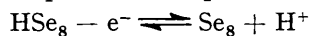


**794.** *The Photochemistry of Selenium. Part IV.\* Photogalvanic Effects with Grey Selenium.*

By R. W. PITTMAN.

Photogalvanic effects at gold electrodes coated with grey selenium, in aqueous hydrochloric acid, are described. These are shown to be different from those obtained with red selenium and the difference is accounted for in terms of the molecular structures of the two forms of the element.

PHOTOGALVANIC effects with red selenium in aqueous hydrochloric acid were described in an earlier paper \* and a mechanism capable of giving rise to these effects was suggested. This was, in brief, that  $\text{Se}_8$  rings with trapped, light-induced, positive holes were capable of combining with hydrogen atoms formed by electrolytic discharge and that the labile entities so produced could participate in the equilibrium



and thus allow such electrodes to behave reversibly in certain circumstances. If it is assumed that electron switching between light-excited  $\text{Se}_8$  rings and adjacent  $\text{Se}_8$  molecules

\* Part III, *J.*, 1953, 855.

is relatively improbable, then an immediate implication of this argument is that the nature of these effects is directly associated with the particular molecular structure of red selenium and its validity would be enhanced if it were shown that grey selenium, with its infinite chains of covalently bound atoms (in which localisation of positive holes appears less likely) manifested a behaviour of different character. The experiments described here were directed towards that end.

#### EXPERIMENTAL

The apparatus used was as described in Part III, except that the selenium films were of the grey form. The preparation of the red selenium electrodes used in earlier experiments was a somewhat empirical process in which damage of the film by hydrogen evolution was frequent. However, increased experience enabled a more controllable technique to be developed, in which hydrogen evolution was reduced to negligible proportions. This may be outlined as follows. The gold electrode, *in situ* in the cell, was covered with a 20% aqueous solution of selenium dioxide and uniformly illuminated by two 100-w tungsten lamps placed at a distance of a few inches. It was then made cathodic, using a platinum-wire ring anode, and the applied potential was adjusted until a current of approx. 100  $\mu\text{A}$  passed. After some minutes a thin bloom of selenium appeared on the gold. The lamps were then turned off and with the electrode in complete darkness the applied potential was varied until cathodic current just ceased to flow. The electrode was again illuminated and it was found that a cathodic current dependent upon light intensity, and of the order of 50  $\mu\text{A}$  for these conditions, flowed through the circuit. This was allowed to continue until a selenium deposit of the required thickness was formed. The cell was then repeatedly washed with conductivity water to remove all traces of selenious acid. The films so obtained were bright red and highly uniform and adherent. Conversion into the grey modification was accomplished by 15 hours' heating at 120°.

If 4 faradays of charge are required to reduce one mole of selenium dioxide, then the passage of one coulomb should deposit 0.2 mg. of selenium. The radius of the electrode was 0.7 cm., hence, as the density of the grey allotrope is 4.79 g./c.c., the thickness of film for one coulomb is approx. 0.028 mm.

Aqueous hydrochloric acid solutions of various strengths were used as electrolytes and the experiments were carried out anaerobically. The greatest care was exercised in the purification, by normal methods, of the materials used, and solutions were prepared with conductivity water.

In the terminology of Part III, the gold electrode with its grey selenium film will be called the grey selenium electrode and all electrode potentials will be referred to a hydrogen electrode bathed in the same solution.

#### RESULTS

The behaviour, in darkness, of grey selenium electrodes was similar to that of red ones, *i.e.*, they tended to act as polarised electrodes over a considerable potential range, approx. from 0 to +1.0 v. The rate of positive drift, already noted with the red modification, was greater and all the many electrodes examined attained potentials of the order of +0.5 to +0.8 v on resting in the dark for several hours after cathodisation. The values of the dark-rest potentials appeared to be independent of acid concentration and dependent only on the nature of the selenium film. The more perfect the film the higher the rest potential.

The maximum responses of these electrodes, on open circuit, to variation of light intensity were not immediately attained (see Figs. 1 and 2). In the many observations made over the potential range in which these electrodes showed polarised behaviour, the sign of  $\Delta E$ , the change in potential on illumination on open circuit, was always positive. The magnitude of  $\Delta E$  could not be directly correlated with light intensity, and the static behaviour of these electrodes is best described by saying that on illumination they always take up a potential more positive than their dark-rest potential and that its value is a function of the incident-light intensity, and also of some property of the film which frequently seems to run parallel with film thickness. The differences in the static behaviours of red and grey selenium electrodes may be tabulated:

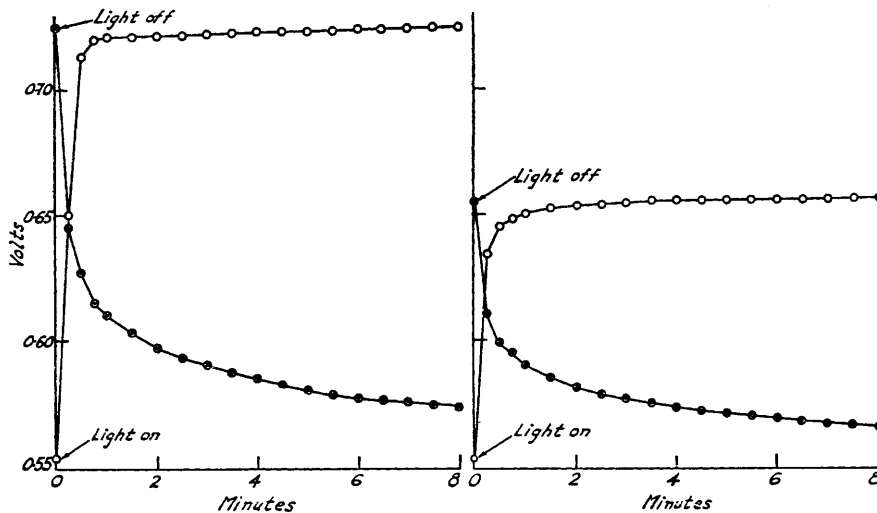
Red	Grey
$\Delta E$ negative or positive according to whether dark rest potential is greater or less than +0.524 v.	$\Delta E$ always positive.
Illuminated rest potential constant at +0.524 v, independent of acid concentration, film thickness and at high light intensities, of incident light flux.	Illuminated rest potential not constant, dependent both on film thickness and light intensity; independent of acid concentration.

In dynamic experiments, also, the behaviour of grey selenium was different from that of red. The shapes of the cathodic branches of the polarisation-current curves were dissimilar and the hysteresis due to the enhancement of reversibility by cathodisation, occurring with

*Potentials on open circuit. Grey selenium electrode in 0.01N-HCl.*

FIG. 1. *With high light intensity.*

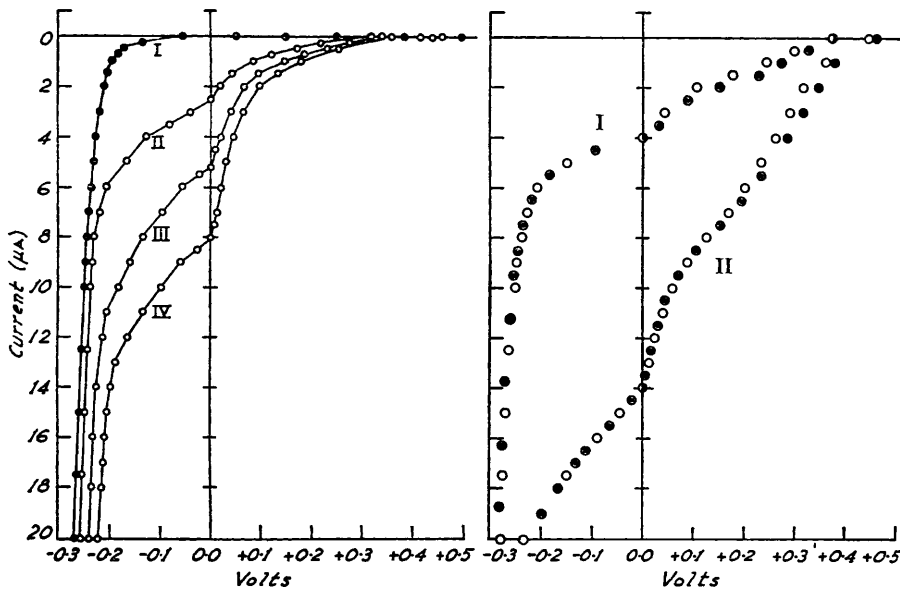
FIG. 2. *With low light intensity.*



*Polarisation-current curves. Grey selenium electrodes.*

FIG. 3. *Film B in 0.01N-HCl.*

FIG. 4. *Film D, o in 1.0N-HCl, • in 0.01N-HCl.*



I, in darkness. II, III, IV, illuminated: relative light intensities, II 1.0, III 2.2, IV 3.3.

Relative light intensities, I 1.0, II 3.3.

red selenium, was lacking. The form of such polarisation-current curves is illustrated in Fig. 3. These curves with cusps are quite characteristic and reproducible, and the null current on illumination for a particular film, as defined by the discontinuity at zero potential, was shown to be directly proportional to light intensity (curves II, III, and IV, Fig. 3). At any

particular light flux the value of this null current appeared to be a function of film thickness, though it is believed that a less easily definable term "perfection" should also be included. The effect of film thickness, in this respect, is shown by comparison of curves II and IV of Fig. 3 (film B) with curves I and II of Fig. 4 (film D). The quantities of electricity allowed to pass in the formation of these films were 1.0 coulomb for film B, and 2.2 coulombs for film D. The thicknesses should be proportional to these quantities.

The null current for a given film, with a given light intensity, remains constant for some time and then diminishes. This is definitely associated with dissolution of the grey selenium with the consequent production of hydrogen selenide, as shown by the precipitation of cadmium selenide in the micro-bubbler, containing half-saturated cadmium sulphate solution, through which the effluent gas from the main compartment of the cell was passed.

It is believed that the passage of cathodic photo-current at zero polarisation and at more positive potentials results solely in the production of hydrogen selenide. Certainly at no time during the flow of such currents were hydrogen bubbles observed at the electrodes, though this, admittedly, has little significance as the quantities of electricity involved were so small. However, supporting evidence may be adduced from observations on grey selenium electrodes in selenious acid. A number of experiments were performed, using a similar procedure to that described in the Experimental section for preparation of the films except that the initial deposit was of grey selenium formed by the standard method. With zero dark currents, photo-currents of up to 200  $\mu\text{A}$  were obtained, greater, it will be noted, than those given by the less stable modification. In no case was there any visible hydrogen production even after many hours. The selenium deposited in these experiments was always of the "grey" form. The resulting films had a black matt appearance and were almost certainly microcrystalline. They showed the same general characteristics as the films produced by heat treatment. On the other hand, if cathodic dark currents were allowed to flow, hydrogen bubbles were observed at the electrodes after relatively short illumination. In experiments with hydrochloric acid solutions, hydrogen evolution increased markedly as the potential of the illuminated electrode was made increasingly negative, and this was undoubtedly at the expense of hydrogen selenide production, which at sufficiently negative polarisations was completely suppressed. As an instance of this a typical experiment is quoted. A grey selenium electrode in 0.1N-hydrochloric acid gave a null current of 12.5  $\mu\text{A}$ , which after 95 min. had fallen to 8.5  $\mu\text{A}$ . By this time there was a deposit of cadmium selenide in the effluent bubbler. The circuit was then broken, the cell swept out with nitrogen, and the potential of the illuminated electrode made sufficiently negative (*ca.* -0.32 V) for a cathodic current of 60  $\mu\text{A}$  to pass. After 15 min. hydrogen bubbles were apparent at the electrode but even after 17 hr., no trace of cadmium selenide was observed in the appropriate bubbler. This prolonged cathodisation had drastic effects, small flakes of selenium being torn from the gold base. The null current on illumination had also fallen to 2.0  $\mu\text{A}$ , but after this current had been allowed to flow for 12 hr. a slight but definite deposit of cadmium selenide had been formed in the effluent bubbler. It is noteworthy that no signs of hydrogen selenide formation were ever observed with grey selenium electrodes in the dark.

Variation of hydrochloric acid concentration in the electrolyte exercised little effect on the polarisation-current curves of grey selenium electrodes (*cf.* Fig. 4). It will be noted that the curves for identical light intensities but differing acid concentrations are almost superposed, only slight deviations being shown on the positive branches.

With red selenium electrodes the effect of variation of acid concentration is quite marked (Part III), for, while the illuminated rest potentials of these electrodes are independent of this factor, the area enclosed between the polarisation curves in light and in darkness is greater the higher the acid concentration.

The anodic branches of the curves for grey selenium greatly resemble those for red and hence those of the bare gold electrode. Some difficulties, which might arise from desorption phenomena, were, however, experienced in obtaining reproducible readings in the region just previous to the onset of steady flow of anodic current, but this phenomenon could not be examined by the techniques used in this work and further investigation in this region awaits the development of more refined methods.

#### DISCUSSION

It is difficult to discuss the results described in the previous section from the point of view of potential gradients originating in the separation of charge due to the interaction of light quanta and selenium atoms: first, because of the difficulty of dealing with such

gradients in a polyphase system and, secondly, because of the possibility of non-ohmic conduction. It seems easier and indeed, more fundamental, to consider that in certain circumstances a current, of magnitude proportional to incident-light flux, is generated at the illuminated selenium-solution interface. In fact the so-called null current, passing when the illuminated cell is short-circuited, is such a current and a plausible mechanism for its generation may be envisaged as follows.

The interaction of a light quantum and a selenium atom produces an electron and a positive hole. It is suggested (Tamm, *Z. Physik*, 1932, **76**, 849) that the bulk of such incipient-current carriers in semi-conductors becomes lodged in surface states. Bardeen (*Phys. Review*, 1947, **71**, 717) suggests that this may result in a conduction band at the surface of the semi-conductor and that if the density of the surface levels is sufficiently high there will be an appreciable double layer at a free surface formed from a net charge due to electrons in surface states and a space charge of opposite sign extending into the bulk. This seems to have been confirmed by Brattain (*ibid.*, 1947, **72**, 345) by examination of changes in contact potential produced by illumination of semi-conductors. This tendency to formation of a double layer of specific orientation at the selenium-solution surface would be enhanced because the volume relations between  $H_3O^+$  ions and electrons are more favourable than those between positive holes and chloride ions. If the potential of electrons at this surface is sufficiently high, discharge of hydrogen ions can occur. Now, the light-excited selenium atom, part of an infinite chain, can be considered as an odd molecule capable of combining with the newly formed hydrogen atom, with its odd electron, to give the entity  $(HSe_n)^+$ ,  $n$  being large. This unstable entity may then disrupt, extruding an  $HSe^-$  ion into the solution and generating two positive charges which migrate to the dark face by  $p$ -type conduction in the chains. At first sight it would appear that this migration of charge needs a specific orientation of chains, but, if interaction between chains is assumed—and such an interaction involving chain endings seems highly probable—then the passage of positive holes from the illuminated face to the gold substrate can be visualised, even with random orientation. The overall cell reaction is completed by the charging of two hydrogen atoms at the hydrogen electrode to give the two positive ions required to fulfil the demands of electroneutrality in the solution.

The magnitude of the null current generated by this mechanism will be proportional to incident-light intensity and also to the fraction of the total number of light-induced charges lodged in the surface states, and this fraction may well be a function of film thickness; thus we have a ready explanation of the experimentally observed dependence of null current upon film thickness.

The effect of polarisation of the electrodes by applied potentials must next be considered. A point of great importance here is the occurrence of discontinuities in the polarisation-current curves at zero polarisation. These are quite definite and reproducible phenomena, the uniqueness of which is confirmed by the results of experiments in which a small 50-cycle alternating component (approx., 0.1 v r.m.s.) was superimposed upon the steady polarising potential. This, in general, caused a change ( $\Delta i$ ) in the current flowing through the cell.  $\Delta i$  was positive and at a maximum for zero polarisation; for many films the null currents on illumination were almost doubled. As the positive polarisation was increased  $\Delta i$  rapidly decreased, becoming zero at approximately +0.1 v. At greater positive polarisations it changed sign, but it never became greater in magnitude than about 20% of the current due to steady polarisation. For polarisations in the opposite sense,  $\Delta i$  slowly diminished, becoming zero at approx. -0.25 v but never changing in sign no matter how great the negative polarisation.

The discontinuity, so strikingly displayed by this maximum rectifying effect at null D.C. potential, must undoubtedly arise from a change in mechanism, and such a change may be discussed in terms of the two processes of conduction possible in grey selenium,  $p$ -type involving the covalently linked selenium chains and  $n$ -type occurring in the interstices between the chains. These two processes may be considered as separate but not necessarily independent. It is reasonable to suppose that the flow of null current on illumination is confined to  $p$ -type conduction and that the flow of charge on external polarisation is, to a first approximation, limited to  $n$ -type. Comparison of the relative

mobilities of the two current carriers adds weight to this suggestion. The flow of current through the cell, arising from external polarisation, should give rise to an  $iR$  drop across the selenium layer and it would seem that this potential difference is capable of polarising the mechanism of positive-hole conduction. This implies that the two current-carrying processes are independent within the bulk of the selenium but interact at the two surfaces. The theory of surface states is of assistance here, for the interaction can be explained by the lateral translation of charge within these states.

Consider, first, the negative branches of the current-polarisation curves in the light of these suggestions. The gold-selenium surface will be negative with respect to that between selenium and solution, and the consequent potential gradient will facilitate the flow of positive holes towards the gold, thus depleting their concentration at the site of interaction with hydrogen atoms and diminishing the flow of pure photo-current. If the potential gradient is sufficiently steep the photo-current will be completely suppressed, the positive holes acting only as current carriers in the ordinary sense. This picture is certainly supported by the observed diminution in the yield of hydrogen selenide with increasing negative polarisation.

With polarisations in the opposite direction, *i.e.*, on the positive branches, photo-electrons will be drained from the illuminated face, thus lowering the rate of hydrogen-ion discharge. Also the secondary positive holes produced by the transformation



will be retarded in their passage to the gold, hence again the pure photocurrent will decrease and become completely suppressed at sufficiently high positive polarisations. In fact the illuminated selenium-solution interface may be considered as a current generator, the output of which is diminished by polarisation in either sense, thus giving rise to the discontinuity at zero polarisation.

Thanks are offered to the Central Research Fund of the University of London for financial assistance in the purchase of apparatus.

BIRKBECK COLLEGE, LONDON, W.C.1.

[Received, July 16th, 1953.]

---