176. *The Photochemistry of Selenium. Part III.* Photogalvanic Effects with Red Selenium.*

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Photogalvanic effects at gold electrodes coated with red selenium, immersed in aqueous hydrochloric acid, show that such electrodes tend to behave reversibly on illumination, this tendency being increased by cathodic prepolarisation. An explanation of this behaviour is given in terms of localised adsorption of hydrogen atoms on illuminated red selenium.

THIS work was undertaken to collect evidence concerning the suggestion that photochemical oxidation of hydrogen selenide by gaseous oxygen, in the presence of liquid water and solid selenium, involves a step in which the discharge of hydrogen ions at a selenium surface is facilitated by light (Pittman, *J.*, 1949, 1811). To this end, an examination was made of photogalvanic effects at selenium electrodes. These effects have long been known (Ries, " Das Selen," 1918, J. C. Hubers) but the only recent investigations appear to be those of von Hippel *et al.* (*J. Appl. Physics*, 1946, **17**, 215.) The results of the earlier workers may be unreliable for at least two reasons: (*a*) lack of knowledge of the allotropic form of selenium used, and (*b*) neglect of the considerable effects of impurities, particularly of oxygen.

EXPERIMENTAL.

The system chosen for examination was the cell Au|Se(red),HCl(aq.)|Pt,H_2, the experimental arrangement being such that only one side of the gold electrode, that coated with selenium, was in contact with the cell fluid. This was accomplished by attaching a disc of gold foil to the bottom of a cylindrical glass cell (Fig. 1) by means of heat-cured D.C. 996 Silicone. There was no evidence of possible contamination of the electrode by the surface-active Silicone: for example, the selenium coatings were formed by electro-reduction; the films obtained were highly uniform and adherent and showed no effects compatible with surface contamination of the gold. Also the results given by such Silicone-adhesed electrodes were very similar to those obtained with platinum electrodes fused to glass.

The difficulties associated with the production of films of selenium in a known allotropic form were overcome by electrodeposition of the element. This could be effected either by anodic oxidation of hydrogen selenide in aqueous solution or by cathodic reduction of aqueous selenious acid. The latter method was used on the score of convenience. Independently, von Hippel and Bloom (*J. Chem. Physics*, 1950, **18**, 1243) investigated the electrodeposition of selenium from selenious acid solutions and, though their methods differ in detail from that used in this work, there is, in general, a close concurrence of results. With this electrodeposition technique it was possible to prepare films of selenium which appeared to be unambiguously of the red variety, and these could be transformed into the grey modification by annealing for several hours at 100—120°. The experiments described here are, however, concerned only with coatings of the red form. Though the description is not accurate, the gold electrodes covered with red selenium film will be referred to as selenium electrodes.

The method of illuminating the selenium electrode is shown in Fig. 1. Preliminary observations indicated that at high light intensities the magnitude of the photo-galvanic effects shown by these electrodes was either independent of, or dependent only on a small fractional power of,

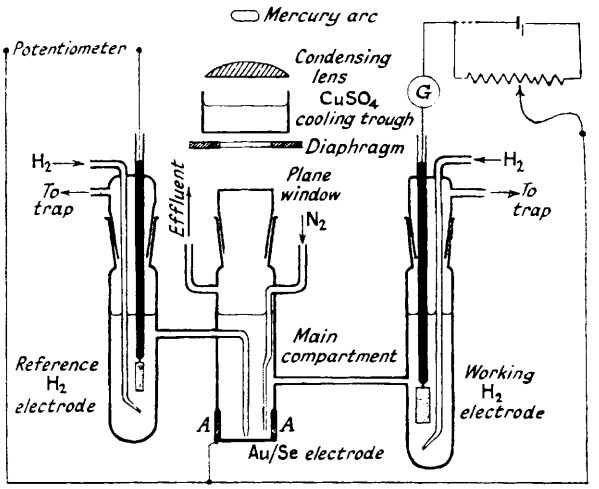
* Part II, *J.*, 1949, 1811.

the incident light flux. To eliminate a variable not of immediate interest, a light source of constant intensity was used. This consisted of a 125 w " Osira " mercury arc, removed from its glass envelope, the power consumption and light output of which were under continuous control. The latter quantity was measured with an E.E.L. selenium cell and a uranyl oxalate actinometer.

Early experiments with the main electrode compartment open to the air gave erratic results, and bubbling of oxygen through this part of the cell increased the erratic behaviour. For subsequent work, therefore, a closed cell was used, with a stream of nitrogen, deoxygenated by passage over red-hot copper, passing through the solution in the main electrode vessel. With these conditions the behaviour of the cell was much more stable and reproducible.

Two kinds of experiments were performed with this type of cell: one " static," in which potentials on open circuit were measured, either with a Tinsley potentiometer or with a high impedance valve-voltmeter. The other, " dynamic," in which current passing through the cell was measured at various applied polarising potentials. In all experiments the electrode potentials were measured against a hydrogen electrode immersed in the same solution. From now on, all potentials quoted will be referred to such an electrode.

FIG. 1.



In hydrochloric acid, over a wide concentration range (4·8, 1·0, 0·10, 0·01N), the selenium electrodes behaved, in the dark, in a similar way to bare gold electrodes. Between 0 and about +0·8 v they acted as almost ideal polarised electrodes, the open circuit potential being determined only by previous polarisation. They showed, however, a tendency to drift positive if left for many days. Comparison of polarisation–current curves (Figs. 2—5) also makes this similarity apparent.

On exposure to light, the open circuit potentials of bare gold electrodes changed, if at all, by less than 1 mv. The selenium electrodes showed marked effects, in some cases the potential becoming more positive and in others more negative (see Table 1). When the light was cut off

TABLE 1.—*Potential changes of red selenium-coated electrodes after 5 minutes' illumination. Electrolyte, 1·0N-hydrochloric acid.*

Potential (v):			Potential (v):			Potential (v):			Potential (v):		
dark	ill'd.	ΔE, v	dark	ill'd.	ΔE, v	dark	ill'd.	ΔE, v	dark	ill'd.	ΔE, v
0·175	0·380	+0·205	0·422	0·442	+0·020	0·539	0·524	−0·015	0·661	0·557	−0·084
0·330	0·396	+0·066	0·453	0·469	+0·016	0·551	0·538	−0·013	0·700	0·582	−0·118
0·380	0·419	+0·039	0·528	0·524	−0·004	0·602	0·550	−0·052			

the electrodes regained their initial potentials, but this change was not instantaneous, 5—10 minutes being required for its completion.

The behaviour of these electrodes was similar in all the concentrations of hydrochloric acid investigated, the sign of ΔE depending on whether the dark potential was greater or less than

FIG. 2. *Current–polarisation curves* : 4·8N-HCl.

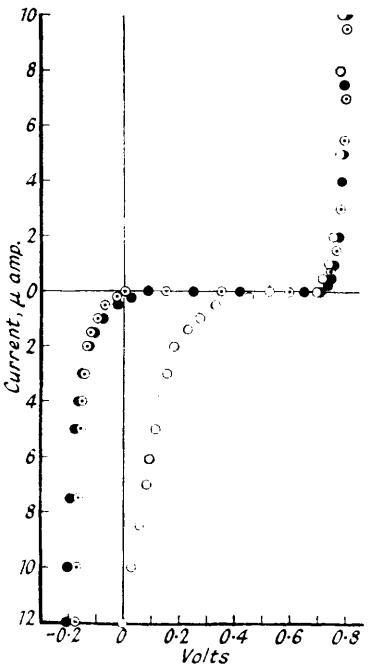


FIG. 3. *Current–polarisation curves* : 1·0N-HCl.

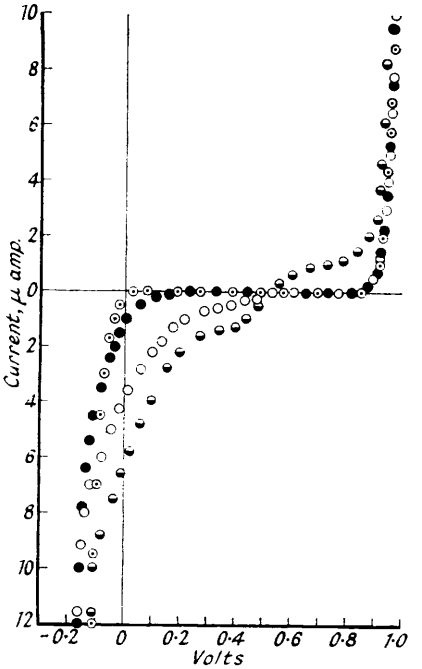


FIG. 4. *Current–polarisation curves* : 0·1N-HCl.

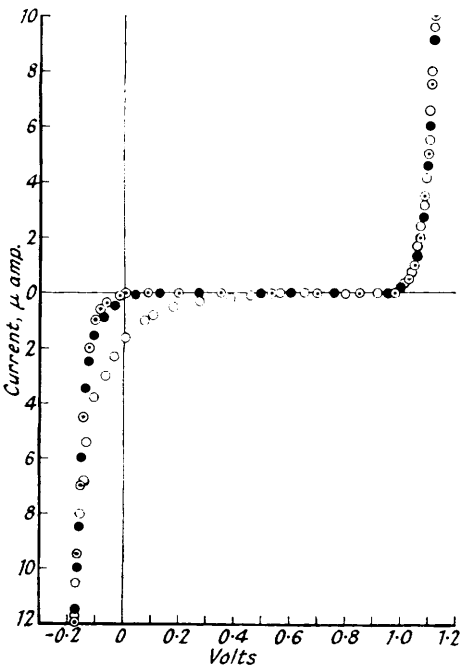
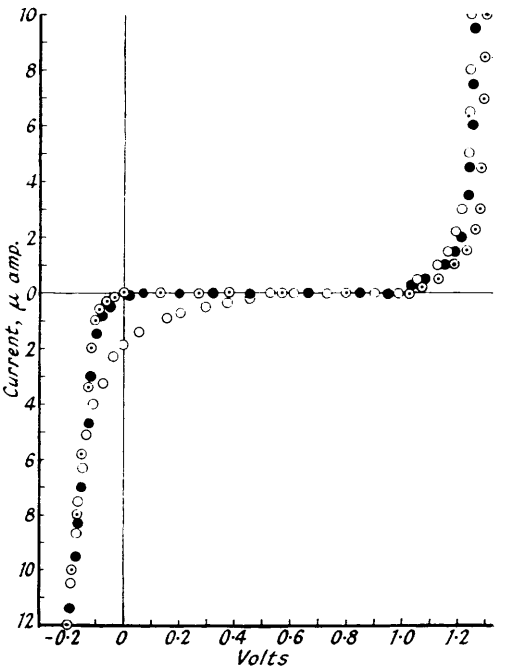


FIG. 5. *Current–polarisation curves*: 0·01N-HCl.



⊙ Bare gold.
● Red selenium in darkness.
○ Illuminated red selenium.
◒ ,, ,, , cathodically more polarized.

about +0·5 v. The change in potential of the electrode, on illumination, was not instantaneous, and if illumination was continued for up to several hours, all the many electrodes used, in all the concentrations of hydrochloric acid, came to a potential of +0·524 ± 0·005 v and remained thereat almost indefinitely while illuminated. Also, if the stream of nitrogen through the main cell was replaced by one of hydrogen, no change was observed in the behaviour of the selenium electrodes, the potential of +0·524 v still being attained on continued illumination.

In the conduct of the " dynamic " experiments a special technique was necessary, for, although gold and the non-illuminated selenium electrodes gave polarisation–current curves which were sensibly unaffected by previous polarisation, both the cathodic and anodic branches in curves for illuminated selenium electrodes showed marked hysteresis (Fig. 3, points ◒), the magnitude of which depended on the degree of cathodic polarisation to which the electrode had been previously subjected. The following procedure was therefore adopted. The illuminated selenium electrode was polarised to approximately +0·6 v and left until the current flowing through the cell fell to zero; in the case of electrodes which had not been cathodised or which had been anodised to remove the effects of cathodisation, this state was reached in less than 5 minutes. This condition of the cell was used as the starting point of both anodic and cathodic polarisations. The applied potential was then varied in a stepwise manner, observations of current and potential being made after each adjustment, only when both quantities had become constant. Again, this condition was invariably attained in less than 5 minutes. Reproducible curves were obtained in this way, the various parameters being independent of the particular selenium electrode used. It will be noted that the potential at which these electrodes began to pass cathodic current became more positive on illumination and that it is, in fact, identical, to a close approximation, with the potential taken up by the illuminated electrodes on open circuit. The anodic branches of the curves were unaffected by illumination.

The effect of cathodic prepolarisation was further investigated, and polarisation–current curves for low current densities (*ca.* 0·2 μa/cm.^{2}) obtained after various cathodic prepolarisations are shown in Fig. 6. The technique described above was not used in these experiments. The electrode was polarised cathodically for an appropriate time and then the applied E.M.F was varied in steps, through zero, to anodic polarisation In all cases potential and current reading became sensibly constant after lapses of 5 minutes. It will be seen that the greater the charge passed in the prepolarisation the more the illuminated electrode tends towards reversible behaviour.

To examine the possibility of formation of hydrogen selenide by the passage of cathodic current through selenium electrodes, the effluent gas from the main compartment of the cell was passed through a micro-bubbler containing half-saturated cadmium sulphate solution. In no case was cadmium selenide precipitated on prolonged cathodisation of selenium electrodes in the dark at the current densities used, but in every one of eight polarisations of illuminated selenium electrodes at potentials between 0 and +0·524 v, *i.e.*, at current densities even less than those used in cathodisations in darkness, a brown precipitate of cadmium selenide was formed. Owing to the smallness of the current densities used it was impossible to relate quantitatively the amount of hydrogen selenide formed with the quantity of electricity passed, but it is noteworthy that precipitates were only formed after cathodisation had been continued for 12 hours or more.

The effect of artificial introduction of hydrogen selenide into the system was investigated by bubbling a mixture of nitrogen (745 mm.) and hydrogen selenide (15 mm.) through the main compartment of the cell. The initial open-circuit potential of the illuminated selenium electrode was +0·528 v, and after 10 minutes' passage of the mixture the potential fell to +0·001 v and after 3 hours to −0·005 v. All the usual photo-galvanic responses were suppressed by this treatment, and they did not reappear even after a lapse of 5 days, with nitrogen alone passing through the cell.

Discussion

For an electrode to act reversibly, both cathodic and anodic depolarisation must occur. Not infrequently the product of one depolarising process acts as a depolariser for the other; *e.g.*, a gold electrode in an acid solution is cathodically depolarised by iodine, and if cathodic current is passed, hydrogen iodide, an anodic depolariser, is formed and the electrode shows reversible behaviour. This, however, does not always obtain. Consider, again, a gold electrode in aqueous acid; atomic hydrogen, an anodic depolariser, is formed by the passage of cathodic current but as this is at once removed as molecular hydrogen, such an

electrode is not reversible. The observations quoted in the previous section show that while red selenium in the dark is inactive, on illumination it acts as a cathodic depolariser.

By one criterion, that of the electrode's acquiring a fixed potential, these illuminated selenium electrodes behave as reversible systems, and as this potential measured against a hydrogen electrode in the same solution is independent of acid concentration, they might be considered as being reversible to hydrogen ions. However, the requirements of a second and necessary criterion, namely, that the potential of an ideal reversible electrode is independent of the current flowing through it, are not approached unless the electrode has been cathodically prepolarised (Fig. 6). It would thus appear that the products of cathodic processes at these electrodes provide an anodic depolariser. Certainly there is no indication of atomisation of molecular hydrogen, for replacement of nitrogen in the main cell by hydrogen has no effect. It might be suggested that hydrogen selenide, a reducing agent, acts as the anodic depolariser. There are two factors which make this improbable. On one

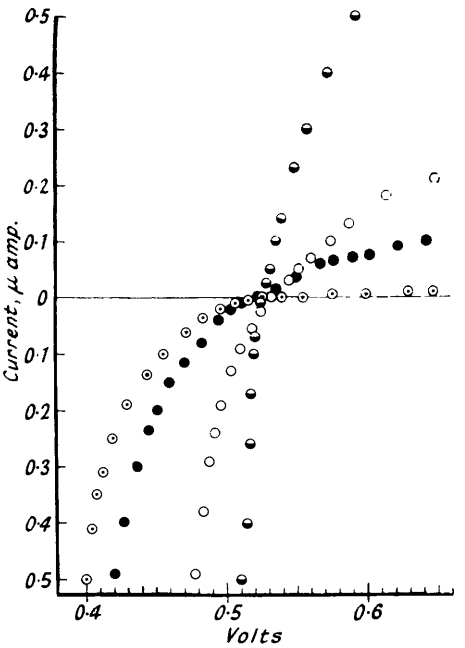


FIG. 6. *Current–polarisation curves (low c.d.) for illuminated red selenium*: 1·0N-HCl.

- ⊙ No prepolarisation.
- ● Cathodic prepolarisation, 0·015 coulomb.
- ○ ,, ,, 0·030 ,,
- ◒ ,, ,, 0·100 ,,

hand, the continuous stream of nitrogen flowing through the solution should rapidly remove any hydrogen selenide formed, and on the other, there is the observation of the poisoning effect of this compound.

The behaviour of these electrodes can be explained if it is assumed that hydrogen atoms, produced by the flow of cathodic current, do not combine to form molecular hydrogen but undergo localised adsorption on illuminated selenium and thus provide a limited store of anodic depolariser. Such an adsorption can be envisaged if the mechanism of photoconduction in red selenium is considered. Von Hippel (*J. Chem. Physics*, 1948, **16**, 372) suggests that photoconduction in this form of the element is of N type, as the positive holes created by the excitation of electrons to a conduction band are localised in the Se_8-ring molecules and thus cannot participate in conduction, as they do in the chain molecules of grey selenium. These light-excited Se_8 molecules may be considered as odd molecules, with which hydrogen atoms, behaving as free radicals, can combine to give the labile systems Se_8H. The fate of these complex entities will be determined by the interstitial space charge within the selenium, which in turn will be dependent on the electrode potential.

The net current flowing through a reversible electrode may be considered as the algebraic sum of the separate currents arising from concurrent anodic and cathodic processes

(Hammett, *Trans. Faraday Soc.*, 1933, **29**, 770; Bockris, *Chem. Reviews*, 1948, **43**, 525; Hills and Ives, *J.*, 1951, 305). It thus becomes necessary to suggest processes likely to give rise to these currents in the prepolarised illuminated red selenium electrode.

If the foregoing theory of hydrogen-atom adsorption is accepted, the anodic process may be described by

$$(1)\ Se_8H - e^- = Se_8 + H^+.$$

This charging of hydrogen ions will take place at a rate proportional to $[Se_8H]e^{-(\omega + \alpha FV)/RT}$, where ω is the activation energy of process (1), V is the polarisation of the electrode, and α is a transfer factor. The anodic component of the exchange current thus becomes

$$I_a = k_1[Se_8H]e^{-(\omega + \alpha FV)/RT}$$

which is proportional to the population of adsorbed hydrogen atoms on the selenium and is self-destroying.

The explanation of the cathodic process presents more difficulty, for it must embrace the facts that the cathodic products appear to enhance the rate of the cathodic process and that the equilibrium potentials of these electrodes depend on hydrogen-ion concentration in the same way as for the H_2–Pt electrode. These difficulties are resolved if it is assumed that the cathodic product, Se_8H, catalyses the further discharge of hydrogen ions, thus enabling the cathodic component of the current to be written as

$$I_c = -k_2[H^+][Se_8H]e^{-(\omega' - \beta FV)/RT}$$

where ω' is the activation energy of hydrogen-ion discharge and β is a transfer factor related to α.

It will thus be seen that the equilibrium potential at which the resultant current vanishes *i.e.*, when

$$I_a + I_c = 0 = k_1[Se_8H]e^{-(\omega + \alpha FV)/RT} - k_2[Se_8H][H^+]e^{-(\omega' - \beta FV)/RT}$$

will depend, not upon the concentration of adsorbed hydrogen atoms, but only upon the hydrogen-ion concentration of the solution.

A problem still remains with regard to the formation of hydrogen selenide during cathodisation of the illuminated selenium electrodes. This has not been closely investigated but the impression has been gained that it is a secondary process as it only occurs after prolonged passage of cathodic current. It is possible that the hydride is produced by attack on the Se_8H entities by some process such as (2) $Se_8H + H = H_2Se + Se_7$ or (3) $Se_8H + e = HSe^- + Se_7$. There is a slight balance of evidence in favour of process (3), for this would occur at potentials more negative than the equilibrium potential and might offer some explanation for the appearance of plateaux in the cathodic limbs of polarisation–current curves from prepolarised illuminated electrodes (Fig. 3, points ◒). The disrupted remnants of the Se_8 rings could combine to form chain molecules, resulting in formation of amorphous or grey selenium. Careful examination of all the electrodes used showed no trace of either of these transformations. It is more likely that the Se_7 residues, as they are diradicals, are destroyed by attack by hydrogen atoms with formation of more hydrogen selenide.

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