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IX. *Some Experiments with Selenium Cells.*

By SHELFORD BIDWELL, M.A., F.R.S.*

It is well known that selenium, like sulphur, which it closely resembles in its chemical properties, is capable of existing in several distinct forms, differing greatly in appearance. The modifications most commonly met with are known as the black amorphous or vitreous, the red amorphous, and the crystalline forms. Selenium is, I believe, always supplied commercially in the vitreous condition. Vitreous selenium is as structureless as glass, and, when its surface is smooth and clean, it is very like black sealing-wax in appearance. In thin films, however, it is seen to be transparent and of a ruby-red colour. It melts, after first softening, at a temperature of about 100° C. Red amorphous selenium is a finely divided brick-red powder, which, at a temperature of from 80 to 100° , becomes transformed into the ordinary dark-coloured vitreous form. Crystalline selenium is obtained by keeping melted vitreous selenium at a temperature of from 100° to 200° for some time, the black liquid mass being gradually converted into a hard slate-coloured solid. This form of selenium melts at 217° : it resembles a metal in appearance, and even in the thinnest films it is quite opaque to light.

In the vitreous condition selenium is a practically perfect non-conductor of electricity: so it is also in the powdery condition if perfectly dry. Crystalline selenium, on the other hand, is, according to the books, a good conductor. In comparison with true metals, however, it conducts rather badly. I found some time ago that the specific resistance of a plate of crystalline selenium, which had been annealed for several hours in a glass mould, out of contact with any metal, was 2500 megohms, while that of another specimen annealed in contact with copper electrodes was 0.9 megohm, the lower resistance in the latter case being due, as I then suggested and still think probable, to the formation of copper selenide during the heating.

A very remarkable fact, first published by Mr. Willoughby

* Read December 12, 1890.

Smith in 1873, is that the resistance of crystalline selenium appears to be temporarily diminished by the action of light. This effect is easily shown by means of a small piece of crystalline selenium fitted with wire electrodes and joined up in circuit with a battery and a reflecting-galvanometer. The galvanometer-deflexion is increased when the selenium is illuminated.

In order that the resistance of a so-called "selenium cell" may be kept as low as possible, and the light made to produce a maximum effect, three conditions have to be aimed at. The electrodes should be large; they should be near together; and the selenium, in order to expose a large surface relatively to its volume, should consist of a thin film. Several contrivances have been proposed with the view of fulfilling these requirements. A simple and, I believe, effective one is that which I suggested ten years ago (*'Nature,'* vol. xxiii. p. 58). A fine copper wire is wound upon an oblong strip of mica from end to end, the number of turns being about 20 to the inch: a second wire is then wound on, parallel to the first, the turns of the second wire alternating with those of the first; great care is taken that the two wires do not touch each other anywhere. A thin layer of melted selenium is spread over one surface of the mica, filling the spaces between the wires. The film is first quickly cooled by placing the mica upon any convenient cold surface, then it is crystallized by heating at a temperature of about 200° , and, lastly, it is annealed by gradually lowering the temperature for several hours. A cell made in this manner, with a surface of about 10 sq. cm., is generally found to have a resistance in the dark of from 50,000 to 100,000 ohms. As a rule, those cells which have an unusually low resistance are less sensitive to light than others. In a cell of average quality the resistance is reduced about 50 per cent. by the light of an ordinary gas-flame at the distance of one foot.

I made a number of cells on this plan in the years 1880 and 1881. Up to the end of 1882 they were frequently used, and no material falling off in their sensitiveness was noticed. Thirteen of these cells were laid aside until 1885. They had then for the most part deteriorated more or less,

one or two of them being quite useless. They were again put away until the present year, 1890, when it was found that only one of the thirteen retained its original sensitiveness and resistance unimpaired.* A second one worked fairly well with a feeble current, its resistance with a single Leclanché cell being in the dark 14,000 ohms, and when illuminated by a gas-flame at 12 inches, 8000 ohms; but with a battery of six cells the resistance became variable and unsteady, as if there were a loose contact somewhere, and a continuous boiling noise was heard in a telephone introduced into the circuit. The resistance of the remaining eleven cells had fallen enormously, in some cases to less than 10 ohms, and they were quite insensitive to the action of light. An attempt was made to restore most of them by melting down the selenium and recrystallizing and annealing; but though the resistance could in this manner be brought up again to a high point, the sensitiveness of the renovated cells was in all cases found to be very poor.

Prof. Adams states (Phil. Trans. vol. clxvii. p. 348) that in the course of a year the resistance of most of the pieces of selenium with which he performed his well-known experiments fell very considerably, and it would be of great interest to know what is the cause of this curious phenomenon. In the case of my own cells, I satisfied myself that it certainly was not due to any short-circuiting of the wires by contact; and I suggest that it may be owing to the presence of an excessive amount of conducting selenide formed by the union of the selenium with the metal of the electrodes. Each wire is covered with a layer of selenide, which gradually increases in thickness at the expense of the free, badly-conducting selenium, and thus the resistance of the cell slowly falls. At length the layers of selenide become so thick that the coatings upon the two wires actually meet and touch each other. Thereupon the cell is short-circuited; its resistance no longer depends upon the selenium but upon the metallic selenide, which is a good conductor.

I have in a former paper (Proc. Phys. Soc. vol. vii. p. 129; Phil. Mag. Aug. 1885, p. 178) given reasons for believing

* This cell had the unusually high resistance of 400,000 ohms, reduced by the light of a gas-jet at one foot to 190,000 ohms.

that the presence of a certain amount of metallic selenide is essential to the sensitiveness of a cell, and I have stated my opinion that the true function of the prolonged heating, generally termed "annealing," is the formation of this necessary selenide, which, when a current passes through the cell, is electrolysed, selenium being deposited upon the anode wire. With the weak currents generally used, the quantity of deposited selenium would be very small, and would at once unite with the metal of the electrode. But if a sufficiently strong current were passed, it is conceivable that the selenium might be separated in quantities too great to be disposed of in this manner. Then the free selenium around the electrode ought to be visible. This view is confirmed by a recent experiment. A cell was made last October with new selenium and the usual copper-wire electrodes. It was well annealed, and its resistance was about 50,000 ohms. The cell was connected to a 26-volt battery, and left for two days. At the end of that time the cell presented a remarkable appearance, those portions of the anode wire where the selenium coating happened to be thin being covered with red feathery tufts, some of which had dropped off and fallen upon the paper on which the cell was lying. Ordinary tests showed that the red stuff consisted, mainly at all events, of red amorphous selenium. But it was clearly moist. All very fine powders seem to attract moisture from the atmosphere; but in the present case the moisture appeared to be greater than could be thus accounted for. An examination under the microscope disclosed the presence of a number of minute lumps of a white substance, intermixed with the red stuff. The lumps had the appearance of pieces of calcium chloride which had been exposed to the air, and they were clearly the origin of the moisture. They consisted, no doubt, of selenium oxide or hydroxide, which is probably a deliquescent substance.* This oxide might perhaps be formed by the direct combination of some of the freshly separated selenium with the oxygen of the air, or with that resulting from the electrolysis of traces of water existing in the cell.

In the discussion which followed the reading of my former

* Since the above was written, Prof. S. U. Pickering, F.R.S., has told me that the oxides of selenium are deliquescent.

paper, the late Mr. J. W. Clark took exception to a hypothesis therein put forward as to the probable action of the selenides formed in selenium cells, on the ground that selenide of copper conducted metallically and not electrolytically. This he stated to have been experimentally proved by Hittorf (*Pogg. Ann.* vol. lxxxiv. 1857, quoted by J. W. Clark, *Proc. Phys. Soc.* vol. vii. pp. 119, 120*; *Phil. Mag.* July 1885, pp. 38, 39). But if the amorphous selenium surrounding the anode in my recent experiment was formed otherwise than by electrolysis, it is difficult to imagine why it should be confined to the anode, as was seen to be the fact, and not extend also to the kathode and other portions of the cell. The inference seems to be that copper selenide does conduct electrolytically †.

When the resistance of this cell was tested with the Wheatstone's bridge, it was found to have diminished enormously. It was also not sensibly affected by illumination, but, on the other hand, it appeared to be dependent in a curious way on the direction of the current used in testing. With one Leclanché cell and equal proportional coils of 100 ohms each, the resistance with a current from anode‡ to kathode was 4500 ohms, and with a current in the opposite direction only 2900 ohms. The change occurred with great regularity as often as the current was reversed.

The cell was then connected directly to the galvanometer without any battery, and a very small polarization current from kathode to anode through the cell was indicated. While thus connected, a piece of magnesium ribbon was burnt near the cell. Instantly the spot of light was deflected off the scale by a current in the opposite direction (*i. e.* from anode to kathode internally), returning to its former position as soon as the magnesium was extinguished. This was not a thermoelectric effect, for the approach of a hot brass rod caused a smaller current *from kathode to anode*, which subsided slowly and not suddenly when the rod was withdrawn.

* This paper of Mr. Clark's, though printed in the 'Proceedings' before my own, was in fact read after it.

† The cell with the red amorphous selenium on the anode was exhibited to the meeting.

‡ The wire upon which the amorphous selenium was deposited is here and afterwards called the anode.

Photoelectric currents of this character had been previously observed by Prof. Adams and by Mr. Fritts of New York, but no explanation of their origin has been attempted. Perhaps the behaviour of my cell may suggest the direction in which the source of such currents should be looked for, but I have not yet followed up the inquiry.

In the illustration of lectures it is often desirable to be able to exhibit experimental effects in a striking and attractive manner. The movements of a spot of light upon a scale may be convincing, but they are hardly impressive. Yet the resistance of sensitive selenium cells is so high that the variation, under the influence of light, of currents passing through them cannot easily be demonstrated to an audience in any other manner than by their action upon a reflecting-galvanometer. With sufficient battery-power they may, however, be made to work a delicate relay, and thus to produce indirectly a great variety of startling effects. For example, a selenium cell may be connected with a relay and a battery in such a manner that a bell is rung when the cell is in the dark and ceases to ring when the cell is illuminated; the bell circuit remaining closed when the current through the selenium circuit is below a certain strength, and being broken by the relay when the selenium current is increased by the action of light. It is possible that if selenium cells could be made to retain their sensitiveness for a reasonable time, an arrangement of this kind might receive a practical application. It might be used to give notice of the accidental extinction of railway signal-lamps or of ships' lights; and if the connexions were so made that light and not darkness set the bell in action, it might be employed for the protection of safes and strong-rooms, the mere light of a burglar's lantern being sufficient to give an alarm.

Again, if the relay is connected with an electric lamp instead of a bell, it constitutes a contrivance by means of which a light is provided automatically when required, and extinguished when no longer wanted. It gives us a lamp which will light itself in the dark and put itself out in the light. The relay can be adjusted so that the lamp may be turned out when the external illumination reaches any desired

point, the diffused light of a dull December day being quite sufficient to act upon the selenium *.

But I do not at present attach any serious importance to such practical applications of these devices. I regard them simply as affording somewhat attractive illustrations of the effect of light upon the resistance of selenium.

X. *Experiments in Photoelectricity.* By GEORGE M. MINCHIN, M.A., Professor of Mathematics in the Royal Indian Engineering College, Coopers Hill †.

NEAR the beginning of the year 1877 I commenced a long series of investigations in Photoelectricity, and I was not then aware that M. Becquerel had previously worked at this subject and had obtained some results which I also obtained independently. In the spring of 1880 I made a verbal communication to this Society, illustrated by experiments, on the generation of electric currents by the action of light on silver plates which were coated with collodion and gelatine emulsions of bromide, chloride, iodide, and other salts of silver, as well as with eosine, fluoresceine, and various aniline dyes. A short summary of these results appears in the Report of the meeting of the British Association that year at Swansea. The chief object which I had then in view in prosecuting such experiments was the solution of the problem of producing a photographic image of an object at a distance by means of a instrument which is still imaginary and which I proposed to call a *telephotograph*.

As these experiments have never been published in adequate detail, I propose to begin this paper with an account of them.

Silver Plates.

Let two strips of cleaned silver foil be each fastened on a plate of glass, by means of pitch or other suitable substance; take some finely powdered chloride of silver and shake it up well in a test-tube containing collodion, the emulsion being,

* Experiments with the bell and the lamp were shown at the meeting.

† Read January 16, 1891.