential for cp electrode in 0.1 M sodium tetraborate. Derived from spectral data obtained as follows:

- A, At 0.03 V after 12 hr maintained at this potential and then after a further 1 hr at -0.3 V. See also Figures 5.2.1 and 2.
- B, At 0.6 V following a slow excursion to -1.2 V, Figure 6.2.3b.
- C, As described in Figure 6.4.1 (* Figure 6.4.2).
- D, As described in Figure 6.4.4.
- E, From photo-voltage measurements under constant applied currents.

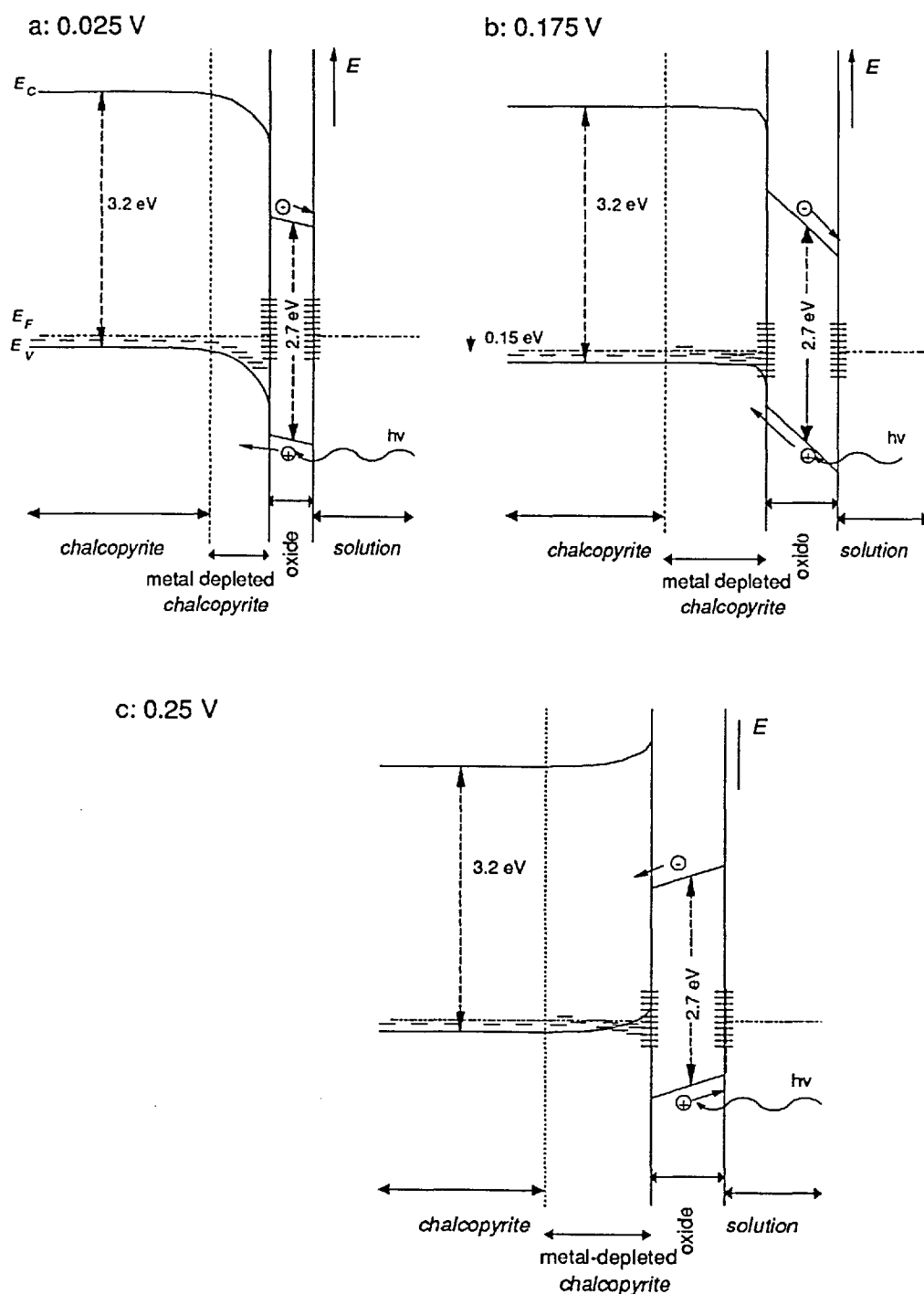


Figure 6.4.8. Electronic energy level diagram for the idealised structure of the cp electrode at equilibrium in 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$ at various potentials. **b** vs **a** shows all the possible effects of increasing the potential from 0.025 V in the experiment during which photocurrent spectra were recorded (see **Figure 6.4.6**). The results conform only to the increase in oxide layer thickness, whereby the effects of band bending in **a** are exaggerated. The principle source of photocurrent generation is illustrated. All diagrams pertain to the model presented in **Figure 6.3.4d**.

6.5 Cyclic photovoltammetry on cp at oxidising potentials.

p-type Cu_2O formation from $\text{Cu}(\text{OH})_2$ on cp has already been suggested in Section 6.3 as giving rise to the large transient photo-cathodic response at -0.3 V following positive potential excursions. The emergence of this peak was further investigated by cyclic photo-voltammetry from -0.5 V - a potential at which reduction of underlying cp was negligible - to increasingly positive potential sweep limits. Figure 6.5.1 shows photocathodic peaks below -0.3 V in the negative-going sweeps following excursions to 0.5, 0.6 and 0.7 V. Similar behaviour had been displayed by the Cu electrode, (Figure 6.3.2), and attributed to the reductive formation of p-type Cu_2O from $\text{Cu}(\text{OH})_2$. As with Cu, the photocathodic peak was associated with an enhanced total cathodic current shown in Figure 6.5.2. There were further similarities. On the copper electrode a stable photoactive p-type film had been grown at 0.0 V; probably Cu_2O . If the same had occurred on cp, at least some photocathodic currents would be expected positive of the Cu_2O reduction potential at pH 9.2, -0.271 V. There was such activity on reverse scans following all positive potential excursions. There was, however, one significant difference. Figure 6.5.1 indicates photocathodic currents above the flatband potential of p-type Cu_2O ; 0.1 V. In Section 6.4, spectral photocurrents at potentials between 0.025 V and 0.4 V were identified with the formation of a thin ternary oxide interphase whose reduction potential could easily have coincided with that of Cu_2O (*cf* reaction (6.4.5)). However, on sweeps 5-7 in Figures 6.5.1 and 2 the potential exceeded 0.4 V. Thereupon, rapid ion migration from a metal - particularly iron - depleted cp substrate through the oxide interphase is expected, and cathodic photoactivity arising from copper oxidation products can be entertained.

In order to detect transitory photocurrents in potential sweep experiments it was necessary to employ much shorter lock-in time constants than were employed in the spectral sweeps above. This necessitated directing "white" light from the xenon lamp onto the electrode surface. For reasons not clearly understood, "white" light had the effect of reversing photocurrents under the reducing conditions encountered in Chapter 5. Likewise, during the initial positive going sweep 3 in Figure 6.5.1, the familiar small cp "white" light anodic photocurrent signal was observed. In Section 6.4, with reference to Figure 6.4.8c, 0.2 V was identified as the 'flatband' potential of the metal-depleted cp layer near the sulphide / oxide interface, giving rise to reversed photocurrents at higher potentials. "White" light photocurrents also reversed at 0.2 V, turning cathodic. They remained cathodic, during the reverse potential sweep, and the positive going potential sweep 4 until prevailing total currents turned anodic. This indicated not so much the persistence of the photoactive oxide interphase as the permanence of the field change E_z within it,

once the potential 0.2 V had been surpassed. Both Fermi level pinning at the metal-depleted sulphide / oxide interphase and the interphase itself may have presented a barrier to any metal ion migration back into the sulphide layer, preventing a reverse in the changes that occurred moving positive of 0.2 V.

In the next positive going sweep 4, above -0.3 V, I_{ph} and I_{tot} closely followed their previous potential dependent profile, consistent with the reversibility of cp oxidation to 0.3 V discussed in the next section. The significant change in sign of photocurrents at 0.36 V remained not only for the 16 seconds taken for the potential to return to 0.36 V from 0.4 V, but for an additional 30 seconds it took for the potential to reach 0.2 V. In accordance with the interpretation presented in Section 6.5, it is suggested that approaching 0.4 V, the integrity of the sulphide / oxide interface began to break down. Coincidentally, total currents increased sharply, as shown in Figure 6.5.2. Possibly, at isolated sites, the migration of Cu^+ and Fe^{3+} from the sulphide substrate to the oxide / electrolyte interface was facilitated by the removal of the sulphide / oxide interfacial Schottky barrier. The larger charge and smaller size of Fe^{3+} would certainly favour its migration over Cu^+ , and so n-type hematite, positive of its flatband potential, may have formed heterogeneously over the electrode surface at potentials exceeding 0.36 V, giving rise to a photoanodic effect. On the negative-going potential sweep from 0.4 V, Fe_2O_3 or a similar n-type phase could have approached a characteristic flat band potential. By 0.2 V, the associated weakening in band bending in this phase may have caused photocathodic currents from the extant oxide interphase to prevail once again.

However, Figures 6.5.1 indicates that +0.36 V may also be a critical potential required for the formation of p-type Cu_2O at more negative potentials, because the profile of $I_{ph} \cdot \sin \theta$ vs potential on the negative-going potential sweep from 0.4 V is quite different from the profile for the previous negative potential excursion from 0.3 V. The most negative value of $I_{ph} \cdot \sin \theta$ at -0.26 V coincides with the reversible potential for the Cu_2O / Cu couple. It is conceivable that the Fermi level unpinning at the metal-depleted sulphide / oxide interface near 0.36 V resulted in a reversed field in the oxide that could not be sustained. The formation of oxides of copper would then be expected. In conformity with the discussion presented at the end of Section 6.3, the model presented in Figure 6.3.4c increasingly accounts for the observed behaviour, on potential excursions increasingly positive of 0.4 V.

Further cathodic photocurrent peaks are evident on below -0.3 V after the ensuing positive-going potential scans 5, 6 and 7. The profiles of $I_{ph} \cdot \sin \theta$ vs potential on negative potential excursions from 0.5 V and 0.6 V show a remarkable resemblance to the photocurrent vs potential profile of the copper electrode, shown in Figure 6.3.2. The

increased migration of Cu^{2+} ions to the electrode surface above 0.38 V could account for these photocurrents. An enhanced rate of electron transfer as the positive potential limit was increased could be expected to exceed the rate of the subsequent relatively potential independent process by which the resultant $\text{Cu}(\text{OH})_2$ dehydrated to form CuO . The increased magnitude of reverse scan negative I_{tot} and $I_{\text{ph}} \cdot \sin \theta$ peaks which commenced near -0.3 V following excursions to 0.5, 0.6 and 0.7 V provide strong evidence for the formation of $\text{Cu}(\text{OH})_2$ in this way, and is directly comparable to the critical effect p-type Cu_2O had on the alkaline oxidation of copper. The fact that the $I_{\text{ph}} \cdot \sin \theta$ signal between +0.2 and -0.3 V was coincidentally and increasingly diminished following excursions to 0.5, 0.6 and 0.7 V suggests that Cu_2O was increasingly removed from the cp product layer, probably by its oxidation to $\text{Cu}(\text{OH})_2$.

If p-type Cu_2O and $\text{Cu}(\text{OH})_2$ were the only oxidation products above 0.4 V exposed to incident radiation, then no photoactivity would be expected, and the profile of $I_{\text{ph}} \cdot \sin \theta$ in **Figure 6.5.1** would closely resemble **Figure 6.3.2**, obtained from the copper electrode. In the event, $I_{\text{ph}} \cdot \sin \theta$ increased rapidly over positive going potential sweeps beyond 0.4 V, for some cp electrodes giving rise to photoanodic responses greater in magnitude than the photocathodic peaks just discussed, as shown top right in **Figures 3.7.1-6**. In **Section 6.2** the source of this photoanodic behaviour was identified with the formation of $\alpha\text{-Fe}_2\text{O}_3$ but attempts to obtain spectral measurements at these potentials were defeated due to the significantly increased total currents, and instability of $I_{\text{ph}} \cdot \sin \theta$ above 0.4 V. Whilst the photocurrent phase angles (not shown) on return sweeps from 0.5 and 0.6 V were $85 \pm 5^\circ$ down to potentials of 0.2 V, the return sweep from 0.7 V showed marked deviation, following the same path as the direct excursion to and from 0.8 V, shown in **Figure 6.3.1**. Perhaps only at potentials > 0.6 V had the passivating oxide $\text{Cu}_x\text{Fe}_y\text{O}_z$, collapsed under the applied potentials. The oxidation products were then chiefly $\text{Cu}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$.

Two other experiments were performed to investigate the trends discussed above. In **Figure 6.5.3** potential sweeps from +0.4 V to and from increasingly negative potentials confirm, by the absence of a photocurrent peak at -0.3 V, the probable formation $\text{Cu}(\text{OH})_2$ only at potentials exceeding 0.4 V. In addition, the photocathodic signal on reverse scans, ascribed to Cu_2O , increased following increasingly negative potential excursions. This is thought to be due to the increased copper enrichment on going to more negative potential limits, sulphur being lost reductively as HS^- . Thereby, thicker layers of Cu_2O may have formed oxidatively, consistent with the lower positive potential required for Cu_2O formation from copper as compared with cp, between which metal-enriched cp is an intermediate case.

In the second experiment, the results of which are shown in **Figure 6.5.4**, the potential was maintained at 0 V for 180 s, then swept at 10 mV s^{-1} to -0.6 V, where the potential was kept constant until the current reached $< 0.5 \text{ } \mu\text{A cm}^{-2}$. Thereupon the potential was abruptly increased to 0.1 V, maintained at 0.1 V for 180 s, then swept back to -0.6 V again. The process was repeated at 0.2, 0.3, 0.4, 0.5 and 0.6 V. The object of this experiment was chiefly to determine the reversibility of cp electrochemical oxidation at pH 9.2 by obtaining from I_{tot} measurement the total charge passed under successive oxidising and reducing potentials. In addition, **Figure 6.5.4a** shows the rapid attainment of steady state photocurrents at potentials $\leq 0.4 \text{ V}$. Also, **Figure 6.4.6** conveys that the stable "white" light photocurrents were never cathodic, whereas **Figure 6.5.1**, **6.4.3** and **3.7. 1 - 6** show consistent transitions from photocathodic to photoanodic behaviour at 0.2 V. **Figure 6.5.5** shows these photocathodic currents to be transitory, confirming that the photocurrent cross-over at about 0.15 V under "white" light on negative-going potential excursions is not related to the reversal in photocurrents under monochromatic light between 0.175 V and 0.25 V as discussed in **Section 6.4**

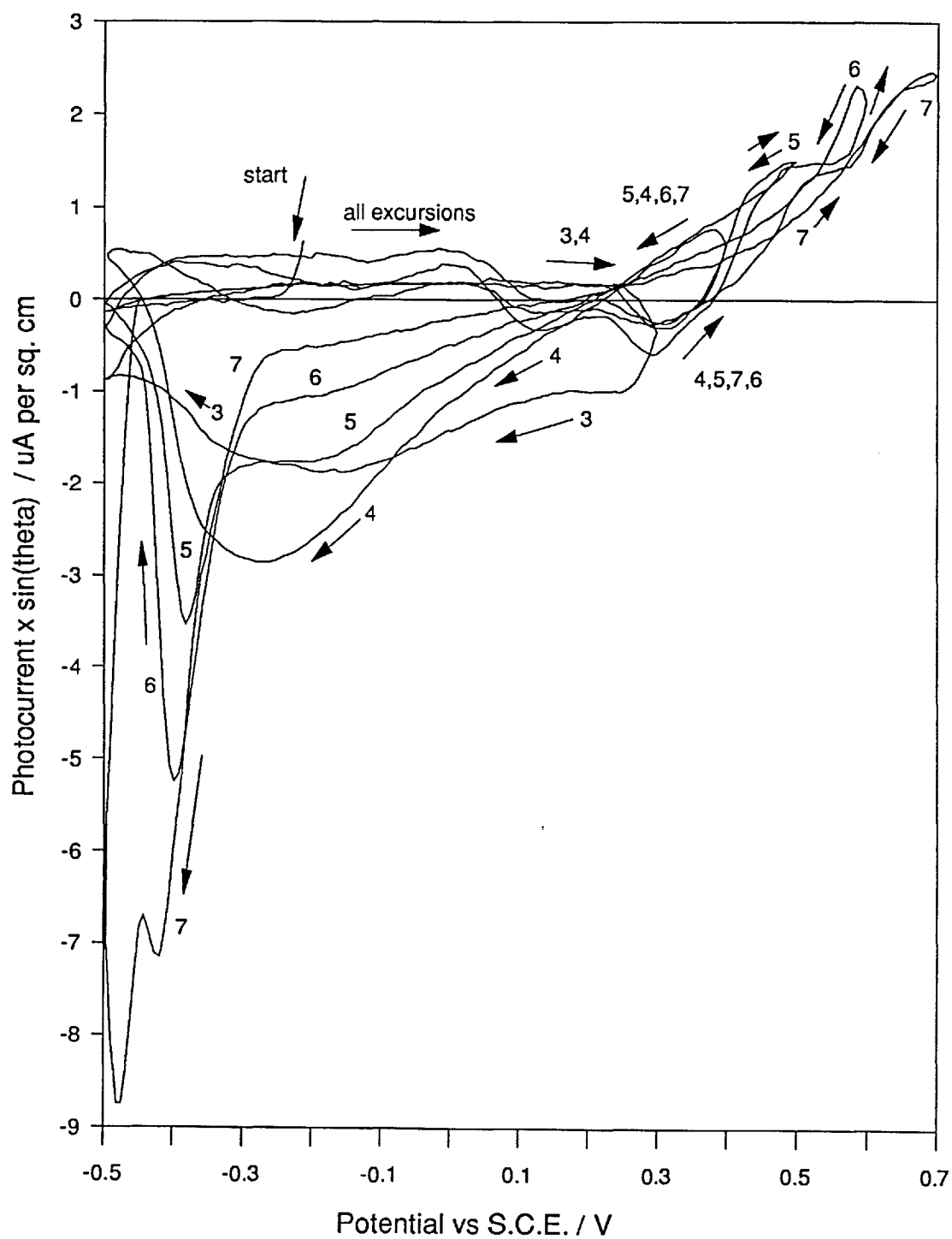


Figure 6.5.1. $I_{ph} \cdot \sin\theta$ vs applied potential for cp electrode in 0.1 M sodium tetraborate solution under "white" light following potential excursions from -0.2 V to -0.5 V, then successively to and from:
 3: 0.3 V; 4: 0.4 V; 5: 0.5 V; 6: 0.6 V; 7: 0.7 V.
 5 mV s^{-1} sweep rate. See also Figure 6.5.2.

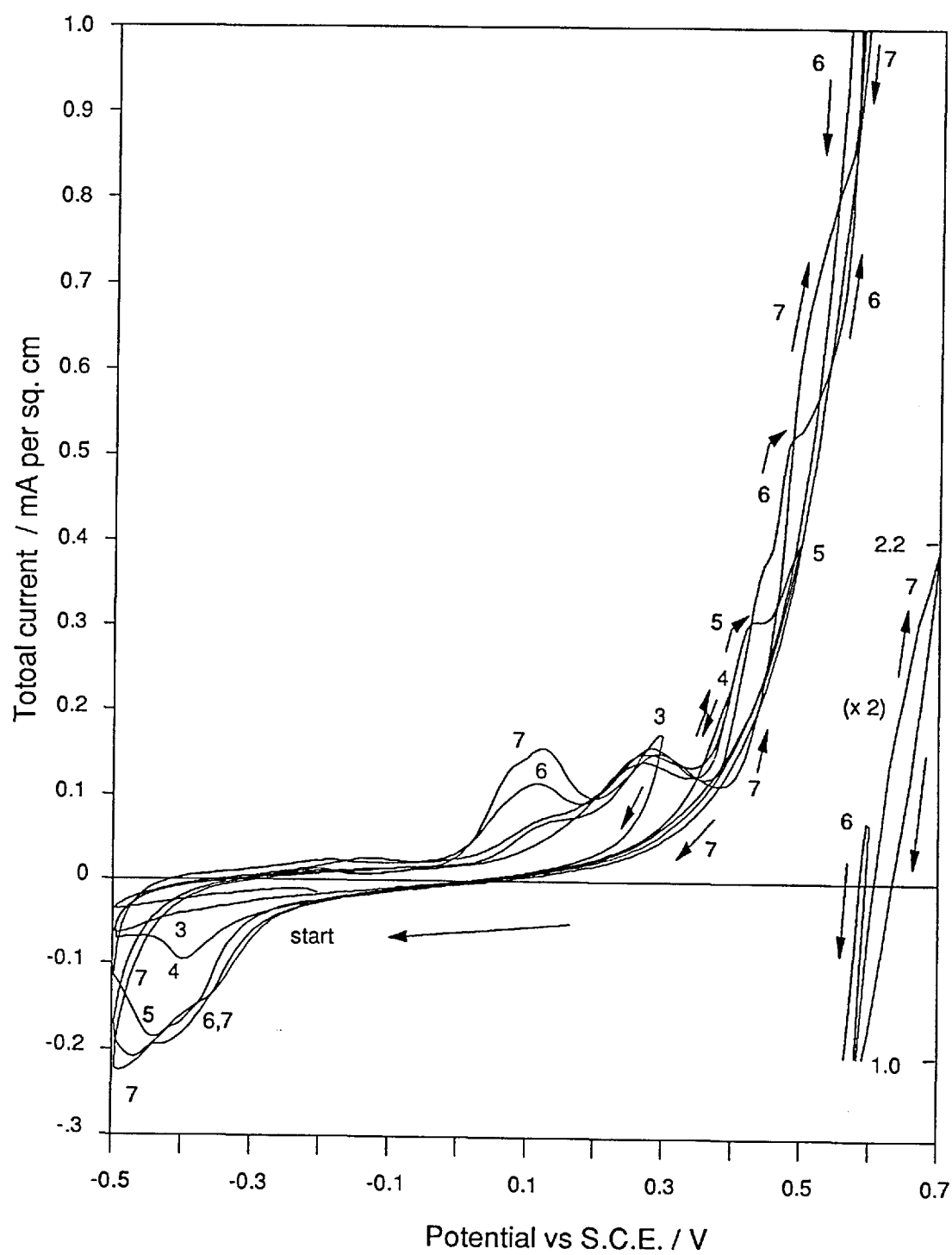


Figure 6.5.2. I_{tot} vs applied potential, during experiment pertaining to Figure 6.5.1.

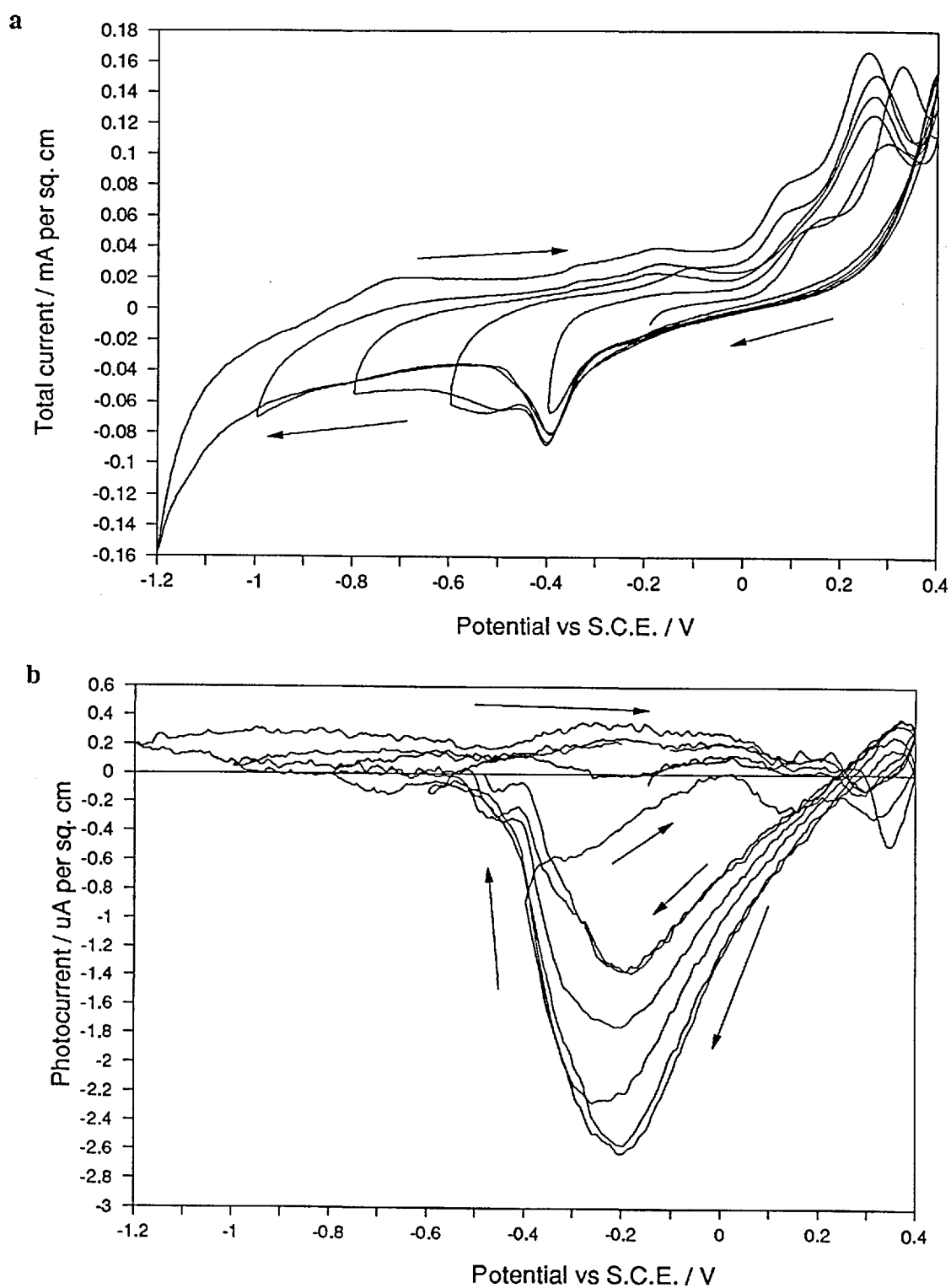


Figure 6.5.3. a, I_{tot} and b, $I_{\text{ph}} \cdot \sin \theta$ vs applied potential for cp electrode in 0.1 M sodium tetraborate solution under "white" light. 5 mV s^{-1} sweep rate.

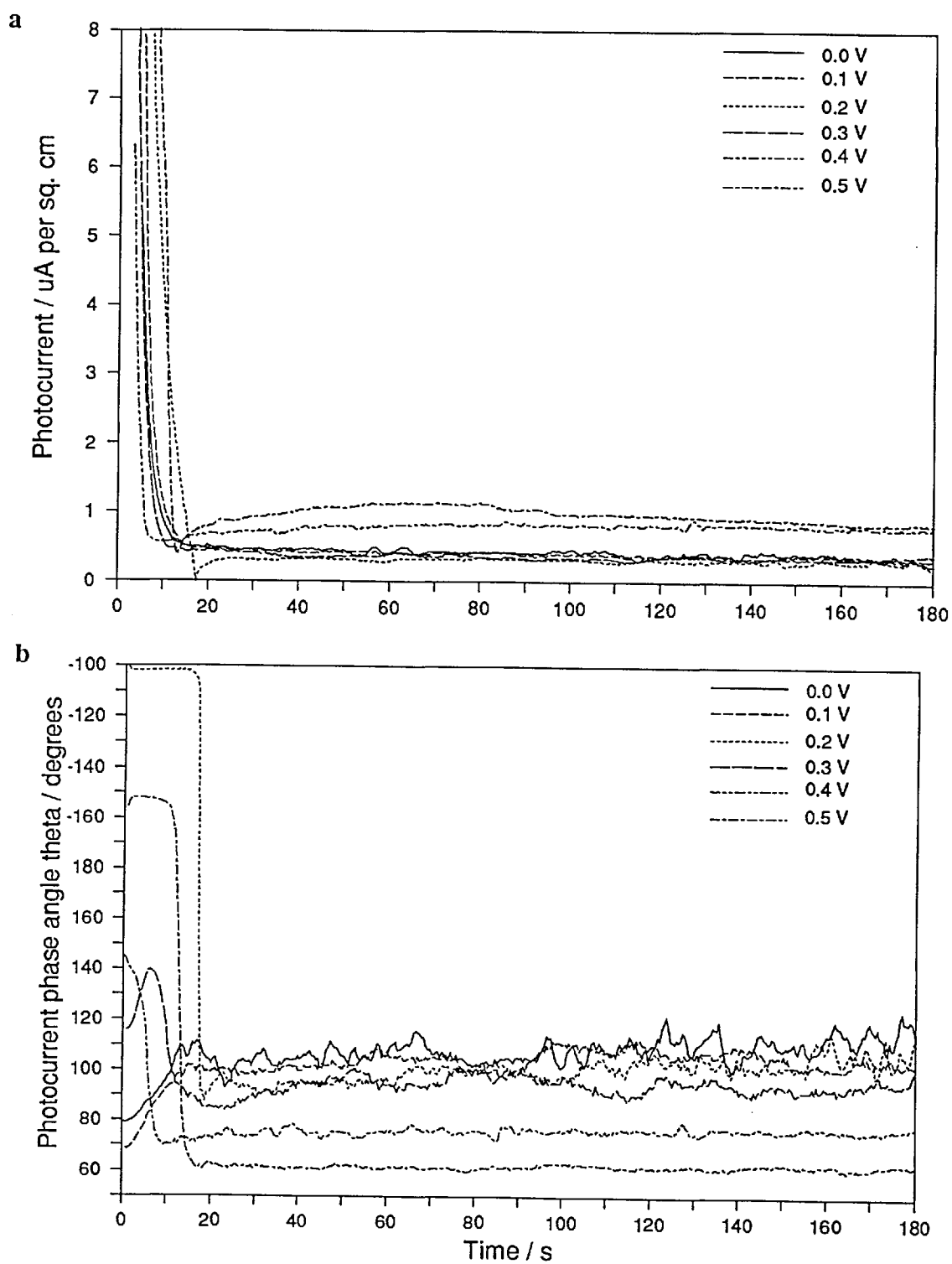


Figure 6.5.4. The time dependence of **a**, I_{ph} and **b**, θ at succeeding positive constant potentials, applied for 180 s, following potential excursions to -0.6 V. Cp electrode in 0.1 M sodium tetraborate solution under "white" light. See text.

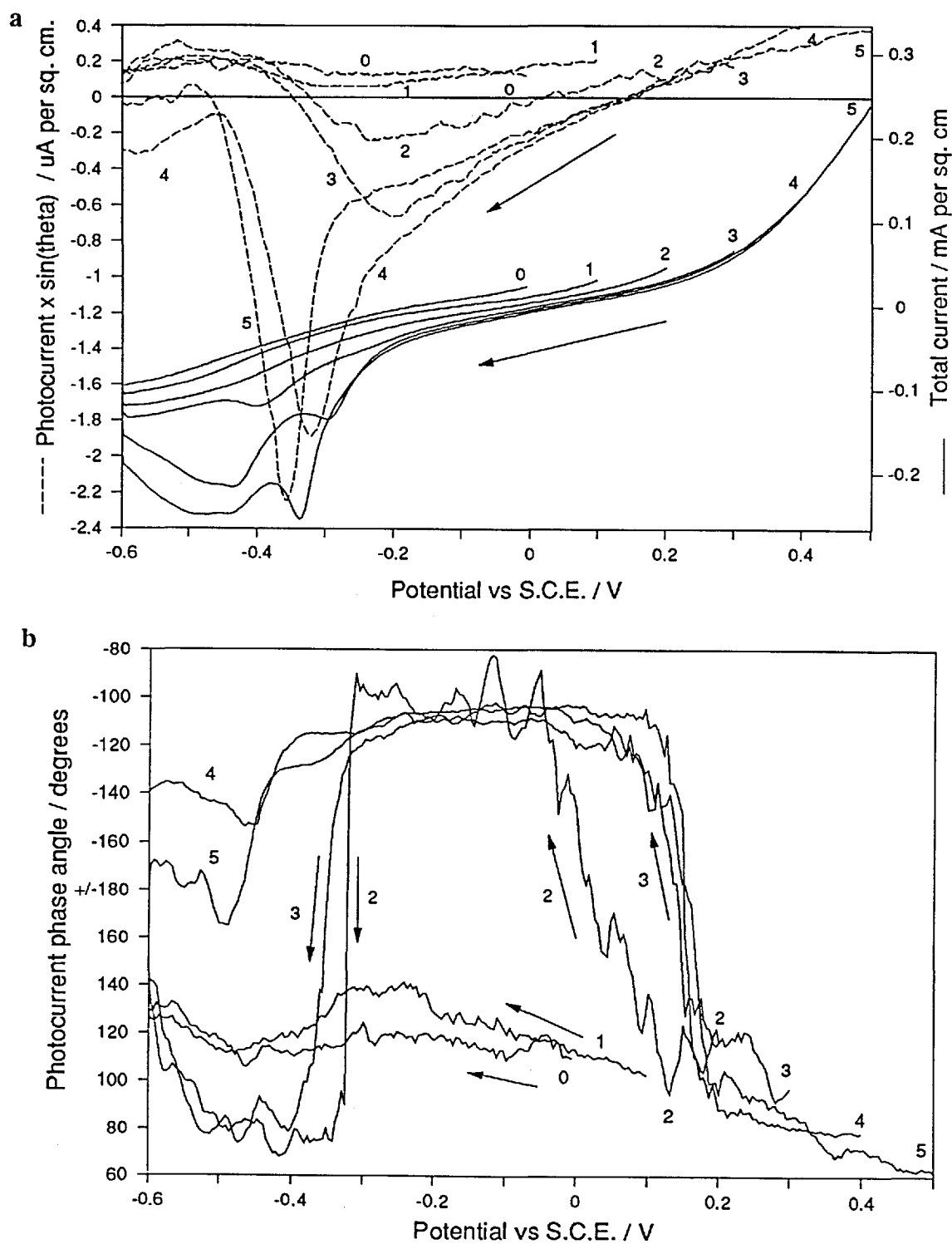


Figure 6.5.5. The potential dependence of a, I_{tot} and $I_{\text{ph}} \cdot \sin \theta$ and b, θ , during negative-going potential sweeps to -0.6 V from the positive potential limit, as in Figure 6.5.4. 10 mV s^{-1} sweep rate.

6.6 Coulometry

The total current decay at the positive potentials referred to in Figure 6.5.4, is shown in Figure 6.6.1 in the form of a plot of $\ln(I_{\text{tot}})$ vs $\ln(t)$, where t is the time after applying each positive potential. These currents were measured concurrently with the data presented in Figure 6.5.4 and 5. Initial data points in Figure 6.6.1 were uncertain because measurements were acquired every 0.5 s. Current decay at times < 1 s was measured in a different experiment, from which Figure 6.6.2 was obtained.

Figure 6.6.1a shows linearity at all positive potentials (except 0.4 V), some 15 seconds after each positive potential was applied. The slopes of the plots x at increasing potentials are: -0.56 (0 V and 0.1 V); -0.52 (0.2 V); -0.45 (0.3 V); -0.32 (0.4 V). The 0.2 V data, plotted as I vs $t^{-1/2}$, was analysed for linear correlation. The correlation coefficient was 0.9998 over the time period between 20 to 200 s and the plot approached $t^{-1/2} = 0.004$ at zero current. This is indicative of a diffusion limited current for which the boundary conditions of the Cottrell equation were valid. From the measurement of the slope, $D^{1/2} \cdot C_R^\infty = 1.22 \times 10^{-4} \text{ A m}^{-2} \text{ s}^{1/2}$. This limited current could not be attributed to the oxidisable solution species, $10^{-4.8}$ M hydroxide ions, because the absurdly high value for D obtained would be $6 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. If the I vs $t^{-1/2}$ dependency does indeed convey true diffusion control, it must conform to the existence of completely different boundary conditions than govern Cottrell-type behaviour, and involve diffusion of metal ions, presumably Fe^{3+} . The decrease in x with increasing potential mitigates against diffusion control in a product interphase or (pores therein), as the increase in interphase thickness with increasing constant applied potential would be expected to lead to more rapidly diminishing currents. The alternative is more consistent with the conclusions reached in Section 6.4 and electrochemical oxidation in acid conditions. A substantial portion of the applied potential difference fell within a space charge layer of metal-depleted cp. Fe^{3+} ion migration to the metal-depleted cp / oxide interface was opposed by the field E_z within that layer, but E_z decreased as the potential was increased. Logarithmic plots at higher potentials showed poorer linearity, at 0.5 V there being a distinct enhancement in total current after some 30 seconds, co-incident with the change to positive photocurrent as depicted in Figure 6.5.4.

The validity of the Cottrell equation at $t < 1$ s for positive stepped potential excursions from the rest potential is shown in Figure 6.6.2. At potentials < 0.2 V the plots show two approximately linear regions above and below $t^{-1/2} = 20 \text{ s}^{-1/2}$. Again, much higher gradients were obtained from these plots than could be reasonably expected from diffusion control by hydroxide ions.

Returning to **Figure 6.6.1**, the oxide products formed at positive potentials were reduced by an applied potential of -0.6 V, maintained until the current was $< 1.0 \mu\text{A cm}^{-2}$. It is interesting that the $\ln(-I)$ vs $\ln(t)$ plots at -0.6 V shown in **b** all have much the same profile, suggesting that the oxide layer grown anodically governed the rate of ensuing reduction at -0.6 V.

In an attempt to find how reversible oxidation was after successive constant positive potentials had been applied, the current was integrated numerically with respect to time. Current spikes on stepping to positive potentials were monitored on an oscilloscope and found to add insignificantly to the summed charge. The positive to negative charge passed for each positive potential excursion and the following negative potential excursion is shown in **Figure 6.6.3a**. The results of similar experiments on Cu_2S , chalcocite, are included for comparison. The positive charges passed through the same cp electrode on the initially applying a potential of 0.0 V should, of course, be identical. That they were not is indicative of the fluctuations in experimental conditions, which in large part is thought to be manifest in different oxide growth at the rest potential due to adventitious oxygen even though, as usual, every effort was made to exclude it. In other respects **Figure 6.6.3a** shows clear trends in the charge passed, as described below.

A smaller anodic charge passed on the excursion to 0.4 V than on the previous excursion to 0.3 V when the negative potential limit was -0.2 V, but not when it was -0.6 V. This provides further evidence that subjected abruptly to potentials of > 0.3 V, cp does not form the same passivating oxidation product as was evident from spectral and photocurrent-potential sweep experiments. Consistent with the conclusions reached in **Section 6.5**, this same passivating film was not reduced at -0.2 V, and indeed the reductive charge passed at -0.2 V never exceeded one quarter of the charge passed anodically. **Figure 6.6.3a** also illustrates a distinct rise in anodic charge passed on stepping the potential from -0.2 V to +0.4 V, and to +0.7 V, consistent with **Figure 6.5.2**.

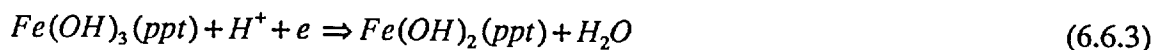
Figure 6.6.3b shows the ratio of anodic to cathodic charge passed at the end of each period at the constant negative potentials ($Q_c:Q_a$). It is seen that the oxide product layer formed at 0.0 V may have been entirely reduced at -0.6 V and -0.4 V. This is unexpected, considering the reduction potentials of some oxidation products of cp, previously supposed to occur at pH 9.2 and 0.0 V (see also the **Appendix 1** figure):



$$E = -0.312 \text{ V}$$



$$E = -0.582 \text{ V}$$

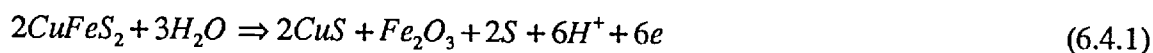


$$E = -0.541 \text{ V}$$



$$E = 0.07 \text{ V}$$

Specifically, at -0.4 V the impossibility of reactions (6.6.1 - 3) occurring to any significant extent discredits the hypothesis that these are the oxidation products at 0.0 V *via* reactions such as



$$E = -0.385 \text{ V},$$

because oxidation of cp to S (0), Fe(III) and Cu(II) at 0.0 V followed by reduction of Cu(II) to Cu(0) at -0.4 V, would yield a maximum charge ratio of 0.4. From -0.4 V to the increasingly positive potential limits up to 0.3 V, sulphate formation was unlikely, (see Section 1.3.1), the oxidation state of the iron in the product layer was certainly (III), leaving only reaction (6.6.4) as being able to give rise to enhanced $Q_c:Q_a$ ratios to a theoretical limit of 1. After an initial fall, $Q_c:Q_a$ did indeed approach 1. The effect was more pronounced for chalcocite, Cu_2S . It is understood to form CuO and $Cu_{2-x}S$ oxidatively [219]. The underlying trend remains that there is a decrease in $Q_c:Q_a$ at increasing positive potentials. One limitation of the experiment to -0.6 V had been the negative potential limit at which cp itself is reducible, thereby contributing a cathodic current. If the conclusions drawn regarding Figure 6.6.1b are correct, this contribution was small. Therefore Figure 6.6.3b would appear to convey a genuine increase in the irreversibility of cp oxidation as the positive potential is increased.

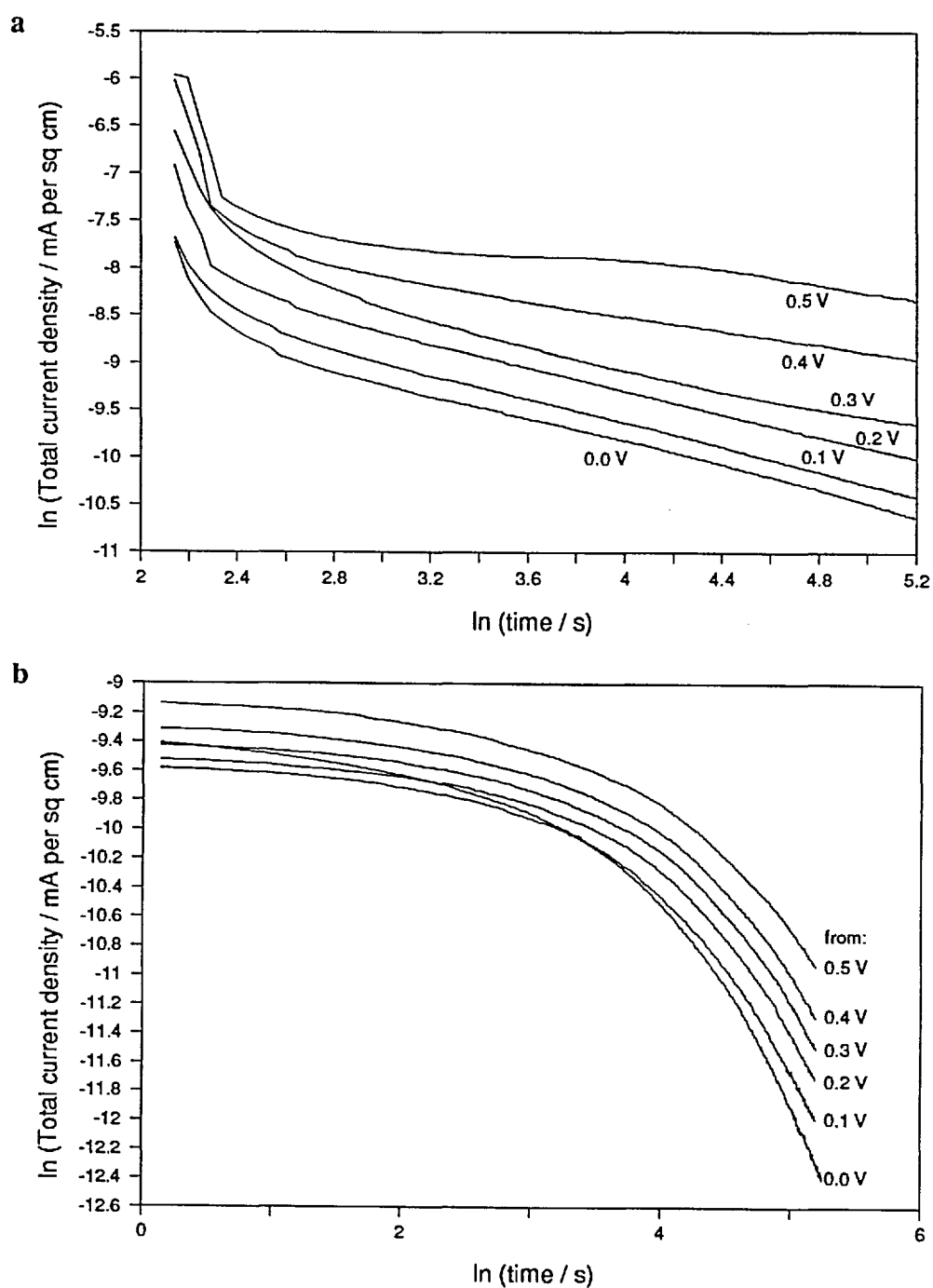


Figure 6.6.1. Plots of $\ln(I_{\text{tot}})$ vs $\ln(t)$ for cp electrode in 0.1 M sodium tetraborate solution under "white" light. **a** at increasing positive potentials maintained for 180 s and **b**, at -0.6 V following sweep from these positive potentials. See also Figure 6.5. 4 - 5 and 6.6.2.

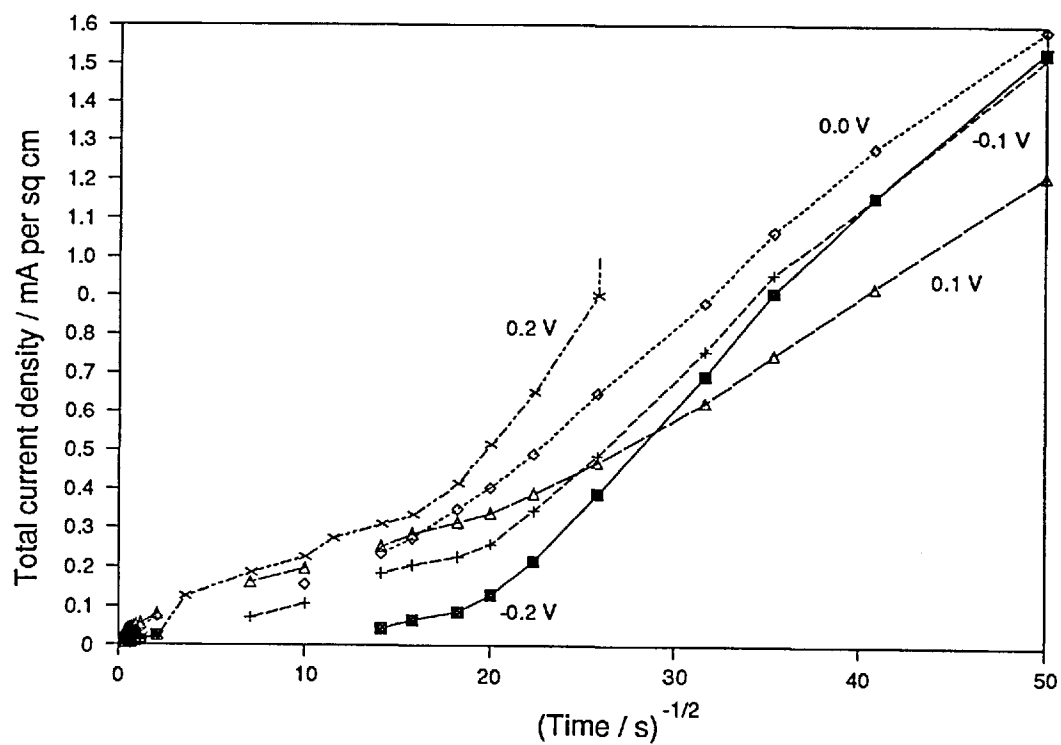


Figure 6.6.2. Cottrell type plots of I_{tot} vs $t^{-1/2}$ for cp electrode in 0.1 M sodium tetraborate solution under "white" light at positive potentials positive of the rest potential, maintained for 300 s, then stepped positively 0.1 V.

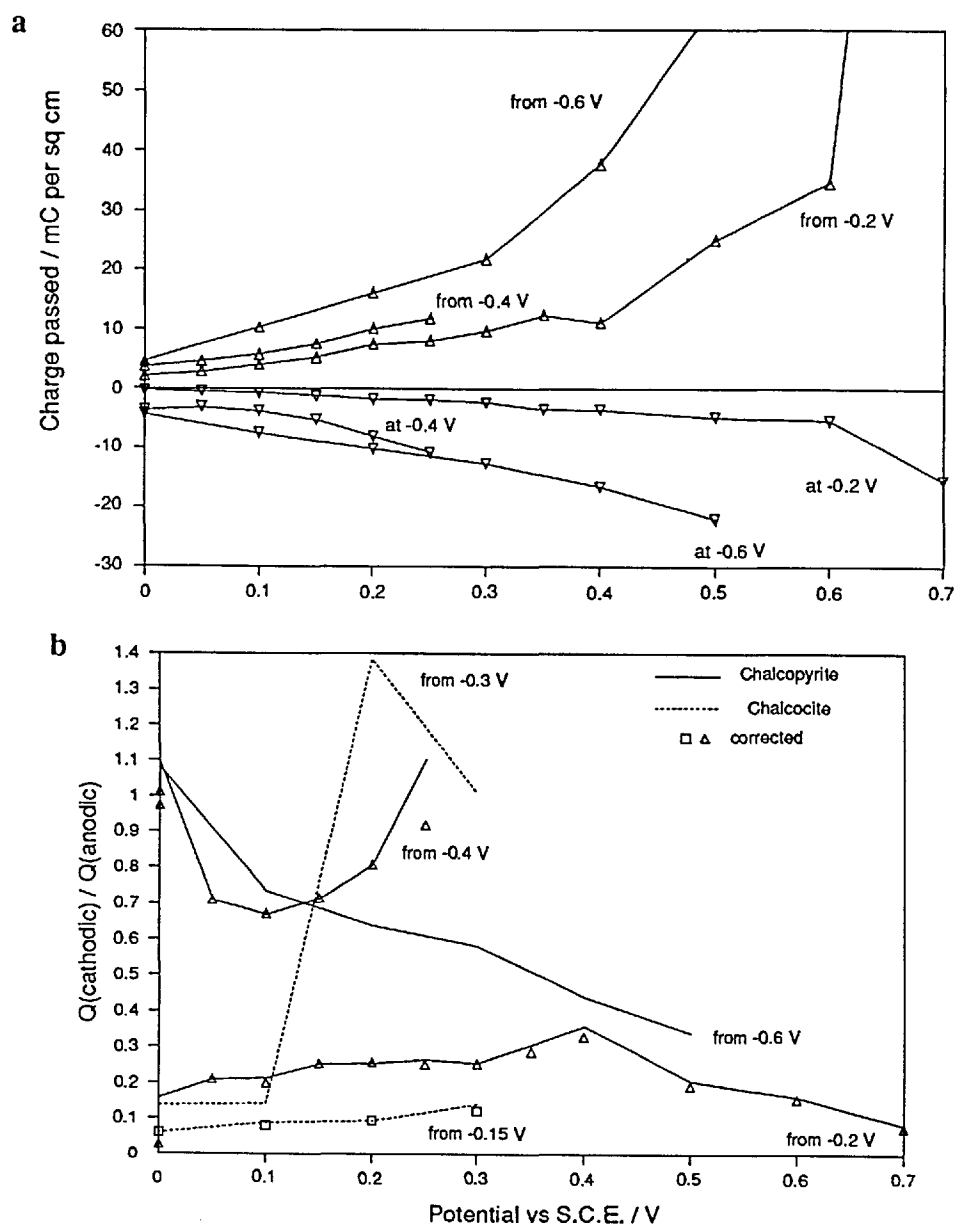


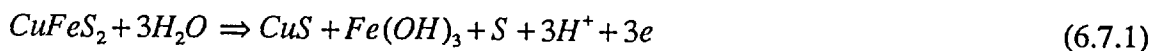
Figure 6.6.3a. Total cathodic charge Q_c and anodic charge Q_a passed for cp under xenon light in 0.1 M borax solution vs positive potential excursion limit. This potential was maintained for 180 s. There followed a negative-going potential sweep at 10 mV s^{-1} to the annotated negative potential limits. These potentials were maintained until $I_{\text{tot}} > -0.1 \mu\text{A cm}^{-2}$.

b. $Q_c:Q_a$ vs positive potential excursion limit, as described above, and for a Cu_2S (chalcocite) electrode. The "corrected" values pertain to certain experiments in which the cathodic currents took $> 1 \text{ hr}$ to reach $-0.2 \mu\text{A cm}^{-2}$. Cottrell-type plots were linear in this range, allowing an additional cathodic charge to be considered by integration of the function $I = mt^{1/2} + c$ with respect to time.

6.7 Cyclic voltammetry.

On the strength of the observations described in the preceding sections of this chapter, an attempt can be made to provide a fresh account of cp oxidation in alkaline solutions, and attribute the current peaks shown in Figures 3.7.1-7, 6.1.1 and 6.3.1 to specific redox processes.

Initial positive going potential excursions in all these diagrams showed a peak, labelled I in Figure 6.1.1, arising immediately upon sweep commencement from -0.2 V. This was attributed by Gardner and Woods [6] to the reaction:



$E = -0.309 \text{ V}$ at pH 9.2.

The present work demonstrates the unlikelihood that any such reaction occurred. The photoelectrochemical evidence at similar potentials is indicative of the formation of an oxide, similar to CuFe_2O_4 , by the depletion of metal ions from the underlying cp substrate. Gardener and Woods [6] observed an appropriate shift in the potential corresponding to current peak I upon varying the pH, *ie* 0.059 V per pH unit. However, the same shift is to be expected from the formation of any metal oxide or hydroxide, so long as there was no concurrent dissolution of metal ions or formation of sulphony species. Gardener and Woods [6] interpreted the increase in current at peak II to arise from:

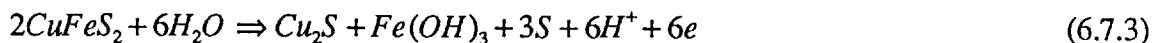


(at pH 9.2, $E = 0.086 \text{ V}$.)

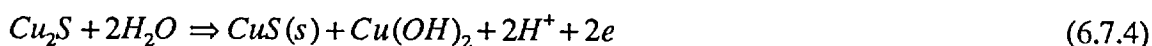
The present work showed from progressively decreasing sweep rates a more marked cross-over of positive and negative current profiles, as in Figure 3.7.1 vs 2. This suggests that the broad rise in current beyond peak I could not be attributed simply to a sequence of reactions such as (6.7.1)/(2), or by reactions (6.4.1 - 4), all of which are alternative reaction routes, having sufficiently low standard potentials. The distinct change in photocurrent phase angle and magnitude always associated with peak II and closely associated with decay in spectral photocurrents at 0.4 V provides a reasonable explanation: the passivation of cp on positive-going sweeps depended on the time required for surface coverage of the passivating interphase. Therefore at the slower sweep rate, passivation was more effective. At potentials positive of 0.37 V, the Schottky barrier at the sulphide / oxide interface essentially collapsed, and ion migration to the electrode interface was now restricted by the oxide interphase itself. n-type Fe_2O_3 was a likely photoactive product associated with peak II. Above 0.6 V the interphase itself decomposed, and direct oxidation of cp ensued, increasingly with concomitant sulphate

formation. This was associated with the shoulder III in **Figure 6.1.1** (see below). The slower potential sweep to 0.8 V ensured more effective surface passivation to 0.6 V, and ensured that between 0.4 V and 0.8 V the underlying oxide matrix was destroyed, giving rise to larger anodic currents on the reverse scan. Hence the distinctive total current cross-over in **Figure 6.1.1**.

Gardener and Woods' findings differed from that of Page [11], who reasoned that cp oxidation in alkali may follow more the course predicted by thermodynamic considerations, which from his data meant chalcocite *via* bornite formation. In effect,

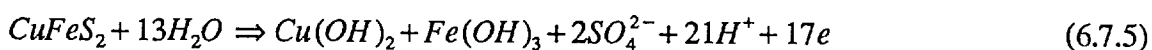


at pH 9.2, $E = -0.276$ V, and gave rise to peak I. Then,



at pH 9.2, $E = -0.012$ V

followed by oxidation of CuS by reaction (6.7.2) at peak II. Page [11] attributed the shoulder III to the delayed formation of sulphate:

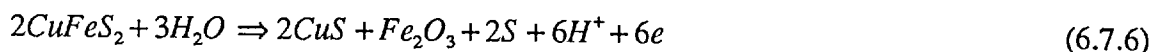


(at pH 9.2, $E = -0.477$ V).

This reaction would cause the dissolution of $\text{Cu}(\text{OH})_2$, concomitant with a decrease in the interfacial pH, thereby breaking down $\text{Cu}(\text{OH})_2$ formed at lower potentials. The results of this chapter comply with Page's findings insofar as **Figures 3.7.1-7** (top left) and **Figure 6.1.1** show a steep current rise on sweeping the potential positive of 0.6 V from the cp rest potential. On the other hand, these figures indicate that following a subsequent potential excursion to -1.2 V, the cp surface was passivated at considerably more positive potentials. In **Section 6.3** it was shown that this behaviour was similar to that of iron, passivated by n-type Fe_2O_3 . The resemblance was closest following slow negative potential excursions. Whilst the formation of $\text{Cu}(\text{OH})_2$ at the oxide / electrolyte interface is to be expected above 0.4 V as described in **Section 6.5**, surface passivation could not be attributed to $\text{Cu}(\text{OH})_2$ formation. It is now understood that the thickness of an underlying oxide layer determines the onset of transpassivity. As was pointed out in **Section 1.3**, thermodynamically predicted cp oxidation products depend on the chosen Gibbs energy data, but in this work the effect of field and concentration gradients within an oxide product are identified as the dominant factor in determining reaction products.

On the subsequent, negative-going sweep from +0.8 V, the current turned cathodic only at potentials below 0.0 V vs S.C.E.. From measurements of charge passed under the anodic and cathodic peaks, and by incrementally increasing potential scanning limits, the present and previous work is only agrees in that oxidation of chalcopyrite is reversible after potential excursions to < 0.1 V. Previously, it was uncertain which reversed series of reactions accounted for the observed reversibility: reactions (6.7.1)/(2), or (3)/(4)/(2). It is established in Section 6.5 that such reactions are not realistic, at least to +0.6 V, where forward and reverse scan photocurrents suggest the prevalence of a single oxide phase of a semiconductivity which determined the total current flow through the electrode.

The reduction of any oxidatively formed sulphur to HS⁻ ions (reaction (6.6.3)) would be indicated by enhanced cathodic currents at potentials < 0.58 V. There is no sign of any enhanced current in either Figures 6.3.1 and 6.5.3, in support of the hypothesis that no sulphur formed oxidatively. The reduction of ferric hydroxide to ferrous hydroxide (reaction (6.6.2)) has been assigned to peaks below its standard potential of -0.54 V [11]. It is now expected that an iron-rich oxide layer formed at positive potentials. Its reduction exemplified by:



could be expected below a standard potential of -0.365 V, which is suggested especially by Figure 6.1.1 at peak IV'. At slightly less negative potentials an increasing cathodic current was associated with enhanced photocurrents, as exemplified in Figures 6.5.1 and 2. It was attributed to the reduction of CuOH)₂ which had formed > 0.4 V, analogous to its formation on elemental copper.

The much pronounced I_{tot} peak below -0.2 V on negative-going potential scans in Figure 6.5.3 at the very potentials at which there were small current responses following positive excursions to 0.8 V can be understood in terms of the pervasive effect of the oxide interphase. Approaching 0.4 V, p-type Cu₂O was concentrated at the oxide surface, possibly because an electric field there opposed the flow of metal ions from the cp/oxide interface to the oxide/electrolyte interface, particularly the highly charged Fe³⁺ ions. Thereby a layer of Cu₂O of finite thickness formed on the oxide interphase surface, and was reduced at lower potentials. Above 0.4 V, (Figure 6.1.1), the field relaxed and under a higher Fe³⁺ concentration gradient these ions rapidly migrated through the Cu₂O film, the surface electric field reversed, favouring Fe₂O₃ formation. Now this film

predominated on the reverse scan, and there was no current response indicative of copper oxide reduction. **Figure 6.1.1** conveys an enhanced current below -0.7 V relative to **Figure 6.5.3**. It is likely that only at this potential was fresh cp exposed.

Positive-going potential sweeps following excursions to -1.2 V exhibited a peak at about 0.13 V, which Gardener and Woods [6] assigned to oxidation of excess CuS by reaction (6.6.1). It is considered more likely that metal oxide formation more readily occurred at this potential as the surface of the electrode became progressively more depleted in sulphur after each potential excursion to -1.2 V.

6.8 *The photoelectrochemistry of other sulphides in alkaline solutions.*

A number of experiments were carried out with bornite (Cu_5FeS_4) and chalcocite (Cu_2S), as they are phases related to chalcopyrite, to aid interpretation of cp oxidation behaviour. Like cp, bornite and chalcocite were found to be photoelectrochemically active under a wide range of conditions; typical cyclic voltammograms are shown in **Figure 6.8.1** and **2** respectively. The photocurrent profile at positive potentials indicated an n-type semiconducting surface most prominent on chalcopyrite but absent altogether in the equivalent voltammograms for Cu_2S , **Figure 6.8.2b**, reinforcing the conclusions above, that anodic n-type behaviour arose from an iron rich oxide. Likewise the broad photocathodic peak near -0.1 V on positive and negative going scans is most prevalent for Cu_2S and least so for CuFeS_2 , as would be most reasonable if this peak is attributed to the presence of a copper species, probably p-type Cu_2O .

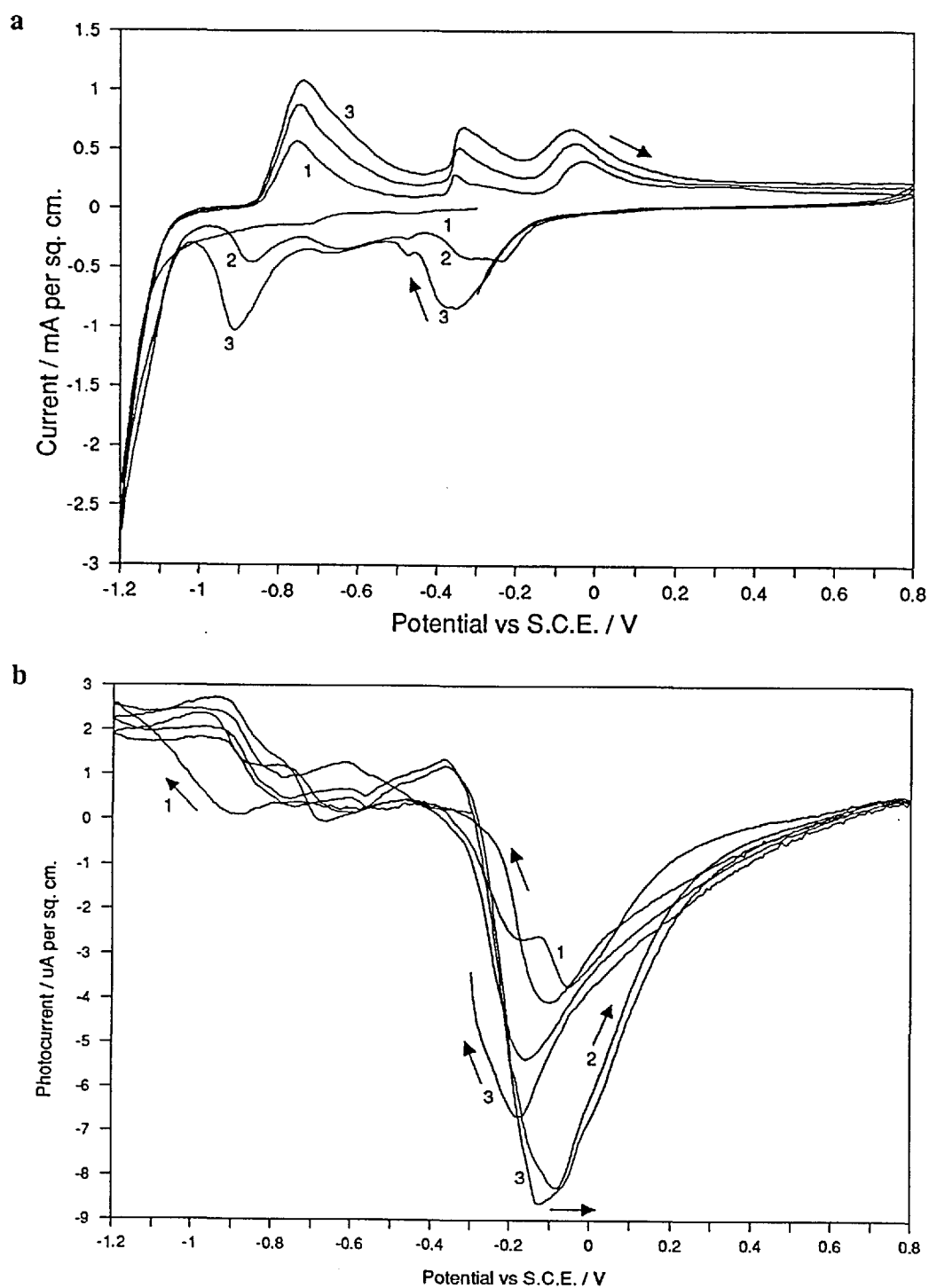


Figure 6.8.1a, cyclic voltammogram for polished bornite electrode in deoxygenated buffer solution at pH 9.2, commencing near the rest potential -0.3 V. 5 mV s^{-1} sweep rate.

b, "White" light photocurrent response of bornite under conditions described above.

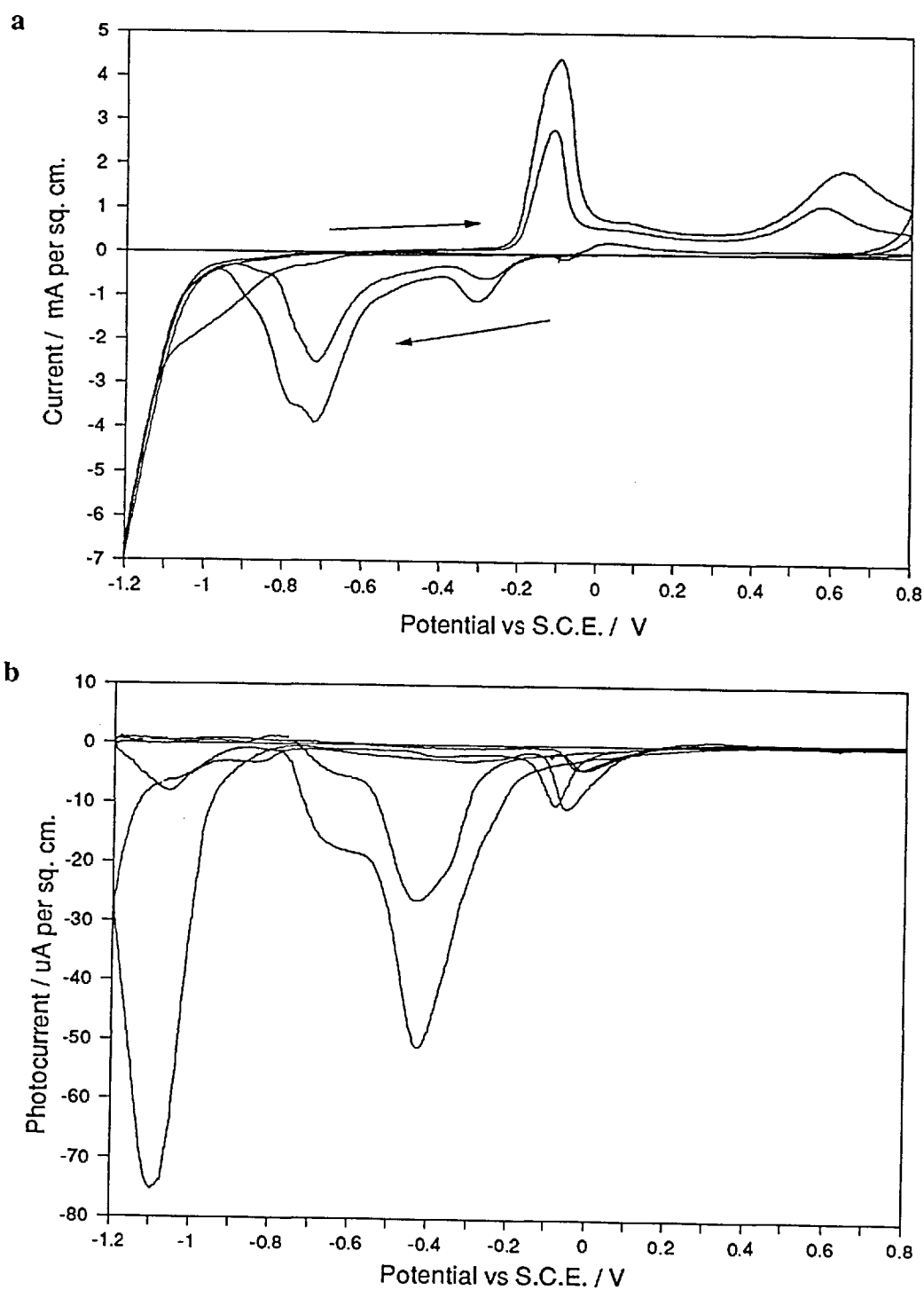


Figure 6.8.2a, cyclic voltammogram for polished chalcocite electrode in deoxygenated buffer solution at pH 9.2, commencing near the rest potential -0.3 V. 5 mV s^{-1} sweep rate.

b, "White" light photocurrent response of chalcocite under conditions described above.

CHAPTER 7.

CONCLUSIONS

This investigation into cp aqueous electrochemistry provided a new insight into phase changes that occur under oxidising and reducing conditions. To begin with, it was established that electrodes fabricated from twenty cp mineral specimens of diverse geological origin exhibited similar current and photocurrent responses to applied potential regimes in both acid and alkali. The X-ray diffraction pattern of a powdered sample from one such specimen was characteristic of the cp structure. Detailed microprobe analysis of another sample revealed a stoichiometry $\text{Cu}_{1.000}\text{Fe}_{1.988}\text{S}_{2.000}$. Electrodes fabricated from this specimen were then studied in more detail.

In solutions of 0.1 M HClO_4 , cyclic photo-voltammetry revealed the formation of an n-type passivating photo-active film at potentials between 0.2 V and 0.6 V vs S.C.E., even subsequent to potential sweep excursions to -1.2 V. Analysis of impedance spectra at potentials positive of the rest potential showed prevailing Warburg-type impedance at low frequency of potential modulation, consistent with a current limited by the diffusion of Fe^{3+} ions away from the electrode surface. Capacitances obtained by fitting semicircular curves to data at high frequencies were stable in the vicinity of 0.3 V. Also they were extremely high, indicating either a chemical charge storing capacity in the semiconducting phase responsible, or a large increase in surface area associated with the removal of iron from the cp lattice. Similar results were obtained in solutions of 2 M H_2SO_4 . The evidence was consistent with the oxidative formation of a semiconducting metal-depleted sulphide on cp. Oxides were unlikely considering their thermodynamic instability at low pH.

Photo-cathodic currents were also observed from cp in acid solutions near -0.1 V. Photocurrent spectroscopy revealed indirect electron transition and a threshold energy of 2.45 eV. With the aid of linear sweep voltammetry to ever-widening sweep limits, the emergence and disappearance of the photo-cathodic response and total current peaks were closely identified with the formation of a Cu_2S -like phase at < -0.5 V. It was possibly djurlite, $\text{Cu}_{1.96}\text{S}$, because chalcocite itself is not considered photo-active. This phase did not form anodically, whereas chalcocite has been frequently cited in the literature as forming oxidatively on the basis of conventional voltammetry. Voltammetric current peaks were assigned on the strength of the combined evidence. It was demonstrated that Cu^{2+} forms oxidatively only at potentials exceeding 0.4 V.

These above results are pertinent to the industrial copper extraction from cp by oxidative leaching in acid solutions. The 'n-type' product layer was clearly associated with surface

passivation at oxidising potentials on all twenty cp specimens. It is now established that copper leaching from cp in strongly acidic solutions requires potentials in excess of 0.4 V vs S.C.E. in at room temperature.

A more extensive survey of cp electrochemistry was carried out in sodium metaborate solutions of pH 9.2; the pH at which cp is frequently separated from associated minerals during froth flotation. At the rest potential and reducing potentials, a "white light" photo-anodic response was observed. It was stable over several days. From photocurrent and photovoltage spectroscopy the response above 2 eV was found to be photo-cathodic. Even at potentials as low as -1.0 V, there was linear dependency in plots of $(\Phi \cdot h\nu)^{1/2}$ vs $h\nu$, appropriate to non-direct electron transition and a threshold energy of about 3.3 eV. This behaviour cannot be assigned to any of the reduction products predicted by the thermodynamic description of the Cu-Fe-S-H₂O system except cp. Chalcopyrite is understood to be a degenerate semiconductor with a 0.5 eV band-gap, but the photocurrent spectra closely resembled cp absorption spectra, between 3.3 and 4.8 eV, as indeed the linear dependency of the above plot would require if the photoactive phase in question was cp. The photocurrent spectra obtained from bornite, Cu₅FeS₄, and chalcocite, Cu₂S, were compared with that for chalcopyrite. They were entirely dissimilar. From the above evidence it was concluded that in solutions of pH 9.2, the electronic and physical structure of chalcopyrite prevails at potentials as low as -1.0 V vs S.C.E.. The significant total cathodic charge passed on reaching this potential would require metal ion diffusion into the electrode interior. Linear dependence of I vs $t^{1/2}$ confirmed that this diffusion was rate limiting.

In alkaline solutions photocurrent voltammetry indicated the formation of a complex photo-active film on cp at oxidising potentials. Following anodic and cathodic pre-treatment, cyclic photocurrent spectroscopy and the photocurrent spectrum at 0.7 V vs S.C.E. showed behaviour very similar to that of n-type Fe₂O₃ formed on iron electrodes. However, the photoelectrochemical behaviour of cp subjected to less oxidising potentials directly from its rest potential revealed a photo-active electrode surface whose composition was more difficult to ascertain. Photocurrent and photovoltage spectra indicated the formation of one interphase for which the characteristic threshold energy was 2.6 eV. The emergence of this interphase was identified from spectra at applied potentials as low as -0.2 V, just positive of the rest potential, and it persisted at potentials as high as 0.4 V. It is believed to consist of a homogeneously distributed oxide film of composition similar to CuFe₂O₄, overlying metal-depleted cp. Spectral photocurrents arising from the interphase reversed direction near 0.2 V. It is proposed that the electric

field normal to the electrode surface within this interphase was sensitive to the band structure of the underlying metal-depleted sulphide layer, which in turn was sensitive to the extent of metal depletion - *i.e.* hole donor concentration - within it.

At potentials exceeding 0.4 V photocurrents were no longer stable enough for spectroscopy to be undertaken, but the progress of oxidation was demonstrated to depend very much on the semiconducting nature of the oxide formed at lower potentials. At increasing potential, coulometry and "white" light photocurrent cyclic voltammetry in particular indicated the formation of cupric oxide, cupric hydroxide, iron (III) (hydr-)oxides and finally sulphate ions. At no point was sulphur detected. The photoelectrochemical behaviour is consistent with the heterogeneous surface distribution of these oxide products. It is interesting that the presence of copper oxidation products on cp was evident only on applying potentials > 0.4 V vs S.C.E. in both acidic and alkaline solutions.

Although it was not possible to determine the exact composition of chalcopyrite oxidation and reduction products, this work enabled the behaviour of chalcopyrite to be more easily interpreted. The previous widely held view that chalcopyrite forms heterogeneously distributed and well known products, especially under mild oxidising and reducing conditions, is discredited, whilst, for instance, the reversibility of mild oxidation of chalcopyrite in alkaline solutions can now be more clearly understood. The mixed potential of 0.2 V established in flotation cells containing cp and aerated alkaline solutions can be readily appreciated as a result of this work. It is thought that chalcopyrite brought slowly to that potential is entirely covered by a thin oxide layer which presents a formidable barrier to metal ion migration from within and electron conduction from without. A more hydrolysed, non-passivating and heterogeneous surface is expected from the rapid application of this potential, or the imposition of higher potentials, and could be effected in a fluidised bed electrochemical cell. This could lead to improved CuFeS_2 flotation selectivity and recovery.

Future Work

This investigation was severely hampered by the inability to determine the semiconductor characteristics of chalcopyrite itself. Apart from the difficulties faced in fabricating a cruciform specimen from this friable material, it is believed that several attempts at Hall voltage measurements on apparently defect-free chalcopyrite failed on account of a small Hall voltage arising from the degenerate nature of the bulk phase. The van der Pauw method [221] demands 'suitably small ohmic contacts', for which a suitably large specimen of chalcopyrite could not be fabricated. The Seebeck effect could and should be implemented in future studies involving the semiconducting nature of chalcopyrite, granted the heating of cp would require that oxygen were carefully excluded.

The difficulty with using purely electrochemical measurements analytically, including the very surface sensitive methods described in this work, is that the identification of reaction products is always made inferentially. Other *in situ* electrochemical studies on cp could complimentary discoveries made hitherto. In particular Fourier transform IR and laser Raman reflectance spectroscopy could provide direct identification of molecular surface species.

APPENDICES

Appendix 1. Thermodynamic Data for Cu-Fe-S-H₂O Systems at 298 K

Species	ΔG_f° / kJ mol ⁻¹	Species	ΔG_f° / kJ mol ⁻¹
H ₂ O	-237.178	Cu(OH) ₂ (ppt)	-359.5
H ₂ S (g)	-33.56	HCuO ₂ ⁻	-258.9
H ₂ S	-27.87	CuO ₂ ²⁻	-183.9
HS ⁻	12.05	CuSO ₄ (c)	-663.
S ²⁻	86.31	CuSO ₄ ·H ₂ O (c)	-916.4
	120[84]	CuSO ₄ ·3H ₂ O (c)	-1399
S ₂ ²⁻	79.5	CuSO ₄ ·5H ₂ O (c)	-1880
S ₃ ²⁻	73.6	Cu ₂ S (chalcocite)	-87.6
S ₄ ²⁻	69.0		-85.57[86]
S ₅ ²⁻	65.7	Cu _{1.96} S (djeurlite)	-84.64[86]
S _{rhombic}	0	Cu _{1.934} S (digenite)	-83.85[86]
S _{monoclinic}	0.188	Cu _{1.75} S (anilite)	-78.54[86]
S ₈ (g)	49.66	Cu _{1.4} S (blue-remain. covellite)	-64.34[86]
S ₂ (g)	79.33		-83.69[87]
S (g)	238.28	Cu _{1.93} S	-84.01[87]
S ₂ O (g)	-138.833	Cu _{1.83} S	??[87]
SO	-19.836	Cu _{1.665} S	-66.06[87]
S ₂ O ₃ ²⁻	-518.8	Cu _{1.38} S	-53.2
S ₅ O ₆ ²⁻	-956.0	CuS	0
S ₄ O ₆ ²⁻	-1022.2	Fe (α)	0
S ₂ O ₄ ²⁻	-600.4	Fe ₂ O ₃ (c) (hematite)	-743.60
HS ₂ O ₄ ⁻	-614.6	Fe(OH) ₃ (ppt)	705.535
H ₂ S ₂ O ₄	-616.7	Fe ₃ O ₄ (c) (magnetite)	-1015.359
S ₃ O ₆ ²⁻	-958	Fe(OH) ₂ (ppt)	-486.6
SO ₂ (g)	-300.194	FeOOH (c) (goethite)	-490
SO ₂	-300.708	Fe _{0.942} O (wustite)	-245.211
H ₂ SO ₃	-537.90	FeO (c)	-251.454
HSO ₃ ⁻	-527.81	Fe ²⁺	-91.5
SO ₃ ²⁻	-486.6	Fe ³⁺	-16.7
S ₂ O ₅ ²⁻	-791	FeOH ²⁺	-229.41
S ₂ O ₆ ²⁻	-966	Fe(OH) ₂ ⁺	-438.1
SO ₃ (g)	-371.08	Fe(OH) ₂ (aq)	-441.0
H ₂ SO ₄ (g)	-662.91	FeOH ⁺	-277.4
H ₂ SO ₄	-744.63	Fe(OH) ₃ (undissoc.)	-660.0
HSO ₄ ⁻	-756.01	Fe(OH) ₃ ⁻	-605.1
SO ₄ ²⁻	-744.63	HFeO ₂ ⁻	-376.4
S ₂ O ₈ ²⁻	-1110.4	Fe(OH) ₄ ²⁻	-769.9
H ₂ S ₂ O ₈	-1110.4	Fe(OH) ₄ ⁻	-842.2
		FeO ₂ ²⁻	-301
CuFeS ₂ (c)	-190.58[85]	Fe ₂ (OH) ₂ ⁴⁺	-467.27
Cu ₃ FeS ₄ (c)	-392.72[85]	FeS (c)	-100.738
CuFeO ₂ (c)	-479.9	FeS ₂ (c)	-166.012
CuFe ₂ O ₄ (c)	-858.8	Fe ₇ S ₈ (c)	-748.5
		FeSO ₄ ⁺	-772.8
		Fe(SO ₄) ₂ ⁻	-1524.6
Cu ⁺	50.3	Fe ₂ (SO ₄) ₃	-2243
Cu ²⁺	65.7	Fe ₂ (SO ₄) ₃ (c)	-2263.065
Cu ₂ O (s)	-148.1		
CuO (s)	-134		

Table. Gibbs energies of formation of species in the copper - iron - sulphur - water system. All data was obtained from reference [BP4:28], unless marked otherwise.

The following reactions are predicted to occur under the conditions of **Figure 1.3.1.2**.



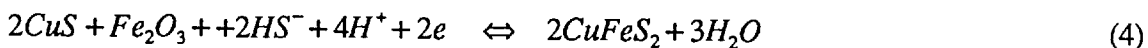
$$E / V = -0.183 - 0.0296 \log(\text{Fe}^{2+})$$



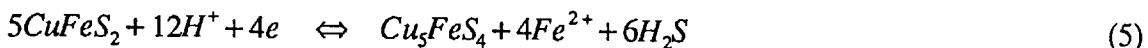
$$E / V = -0.006 + 0.0591 \log(\text{Fe}^{2+})$$



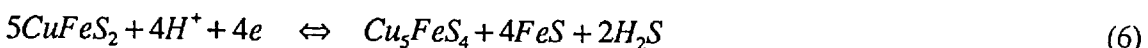
$$E / V = 0.125 - 0.0591 \text{pH}$$



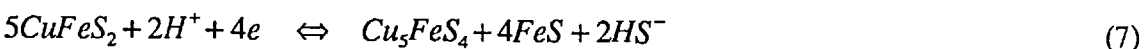
$$E / V = 0.919 - 0.1182 \text{pH}$$



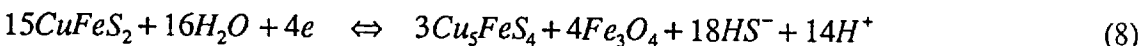
$$E / V = -0.070 - 0.1773 \text{pH} - 0.0591 \log(\text{Fe}^{2+}) - 0.088 \log(\text{H}_2\text{S})$$



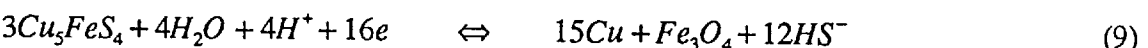
$$E / V = -0.263 - 0.0591 \text{pH} - 0.0295 \log(\text{H}_2\text{S})$$



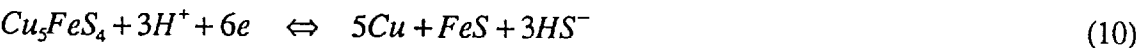
$$E / V = -0.470 - 0.0295 \text{pH} - 0.0295 \log(\text{HS}^-)$$



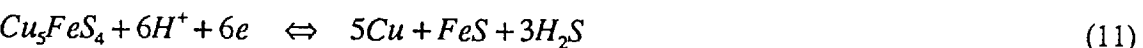
$$E / V = -4.226 + 0.2068 \text{pH} + 0.2600 \log(\text{HS}^-)$$



$$E / V = -0.814 - 0.0148 \text{pH} - 0.0443 \log(\text{HS}^-)$$



$$E / V = 0.567 - 0.0296 \text{pH} - 0.0296 \log(\text{HS}^-)$$



$$E / V = -0.360 - 0.0591 \text{pH} - 0.0296 \log(\text{H}_2\text{S})$$

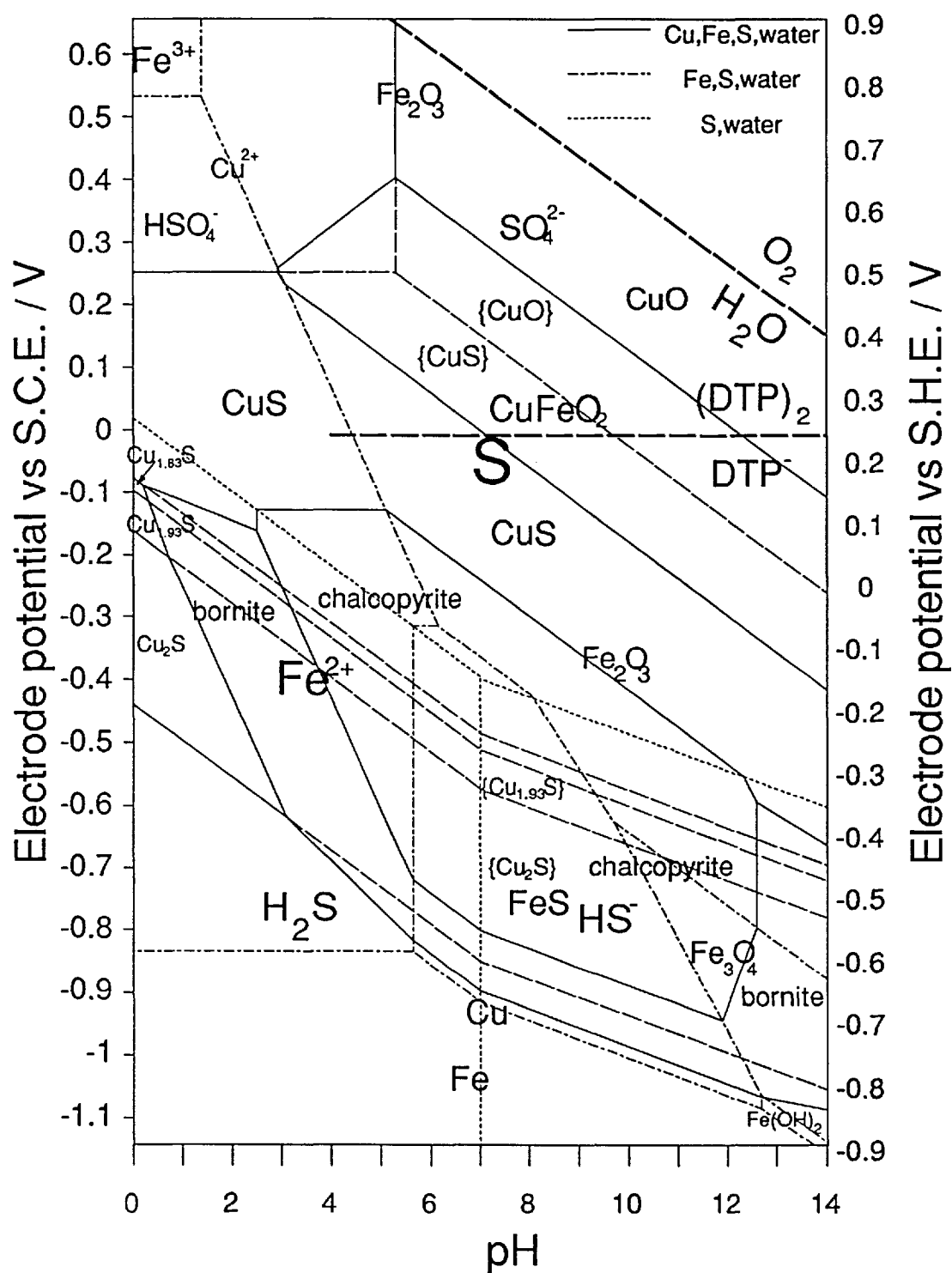


Figure. Metastability diagram for the Cu-Fe-S-H₂O system calculated from the data above excluding FeS₂ and sulphur species of oxidation state greater than 0, and for dissolved copper, iron and sulphur activities of $10^{-4.01}$, 10^{-4} , and $10^{-3.99}$, respectively.

See also Section 1.3.1.

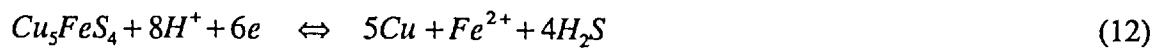
Appendix 2.

The following computer program was written in Turbo Pascal version 3.0 for data acquisition and control of a Schlumberger Solartron 1286 Electrochemical Interface and 1250 Frequency Response Analyser, and EG&G 1252 Phase Sensitive Lock-in Amplifier, via an IEEE-488 interface bus. The program is a modified version of one written by Z.Liang [219]. The modifications enabled the recording of photocurrent phase angles and photovoltage measurements. They also afforded greater user control of the above instruments, and facilitated experiments in cyclic photo-voltammetry to variable sweep limits.

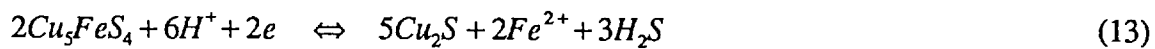
```

program acqu12;
const
  T1 = 3000; T2 = 1000; T3 = 15; T4 = 10000; T5 = 20; V0 = 0;
  I0 = 0; F0 = 448; AM0 = 0.350; ha = 1; Od = 1; tim1 = 10000;
type
  sdesc = record len : byte; addr : integer end;
  CMDSTR = string[80];
  DATASTR = string[50];
  ClockType = record
    Hour,Minute,Second,Sec100 : integer;
    TotalHours,TotMin,TotalSecs,Tots100 : integer;
    Number : integer;
  TotalTime : real;
  end;
  RegPack = record
    AX,BX,CX,DX,BP,SI,DI,DS,ES,Flags : integer;
  end;
  Registers = record
    AX,BX,CX,DX,BP,SI,DI,DS,ES,Flags : integer;
  end;
var
  trate,sam,check,rseg,stp,stp1,stp2,stp3,stp4,rstp,dstp:real;
  del,count,rrate,csam: integer;
  Offset : integer; Output_File : TEXT; FileName : DATASTR;
  Mode,ptc,Lock_in_OP : integer; RR, sst : real; rfq : DATASTR;
  V1,V2,dV,F1,F2,dF,L1,L2,dL:real;
  w1,V,F : real; I : integer; Total_I : real; TF,V_and_I : DATASTR;
  Freq_Sweep_mode,Sweep_Mode,vs : char;
  ch : char; j : integer;
  v01,v02,v03,v04,v05,v06,v07,v08,v09,v10,v11,v12,v13,v14,v15,v16,v00,
  i01,i02,i03,i04,i05,i06,i07,i08,i09,i10,i11,i12,i13,i14,i15,i16,i00 : real;
  sgs,T0,Sn,nfr : integer; I_and_T : DATASTR; N : integer;
  Nstr : string[3]; Clock : ClockType; RecPack : RegPack;
  Regs : Registers; dt : real; fd,fit,fh,fo : integer;
  sfr : char; hz1,hz2,dg : real;
  N_read : integer;
  Day,Month,Year,Hour,Min,Sec : integer;
  TC,GO,time,Xmax,Xmin,Xkeep,Curr : real;
  addr_1286,my_address,system_controller : integer;
  status,len,poll : integer;
  cmd,recv : CMDSTR;
  cmddesc,recvdsc : sdesc;
procedure transmit (var s : sdesc; var status : integer); external 't488xmit';
procedure receive (var r : sdesc; var len,status : integer); external 't488recv';
procedure Xmit;
begin
  cmddesc.len := length(cmd);
  transmit(cmddesc,status);
  if status <> 0 then
    begin
      writeln('Error in ',cmd);
      writeln('status = ',status);
    end
  end;
end;
procedure Tell_1286_to(s:CMDSTR);
begin
  cmd:='UNL UNT MTA LISTEN 18 DATA '''+s+''''; Xmit
end;
procedure Tell_5210_to(s:CMDSTR);
begin
  cmd:='UNL UNT MTA LISTEN 42 DATA '''+s+''''; Xmit
end;
procedure Tell_1250_to(s:CMDSTR);
begin
  cmd:='UNL UNT MTA LISTEN 2 DATA '''+s+''''; Xmit
end;

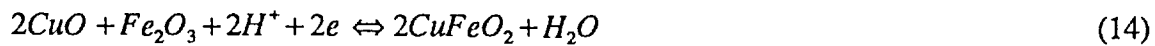
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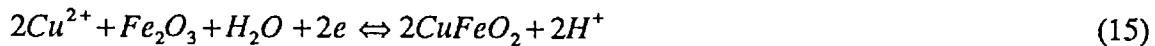
$$E / V = -0.328 - 0.0788pH - 0.0394 \log(H_2S) - 0.0098 \log(Fe^{2+})$$



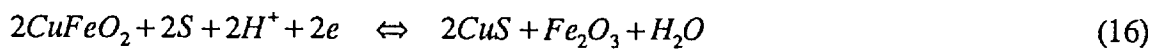
$$E / V = -0.419 - 0.0886 \log(H_2S) - 0.0591 \log(Fe^{2+}) - 0.1773pH$$



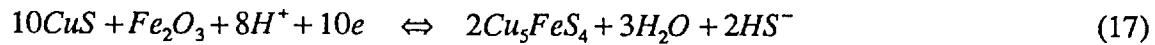
$$E / V = 0.961 - 0.0591pH$$



$$E / V = 0.572 + 0.0591pH + 0.0591 \log(Cu^{2+})$$



$$E / V = 0.660 - 0.0591pH$$



$$E / V = 0.382 - 0.0118pH$$

```

procedure Prepare_to_read_1286;           {gen}
begin
  cmd:='IFC UNL UNT MLA TALK 18'; Xmit
end;
procedure Read_1286(var V_and_I : DATASTR); {gen}
var code : integer;
begin
  recv:= ' ';
  recvdesc.len:=length(recv);
  receive(recvdesc,len,status);
  V_and_I := Copy(recv,1,25)
end;

procedure DVM_On;           {gen}
begin
  Tell_1286_to('RU 1;');
end;
procedure Start_Sweep;      {gen}
begin
  Tell_1286_to('SW '+Sweep_mode+');
end;
procedure StandbyOn_Off;    {gen}
begin
  Tell_1286_to('PW 0;');
end;
procedure StandbyOn_On;     {gen}
begin
  Tell_1286_to('PW 1;');
end;

procedure GPIB_1286_Off;
begin
  Tell_1286_to('GP 0;');
end;

procedure Apply_I_To_Cell(Curr:real); {6}
var Vstr : DATASTR;
begin
  Str(Curr:7:4,Vstr);
  Tell_1286_to('PO '+1+');
  Tell_1286_to('PC '+Vstr+');
  StandbyOn_On;
  delay(1200);
end;
procedure Get_Current_Par(var Curr,time,GO : real); {6}
begin
  write(' Constant Current : '); readln(Curr);
  writeln(' NOTE! TOTAL DELAY TIME = PAUSE + SWEEP TIME,');
  writeln(' SWEEP TIME MUST BE ACCOUNTED FOR EXTERNALLY!');
  Write(' Pause between Readings (Secs) : '); readln(time);
  time := time * 1000;
  write(' Number of Measurements : '); readln(GO);
  writeln;
end;
procedure wait;
begin
  delay(1);
  Xmax := Xmax - 1;
end;
procedure Analyser_Recycle;           {5}
begin
  Tell_1250_to('RE;'); delay(T5);
end;
procedure Prepare_F_Sweep_Fill(TC:real); {5}
var FullName,suffix : DATASTR;
begin
  Str(TC:1:0,suffix);
  FullName := FileName + suffix + '.pm';
  writeln('Output File : ',FullName);
  Assign(Output_File,FullName);
  Rewrite(Output_File);
  Writeln(Output_File,'File Name : ',FullName);
  Writeln(Output_File,'Frequency Sweep Response. ');
  Writeln(Output_File,'Sweep mode : ',Freq_Sweep_mode);
  Writeln(Output_File,'Potential : ',TC:7:3);
  Writeln(Output_File,' Freq(Hz) Real Imaginary');
  Writeln(Output_File,'-----');
end;

procedure Original_1250_Range;           {4}
begin
  Tell_1250_to('RA 1,0;'); delay(T5);
  Tell_1250_to('RA 2,0;'); delay(T5);
end;

```

```

procedure Stop_Analyser;      {4}
begin
  Tell_1250_to('SA;'); delay(T5);
end;
procedure CONDITION_Off;      {4}
begin
  Tell_1286_to('BR 0;');
end;
procedure Read_1250(var TF : DATASTR); {4}
var code : integer;
begin
  recv:= '          ';
  recvdesc.len:=length(recv);
  receive(recvdesc,len,status);
  TF := Copy(recv,1,35)
end;
procedure Prepare_to_Read_1250; {4}
begin
  cmd:='IFC UNL UNT MLA TALK 2'; Xmit;
end;

procedure Prepare_F_Sweep_File(v:real); {4}
var FullName,suffix : DATASTR;
begin
  Str(v:5:3,suffix);
  FullName := FileName + suffix;
  writeln('Output File : ',FullName);
  Assign(Output_File,FullName);
  Rewrite(Output_File);
  WriteLn(Output_File,'File Name : ',FullName);
  WriteLn(Output_File,'Frequency Sweep Response. ');
  WriteLn(Output_File,'Sweep mode : ',Freq_Sweep_mode);
  WriteLn(Output_File,'Potential : ',v:7:3);
  WriteLn(Output_File,'Freq/Hz Real Imag. ');
  WriteLn(Output_File,'-----');
end;
procedure Apply_V_To_Cell(V:real); {4}
var Vstr : DATASTR;
begin
  Str(V:7:3,Vstr);
  Tell_1286_to('PV '+Vstr+');
  StandbyOn_On; delay(1200); {gen}
end;
procedure Start_Freq_Sweep; {4}
begin
  Tell_1250_to('SC '+Freq_Sweep_mode+'); delay(T5);
end;
procedure Get_Potential_Par(var V1,time,GO : real); {4}
begin
  write(' Constant Potential : '); readln(V1);
  writeln(' NOTE! TOTAL DELAY TIME = PAUSE + SWEEP TIME. ');
  writeln(' SWEEP TIME MUST BE ACCOUNTED FOR EXTERNALLY! ');
  Write(' Pause between Readings (Secs) : '); readln(time);
  time := time * 1000;
  write(' Number of Measurements : '); readln(GO);
  writeln;
end;
procedure CONDITION_On; {4}
begin
  Tell_1286_to('BR 1;');
end;
procedure Get_Potential_Pars(var V1,V2,dV:real); {4}
begin
  write(' Starting Potential : '); readln(V1);
  write(' Terminating Potential : '); readln(V2);
  write(' Increment : '); readln(dV);
  writeln;
end;
procedure On_1286_LPfilter;
begin
  Tell_1286_to('FI 1;');
end;
procedure Set_1250_Freq(f : real);
var Fstr : DATASTR;
begin
  Str(f:9:3,Fstr);
  Tell_1250_to('FR '+Fstr+'); delay(T5);
end;

```

```

procedure Fundamental_F_Setting;
begin
  write('Please enter the fundamental frequency in Hz ( max 4 KHz ) : '); readln(f);
  Set_1250_Freq(f);
  writeln;
end;
procedure Set_Freq_Sweep_Pars(sfr : char;hz1,hz2,dg : real); {4}
var hs : char;
    Fstr,Lstr : DATASTR;
begin
  write('Would you like to do the HARMONIC sweep ? (y)'); readln(hs);
  if (hs = 'y') or (hs = 'Y') then
    begin
      writeln; hs:= 'y';
      Fundamental_F_Setting;
      Freq_Sweep_Mode := '0';
    end
  else
    begin
      writeln; hs:= 'n';
      write('Please enter FR MIN in Hz '); readln(hz1);
      Str(hz1:7:3,Fstr);
      Tell_1250_to('MI '+Fstr+'); delay(T5);
      write('Please enter FR MAX in Hz '); readln(hz2);
      Str(hz2:7:3,Fstr);
      Tell_1250_to('MA '+Fstr+'); delay(T5);
      writeln;
      writeln('Sweeping frequency range ( 1E-5 to 6.5E+4 ) is divided');
      writeln('into two sub-range, i.e. f < 10 Hz and f >= 10 Hz. ');
      writeln('Please enter the required sub-range --- 1 for f < 10 Hz. ');
      write('2 for f >= 10 Hz and 3 for the whole range : '); readln(sfr);
      if (sfr = '1') then
        begin
          On_1286_LPfilter;
          writeln;
          write('Please enter dLin in Hz/st '); readln(dl);
          Str(dl:4:2,Lstr);
          Tell_1250_to('NH '+Lstr+'); delay(T5);
          writeln;
          writeln('Please enter Frequency Sweep mode --- ');
          write('3 = Lin up ');
          write('4 = Lin down : ');
          readln(Freq_Sweep_Mode);
          writeln;
        end
      else
        begin
          writeln;
          write('Please enter dLog in st/dec '); readln(dg);
          Str(dg:5:2,Lstr);
          Tell_1250_to('GD '+Lstr+'); delay(T5);
          writeln;
          writeln('Please enter Frequency Sweep mode --- ');
          write('1=Log up ');
          write('2=Log down : ');
          readln(Freq_Sweep_Mode); writeln;
        end;
      end;
    end;
  procedure Reformat_1250_On;
  begin
    Tell_1286_to('RR 0'); delay(T5);
  end;
  procedure FRA_Order_Setting(fo : integer); {4}
  var Dstr : DATASTR;
      Od : char;
  begin
    write('Would you like to use the ORDER analysis facility ? '); readln(od);
    if (Od = 'y') or (Od = 'Y') then
      begin
        Od:= 'y';
        Reformat_1250_On;
        writeln;
        write('Please enter 1250 order number (1 to 16) : '); readln(fo);
        if fo > 1 then
          begin
            Str(fo:2,Dstr);
            Tell_1250_to('OR '+Dstr+'); delay(T5);
            writeln;
          end
        else writeln;
      end
    else writeln; Od:= 'n';
  end;
end;

```

```

procedure DC_Couple_1250;      {4}
begin
  Tell_1250_to('DC 1,0;'); delay(T5);
  Tell_1250_to('DC 2,0;'); delay(T5);
end;
procedure New_1250_Range;      {4}
begin
  Tell_1250_to('RA 1,0;'); delay(T5);
  Tell_1250_to('RA 2,0;'); delay(T5);
end;

procedure Stop_F_Sweep;        {4}
begin
  Tell_1250_to('SS;'); delay(T5);
end;

procedure TenV_1286;           {4}
begin
  Tell_1286_to('VX 1;');
end;
procedure TenI_1286;           {4}
begin
  Tell_1286_to('IX 1;');
end;
procedure Vreje_1286;          { Auto } {4}
begin
  Tell_1286_to('VT 0;');
end;
procedure Ireje_1286;          { Auto } {4}
begin
  Tell_1286_to('IT 0;');
end;
procedure GPIB_1250_Off;
begin
  Tell_1250_to('OP 2,0;'); delay(T5);
end;
procedure Reset_1250;          {3}
begin
  Stop_Analyser;
  GPIB_1250_Off;
end;
procedure Stop_Generator;      {3}
begin
  Tell_1250_to('SQ 0;'); delay(T5);
end;
procedure Read_1250_ShortForm(var TF : DATASTR);      {3}
var code : integer;
begin
  recv:= ' ';
  recvdesc.len:=length(recv);
  receive(recvdesc.len,status);
  TF := Copy(recv,1,35);
  Delete(TF,1,12)
end;
procedure Analyser_Single;      {3}
begin
  Tell_1250_to('SI;'); delay(15);
end;
procedure Remove_Blank(var s : DATASTR);
var i:integer;
begin
  i:=0;
  repeat i:=i+1 until s[i]<>' ';
  Delete(s,1,i-1);
end;
procedure Prepare_Fixed_F_File(f:real);      {3}
var FullName,suffix : DATASTR;
begin
  Str(f:9:3,suffix);
  Remove_Blank(suffix);
  FullName := FileName + suffix;
  writeln('Output File : ',FullName);
  Assign(Output_File,FullName);
  Rewrite(Output_File);
  Writeln(Output_File,'File Name : ',FullName);
  Writeln(Output_File,'Fixed frequency (v sweep).');
  Writeln(Output_File,'Sweep mode(1=Ramp, 2=Step) : ',Sweep_mode);
  Writeln(Output_File,'Frequency : ',f:7:3);
  Writeln(Output_File,'Potential(V) I(A) 1286 Real Imaginary');
  Writeln(Output_File,'-----');
end;

```

```

Procedure Start_Generator;           {3}
begin
  Tell_1250_to('RG;'); delay(T5);
end;
procedure GPIB_1250_All;
begin
  Tell_1250_to('OP 2,1; OS 0;'); delay(T5);
end;
procedure Initialise_1250_Bus;       {3}
begin
  cmd:='UNL REN MTA LISTEN 2'; Xmit; Delay(500);
  GPIB_1250_All;
end;
procedure FRA_Harmonic_Setting(fh : integer); {3}
var Hstr : DATASTR;
begin
  writeln('Please enter 1250 harmonic number (1 to 16) , ');
  write ('(default HARMONIC sweep = 1): '); readln(fh);
  if fh > 1 then
    begin
      Str(fh:2,Hstr);
      Tell_1250_to('HA '+Hstr+'); delay(T5);
      writeln;
    end
  else fh:= 1; writeln;
end;
procedure FRA_Integration_Time(dt : integer); {3}
var Tstr : DATASTR;
begin
  write('Please enter 1250 analyser integration time in cycle : '); readln(dt);
  Str(dt:2,Tstr);
  Tell_1250_to('IC '+Tstr+'); delay(T5);
  writeln;
end;
procedure FraDelay_1250(dt : integer); {3}
var Tstr : DATASTR;
begin
  write('Please enter 1250 measurment delay in cycle : '); readln(dt);
  Str(dt:2,Tstr);
  Tell_1250_to('MC '+Tstr+'); delay(T5);
  writeln;
end;
procedure Get_Frequency_Pars(var F1,F2,dF:real); {3}
begin
  write(' Starting Frequency : '); readln(F1);
  write('Terminating Frequency : '); readln(F2);
  write(' Increment : '); readln(dF);
  writeln;
end;
procedure AC_Couple_1250; {3}
begin
  Tell_1250_to('DC 1,1;'); delay(T5);
  Tell_1250_to('DC 2,1;'); delay(T5);
end;
procedure Step_Multisegments; {2}
begin
  write('Please enter V5 in volt '); readln(v05);
  write('Please enter V6 in volt '); readln(v06);
  write('Please enter V7 in volt '); readln(v07);
  write('Please enter V8 in volt '); readln(v08);
  writeln;
  case sgs of
    12,16:
      begin
        write('Please enter V9 in volt '); readln(v09);
        write('Please enter V10 in volt '); readln(v10);
        write('Please enter V11 in volt '); readln(v11);
        write('Please enter V12 in volt '); readln(v12);
        writeln;
      end;
  end;
  case sgs of
    16:
      begin
        write('Please enter V13 in volt '); readln(v13);
        write('Please enter V14 in volt '); readln(v14);
        write('Please enter V15 in volt '); readln(v15);
        write('Please enter V16 in volt '); readln(v16);
        end;
  end;
end;

```

```

procedure Ramp_Multisegments; {2}
begin
  write('Please enter V5 in volt '); readln(v05);
  write('Please enter T5 in sec '); readln(t05);
  write('Please enter V6 in volt '); readln(v06);
  write('Please enter T6 in sec '); readln(t06);
  write('Please enter V7 in volt '); readln(v07);
  write('Please enter T7 in sec '); readln(t07);
  write('Please enter V8 in volt '); readln(v08);
  write('Please enter T8 in sec '); readln(t08);
  writeln;
  case sgs of
    12,16:
      begin
        write('Please enter V9 in volt '); readln(v09);
        write('Please enter T9 in sec '); readln(t09);
        write('Please enter V10 in volt '); readln(v10);
        write('Please enter T10 in sec '); readln(t10);
        write('Please enter V11 in volt '); readln(v11);
        write('Please enter T11 in sec '); readln(t11);
        write('Please enter V12 in volt '); readln(v12);
        write('Please enter T12 in sec '); readln(t12);
        writeln;
      end;
  end;
  case sgs of
    16:
      begin
        write('Please enter V13 in volt '); readln(v13);
        write('Please enter T13 in sec '); readln(t13);
        write('Please enter V14 in volt '); readln(v14);
        write('Please enter T14 in sec '); readln(t14);
        write('Please enter V15 in volt '); readln(v15);
        write('Please enter T15 in sec '); readln(t15);
        write('Please enter V16 in volt '); readln(v16);
        write('Please enter T16 in sec '); readln(t16);
        writeln;
      end;
  end;
end;
procedure Var_segments; {2}
begin
  write('Are more than 4 invariant sweep segments required (n) ? ');
  readln(vs);
end;
procedure Read_Standard_Resistor(var r:real); {2}
var code,sr : integer;
begin
  Tell_1286_to('?RR;');
  cmd:='UNL UNT MLA TALK 18'; Xmit;
  rcv:='';
  rcvdesc.len:=length(rcv);
  receive(rcvdesc,len,status);
  Val(rcv,sr,code);
  case Sr of
    1: r:=0.1;
    2: r:=1;
    3: r:=10;
    4: r:=100;
    5: r:=1000;
    6: r:=10000;
    7: r:=1E5;
  else writeln('Error reading Standard Resistor!!'); Halt;
  end;
end;
procedure Read_RFQ_5210(var rfq: DATASTR);
var code : integer;
begin
  cmd:='IFC UNL UNT MTA LISTEN 42 DATA'+ 'FRQ'#13#10+'''; Xmit;
  rcv:='';
  rcvdesc.len:=length(rcv);
  cmd:='IFC UNL UNT MLA TALK 74'; Xmit;
  receive(rcvdesc,len,status);
  rfq:=rcv;
  writeln('chopper reference frequency: ',rfq,'mHz'); writeln;
end;
procedure Read_TC_5210(var ptc:integer); {2}
var code : integer;
begin
  cmd:='IFC UNL UNT MTA LISTEN 42 DATA'+ 'TC'#13#10+'''; Xmit;
  rcv:='';
  rcvdesc.len:=length(rcv);
  cmd:='IFC UNL UNT MLA TALK 74'; Xmit;
  receive(rcvdesc,len,status);
  Val(rcv,ptc,code);

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case ptc of
4: ptc:=100; 5: ptc:=300; 6: ptc:=1000; 7: ptc:=3000; 8: ptc:=10000; end;
writeln('5210 time constant = ',ptc,'ms'); writeln;
end;
procedure Read_5210_MP;      {2}
begin
cmd:='IFC UNL UNT MTA LISTEN 42 DATA'''+MP'#13#10+'''; Xmit;
recv:=
;
recvdsc.len:=length(recv);
cmd:='IFC UNL UNT MLA TALK 74'; Xmit;
receive(recvdsc.len,status);
end;
procedure Read_Photo_theta_sweep;      {2}
begin
Read_5210_MP;
writeln(Output_File,V_and_I,',',recv);
writeln(V_and_I,',',recv);
delay(del);
cmd:='UNT TALK 18'; Xmit;
Read_1286(V_and_I);
end;
procedure set_5210_sensitivity (var sst:real);      {2}
var sen : char;
begin
writeln('Codes for 5210 sensitivity in mV (0.3):');
writeln('A = 0.0001; E = 0.01; J = 3;');
writeln('B = 0.0003; F = 0.03; K = 10;');
writeln('C = 0.001; G = 0.1; L = 30;');
writeln('D = 0.003; H = 1; M = 100;');
write('Please enter the appropriate sensitivity code : '); readln(sen);
case sen of
'a', 'A': begin Tell_5210_to('SEN0'#13#10); sst:= 0.0001; end;
'b', 'B': begin Tell_5210_to('SEN1'#13#10); sst:= 0.0003; end;
'c', 'C': begin Tell_5210_to('SEN2'#13#10); sst:= 0.001; end;
'd', 'D': begin Tell_5210_to('SEN3'#13#10); sst:= 0.003; end;
'e', 'E': begin Tell_5210_to('SEN4'#13#10); sst:= 0.01; end;
'f', 'F': begin Tell_5210_to('SEN5'#13#10); sst:= 0.03; end;
'g', 'G': begin Tell_5210_to('SEN6'#13#10); sst:= 0.1; end;
'h', 'H': begin Tell_5210_to('SEN8'#13#10); sst:= 1; end;
'j', 'J': begin Tell_5210_to('SEN9'#13#10); sst:= 3; end;
'k', 'K': begin Tell_5210_to('SEN10'#13#10); sst:= 10; end;
'l', 'L': begin Tell_5210_to('SEN11'#13#10); sst:= 30; end;
'm', 'M': begin Tell_5210_to('SEN12'#13#10); sst:= 100; end;
else begin Tell_5210_to('SEN7'#13#10); sst:= 0.3; end;
end;
end;
procedure Prepare_Fixed_L_File;      {2}
var FullName : DATASTR;
begin
FullName := FileName;
Assign(Output_File,FullName);
Rewrite(Output_File);
Writeln(Output_File,'File Name : ',FullName);
Writeln(Output_File,'I measuring resistor:',RR);
Writeln(Output_File,'lock-in sensitivity:',sst,' mV');
Writeln(Output_File,'reference frequency:',rfq,' Hz');
Writeln(Output_File,'Time constant:',ptc,' ms');
Writeln(Output_File,'Sweep segments/V:',V01,V02,V03,V04);
Writeln(Output_File,'Segment times/s:',T01,T02,T03,T04);
Writeln(Output_File,' V/volts I(dk)/A I(ph) theta ');
end;
procedure Output_delay(var del : integer);
begin
writeln('Input delay between readings required in milliseconds (10):');
readln(del);
end;
procedure Sweep_Mode_1;      {1,2}
begin
Start_Sweep;
delay(T4);
StandbyOn_On;      {gen}
Prepare_To_Read_1286;
repeat Read_1286(V_and_I) until status=0;
end;
procedure Sweep_Mode_2;
begin
StandbyOn_On;      {gen}
Start_Sweep;
DVM_On;
Prepare_To_Read_1286;
repeat Read_1286(V_and_I) until status=0;
end;

```

```

procedure Do_sweep;
begin
  if Sweep_Mode='1' then
  begin
    Sweep_Mode_1;
    case mode of
      1:
      begin
        while status=0 do
        begin
          writeln(Output_File,V_and_I);
          writeln(V_and_I);
          delay(del);
          Read_1286(V_and_I);
        end;
      end;
    2:
    begin
      Tell_5210_to('MP 1'#13#10);
      while status=0 do
      begin
        Read_Photo_theta_sweep;
      end;
    end; {mode case 2}
  end; {mode case}
end {sweep mode 1}
else
begin
  Sweep_Mode_2;
  case mode of
    1:
    begin
      while count<sam do
      begin
        writeln(Output_File,V_and_I);
        writeln(V_and_I);
        delay(del);
        Read_1286(V_and_I);
        count:=count+1;
      end;
    end;
    2:
    begin
      Tell_5210_to('MP 1'#13#10);
      while count<sam do
      begin
        Read_Photo_theta_sweep;
        count:=count+1;
      end;
    end; {mode case 2}
  end; {mode case}
end; {if sweep mode}
end;
procedure DVM_Off; {1}
begin
  Tell_1286_to('RU 0;');
end;
procedure Data_Window; {1}
begin
  Window(1,9,76,20);
  ClrScr;
end;
procedure GPIB_1286_ShortOn;
begin
  Tell_1286_to('GP 2; OS 0;');
end;
procedure Initialise_1286_Bus; {1}
begin
  cmd:='UNL UNT MTA LISTEN 18'; Xmit;
  GPIB_1286_ShortOn;
end;
procedure RMPsw1286_Setting; {1}
var Vstr,Sstr,Tstr : DATASTR;
begin
  if (vs = 'y') or (vs = 'Y') then
  begin
    write('Please enter the number of variant sweep segments (8,12 or 16) '); readln(sgs);
    Sn:=4;
    Str(Sn:5,Sstr);
    Tell_1286_to('SM '+Sstr+');
  end
else
begin
  Sn:=4;vs:='n';

```

```

writeln('Parameters required for a user-selected RAMP sweep :');
writeln('2 segments: V1, T1, V2, T2, (V3 = V1).');
writeln('3 segments: V1, T1, V2, T2, V3, T3, (V4 = V1).');
writeln('4 or more segments: V1, T1, V2, T2, V3, T3, V4, T4. ');
writeln;
write('Please enter the number of sweep segments (2 to 99999) required (4): '); readln(Sn);
Str(Sn:5,Sstr);
Tell_1286_to('SM '+Sstr+');
ClrScr;
end;
write('Please enter RMP V1 in volt '); readln(v01);
Str(v01:7:3,Vstr);
Tell_1286_to('VA '+Vstr+');
write('Please enter RMP T1 in sec '); readln(t01);
Str(t01:5:1,Tstr);
Tell_1286_to('TA '+Tstr+');
write('Please enter RMP V2 in volt '); readln(v02);
Str(v02:7:3,Vstr);
Tell_1286_to('VB '+Vstr+');
write('Please enter RMP T2 in sec '); readln(t02);
Str(t02:5:1,Tstr);
Tell_1286_to('TB '+Tstr+');
case Sn of
  2 : begin
    v03:=v01;
    Str(v03:7:3,Vstr);
    Tell_1286_to('VC '+Vstr+');
  end;
  3 : begin
    write('Please enter RMP V3 in volt '); readln(v03);
    Str(v03:7:3,Vstr);
    Tell_1286_to('VC '+Vstr+');
    write('Please enter RMP T3 in sec '); readln(t03);
    Str(t03:5:1,Tstr);
    Tell_1286_to('TC '+Tstr+');
    v04:=v01;
    Str(v04:7:3,Vstr);
    Tell_1286_to('VD '+Vstr+');
  end;
else
  write('Please enter RMP V3 in volt '); readln(v03);
  Str(v03:7:3,Vstr);
  Tell_1286_to('VC '+Vstr+');
  write('Please enter RMP T3 in sec '); readln(t03);
  Str(t03:5:1,Tstr);
  Tell_1286_to('TC '+Tstr+');
  write('Please enter RMP V4 in volt '); readln(v04);
  Str(v04:7:3,Vstr);
  Tell_1286_to('VD '+Vstr+');
  write('Please enter RMP T4 in sec '); readln(t04);
  Str(t04:5:1,Tstr);
  Tell_1286_to('TD '+Tstr+');
end;
case vs of 'y', 'Y':
  Ramp_Multisegments;
end;
writeln('Ready?'); readln(check);
end;
procedure STPsw1286_setting; {1}
var Vstr,Sstr,Tstr: DATASTR;
begin
  if (vs = 'y') or (vs = 'Y') then
    begin
      write('Please enter the number of variant sweep segments (8,12 or 16): ');
      readln(sgs);
      Sn:=4;
      Str(Sn:5,Sstr);
      Tell_1286_to('SM '+Sstr+');
    end
  else
    begin
      Sn:=4;vs:='n';
      writeln('Parameters required for a user-selected STP sweep :');
      writeln('2 segments: V1, V2, (V3 = V1), V0, T0. ');
      writeln('3 segments: V1, V2, V3, (V4 = V1), V0, T0. ');
      writeln('4 or more segments: V1, V2, V3, V4 (<= V1), V0, T0. ');
      writeln;
      write('Please enter the numbers of sweep segments (2 to 99999) required (4): '); readln(Sn);
      Str(Sn:5,Sstr);
      Tell_1286_to('SM '+Sstr+');
      ClrScr;
    end;
  write('Please enter volts/step '); readln(v00);
  Str(v00:7:3,Vstr);

```

```

Tell_1286_to('VS '+Vstr+','');
write('Please enter sec/step '); readln(i00);
Str(i00:5:1,Tstr);
Tell_1286_to('TE '+Tstr+','');
write('Please enter STP V1 in volt '); readln(v01);
Str(v01:7:3,Vstr);
Tell_1286_to('SA '+Vstr+','');
write('Please enter STP V2 in volt '); readln(v02);
Str(v02:7:3,Vstr);
Tell_1286_to('SB '+Vstr+','');
case Sn of
  2 :
    begin
      v03:=v01;
      Str(v03:7:3,Vstr);
      Tell_1286_to('SC '+Vstr+','');
      stp1:=1+sqrt(sqrt(Int((v02-v01)/(1.001*v00))));
      stp2:=1+sqrt(sqrt(Int((v03-v02)/(1.001*v00))));
      rstp:=stp1+stp2; dstp:=0;
    end;
  3 :
    begin
      write('Please enter STP V3 in volt '); readln(v03);
      Str(v03:7:3,Vstr);
      Tell_1286_to('SC '+Vstr+','');
      v04:=v01;
      Str(v04:7:3,Vstr);
      Tell_1286_to('SD '+Vstr+','');
      stp1:=1+sqrt(sqrt(Int((v02-v01)/(1.001*v00))));
      stp2:=1+sqrt(sqrt(Int((v03-v02)/(1.001*v00))));
      stp3:=1+sqrt(sqrt(Int((v04-v03)/(1.001*v00))));
      rstp:=stp1+stp2+stp3; dstp:=0;
    end;
  else
    begin
      write('Please enter STP V3 in volt '); readln(v03);
      Str(v03:7:3,Vstr);
      Tell_1286_to('SC '+Vstr+','');
      write('Please enter STP V4 in volt '); readln(v04);
      Str(v04:7:3,Vstr);
      Tell_1286_to('SD '+Vstr+','');
      stp1:=1+sqrt(sqrt(Int((v02-v01)/(1.001*v00))));
      stp2:=1+sqrt(sqrt(Int((v03-v02)/(1.001*v00))));
      stp3:=1+sqrt(sqrt(Int((v04-v03)/(1.001*v00))));
      stp4:=1+sqrt(sqrt(Int((v01-v04)/(1.001*v00))));
      stp:=stp1+stp2+stp3+stp4;
      dstp:=stp*Int(Sn/4);
      rseg:=Int(Sn-4*dstp/stp);
      if rseg=0 then rstp:=stp1;
      if rseg=1 then rstp:=stp1+stp2;
      if rseg=2 then rstp:=stp1+stp2+stp3;
      if rseg=3 then rstp:=stp1+stp2+stp3+stp4;
    end;
  end;
sam:=T0+(i00*trate*(dstp+rstp));
case vs of 'y', 'Y':
  begin
    Step_Multisegments;
    writeln('1st 4 segs only:');end;
end;
writeln('Delay: ',T0,'s, DVM readings: ',rrate,' /s, filed:',trate,'/s. ');
writeln('No. Of segments: ',Sn);
writeln('No. Of steps: ',dstp+rstp,' ');
writeln('No. Of readings: ',Sam);
writeln('Duration of sweep: ',sam/trate,'s. ');
writeln('ok?');readln(check);
end;
procedure Rccycle_Trigger; {1}
begin
  Tell_1286_to('TR 1:');
end;
procedure Sync_Trigger; {1}
begin
  Tell_1286_to('TR 3:');
end;
procedure SWdelay_1286; {1}
var Tstr : DATASTR;
begin
  T0:=0;
  write('Please enter sweep delay in sec (0): '); readln(T0);
  Str(T0:5,Tstr);
  Tell_1286_to('DL '+Tstr+','');
  writeln;
end;

```

```

procedure Set_Sweep_Pars;      {1}
begin
  Sweep_Mode:= '2';
  write('Please enter sweep mode: 0=User controlled; 1=Ramp; 2=Step; (2): ');
  readln(Sweep_Mode);
  writeln('sweep mode=',Sweep_Mode);
end;
procedure Status_Window;
begin
  Window(1,22,80,25);
  ClrScr;
end;
procedure STPsw1286_New_Setting( T0:integer;v01,v02,v03,v04,t00,v00:real);
var Vstr: DATASTR;
begin
  Str(v01:7:3,Vstr);
  Tell_1286_to('SA '+Vstr+');
  Str(v02:7:3,Vstr);
  Tell_1286_to('SB '+Vstr+');
  Str(v03:7:3,Vstr);
  Tell_1286_to('SC '+Vstr+');
  Str(v04:7:3,Vstr);
  Tell_1286_to('SD '+Vstr+');
  stp1:=1+sqrt(sqr(Int((v02-v01)/(1.001*v00))));
  stp2:=1+sqrt(sqr(Int((v03-v02)/(1.001*v00))));
  stp3:=1+sqrt(sqr(Int((v04-v03)/(1.001*v00))));
  stp4:=1+sqrt(sqr(Int((v01-v04)/(1.001*v00))));
  stp:=stp1+stp2+stp3+stp4;
  dstp:=stp*Int(Sn/4);
  rseg:=Int(Sn-4*dstp/stp);
  if rseg=0 then rstp:=stp1;
  if rseg=1 then rstp:=stp1+stp2;
  if rseg=2 then rstp:=stp1+stp2+stp3;
  if rseg=3 then rstp:=stp1+stp2+stp3+stp4;
  sam:=T0+(t00*trate*(dstp+rstp));
end;
procedure RMPsw1286_New_Setting( v01,v02,v03,v04,t01,t02,t03,t04:real);
var Vstr,Tstr: DATASTR;
begin
  Str(v01:7:3,Vstr);
  Tell_1286_to('VA '+Vstr+');
  Str(t01:5:1,Tstr);
  Tell_1286_to('TA '+Tstr+');
  Str(v02:7:3,Vstr);
  Tell_1286_to('VB '+Vstr+');
  Str(t02:5:1,Tstr);
  Tell_1286_to('TB '+Tstr+');
  Str(v03:7:3,Vstr);
  Tell_1286_to('VC '+Vstr+');
  Str(t03:5:1,Tstr);
  Tell_1286_to('TC '+Tstr+');
  Str(v04:7:3,Vstr);
  Tell_1286_to('VD '+Vstr+');
  Str(t04:5:1,Tstr);
  Tell_1286_to('TD '+Tstr+');
end;
procedure New_segments;
begin
  sgs:=sgs-4;
  if (sgs=4) then vs:='n';
  case sgs of
    4,8,12:
      begin
        v01:=v05;v02:=v06;v03:=v07;v04:=v08;t01:=t05;t02:=t06;t03:=t07;t04:=t08;
      end;
    8,12:
      begin
        v05:=v09;v06:=v10;v07:=v11;v08:=v12;t05:=t09;t06:=t10;t07:=t11;t08:=t12;
      end;
    12:
      begin
        v09:=v13;v10:=v14;v11:=v15;v12:=v16;t09:=t13;t10:=t14;t11:=t15;t12:=t16;
      end;
  end;
end;

```

```

procedure SWdelay_1286_0;
var Tstr : DATASTR;
begin
  T0:=0;
  Str(T0:5,Tstr);
  Tell_1286_to('DL '+Tstr+');
  writeln;
end;
procedure Repeat_Segments;          {new}
begin
  New_segments;
  Writeln(Output_File,'*****'); Writeln('*****');
  if Sweep_Mode='1' then
    begin
      RMPsw1286_New_Setting(v01,v02,v03,v04,t01,t02,t03,t04);
    end
  else
    begin
      STPsw1286_New_Setting( T0,v01,v02,v03,v04,t00,v00);
      count:=1;
    end;
Do_sweep;
end;
function Operating_Mode: integer;    {begin}
var mode : integer;
begin
  ClrScr;
  mode:=1;
  writeln('There are 5 different operation modes --- ');
  writeln;
  writeln(' 1 : Potential Sweep without illumination;');
  writeln(' 2 : Potential Sweep with illumination;');
  writeln(' 3 : Potential Sweep at fixed Frequency;');
  writeln(' 4 : Frequency Sweep at fixed Potential;');
  writeln(' 5 : Frequency Sweep at constant Potential with Time;');
  writeln(' 6 : Frequency Sweep at constant Current with Time;');
  writeln;
  write('Please enter the required operation mode (1): '); readln(mode);
  Operating_Mode := mode;
  writeln;
end;
procedure Common_paras_Setting_1250;
var par : char;
  Astr,Bstr,Dstr,Fstr,Hstr : DATASTR;
begin
  write('Would you like to set the 1250 common parameters ? (n) ');readln(par);
  if (par = 'y') or ( par = 'Y') then
    begin
      writeln;
      TextColor(12);
      write('<< 1250 parameters setting in progress, ');
      TextColor(11);
      Write('PLEASE WAIT !! ');
      TextColor(12);
      writeln('>>');
      TextColor(14);
      sound(1200); delay(250); NoSound;
      Str(AM0:5:3,Astr);
      Tell_1250_to('AM '+Astr+'); delay(T5);
      Str(V0,Bstr);
      Tell_1250_to('BI '+Bstr+'); delay(T5);
      Tell_1250_to('WF 0;'); delay(T5);
      Tell_1250_to('MO 0;'); delay(T5);
      Tell_1250_to('SY 0;'); delay(T5);
      Tell_1250_to('AP 0;'); delay(T5);
      Tell_1250_to('SQ 0;'); delay(T5);
      Str(ha,Hstr);
      Tell_1250_to('HA '+Hstr+'); delay(T5);
      Str(od,Dstr);          {REFORMAT menu must be 'On'}
      Tell_1250_to('OR '+Dstr+'); delay(T5);  {when ORDER facility in use}
      Tell_1250_to('AU 0;'); delay(T5);
      Tell_1250_to('RA 1,0;'); delay(T5);
      Tell_1250_to('RA 2,0;'); delay(T5);
      Tell_1250_to('DE 1,0;'); delay(T5);
      Tell_1250_to('DE 2,0;'); delay(T5);
      Tell_1250_to('IP 1,1;'); delay(T5);
      Tell_1250_to('IP 2,1;'); delay(T5);
    end;
end;

```

```

Tell_1250_to('CO 0;'); delay(T5);
Tell_1250_to('BP 0;'); delay(T5);
Tell_1250_to('FN 3,0;'); delay(T5);
Tell_1250_to('FN 4,0;'); delay(T5);
Tell_1250_to('FN 5,0;'); delay(T5);
Tell_1250_to('OP 0,0;'); delay(T5);
Tell_1250_to('OP 3,0;'); delay(T5);
Str(F0,Fstr);
Tell_1250_to('FS '+Fstr+'); delay(T5);
Tell_1250_to('RH 1;'); delay(T5);
Tell_1250_to('RR 1;'); delay(T5);
end
else
begin
writeln('Previous common-parameter settings will be used');
end;
writeln;
end;
procedure Initialise_1250;
var ini : char;
begin
write('Would you like to INITIALISE the 1250 ? (n) '); readln(ini);
if (ini = 'y') or (ini = 'Y') then
begin
Tell_1250_to('TT 2;'); delay(1200);
end
else
begin
writeln('Warning ! The 1250 is not INITIALised');
end;
writeln;
end;
procedure Option_Setting; {begin}
var fra : char;
begin
write('Is the FRA 1250 going to be used ? (n) '); readln(fra);
if (fra='y') or (fra='Y') then
begin
ClrScr;
Initialise_1250;
Common_Paras_Setting_1250;
end
else writeln;
end;
end;

```

```

procedure DVMprecism_1286; {begin}
var pc : char;
begin
writeln('Codes for 1286 reading precision (13/sec):');
writeln('A : 30/sec, B : 2/sec, C : 8/sec. ');
write('Please enter the appropriate code : '); readln(pc);
case pc of
'a' , 'A' : begin Tell_1286_to('DG 3;'); rrate:=30;trate:=7.3;end;
'b' , 'B' : begin Tell_1286_to('DG 0;'); rrate:=2;trate:=2; end;
'c' , 'C' : begin Tell_1286_to('DG 2;'); rrate:=8;trate:=6.5; end;
else begin Tell_1286_to('DG 1;');rrate:=13;trate:=6.5; end;
end;
writeln;
end;

```

```

procedure Resistor_1286_Setting; {begin}
var csr : char;
begin
writeln('Codes for 1286 current-sensing resistor in ohms (100) :');
writeln('A = 10; B = 1000; C = 0.1;');
writeln('D = 1; E = 10,000; F = 100,000. ');
write('Please enter the appropriate resistance code : '); readln(csr);
case csr of
'a' , 'A' : Tell_1286_to('RR 3;');
'b' , 'B' : Tell_1286_to('RR 5;');
'c' , 'C' : Tell_1286_to('RR 1;');
'd' , 'D' : Tell_1286_to('RR 2;');
'e' , 'E' : Tell_1286_to('RR 6;');
'f' , 'F' : Tell_1286_to('RR 7;');
else Tell_1286_to('RR 4;');
end;
writeln;
end;

```

```

procedure Common_Paras_Setting_1286;           {begin}
var par : char;
  Vstr,Istr,Fstr: DATASTR;
begin
  write('Would you like to set the 1286 common parameters ? (n) ');readln(par);
  if (par = 'y') or (par = 'Y') then
    begin
      writeln;
      TextColor(12);
      write('<< 1286 parameters setting in progress, ');
      TextColor(11);
      Write('PLEASE WAIT !! ');
      TextColor(12);
      writeln('>>');
      TextColor(14);
      sound(1200);Delay(100); NoSound;
      Tell_1286_to('PO 1;');
      Tell_1286_to('OL 1;');
      Tell_1286_to('BY 1;');
      Tell_1286_to('ON 1;');
      Tell_1286_to('PI 1;');
      Tell_1286_to('PB 3;');
      Tell_1286_to('RG 2;');
      Tell_1286_to('DC 0;');
      Tell_1286_to('AV 0;');
      Tell_1286_to('RH 1;');
      Tell_1286_to('EB 0;');
      Tell_1286_to('RR 4;');
      Str(V0,Vstr);
      Tell_1286_to('PV '+Vstr+');');
      Str(I0,Istr);
      Tell_1286_to('PC '+Istr+');');
      Str(F0,Fstr);
      Tell_1286_to('FS '+Fstr+');');
      Tell_1286_to('UL 3;');
      Tell_1286_to('UR 5;');
    end
  else
    begin
      writeln('Previous common-parameter settings will be used');
    end;
  writeln;
end;
procedure Initialise_1286;           {begin}
var ini : char;
begin
  write('Would you like to INITIALISE the 1286 ? (n) '); readln(ini);
  if (ini = 'y') or (ini = 'Y') then
    begin
      Tell_1286_to('BK 4;');
    end
  else
    begin
      write('n');
    end;
  writeln;
end;
procedure Normal_Window;           {begin}
begin
  Window(1,3,80,20);
  ClrScr;
end;
procedure General_Message;           {begin}
begin
  ClrScr;
  TextColor(11);
  writeln('Electrochemical Data Acquisition - ');
  TextColor(14);
  writeln('-----');
  writeln;
  GotoXY(1,21);
  write('-----');
end;
procedure init488 (var addr,level : integer); external 't488init';
begin
  ClrScr;
  cmddesc.addr := ofs(cmd)+1;
  recvdesc.addr := ofs(recv)+1;
  addr_1286 := 18;
  my_address := 21; system_controller := 0; count:=0; del:= 10;
  init488(my_address,system_controller);
  Offset := 18;
  TextMode(C80);
  TextBackground(10);

```

```

window(1,1,80,25);
General_Message; Normal_Window;
cmd:='REN'; xmit;
Initialise_1286;
Common_Paras_Setting_1286;
Resistor_1286_Setting;
DVMprecision_1286;
Option_Setting;
write('Output File Group Name : '); readln(FileName);
if (FileName='') then FileName:='test';
Mode := Operating_Mode;
Status_Window; writeln('Operating mode : ',Mode);
Normal_Window;
case Mode of
  1 : { potential sweep without illumination mode }
begin
  Set_Sweep_Pars;
  case Sweep_Mode of
    '0':
begin
  Output_delay(del);
  Recycle_Trigger;
  sam:=20000;
end;
    '1':
begin
  writeln('Ramp Sweep');
  Sync_Trigger;
  SWdelay_1286;
  Var_segments;
  RMPsw1286_Setting;
end;
    '2':
begin
  Sweep_Mode:='2';
  writeln('Step Sweep');
  Recycle_Trigger;
  SWdelay_1286;
  Var_segments;
  STPsw1286_Setting;
end;
  end;
Status_Window;
write('Potential sweep without illumination mode ');
Assign(Output_File,FileName);
Rewrite(Output_File);
WriteLn(Output_File,'File Name : ',FileName);
writeln(Output_File,'No illumination (V sweep).');
writeln(Output_File,'Potential(V) I (A) from 1286');
writeln(Output_File,'-----');
Normal_Window;
writeln('Output file : ',FileName); writeln;
writeln('Acquiring data...'); writeln;
writeln('Potential(V) I (A) from 1286');
writeln('-----');
Data_Window;
Initialise_1286_Bus; { GPIB ShortOn (PAR1/PAR2)}
Do_sweep;
if (vs='y') or (vs = 'Y') then Repeat_Segments; {new}
if (vs='y') or (vs = 'Y') then Repeat_Segments;
if (vs='y') or (vs = 'Y') then Repeat_Segments;
writeln('End of Sweep');
Close(Output_File);
end; { mode 1 }
  2 : { potential sweep under monochromatic light illumination }
begin
  Writeln('Turn 5210 on ok?'); readln(check);
  Tell_5210_to('DD44'#13#10);delay(300);
  Tell_5210_to('TC 5'#13#10);delay(300);
  Read_Standard_Resistor(RR);
  Set_5210_sensitivity(sst);delay(500);
  Read_TC_5210(pte);
  Read_RFQ_5210(rfq);
  Set_Sweep_Pars; {1}
  case Sweep_Mode of
    '0':
begin
  Output_delay(del);
  Recycle_Trigger;
  sam:=20000;
  Tell_1286_to('ON 0;');
  Tell_1286_to('PO 1;');
end;
    '1':

```

```

begin
  writeln('Ramp Sweep');
  Sync_Trigger;      {1}
  SWdelay_1286;      {1}
  Var_segments;
  RMPsw1286_Setting; {1}
end;
'2':
begin
  Sweep_Mode:='2';
  case
    rate of
      30 : rate:=3.35;
      8  : rate:=3.3;
      13 : rate:=3.35;
    end;
  writeln('Step Sweep');
  Recycle_Trigger;    {1}
  SWdelay_1286;       {1}
  Var_segments;
  STPsw1286_Setting;  {1...}
end;
end;
Status_Window;
write('Potential Sweep with illumination');
Normal_Window;
Prepare_Fixed_L_File;
writeln('Output File : ',FileName); writeln;
writeln('Acquiring data...'); writeln;
writeln('Potential(V) I(A) I(ph) theta');
writeln('-----');
Data_Window;          {1...}
Initialise_1286_Bus;
Do_sweep;
if (vs='y') or (vs='Y') then Repeat_Segments; {new}
if (vs='y') or (vs='Y') then Repeat_Segments;
if (vs='y') or (vs='Y') then Repeat_Segments;
Tell_5210_to('TC 13'#13#10);
writeln('End of Sweep');
Close(Output_File);
end;
{ mode 2 }
3 : { Potential Sweep at fixed frequency }
begin
  Stop_Analyser;
  AC_Couple_1250;
  Get_Frequency_Pars(F1,F2,dF);
  FraDelay_1250(fd);
  FRA_Integration_Time(fit);
  FRA_Harmonic_Setting(fh);
  Set_Sweep_Pars;      {1...}
  if Sweep_Mode='1' then
    begin
      writeln('Ramp Sweep');
      Sync_Trigger;
      SWdelay_1286;
      RMPsw1286_Setting;
    end
  else
    begin
      writeln('Step Sweep');
      Recycle_Trigger;
      SWdelay_1286;
      STPsw1286_Setting;
    end;
  Initialise_1286_Bus;      {...1}
  Initialise_1250_Bus;
  Status_Window;           {1}
  write('Potential Sweep at Fixed Frequency ');
  if Sweep_Mode='1' then writeln('Ramp Sweep') else writeln('Step Sweep');
  writeln('F1 : ',F1:7:3,' F2 : ',F2:7:3,' dF : ',dF:7:3);
  F:=F1;
  While F<=F2 do
    begin
      Set_1250_Freq(F);
      Start_Generator;
      Normal_Window;        {1}
      Prepare_Fixed_F_File(F);
      writeln('Frequency = ',F:7:2);
      writeln('Acquiring data...'); writeln;
      Writeln('Potential(V) I(A) 1286 Real Imaginary');
      Writeln('-----');
      Data_Window;          {1...}
      if Sweep_Mode='1' then Sweep_Mode_1 else Sweep_Mode_2;
      while status=0 do

```

```

begin
  Analyser_Single;
  cmd:='UNT UNL MLA TALK 2'; Xmit;
  Read_1250_ShortForm(TF);
  writeln(Output_File,V_and_I,',',TF);
  writeln(V_and_I,',',TF);
  cmd:='UNT UNL MLA TALK 18'; Xmit;
  Read_1286(V_and_I)      {1}
end;
if Sweep_Mode='2' then DVM_Off;
Stop_Generator;
writeln('End of Sweep');
Close(Output_File);
F:=F+dF;
end; { F Loop }
Reset_1250;
end; { mode 3 }
4: { Frequency Sweep at fixed potential }
begin
  Sync_Trigger;          {1}
  Vrejc_1286;
  Irejc_1286;
  TenV_1286;
  TenI_1286;
  Tell_1286_to('ON 0;');
  Stop_Analyser;          {3}
  Stop_F_Sweep;
  New_1250_Range;
  DC_Couple_1250;
  FraDelay_1250(fd);      {3}
  FRA_Integration_Time(fit);
  FRA_Harmonic_Setting(fh); {3}
  FRA_Order_Setting(fo);
  Set_Freq_Sweep_Pars(sfr,hz1,hz2,dg);
  Get_Potential_Pars(V1,V2,dV);
  GPIB_1286_Off;          {6:Reset 1286}
  Initialise_1250_Bus;     {3}
  Status_Window;          {1}
  write('Frequency Sweep at Fixed Potential ');
  Case Freq_Sweep_Mode of
    '0': writeln('Harmonic');
    '1': writeln('Log up');
    '2': writeln('Log down');
    '3': writeln('Lin up');
    '4': writeln('Lin down');
  end;
  writeln('V1:',V1:7:3,' V2:',V2:7:3,' dV:',dV:7:3);
  V:=V1;
  While ((dV>0)and(V<=V2))or((dV<0)and(V>=V2)) do
  begin
    Start_Freq_Sweep;
    Apply_V_to_Cell(V);
    DVM_On; delay(100);    {1}
    CONDITION_On; delay(15);
    DVM_Off;              {2}
    Normal_Window;        {1}
    Prepare_F_Sweep_File(V);
    writeln('Potential =',V:7:2);
    writeln('Acquiring data...'); writeln;
    Writeln(' Freq(Hz)   Real   Imaginary');
    Writeln('-----');
    Data_Window;
    Analyser_Recycle;
    Start_Generator;      {3}
    Prepare_to_Read_1250;
    Repeat Read_1250(TF) until status=0;
    While status=0 do
    begin
      writeln(Output_File,TF);
      writeln(TF);
      Read_1250(TF);
    end;
    writeln('Frequency sweep ended. ');
    CONDITION_Off;
    StandbyOn_Off;
    Stop_Generator;        {3}
    Stop_Analyser;
    Stop_F_Sweep;          {rpt}
    Close(Output_File);
    V:=V+dV;
  end; { V Loop }
  Original_1250_Range; { 30 mV }
  Reset_1250;            {3}
end; {mode 4}

```

```

5:      ( Frequency Sweep at fixed potential )
begin
  Sync_Trigger;           {1}
  Vreje_1286;             {4...}
  Ireje_1286;
  TenV_1286;
  TenI_1286;
  Stop_Analyser;          {3}
  Stop_F_Sweep;
  New_1250_Range;
  DC_Couple_1250;         {...4}
  FraDelay_1250(f);       {3}
  FRA_Integration_Time(fit); {4...}
  FRA_Harmonic_Setting(fh);
  FRA_Order_Setting(fo);
  Set_Freq_Sweep_Pars(sfr,hz1,hz2,dg);
  Get_Potential_Par(V1,time,GO); {...4}
  GPIB_1286_Off;          {6:Reset 1286}
  Initialise_1250_Bus;     {3}
  Initialise_1286_Bus;     {1}
  Status_Window;
  write('Frequency Sweep at Fixed Potential      ');
  Case Freq_Sweep_Mode of
    '0' : writeln('Harmonic');
    '1' : writeln('Log up');
    '2' : writeln('Log down');
    '3' : writeln('Lin up');
    '4' : writeln('Lin down');
  end;
  writeln('V1 : ',V1:7:3,' V2 : ',V2:7:3,' dV : ',dV:7:3);
  V:=V1;
  begin
    Apply_V_to_Cell(V);    {4}
    TC := 0;
    Xmax := time / tim1;
    Xkeep := Xmax;
    Xmin := 0;
  repeat
    Start_Freq_Sweep;      {3}
    DVM_On; delay(1100);   {1}
    CONDITION_On; delay(15); {3}
    DVM_Off;               {1}
    Normal_Window;         {1}
    Prepare_F_Sweep_Fill(TC);
    writeln('Potential = ',V:7:2);
    writeln('Acquiring data...'); writeln;
    Writeln(' Freq(Hz) Real Imaginary');
    Writeln('-----');
    Data_Window;           {1}
    Analyser_Recycle;
    Start_Generator;       {3}
    Prepare_to_Read_1250;   {4...}
    Repeat Read_1250(TF) until status=0;
    While status=0 do
      begin
        writeln(Output_File,TF);
        writeln(TF);
        Read_1250(TF);      {...4}
      end;
    Prepare_to_read_1286;   {1...}
    writeln(Output_File,' ');
    Writeln(Output_File,'Potential (V) I (A) from 1286');
    writeln(Output_File,'-----');
    Read_1286(V_and_I);
    writeln(Output_File,V_and_I);
    writeln(' ');
    writeln('Potential (V) I (A) from 1286');
    writeln('-----');
    writeln(V_and_I);
    Read_1286(V_and_I);     {...1}
    writeln('Frequency sweep ended. ');
    Stop_Generator;        {3}
    Stop_Analyser;         {3}
    Stop_F_Sweep;
    writeln(V_and_I);
    Close(Output_File);
    writeln(' Delay = ',Xmax * 10,' seconds. ');
    sound(1200); delay(250); Nosound;
    While Xmax > Xmin do wait;
    sound(1200); delay(250); Nosound;
    Xmax := Xkeep;
    TC := TC + 1;
    until TC > GO
  end; { V Loop }

```

```

Original_1250_Range; { 30 mV } {4}
Reset_1250; {3}
end; { mode 5 }
6 : { Frequency Sweep at fixed Current }
begin
  Sync_Trigger; {1}
  Vreje_1286; {4...}
  Ireje_1286;
  TenV_1286;
  TenI_1286;
  Stop_Analyser;
  Stop_F_Sweep;
  New_1250_Range;
  DC_Couple_1250;
  FraDelay_1250(fd);
  FRA_Integration_Time(fit);
  FRA_Harmonic_Setting(fh); {3}
  FRA_Order_Setting(fo);
  Set_Freq_Sweep_Pars(sfr,hz1,hz2,dg); {...4}
  Get_Current_Par(Curr,time,GO);
  GPIB_1286_Off;
  Initialise_1250_Bus; {4}
  Initialise_1286_Bus; {1}
  Status_Window; {1}
  write('Frequency Sweep at Fixed Potential ');
  Case Freq_Sweep_Mode of
    '0' : writeln('Harmonic');
    '1' : writeln('Log up');
    '2' : writeln('Log down');
    '3' : writeln('Lin up');
    '4' : writeln('Lin down');
  end;
  writeln('Curr : ',V1:7:3,' Pause : ',time:7:3);
  begin
    Apply_I_to_Cell(Curr);
    TC := 0;
    Xmax := time / tim1;
    Xkeep := Xmax;
    Xmin := 0;
  repeat
    Start_Freq_Sweep; {4}
    DVM_On; delay(1100); {1}
    CONDITION_On; delay(15); {4}
    DVM_Off; {1}
    Normal_Window; {1}
    Prepare_F_Sweep_Fill(TC); {5}
    writeln('Current = ',Curr:7:2);
    writeln('Acquiring data...'); writeln;
    Writeln(' Freq(Hz) Real Imaginary');
    Writeln('-----');
    Data_Window;
    Analyser_Recycle; {5}
    Start_Generator; {3}
    Prepare_to_Read_1250; {4...}
    Repeat Read_1250(TF) until status=0;
    While status=0 do
      begin
        writeln(Output_File,TF);
        writeln(TF);
        Read_1250(TF); {...4}
      end;
    Prepare_to_read_1286;
    writeln(Output_File,' ');
    Writeln(Output_File,'Potential (V) I (A) from 1286');
    writeln(Output_File,'-----');
    Read_1286(V_and_I);
    writeln(Output_File,V_and_I);
    writeln(' ');
    writeln('Potential (V) I (A) from 1286');
    writeln('-----');
    writeln(V_and_I);
    Read_1286(V_and_I);
    writeln('Frequency sweep ended. ');
    Stop_Generator; {3}
    Stop_Analyser; {3}
    Stop_F_Sweep; {4}
    writeln(V_and_I);
    Close(Output_File);
    writeln(' Delay = ',Xmax * 10,' seconds. ');
    sound(1200); delay(250); Nosound;
    While Xmax > Xmin do wait; {5}
    sound(1200); delay(250); Nosound;
    Xmax := Xkeep;
    TC := TC + 1;
  end;
end;

```

```

        until TC > GO
        end; { V Loop }
        Original_1250_Range; { 30 mV }      {4}
        Reset_1250;                          {3}
        end; { mode 6 }
        end; { case }
        StandbyOn_Off;
        writeln('1286 standby'); {removed GPIB_1286_Off;}
        cmd:='GTL'; xmit;
        sound(400);Delay(300);sound(282);delay(300);NoSound;
        writeln('That''s it !');
        Window(1,1,80,25);
        end. {end of program acqu12}

```

Data obtained from the above program was loaded into a Lotus 123 worksheet file and normalised for the electrode cross-sectional area, the current measuring resistance and other instrumental sensitivities where appropriate by macros written for this purpose. Such manipulations were not included in the above program because it was found they significantly decreased the rate of data acquisition.

A further Lotus 123 macro was designed to obtain semicircular curve-fits from the processed data, *ie* real and imaginary impedances, acquired during variable ac frequency response analysis. Because of the increased contribution of a Warburg-type impedance to these impedances at low frequencies, a least squares fit procedure was not adopted in this macro. Instead, sets of three data points pertaining to successively lower ac frequencies were taken from a particular data range. The origins of circles intersecting the three points in each set were deduced and plotted in the complex plane. It was therefore possible to observe the migration of plotted points in a line of gradient -1 if and when, at lower frequencies, the Warburg-type impedance became significant. The circle radius and location of the circle origin was then calculated from average values for data sets unaffected in this way. These values were used to deduce the characteristic values R_{ct} , C and θ .

Converting spectral photocurrents I_{ph} to photocurrent efficiencies required a Lotus 123 macro that performed the following manipulations. Firstly the exact light wavelength, λ in nm, corresponding to each successive photocurrent or photovoltage reading was determined from the time interval between readings, the duration of the sweep, and the initial and final light wavelengths. The power output of the xenon lamp, P in $W\ cm^{-2}$, corresponding to this photocurrent was determined from a list of values such as those plotted in **Figure 2.4.1.3** for a monochrometer slit width of 3mm. The photocurrent efficiency was then calculated from $\Phi = I_{ph} \cdot h\nu / P$, where $h\nu$ in eV is equal to $1239.7/\lambda$.

Appendix 3

Above: View inside the Faraday cage and, *below*, apparatus used in photoelectrochemical experiments.

British Museum specimens from which chalcopyrite sample no. 9 (*above*) and chalcopyrite sample no. 11 (*below*) were obtained. See **Table 3.3.1** for mineral specifications.

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