Ferrocenyl Surface Species on Platinum and Conducting Glass Electrodes, and on Photoelectrochemical n-Silicon Electrodes†

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Cyclic voltammetry on platinum and conducting glass electrodes derivatised with a variety of ferrocenyl compounds has indicated, largely from the scan-rate dependence, peak separation, and coverage, that any particular derivatant might in successive experiments evince behaviour from near-irreversible to near-reversible, though most show the latter. These observations led to studies of the more viable derivatants on n-doped silicon under visible illumination, and considerable stabilisation of the silicon was shown by (dichloromethylsilyl)ferrocene. It was moderately successful also on GaAs.

Photoelectrochemical energy-conversion systems remain important[1] and in such an application, n-silicon with a protective manganese(III)-oxide coating has proved stable in photoelectrolytic use.[2] Wrighton and co-workers' use[3] of ferrocenyl species for the protective derivatisation of photoelectrochemical doped-silicon electrodes prompted the test[4] of alternative substituents and core atoms; our first results[4] proved to be of largely archival interest only, centred on the novelty of the ferrocenes synthesized, since erratic and at best only feeble protection against electrochemical passsivation ensued. We have since achieved a vast improvement by extending the range of compounds, the electrode substrates, conditions for the attachment reactions, and the electrochemical parameters monitored. Driven by strain release, some strained-ring molecules were expected to bond more controllably to the electrodes, and thus show more consistent and thus interpretable behaviour. This prospect, and comparison with the derivatants differently bonded, are accordingly examined in this paper, and comparison is briefly made with gallium arsenide semiconductor as substrate. We report the dark electrochemistry of derivatants on Pt or ITO glass as a pointer to subsequent photoelectrochemical behaviour.

Results and Discussion

Species attached by Strain-release Mechanisms.—The ferrocene species[4] shown in Scheme 1, being intrinsically more stable without the hydrolysable silicon–halogen bonds,[5] were deposited by spraying acetone solution on to the n-doped silicon at 200 °C, thereby effecting dramatic improvement over the original method.[4] While avoiding polymerisation of the silicon–halogen compounds attached by a hydrolytic reaction (below), this procedure will be seen to allow firmer attachment and hence better protection than does dipping. Similar deposition on Pt and ITO glass provided derivatised metal and quasi-metal substrates for initial dark-electrode studies, as yardsticks for the silicon photoelectrochemistry, both being monitored by cyclic voltammetry (c.v.). For compound (1), Figure 1 shows the larger background current with Pt *cf.* ITO, endorsing the use of the latter.

Regarding the dark c.v. data summarised in Table 1, the results at first sight appear to be of so wide a range as to invite chaos-based interpretations. However, these show clear trends when viewed in the light of basic mechanistic tenets. Figure 1 shows anodic and cathodic current peaks i_{p_a} and i_{p_c} at potentials E_{p_a} and E_{p_c}; the difference $\Delta E_p = |E_{p_a} - E_{p_c}|$. Large values of ΔE_p (*i.e.* markedly >59 mV) denote slow ('irreversible') heterogeneous electron transfer (e.t.) at the metal–substrate interface, which thereby controls the net electrode process.[6,7] For rapid, 'reversible', e.t. systems the dependence of

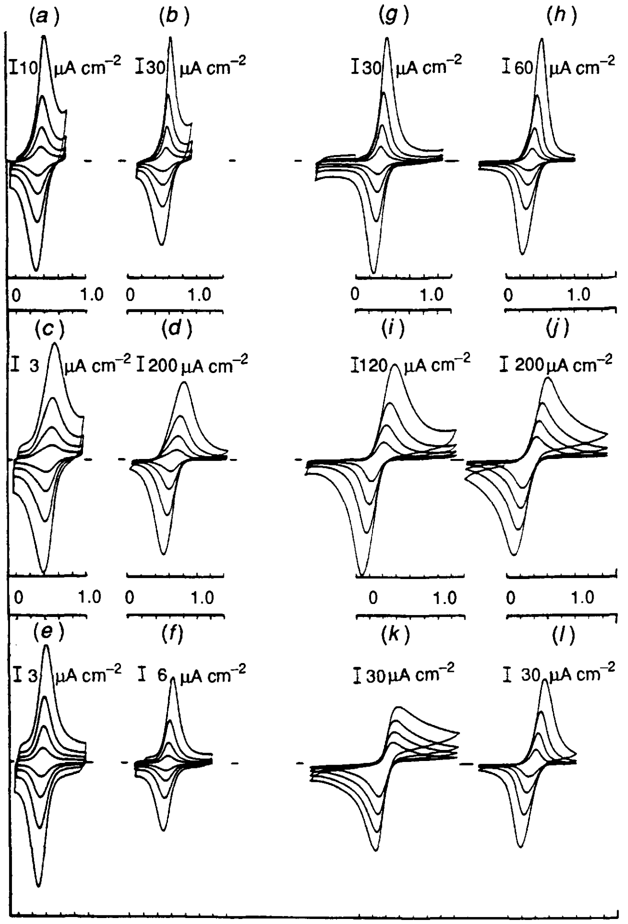

Figure 1. Cyclic voltammetry on electrodes derivatised with compound (**1**) in the media given in Table 1: (*a*), (*b*) A; (*c*), (*d*) B; (*e*)—(*l*) C. Scan rates (downwards from top) 200, 100, 50, 20 mV s^{-1}

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† *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.

Compound	Formula and name	Number used in ref. 4
(1)	$Si[(C_5H_4)_2Fe]_2$ Bis(1,1′-ferrocenediyl)silane	**(11)**
(2)	$Si[(C_5H_4)_2Fe]Ph_2$ (1,1′-ferrocenediyl)diphenylsilane	**(12)**
(3)	$Si[(C_5H_3Cl)_2Fe]_2$ Bis(1,1′-dichloro-2,2′-ferrocenediyl)silane	**(5)**
(4)	$Ge[(C_5H_4)_2Fe]_2$ Bis(1,1′-ferrocenediyl)germane	**(3)**
(5)	$P[(C_5H_4)_2Fe]Ph$ (1,1′-Ferrocenediyl)phenylphosphine	**(10)**

Scheme 1.

Table 1. Ranges of c.v. parameters for ferrocene species in various systems at four v values 200—20 mV s^{-1} (200 mV s^{-1} data cited) 20 °C

Surface compound	System	No. of experiments	E_{p_a}/mV E_{p_c}/mV	i_{p_a}/μA i_{p_c}/μA	δ_a/mV δ_c/mV	100$\bar{x}$	100Γ/ nmol cm^{-2}
(1)	A	3	425—460 270—300	94—375 84—255	12—22 24—28	91—97	28—430
	B	2	540—620 340—370	13—570 13—700	36, 36 28—36	90—93	25—1 270
	C	11	410—640 70—480	13—930 14—920	20—40 24—40	42—101	14—1 670
(2)	B	1	620 430	9 7	36 28	75	38
	C	10	400—760 120—340	11—29 11—28	20—68 22—44	54—83	51—158
(3)	B	1	840 420	25 14	broad broad	71	87
	C	4	710—840 300—510	18—46 10—36	48—56 32—72	14—86	91—202

Systems: A, Pt–NaClO$_4$–water; B, ITO-NBu$^n_4$ClO$_4$-acetonitrile; C, ITO–NaClO$_4$–water. Γ for any one system follows the approximate sequence of i_{p_a}, and in any one experiment increases by ≈ 1.2—1.5 with decreasing v; ΔE_p approximately doubles with increasing v. Derived film thicknesses (∝ Γ) are 0.04—2.86 μm.

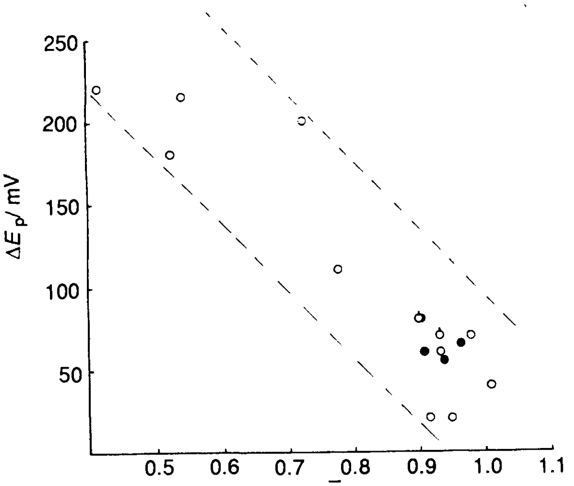

Figure 2. Peak separations ΔE_p *versus* average scan-rate exponents $\bar{x}$ for compound (**1**) at 20 mV s^{-1}. ○, ITO; ●, Pt. Tag, acetonitrile; no tag, water

i_p on scan rate v (= dE/dt) has the form $i_p \propto v^{\frac{1}{2}}$, with ΔE_p = 59 mV, when a diffusional process controls i_p; in contrast, an attached electroactive monolayer shows $i_p \propto$ v and ΔE_p = 0 (if reversible).[6] For each derivatant here, the parameters vary apparently independently of substrate or medium [excepting x for (**1**) in medium C, *cf.* media A and B], and as a further complication ΔE_p values (20—220 mV, *i.e.* sometimes exceeding the reversibility-indicating 59 mV) implicate some current constraint from slow heterogeneous e.t. to the electrode metal.[7] The observed exponent of v is x; taking $\bar{x}$, an average for i_{p_a} and i_{p_c} (since x_a and x_c are found to be close) as a heuristic indicator of mechanism, one may expect $\bar{x}$ to track with ΔE_p but with some irreversibility constraints superimposed, and for (**1**) (Figure 2) there is indeed a clear albeit rough correlation corresponding in direction with the simple theoretical extremes. In addition, the thicker the film, the further from monolayer structure it is (Table 1 footnote), and the more will diffusional ($x \longrightarrow \frac{1}{2}$) control in the film take over from monolayer ($x \longrightarrow 1$) response; hence the surface concentration Γ and $\bar{x}$ should correlate negatively. This is in fact found (Figure 3) for all but one point.

For compound (**2**) similar conclusions hold (Figures 4 and 5), while the few data for (**3**) show poor electrochemical response: large half-peak widths δ indicate repulsive electroactive-site interactions,[8] with modest currents and high average ΔE_p values. The ΔE_p (and δ) values follow the sequence (**1**) $\gtrsim$ (**2**) < (**3**), the general scatter indicating variable one- *versus* two-ring strain release, or randomly substantial steric barriers to e.t. within the film. The ΔE_p ranges for all three species betoken electrochemical rate responses in the reversible/quasi-reversible category: a positive $\bar{x}$ correlation with ΔE_p would indicate quasi-reversible/irreversible responses, and slow heterogeneous e.t. causing 'irreversible' constraints would give dE/d log v > 118 mV,[9] which is not found here. The excesses of ΔE_p values over the ideal 59 mV, and the grouping of the larger ΔE_p values with the lower x which tend to $\frac{1}{2}$, are in part explained by the Marcus relation[10] between the mixed-

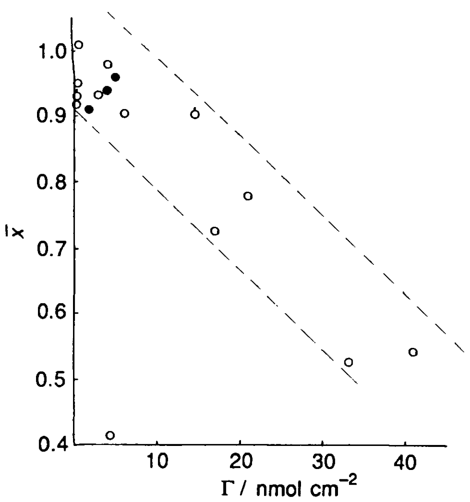

Figure 3. Apparent coverages Γ *versus* average scan-rate exponents $\bar{x}$ for compound (**1**) at 20 mV s^{-1}. Symbols as in Figure 2

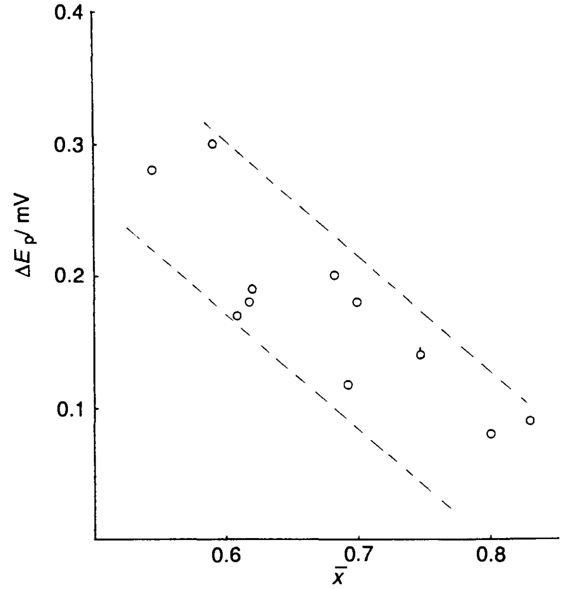

Figure 4. Peak separations ΔE_p *versus* average scan-rate exponents $\bar{x}$ for compound (**2**) at 20 mV s^{-1}. All ITO in water, except tagged (acetonitrile)

valence intersite e.t. rate (governing electronic hopping diffusion in the film) and the *heterogeneous* e.t. rate from film to metal (or quasi-metal).

The germane compound (**4**) behaved like (**3**); the phosphine derivatant (**5**), while forming a deep red coating when an electrode is merely dipped in its solution, still shows no electrochemistry,[4] and a polymeric decomposition product here seems responsible for the passivation. Since poor dark-electrode response predicates poor photoelectrochemical characteristics, only electrodes coated with (**1**) or (**2**) were thus examined under illumination.

Coated n-silicon electrodes under 50 mW cm^{-2} illumination in the most testing milieu, $NaClO_4$ in aqueous solution, gave almost immediate c.v.s of satisfactory reproducibility (Figure 6) with on average but a few per cent decay after hundreds of cycles. In contrast with observations on most halogeno compounds (below) this early stability probably means that there is a substantial oxide layer (from heating), but <30 Å thick, otherwise complete blocking would have followed.[11] The range of responses is given in Table 2. No correlations ensue as in Figures 2—5 for the dark electrochemistry, indicating a sensitivity of the bonding and/or its photoelectrochemical consequences to conditions more marked than for the former. The much greater ΔE_p values than for Pt or ITO (Table 1) can be ascribed in part to the oxide-layer resistance.[11] As expected from the Pt and ITO studies, the response of (**1**) generally outdoes that for (**2**), and also $\bar{x}[(\mathbf{1})] > \bar{x}[(\mathbf{2})]$, even though the latter formed thinner films; thus slower e.t. both within the film and to the substrate electrode are implied for the diphenyl compound.

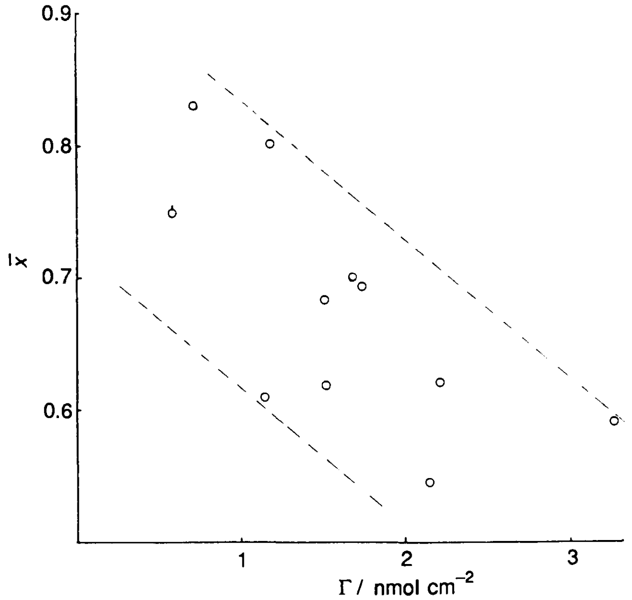

Figure 5. Apparent coverages Γ *versus* average scan-rate exponents $\bar{x}$ for compound (**2**) at 20 mV s^{-1}. Symbols as in Figure 4

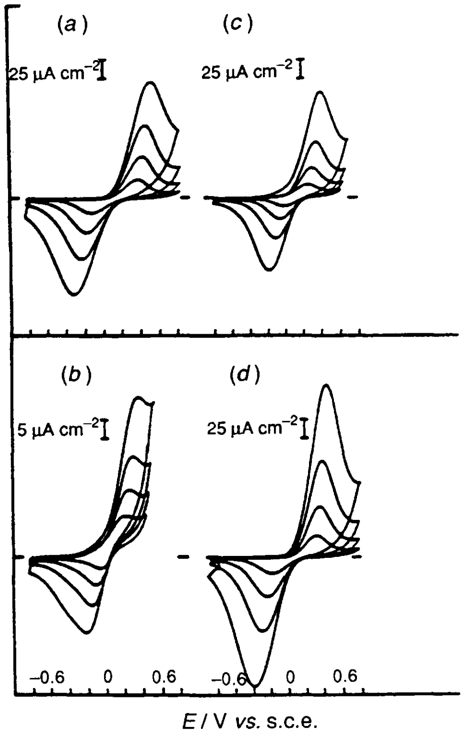

Figure 6. n-Silicon derivatised with compound (**1**) under 50 mW cm^{-2} tungsten illumination in $NaClO_4$–water; scan rates as in Figure 1

Table 2. Cyclic voltammetry of (strain-release) derivatised n-silicon–aqueous $NaClO_4$, in 50 mW cm^{-2} light at 20—200 mV s^{-1} (200 mV s^{-1} data listed), 20 °C

Surface compound	No. of experiments	E_{p_a}/mV E_{p_c}/mV	i_{p_a}/μA i_{p_c}/μA	δ_a/mV δ_c/mV	$100\bar{x}$	100Γ/ nmol cm^{-2}
(1)	7	780 to 360	94—5	560—320	70—93	33—486
		−530 to −190	81—3	560—320		
(2)	6	740 to 440	13—6	600—320	54—72	19—62
		−260 to −100	8.7—3.4	520—260		

Γ for a particular surface follows the approximate sequence of i_{p_a} and in any one experiment increases 1—2 fold with decreasing ν; ΔE_p increases 2—3 fold with increasing ν. Derived film thicknesses ($\propto\Gamma$) 0.05—0.66 μm for (**1**), 0.03—0.08 μm for (**2**).

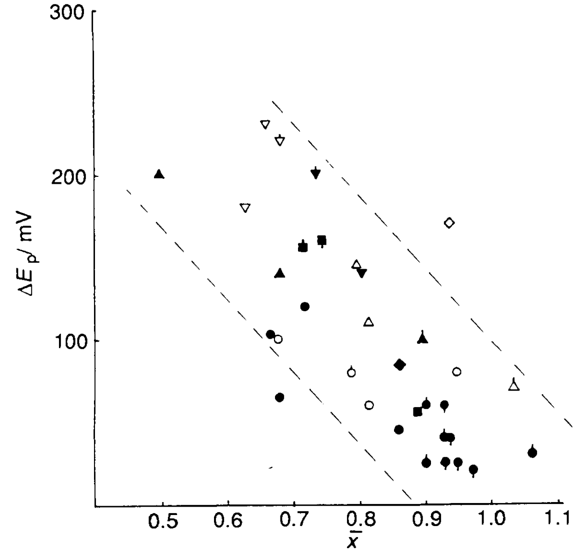

Figure 7. Peak separations ΔE_p *versus* average scan-rate exponents $\bar{x}$ for all Scheme 2 species at 20 mV s^{-1}. Compounds ○, (**6**); △, (**8**); □, (**7**); ▽, (**9**); ◇, (**10**). Filled symbols, Pt; unfilled, ITO; tag up, acetonitrile; tag down, EtOH; no tag, water. One point off diagram at (0.835, 420)

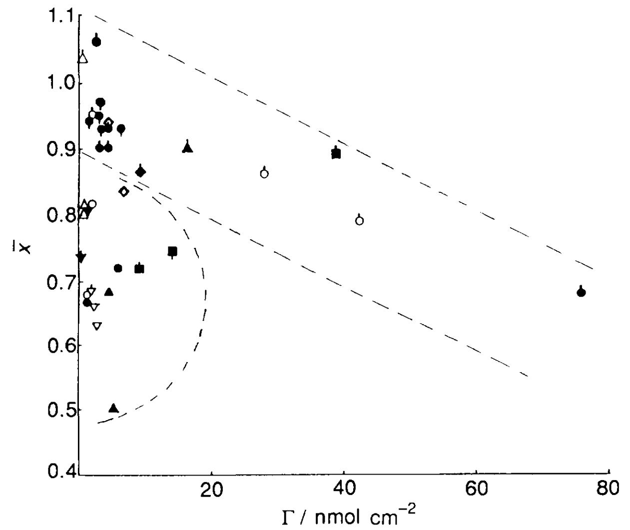

Figure 8. Apparent coverages Γ *versus* average scan-rate exponents $\bar{x}$ for all Scheme 2 species at 20 mV s^{-1}. Symbols as in Figure 7

Species attached by Hydrolytic Reaction of Halogeno-species.—Compared with our earlier efforts,[4] the vast improvement in extent of derivatisation, effected by the heating of the Scheme 1 compounds on the bare substrates, suggested that greater persistence with the less stable, hydrolytically linked, compounds of Scheme 2, which are unstable to heating, would result in improved coating also by these latter. Thus the dipping procedure[4] was systematically extended from hours to days, to allow a variation in the amount of derivatisation. Some control of this amount was possible, but even the carrying of two identical electrodes through all procedures in parallel did not always guarantee the same coverage. Nevertheless, the coverage was always quite substantial. The apparently ring-strained compounds (**1**) and (**2**) will nevertheless bond *via* hydrolysis-driven rather than strain-release-driven reactions.[12]

For this group of derivatants, variations in c.v. parameters (Table 3) for any *one* species overlapped those of the others, again in seemingly random fashion. *All* the Table 3 data, however, plotted as for Figures 2—5, led to (Figures 7 and 8) similar relationships, except that a substantial group of results in Figure 8 (within the dotted semicircle) either are randomly deviant, or may roughly represent behaviour of *incremental* $\bar{x}$ with Γ, to be expected if there is irreversible e.t. to the substrate. This encircled group (all members but one having $\Delta E_p >$ 100 mV) could thus show irreversible-to-quasi-reversible response; the remainder (all but one having $\Delta E_p \leqslant$ 100 mV) are again quasi-reversible to reversible, as argued for the strain-release derivatants.

Some specific points need be noted: aqueous media, and ITO, give somewhat the larger ΔE_p values, the former according with Marcusian results[13] for higher-permittivity media (here within the film), the latter being attributable to resistance. Higher apparent coverages Γ ensue with acetonitrile than with water, *i.e.* hydrophobicity *within* these coatings masks some of the redox sites, contrast Scheme 1 derivatants, resulting also in the larger ΔE_p values (and $x \longrightarrow \frac{1}{2}$ for hopping-diffusional rather than quasi-monolayer behaviour) with the aqueous solvent. The ΔE_p magnitudes are otherwise much as for Scheme 1, though of the latter only compound (**1**) gives comparable coverages Γ. Overall, there are no dramatic contrasts in the dark electrochemistries of the Scheme 1 *cf.* Scheme 2 derivatives.

Under illumination, Figure 9, survival, under repetitive scanning followed the sequence (**6**) > (**7**) > (**8**), the rest failing totally after a few cycles. Compound (**6**) persisted in acetonitrile for > 13 000 cycles (over 76 h) ending up with 9% of its initial peak photocurrent (Table 5); decomposition in water was about ten times more rapid. The more robust species evinced, in the *dark*, lower ΔE_p values and generally a higher coverage Γ (except that the failing germanium compound shows substantial Γ). Comparison of illuminated with non-illuminated responses of the persistent compounds, Table 4 *cf.* Table 3, shows remarkably little effect of change of electrode substrate, or of dark *versus* illumination, on the parameters. However, in detail, the variations observed in the photo-c.v. such as shifts and inversions of E_p values, are as to be expected from the effects of oxide growth, surface states, and resultant influences on the Fermi level of the semiconductor. Again, irreproducibility of

Compound	Formula and name	Ref.
(6)	$[Fe(C_5H_5)(C_5H_4SiCl_2CH_3)]$ (Dichloromethylsilyl)ferrocene	*a*
(7)	$Si[(C_5H_4)_2Fe]Cl_2$ Dichloro(1,1′-ferrocenediyl)silane	*b*
(8)	$[Fe(C_5H_5)(C_5H_4SiCl_2Ph)]$ (Dichlorophenylsilyl)ferrocene	*a*
(9)	$Si[(C_5H_3Cl)_2Fe]Cl_2$ Dichloro(1,1′-dichloro-2,2′-ferrocenediyl)silane	*4* [**(9)**]
(10)	$Ge[(C_5H_4S)_2Fe]Cl_2$ Dichloro(ferrocene-1,1′-diyldithio)germane	*c*

[a] F. R. Mayers, Ph.D. Thesis, Exeter University, 1985. [b] A. G. Osborne, and R. H. Whiteley, *J. Organomet. Chem.*, 1975, **101**, C27. [c] A. G. Osborne, A. J. Blake, R. E. Hollands, R. F. Bryan, and S. Lockhart, *J. Organomet. Chem.*, 1985, **287**, 39.

Scheme 2.

Table 3. Ranges of c.v. parameters for hydrolytically linked ferrocene species in various systems at 200—20 mV s^{-1} (200 mV s^{-1} data cited), 20 °C

Surface compound	System	No. of experiments	E_{p_a}/mV E_{p_c}/mV	i_{p_a}/μA i_{p_c}/μA	δ_a/mV δ_c/mV	100$\bar{x}$	100Γ/ nmol cm^{-2}
(6)	A	2	510—520 300—350	41—216 40—198	260—280 160—200	67—72	63—330
	B	2	570—610 350—390	39—900 35—940	240—320 240—420	79—95	158—2 480
	C	2	500—550 300—340	51—53 55—57	180—280 160—190	68—81	91—173
	D	6	520—630 420—505	116—1 590 101—1 590	180—240 160—200	68—106	175—4 660
	E	5	520—560 420—490	42—156 39—147	180—280 140—240	93—97	117—358
(7)	D	2	500—580 280—470	160—1 290 98—1 460	310—380 230—680	72—89	390—2 700
	E	1	700 250	456 498	480 380	74	595
(8)	A	2	560—600 230—290	126—138 86—100	320—420 280, 280	50—68	173—238
	B	1	495 380	13 12	32 44	104	51
	C	2	515—520 330—345	13—14 12—13	360—380 340, 340	80—82	68—70
	D	1	580 350	40 25	320 320	90	1 280
(9)	A	1	560 305	48 32	44 32	81	71
	B	1	670 330	20 15	40 36	68	91
	C	2	550—560 250—260	23—39 23—30	44, 44 32—36	63—66	115—137
	D	1	680 340	21 7	44 24	74	26
(10)	C	2	800—820 330—570	37—96 19—64	28—48 20—47	840—940	320—420
	D	1	610 385	129 83	25 24	860	380

Systems: A, Pt–$NaClO_4$–water; B, ITO–$NBu^n{}_4ClO_4$–acetonitrile; C, ITO–$NaClO_4$–water; D, Pt–$NBu^n{}_4ClO_4$–acetonitrile; E, Pt–$NBu^n{}_4ClO_4$–EtOH.

response, as often also found by others,[14] precludes useful mechanistic comment on particular observations. We note only that limited oxide growth on derivatised silicon is a desirable stabilising adjunct,[15] and that compound (**6**) does confer quite substantial stabilisation. This could be partly a result of the higher coverages by this species, or the higher coverage could imply stronger intramolecular bonding which carries over to the bonding to silicon. *The main conclusion is that the Me group does confer exceptional photoelectrochemical stabilisation.*

X-Ray photoelectron spectrosopic (x.p.s.) studies of the system (**6**)–n-Si were undertaken (Table 6). Clearly [as observed before with (**7**)] the freshly derivatised uncycled coating comprises some Fe^{III}, as endorsed by the observation of a faint blue colouration on most fresh ferrocene-derivatised electrodes; the band at 711 eV is due to Fe^{III} while that at 708 $\pm$ 0.5 eV is due to Fe^{II}.[17] Notably, Fe is lost on extensive cycling while carbon remains, implying that the coating is polymeric, but prone to iron loss, which accounts substantially for the diminution of electroactivity.

Studies on Gallium Arsenide.—Following the attachment of ferrocenyl species on GaAs,[17] we used our best derivatant (**6**) on n-GaAs for cyclic voltammetry under illumination in acetonitrile or EtOH, with $NBu^n{}_4ClO_4$ electrolyte. In these media hundreds of cycles were achieved with no significant decomposition. However, in water the GaAs failed after $\approx$50 cycles, initial peaks, with reduction peaks on reversal of potential, giving way to huge anodic peaks with no

Table 4. Cyclic voltammetry of hydrolytically ferrocene-derivatised n-silicon in various solutions, in 50 mW cm^{-2} light at 200—20 mV s^{-1} (200 mV s^{-1} data cited), 20 °C

Surface compound	System	No. of experiments	E_{p_a}/mV E_{p_c}/mV	i_{p_a}/μA i_{p_c}/μA	δ_a/mV δ_c/mV	100$\bar{x}$	100Γ/ nmol cm^{-2}
(**6**)	A	4	260 to 440	15—47	240—360	64—74	82—134
			−190 to −120	19—48	200—260		
	B	10	310 to 840	26—144	220—500	65—100	260—290
			−600 to 130	26—93	280—700		
	E	4	20 to 1 060	10—67	220—720	56—124	150—540
			−360 to −70	11—58	200—640		
(**7**)	B	2	300 to 440	7—8	320—380	100—107	220—660
			−110 to −20	6—10	300—320		
	E	1	650	2	640	70	12
			−320	1.5	440		

Systems: A, $NaClO_4$–water; B, $NBu^n{}_4ClO_4$–acetonitrile; E, $NBu^n{}_4ClO_4$–EtOH.

Table 5. Survival of n-silicon derivatised with compound (**6**) under 50 mW cm^{-2} illumination in (*a*) 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$ in acetonitrile and (*b*) 0.1 mol dm^{-3} $NaClO_4$ in water

(*a*)		(*b*)	
t/h	i_p/μA	*t*/h	i_p/μA
0	91	0	63
0.17	70	0.33	57
0.33	60	0.67	48
0.67	48	1	33
1	35	2.7	16
5	19	4	9
30	12	6.7[a]	5
76[b]	8		

[a] 1 200 Cycles. [b] 13 000 Cycles.

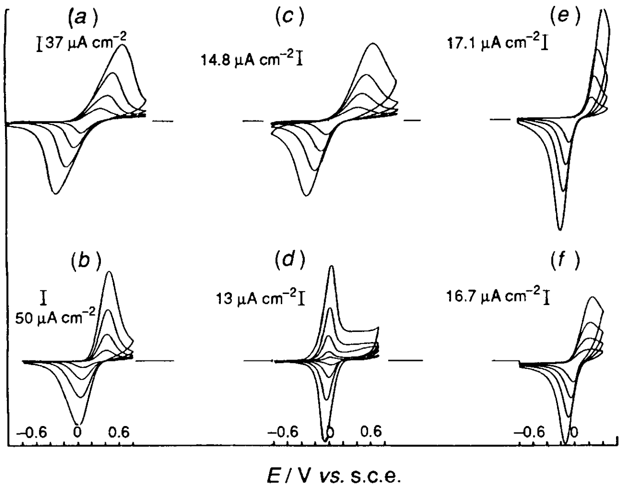

Figure 9. n-Silicon derivatised with compound (**6**) under 50 mW cm^{-2} tungsten illumination in acetonitrile–$NBu^n{}_4ClO_4$ [(*a*), (*b*)], EtOH–$NBu^n{}_4ClO_4$ [(*c*), (*d*)], and water–$NaClO_4$ [(*e*), (*f*)]. Scan rates as in Figure 1

Table 6. X.p.s. data (binding energy relative to C 1*s* = 284.7 eV) for n-Si electrodes with differing surface conditions

	Binding energy/eV		Relative intensity	
Electrode	Si 2*p*	Fe 2*p*	C 1*s*:Si 2*p*	C 1*s*:Fe 2*p*
Bare uncycled	99.9	—	—	—
(**6**) uncycled	102.3	708 711.5	3.3	18 26
	101.2	709.5	20	58
10^3 cycles	102.5	weak Fe^{2+}?	17	Large
100 cycles	102.5	708.8	25	Large
	98.9 102.1	707.9	—	46

accompanying reduction currents. Electronic spectroscopy for chemical analysis again showed iron loss, but residues of Si and C, as on silicon.

Experimental

The materials were prepared following the references in Schemes 1 and 2. Glass-backed platinum-foil squares (1.0 cm^2) were immersed in *aqua regia* (30 s), washed with deionised water, galvanostatted at 50 mA cm^{-2} first of all anodically (60 s) then cathodically (60 s) in 0.5 mol dm^{-3} H_2SO_4, and finally washed in copious amounts of deionised water before use. The 0.5-cm^2 conducting glass electrodes (Saunders Roe, 20 Ω per square) were cleaned in methanol, oven dried, and attached to a crocodile clip. Platinum and glass electrodes were derivatised as below. 100-Face silicon electrodes[4] were pre-treated and derivatised with Scheme 2 species as before[4] but with more varied immersion times. Wide trials with Scheme 1 species led to the spraying of acetone solutions of derivatants on to electrodes pre-heated in an oven to 200 °C. Washing with solvent and drying with nitrogen followed. Wafers (0.5 cm^2) of GaAs (100 face) were attached to copper wires by Ga–In eutectic and silver paint, and mounted (glass-backed) on a glass tube with epoxy resin. It was etched in HF–HNO_3 (3:1) for 15 s, washed in deionised water, immersed in 10 mol dm^{-3} NaOH at 45 °C (60 s), rinsed in water (60 s) and acetone (10 s), and dried in nitrogen (15 min) before derivatisation as above. The electrochemistry (always in 0.1 mol dm^{-3} electrolyte) and illumination apparatus used was as described.[4] The electrode construction, and the cell, of rigid geometry closely reproduced from run to run, are shown in Figure 10. X.p.s. was undertaken on an ESCALab machine at Shell Thornton Research Laboratories by Dr. P. Swift, to whom go our thanks.

Conclusion

In contrast with earlier results,[4] the present observations establish compound (**6**) as being quite efficient in stabilising n-Si against photocorrosion, 13 000 cycles still showing *ca.* 9% residual electrochemistry in non-aqueous solution, a notable result, but the systems are about 10-fold less robust in aqueous media. The photoelectrochemistries as expected are more complicated than the dark electrochemistry on Pt or ITO, but these latter, while also subject to obvious randomness arising

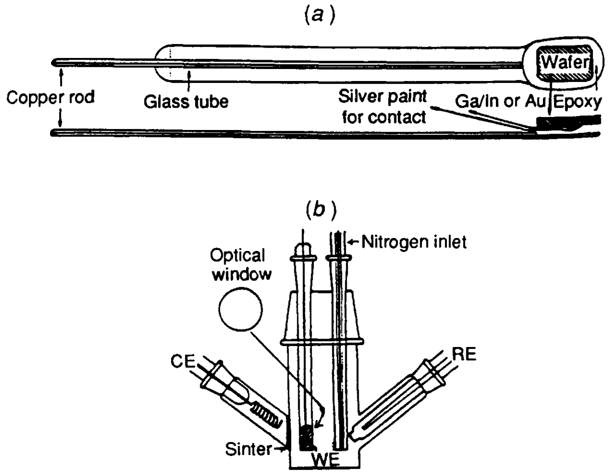

Figure 10. Construction of (*a*) electrodes, (*b*) cell. CE = Counter electrode, WE = working electrode, and RE = reference electrode.

from uncontrollable details under preparative conditions, nevertheless do show approximate correlations which point to classes of behaviour which are the resultants of several current-controlling influences. In the interests of brevity, other available parameters, such as c.v. peak widths δ, have not been widely cited here, even though useful as further experimental touchstones for rationalisation purposes. Effects arising from *e.g.* differential polymer swelling on change of solvent, and the relative effects of cross-linking with the different derivatants, might also have been addressed in the Discussion, but only speculatively; likewise field-dipole effects,[18] theories for which apply to $\Delta E_p = 0$ cases only.

Acknowledgements

We thank Shell Thornton Research Laboratory and the S.E.R.C. for a C.A.S.E. studentship (to F. R. M.), and Dr. R. E. Malpas for extensive advice and discussion.

References

1 'Photoelectrochemical Solar Cells,' eds. K. S. V. Santhanam and M. Sharon, Elsevier, Amsterdam, 1988.
2 R. C. Kainthla, B. Zelenay, and J. O'M. Bockris, *J. Electrochem. Soc.*, 1986, **133**, 248.
3 A. B. Fischer, J. B. Kinney, R. H. Staley, and M. S. Wrighton, *J. Am. Chem. Soc.*, 1979, **101**, 6501 and refs. therein.
4 A. J. Blake, F. R. Mayers, A. G. Osborne, and D. R. Rosseinsky, *J. Chem. Soc., Dalton Trans.*, 1982, 2379.
5 A. B. Fischer, J. A. Bruce, D. R. McKay, G. E. Maciel, and M. S. Wrighton, *Inorg. Chem.*, 1982, **21**, 1766.
6 A. J. Bard and L. R. Faulkner, 'Electrochemical Methods,' Wiley, New York, 1980.
7 E. Laviron, *J. Electroanal. Chem. Interfacial Electrochem.*, 1972, **39**, 1; 1980, **112**, 1.
8 H. Angerstein-Kozlowska, J. Klinger, and B. E. Conway, *J. Electroanal. Chem. Interfacial Electrochem.*, 1977, **75**, 45.
9 L. Roullier and E. Laviron, *J. Electroanal. Chem. Interfacial Electrochem.*, 1982, **134**, 181 and refs. therein.
10 R. A. Marcus, *J. Phys. Chem.*, 1963, **67**, 853.
11 B. H. Loo, K. W. Frese, jun., and S. R. Morrison, *Surface Sci.*, 1981, **109**, 75.
12 C. Eaborn, 'Organosilicon Compounds', Butterworths, London, 1960.
13 R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966.
14 J. A. Bruce and M. S. Wrighton, *J. Electroanal. Chem. Interfacial Electrochem.*, 1981, **122**, 93.
15 M. J. Madou, B. H. Loo, K. W. Freese, jun., and S. R. Morrison, *Surface Sci.*, 1981, **108**, 135.
16 A. B. Fischer, M. S. Wrighton, M. Umaña, and R. W. Murray, *J. Am. Chem. Soc.*, 1979, **95**, 3442.
17 J. M. Bolts and M. S. Wrighton, *J. Am. Chem. Soc.*, 1979, **101**, 6179.
18 H. Gerischer and D. A. Scherson, *J. Electroanal. Chem. Interfacial Electrochem.*, 1985, **188**, 33.

Received 16*th May* 1990; *Paper* 0/02162H