PHOTOELECTRIC CONDUCTION IN SELENIUM

By R. J. Piersol

Abstract

Variation with light intensity of the photo-current in selenium.—A selenium cell is described which gives a photo-current of 10 ma. for a difference of potential of 100 volts and an illumination of 100 foot-candles. The sensitiveness ratio between the currents under light and dark conditions is 100. The characteristics of the cell are very constant. The experimental results establish the existence of a linear relation between the square of the photo-current and the light intensity. It is pointed out that this result substantiates the conclusion that the photo-conduction in selenium is due to a photo-electric liberation of electrons rather than to an allotropic change from an insulating to a conducting form of selenium.

Effect of temperature on the photo-conductivity of selenium.—Under dark conditions the current through a cell immersed in liquid air dropped in 15 sec. to 35 percent of its value at room temperature, and in 10 min. to 0.000046 percent. When the same cell was illuminated with 100 foot-candles and immersed in liquid air, the current increased for 8 min. to about 1.8 times its value at room temperature and then decreased until after 3 hours its value was 82 percent of its value at room temperature. It is concluded that the mechanism of the current conduction under dark conditions is entirely different from that of the photo-conduction.

I. Introduction

DURING the past twenty years approximately one hundred scientific papers have been published presenting experimental data as to the nature of the light sensitive property of selenium. The results have been masked by extraneous effects to such an extent that they have been so contradictory in nature that it has been impossible to establish any one accepted theory. The largest volume of work has been done by Brown[1] and his colleagues, Stebbins,[2] Sieg,[3] Lilah Crum,[4] Kathryn Dieterich,[5] and E. O. Dieterich[6] at the University of Iowa. This research was pursued under the hypothesis that selenium is a composite of three allotropic forms; allotrope A, having zero conductivity; allotrope B, conductivity approaching that of metals; and allotrope C, an intermediate conductivity. The ratios of the three allotropes vary reversibly with light, temperature, and pressure. Their

[1] Brown, Phys. Rev. **20,** 185 (1905); **25,** 501 (1907); **25,** 505 (1907); **26,** 273 (1908); **32,** 237 (1911); **32,** 252 (1911); **33,** 1 (1911); **33,** 403 (1911); **34,** 201 (1912); **1,** 237 (1913); **1,** 245 (1913); **2,** 153 (1913); **2,** 487 (1913); **4,** 48 (1914); **4,** 85 (1914); **4,** 507 (1914); **5,** 72 (1915); **5,** 75 (1915); **5,** 167 (1915); **5,** 235 (1915); **5,** 341 (1915); **5,** 395 (1915); **5,** 404 (1915); Phys. Zeits. **11,** 482 (1911).

[2] Stebbins, Astrophys. J. **32,** 185 (1910).

[3] Sieg, Phys. Rev. **6,** 213 (1915); **7,** 397 (1916); **17,** 411 (1921); Phil. Mag. **28,** 497 (1914).

[4] Crum, Phys. Rev. **33,** 538 (1911).

[5] K. Dieterich, Phys. Rev. **7,** 511 (1916).

[6] E. O. Dieterich, Phys. Rev. **3,** 498 (1914); **4,** 467 (1914); **7,** 415 (1916); **8,** 191 (1916); **9,** 58 (1917).

results were interpreted as substantiation of this theory, which had been advanced previously by Marc[7] to explain the influence of temperature on the conductivity of selenium, and Monten[8] the effect of pressure. On the contrary, Pfund[9] and his students, Nicholson[10] and Eliott[11] at the Johns Hopkins University, have interpreted their results in support of the theory that selenium conductivity is internal photo-electronic in nature.

In order to determine whether the selenium conduction is due to light converting the insulating allotrope to the conducting allotrope or to the light liberating internal photo-electrons, it is necessary to have positive experimental data as to the relation between the photo-current and the light intensity; also the influence of temperature on the light sensitivity. This is because these relations can be predicted accurately if the conduction is photo-electronic. If the conduction is due to allotropic reversion, these predictions would not fit experimental data. The early work on the current: light-intensity ratio is summarized by Brown[12] as follows:

$i^2=aL$	Rosse—Adams—Berndt	$b^i=aL$	Hesehus
$i^3=aL$	Hopius	$i_b/i_a=(b/a)^a$	Ruhmer
$i(i-b)=aL$	Athanasiadis	$i=aL$	Stebbins

where i represents the conduction current; L, the light intensity; and a and b numerical constants. More recently Pfund[13] has shown that for 12.5 seconds exposure

$$ki^B=aL$$

where B is a constant for each wave-length. The value of B was found to be 2.0 for regions of the spectrum from violet to yellow. As red was approached B decreased so that with deep red and infra-red B was unity. Nicholson,[10] working under unfavorably humidity conditions for long exposures, 20 minutes, found B to be approximately 2.0 for the entire spectrum, although for 6000A a repeated value of 2.5 was found. For white light Rankine[14] found the fourth power of the current to be linear to the light intensity. Thirring[15] has found approximately a linear relation between current and light intensity.

Previous results on the influence of temperature on selenium conductivity are also conflicting. Pochettino[16] found that the dark resistance of selenium decreased from 31,000 ohms at room temperature to 2600 ohms at liquid air temperature, while the light resistance decreased 78,000 ohms to 8700 ohms. This corresponds to a reduction of 25 percent in sensitiveness (light-

[7] Marc. Zeits. f. Anorg. Chem. **48,** 5 (1906).
[8] Monten, Archiv. Math. Ast. Och. Physik **4,** 1 (1908).
[9] Pfund, Phil. Mag. **7,** 26 (1904); Phys. Rev. **28,** 324 (1909); **34,** 370 (1912).
[10] Nicholson, Phys. Rev. **3,** 1 (1914).
[11] Eliott, Phys. Rev. **5,** 53 (1915).
[12] Brown, Phys. Rev. **33,** 10 (1911).
[13] Pfund, Phys. Rev. **34,** 370 (1912).
[14] Rankine, Phil. Mag. **39,** 482 (1920).
[15] Thirring, Jour. Sc. Inst. **4,** 54 (1926).
[16] Pochettino, Rend. R. Accad. dei Linc **11,** 286 (1902).

dark ratio). Bidwell[17] claimed that the temperature of maximum resistance for selenium ranged from 14°C to 30°C. Louise McDowell[18] found that the dark resistance of selenium increases with decrease in temperature; 2.9×10^5 ohms at 23°C, 3.6×10^6 ohms at −65°C, 9.0×10^6 ohms at −90°C and 6.0×10^7 ohms at −191°C. Fournier d'Albe[19] found that the dark resistance of selenium increased from 3.7×10^6 ohms at 15°C to 23.4×10^6 ohms at −180°C, while the light resistance increased from 1.95×10^6 ohms at 15°C to 13.5×10^6 ohms at −180°C. This gives a reduction of 10 percent in sensitiveness.

The present article includes the results on the influence[20] of temperature on photo-sensitivity reported before the 1926 meeting of the American Association for the Advancement of Science and the data[21] on the relation of photo-current to light intensity presented at the 1927 Washington Meeting of the American Physical Society.

II. Apparatus and Method

This investigation was undertaken with the object of developing a selenium bridge giving a light current of 10 ma. for 100 volts at 100 foot-candles illumination; possessing a sensitiveness ratio of 100 between light and dark; and having reproducible and constant characteristics. With the technique necessary to build such a selenium cell, the extraneous effects disappeared so that the inherent properties of selenium conductivity became

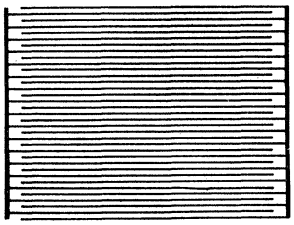

Fig. 1. Schematic diagram of the selenium cell.

unmistakedly evident. Several hundred selenium cells have been made with identical characteristics.

A schematic view of the cell is seen in Fig. 1. The alternate leaves are of brass, 0.005 cm in thickness and insulating micarta, 0.025 cm in thickness. The brass leaves are connected electrically to two electrodes in condenser fashion. The over-all dimensions are 8.75 cm square by 0.65 cm thick. The bridge is composed of 250 brass leaves, each having an effective length of 7.5 cm, with a gap 0.025 cm in width. The surface is ground and polished. Then a film of selenium is deposited over the bridge with uniform thickness

[17] Bidwell, Phil. Mag. **11,** 302 (1906).
[18] McDowell, Phys. Rev. **31,** 524 (1910).
[19] d'Albe, Roy. Soc. Proc. **86,** 452 (1912).
[20] Piersol, Phys. Rev. **29,** 362 (1927).
[21] Piersol, Phys. Rev. **29,** 902 (1927).

of 0.001 cm. Therefore the equivalent length of the bridge is the number of leaves times the effective length of each leaf, which is 1875 cm.

The selenium was obtained from the Baltimore Copper and Smelting Company. But it should be noted that the results are identical using selenium from other sources. To convert the selenium to the light sensitive form, it was annealed at 180°C for five minutes. Neither the temperature nor the time of annealing is as critical as has been supposed. But the thickness of the selenium is of crucial importance for two reasons. Brown[22] has shown that the effective depth for the penetration of light into the surface of light sensitive selenium is 0.0014 cm. The primary light current is due to conductivity only to the depth of light penetration, while the dark current is due to body conductivity. Therefore to obtain a large light current-dark current ratio the thickness of the selenium film should be not greater than 0.0014 cm. Secondly it has been shown by Marc[23] that the action of light is far from being confined to the illuminated portion of the bridge. Also Brown[24] found a change in conductivity of a selenium crystal 10 mm from the point of illumination. This action at a distance is a secondary effect, requiring a long time for an equilibrium state. Therefore the entire depth of selenium should be acted upon directly by the light, as the secondary effects cause conflicting experiment results.

The selenium bridge is sealed in an air-tight hard rubber case with a glass window. The bridge is completely and permanently desiccated by enclosing metallic calcium within the case. Not only does moisture give a surface conductivity which may be several times larger than the dark current, but it also causes electrical polarization as shown by Rankine and Avery.[25]

III. Light Intensity—Current Relation

The source of light is a 400 candle power gas-filled projection lamp, which is moved along an optical bench to obtain different light intensities. Fig. 2*A* gives the data for a typical set of observations of current and light intensity. Fig. 2*B* reproduces the same data by plotting current squared against light intensity. A still more critical graph of the same results is shown in Fig. 3 where the log of the current is plotted against the log of the light intensity. The slope of the line, which is two, gives the exponent of the current.

The relation between photo-current and light intensity was obtained for nine spectral regions by the use of Wratten filters. The experimental method is the same as for white light. The glass of the selenium cell is covered by the filter. The light intensity is in terms of foot-candles of the light falling on the filter. The absolute energy of the transmitted light for each filter could be obtained by multiplying the light energy incident to the filter by a constant which is a function of the transmission of the filter. But

[22] Brown, Phys. Rev. **34,** 201 (1912).
[23] Marc, Zeits. Anorg. Chem. **37,** 459 (1903).
[24] Brown, Phil. Mag. **28,** 497 (1914).
[25] Rankine and Avery, Nature **119,** 338 (1927).

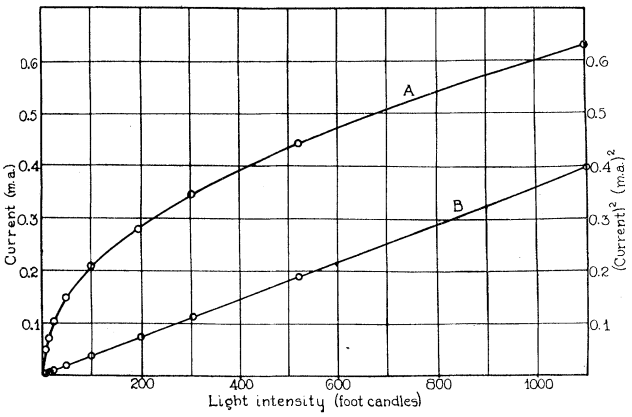

Fig. 2. Variation with light intensity of the photo-current in a selenium cell.

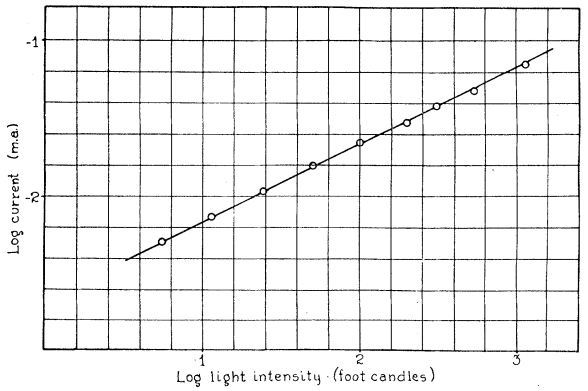

Fig. 3. Variation of the logarithm of the current with the logarithm of the light intensity.

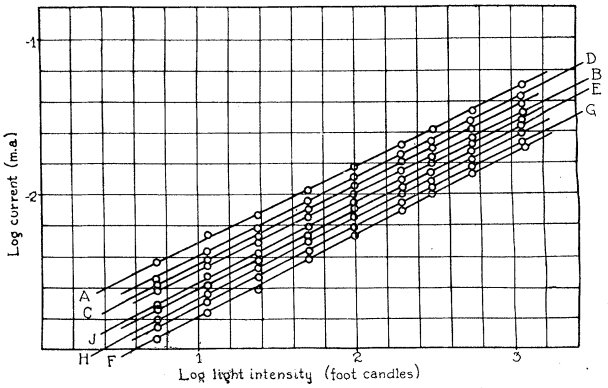

Fig. 4. Variation of the logarithm of the current with the logarithm of the light intensity for light of different spectral compositions.

the relative values give the desired information. In Fig. 4 line A, with 2.04 slope, represents the data for Filter No. 25, Tricolor Red, with transmission from 5800A to infra-red; line B, with 2.02 slope, Filter No. 29, Red, from 6000A to infra-red; line C, with 1.98 slope, Filter No. 50, Blue, from 3600A to 4900A; line D, with 2.00 slope, Filter No. 35, Blue, from 3000A to 4800A with a second transmission band from 6400A to infra-red; line E, with 1.98 slope, Filter No. 45, Green, from 3200A to 3900A and from 4300A to 5500A; line F, with 1.97 slope, Filter No. 53, Naphthol Green, from 4700A to 6300A; line G, with 1.98 slope, Filter No. 49, Blue, from 3600A to 5100A; line H, with 1.96 slope, Filter No. 57, Green, from 4500A to 6400A and from 6700A to infra-red; and line J, with 2.00 slope, Filter No. 74, Green, from 4900A to 5700A. The results, using the nine filters, are shown because they not only indicate the exactitude of the linear relation between the square of the current and the light intensity for various spectral regions, but also the accuracy of the individual readings.

IV. Influence of Temperature

In general, previous investigators have postulated tacitly that the light current and the dark current are of similar nature. In order to study the temperature effects on the light current and dark current separately, a cell was used with a very large dark current, 1 ma. at 100 volts as compared to the corresponding light current of 6 ma. for a light intensity of 100 foot-candles. For the light current experiments the selenium cell was placed in a vacuum thermos bottle, which had not been silvered. At liquid air temperature the light passed through approximately 2 cm of liquid air. For the dark current experiments, the cell was covered with photographic black paper, being placed in a silvered thermos bottle.

For dark condition, at 100 volts, the selenium cell passed a current of 1.08 ma. at 23°C; 6.8×10^{-3} ma. at carbon dioxide snow temperature; and 5.0×10^{-7} ma. at liquid air temperature. The rapidity with which the dark current falls off when changed from room temperature to liquid air temperature is shown by Table I. The third column shows the current at any time

Table I

Decrease with temperature of the "dark" current through selenium, 23°C to −180°C.

Time	Current	Percent	Time	Current	Percent
0 sec.	1.08 ma.	100	2 min.	0.048 ma.	4.4
15	0.38	35.5	3	0.012	1.1
30	0.31	28.7	4	0.0031	0.29
45	0.25	23.2	5	0.00077	0.071
60	0.17	15.7	6	0.00019	0.018
75	0.12	11.1	7	0.00005	0.0046
90	0.093	8.6	10	0.0000005	0.000046
115	0.069	6.4			

in percentage of the current at start of cooling. On submerging the cell the liquid air actively boiled for a period equal to a reduction of the current to about 1 percent. This shows that these results should not be interpreted

as a current temperature lag but as a cooling lag of the selenium cell. If instantaneous cooling were possible, evidence points to the fact that the current would drop to less than 1 percent within a second. The absence of current temperature lag for the dark current is made even more evident in Table II, giving the results on removing the selenium cell from liquid air. During the first 15 seconds the current increases more than 100,000 fold.

TABLE II

Increase with temperature of the "dark" current, −180°C to 23°C.

Time	Current	Percent
0 sec.	0.0000005 ma.	0.000046
15	0.085	7.9
30	0.32	29.6
45	0.66	61.7
60	1.08	100

When the same selenium cell is plunged in liquid air, illuminated with an intensity of 100-foot candles, the results are shown in Table III.

TABLE III

Decrease with temperature of the "light" current, 23°C to −180°C.

Time	Current	Percent	Time	Current	Percent
0 min.	6.15	100	15 min.	9.69	157
3	7.83	126	20	8.85	144
4	8.91	145	25	8.15	133
5	9.92	161	30	7.47	121
6	10.30	168	40	6.95	113
7	10.95	178	60	6.40	104
8	11.00	179	90	5.64	92
9	10.85	177	120	5.02	82
10	10.64	173	180	5.03	82

First, it is noted that at the end of 8 minutes the current has a maximum increase of 79 percent, reaching an equilibrium value, 18 percent decrease, at the end of 2 hours. Secondly, a true time lag is very evident in this cell, in which the thickness of the selenium is approximately 0.025 cm. Repeated observations on different cells gave similar results. Always on cooling the light current increased to a maximum greater than that at room temperature, decreasing to a final value, about 80 percent of the initial value. Table IV

TABLE IV

Increase with temperature of the "light" current, −180°C to 23°C.

Time	Current	Percent
0 min.	5.03	82
10	5.38	87
15	5.69	92
20	6.15	100
25	6.15	100
30	6.15	100

shows data for increasing temperature. Because of the frost on the glass, the first reading was taken 10 minutes after removing the liquid air. Again time lag is noticeable.

V. Theory

On the theory of internal photo-electronic conduction it is possible to calculate the relation between the photo-current and the light intensity. Suppose that light of intensity L falls normally on the surface of the selenium. Let K be the coefficient of absorption of the light by the selenium. Then the amount of light that will reach a layer at distance x within the surface is Le^{-Kx}. If J is the amount of light absorbed in a layer dx in thickness then

$$J = ALKe^{-kx}dx \tag{1}$$

Since the number of photo-electrons N ejected from their orbits is proportional to the light absorbed

$$N = \mu ALKe^{-kx}dx \tag{2}$$

where μ is the proportionality constant. The loss by recombination into the orbits will be $\alpha^2 n^2\ A\ dx$, where n represents the number of electrons per unit volume. This assumes that there are an equal number of electrons and positive ions and that there is random recombination between them. Therefore for equilibrium conditions it follows that

$$\mu ALKe^{-kx}dx = \alpha^2 n^2 A\ dx \tag{3}$$

and hence

$$n = BL^{1/2} \tag{4}$$

Therefore for applied voltage the current will be

$$I = CL^{1/2} \tag{5}$$

The equilibrium condition is reached in a period depending on the average time required for a photo-electron to recombine with a positive ion. The average time of recombination in an ionized gas is a fraction of a second. According to modern theory the time for recombination in a solid should be of the same order as for an ionized gas. This is substantiated by the experimental fact that in a well made selenium cell, with a 100 to 1 ratio, the light current is reduced to less than 5 percent of its previous value within 1 second. In cells where time lag is of the order of hours instead of fractional seconds, the cause must be associated with secondary effects.

The present experimental results for unresolved light are contrary to the theoretical considerations of Pfund[13] and Nicholson[10] who have stated that Eq. (5) does not hold for unresolved light because of the fact that C involves both K and μ, each a function of the wave-length. But it is obvious that when the spectral distribution remains the same for various light intensities, both K and μ are constants. Therefore Eq. (5) should hold in these experiments because the spectral distribution of the light is independent of light intensity.

A photoelectric theory of selenium conductivity would predict a light current practically independent of temperature between 20°C and −180°C; while a chemical allotropic theory would predict a radical change of light current with a change of temperature. In selenium the effect of temperature is different for dark and light current. For a similar temperature difference the dark current is changed 2,000,000 times as compared to 0.2 times for the light current. Also the dark current is reduced to one tenth of its previous value by desiccation. Polarization accompanies large dark current, showing that the dark conducitivity is electrolytic in nature. Also the time lag, the drifting, and the irregularities of the dark current indicate electrolytic conduction. These observations, coupled with the fact that selenium is a hygroscopic substance, indicate that the dark current is spurious, being due to adsorbed vapors.

VI. Conclusions

Experimental results substantiate the conclusion that the photo-conduction in selenium is due to a photo-electric liberation of electrons rather than to an allotropic change from an insulating to a conducting form of selenium. Very exact experimental verification is found for a linear relation between the photo-current squared and the light intensity, both for white light and for different spectral regions. It is shown theoretically that the above relation should hold not only for monochromatic light, but for unresolved light as well. The photo-current is influenced by temperature in a manner similar to the light current in an alkali photo-electric cell. The dark current bears no relation to the photo-current. It disappears with decrease in temperature. It is associated with time lag, drifting, and absence of linear relation between the light current and the square root of the light intensity. The dark current is eliminated practically by the use of a thin film of selenium. These results have been obtained in an attempt to develop a selenium bridge having a high sensitiveness, a large current carrying capacity, and uniformity of operation. A large current has two advantages. It is not necessary to use high sensitivity instruments, in which the accuracy of the results is influenced by insulation leakage. Also a bridge 1800 cm in length averages the results of the 1800 readings for a bridge 1 cm in length.

Research Department,
Westinghouse Elec. & Mfg. Co.,
East Pittsburgh, Pennsylvania,
June 3, 1927.