NEGATIVE ION EMISSION FROM OXIDE COATED FILAMENTS

By Henry A. Barton

Abstract

Using a tube described by Smyth,[1] it was discovered that oxide-coated, platinum filaments emit negative ions as well as electrons. These ions were shown to be due not to gas in the tube or to gas absorbed by the filament, but to disintegration of the oxide coating itself. Electro-magnetic analysis of these ions, described in this paper, gave the value of m/e as about 33 with reference to hydrogen ions and indicated that they consisted only of negative, singly charged, molecular oxygen ions. No evidence of the emission of any positive ions was obtained. This negative ion emission apparently begins at a lower temperature than electronic emission, and increases with temperature, but less rapidly than the electronic. The contribution of the negative ions to the space charge is appreciable because of their relatively large mass, causing the space charge limited current for a given voltage to be less than for a similar non-coated platinum filament. Certain observations by other experimenters are discussed and shown to be in support of the above conclusions.

During a study of the ions formed by electron impact in argon,[2] the writer observed negative ions in large numbers. These were first thought to be formed by argon atoms but subsequently it was discovered that they were produced even when no argon was present in the experimental tube. A more careful examination of their behavior indicated that they came from the filament and were of smaller mass than argon atoms. The filament then in use was a strip of platinum coated with barium and strontium oxides. After substituting a thoriated tungsten filament the negative ions were no longer observed.

More recently a direct study of this phenomenon has been made. The experimental tube was the one described recently by Smyth[1] modified only by the removal of the gauze electrode next to the filament. The result was a simple arrangement for the accurate electromagnetic analysis of the particles from a hot source. A new platinum strip was mounted as a filament and a careful search made for negative ion emission. None was observed. The strip was then taken out and given an oxide coating by the following process: Two sticks of paraffin one containing $BaCO_3$ and the other $SrCO_3$ were touched to the strip

[1] Smyth, Phys. Rev. **25,** 452 (1925).
[2] Barton, Phys. Rev. **25,** 469 (1925).

alternately while it was maintained at a temperature just too low to give visible radiation. After each application time was allowed for the paraffin to burn off. When a good coating was obtained, the strip and leads were heated red hot in a flame to remove the last traces of hydrocarbons. They were then immediately installed and the tube evacuated. In the subsequent work the pressure in the tube was of the order of 10^{-4} mm.

With the filament at red heat, negative ions of the same mass as before were again observed in large numbers, thus proving that the source of these ions was the oxide coating. The range of m/e values from about 5 to 95 times the value for the hydrogen nucleus was ex-

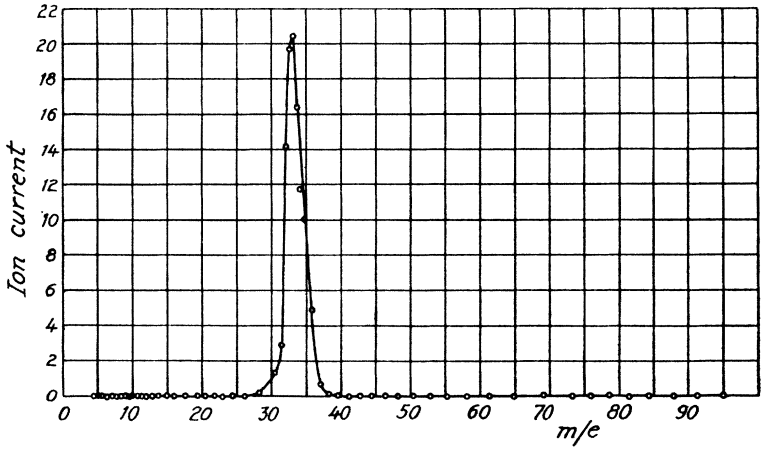

Fig. 1. Mass spectrum of negative ions.

amined and only one group of negative ions was detected. A typical mass spectrum is given in Fig. 1. The fields were then reversed and an attempt made to detect positive ion emission. The m/e ranges examined included those corresponding to barium and strontium atoms, each with single or double charge, and also the hydrogen range. No positive ions whatever were observed. This checks a previous result with the first coated filament.

Identity of the ions. The negative ions observed had an apparent m/e value of 33. The m/e scale had been calibrated by known positive ions and may have been slightly inaccurate for negative ions because of lack of perfect reversibility of the electromagnet used. However, C_2^-, $(CO)^-$ and A^- ions were certainly not present. The paraffin sticks were tested for chlorides and none found to be present. The conclusion, therefore, is that the ions are oxygen molecules, i.e. O_2^-.

Other results. The apparatus was not adapted to a careful study of thermionic emission and no further results were obtained except some determinations of the variation of ion current with the temperature. These merely indicated inconclusively that the ions were first emitted at a temperature too low for electron emission and increased in number as the temperature was raised well into the range in which the electron current was large.

The evidence does not clearly indicate whether the O_2 molecules came off the filament already charged or picked up an electron after emission. The fact mentioned in the previous paragraph favors the former process.

The objection may be raised that not enough time was allowed for the absorbed gases in the oxide coating to be evolved. This objection might be valid in the case of the second filament but not in the case of the first, which had stood continuously in a high vacuum (except for argon at low pressures) for several months and had been burned two or three hundred hours at least.

Discussion

The above conclusions receive indirect support from the earlier experiments of several observers. For example, Wehnelt and Jentsch[3] observed that at a given temperature the current from a Wehnelt cathode never quite reached a saturation value as the applied voltage was raised. This is different from the behavior of a pure metal filament in a high vacuum but analogous to its behavior in the presence of a small amount of gas. In other respects oxide filaments have similar properties to pure metal filaments so it is quite likely this difference is due to the oxygen gas which is produced. The nature of the action is not clear.

Fredenhagen[4] observed (1) that the oxide disappears much more rapidly if the filament is heated with a properly directed field applied than with no field, (2) gas is given off when the cathode is in action, and (3) the metal under surface shows corrosion as if an alloy had been formed with the residual barium and strontium metals. The first of these suggests strongly the formation of O_2^- ions. This is also supported by Horton's[5] conclusion that the conductivity of hot oxides is partly electrolytic. The third observation is in line with the recent suggestion

[3] Wehnelt and Jentsch, Verh. d. D. Phys. Gesell. **10,** 605 (1908).
[4] Fredenhagen, Phys. Zeits. **15,** 21 (1914).
[5] Horton, Phil. Mag. **11,** 505 (1906).

of Koller[6] that the emissive property of the Wehnelt type of filament is due to the deposit of a surface film of the metal reduced from the oxide.

The nearest approach to the writer's work has been done by Schmidt[7] and his collaborators. They found that no positive ions were given off by heated oxides of cadmium and zinc although many salts of these metals do yield positive ions. It appears to be characteristic of oxides that the metal atoms are not emitted, at least not as ions. In regard to the emission of negative particles by these oxides, Schmidt merely mentions their action as Wehnelt cathodes emitting electrons. The construction of his tube apparently did not permit distinguishing between electrons and negative ions.

The effect of the negative ions in contributing to the space charge is very simple. Where the current as limited by space charge consists of two parts, i due to electrons (mass m), and I due to negative ions (mass M), Langmuir's equation for cylindrical electrodes may be rewritten

$$i\sqrt{m}+I\sqrt{M}=(2\sqrt{2}/9)\sqrt{e}\,V^{3/2}/r\beta^2$$

where e is the electronic charge, V the applied voltage, r the radius of the receiving electrode and β a geometrical constant. Since I is small compared with i, the latter is practically the observed total current. Therefore the total current is given approximately by

$$i=\frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\,\frac{V^{3/2}}{r\beta^2}-I\sqrt{\frac{M}{m}}.$$

Although I is small, $\sqrt{M/m}$ is quite large so that to obtain the same space charge limited current from an oxide coated filament as from a plain filament, it is necessary to apply a higher voltage. Katsch[8] has recently compared filaments of several types in identical geometrical situations. As would be expected from the above consideration, he finds it necessary to apply a larger potential to get the same current in the case of oxide coated filaments than in the case of tungsten or thoriated tungsten filaments.

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[6] Koller, Phys. Rev. **25**, 671 (1925).
[7] Schmidt, Ann. der Phys. **75**, 337 (1924); contains summary of earlier papers.
[8] Katsch, Zeits. f. Techn. Phys. **5**, 11, 505 (1924).