CCCXIII.—*The Electrolytic Deposition of Tungsten at a Mercury Cathode.*

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FÉRÉE (*Bull. Soc. chim.*, 1898, **19**, 213) is the only worker on this subject who has claimed to deposit tungsten electrolytically from an aqueous solution. He stated that at a mercury cathode tungsten amalgam may be prepared by the electrolysis of the trioxide in hydrofluoric acid solution, but he gave no other particulars. Rosenheim and Bernhardi Grisson (*Intern. Congr. Appl. Chem.*, 1911, **10**, 120) electrolysed solutions containing 10% of tungsten trioxide in 50% hydrofluoric acid at *C. D.*'s of less than 0·5 amp./cm.^{2}, and also in alcoholic solutions of hydrogen chloride, but obtained no tungsten; they infer that their results contradict those of Férée, but, although details are not available, it is improbable that he used such concentrated acid or such low current densities, for, in the deposition of chromium and molybdenum, he used *C. D.*'s of 2·73 and 5 amp./cm.^{2}, respectively. Fischer (*Z. anorg. Chem.*, 1913, **81**, 170) failed to obtain a deposit of tungsten by electrolysing various aqueous solutions; he examined a German patent claiming the deposition of the metal from a solution of a pertungstate, and concluded that the deposit was oxide and not metal. McCay and Furman (*J. Amer. Chem. Soc.*, 1916, **38**, 640) obtained no deposit from solutions of tungsten trioxide in mixtures of hydrofluoric acid with nitric or sulphuric acid. Mann and Halvorsen (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 493), using an iron cathode and various aqueous solutions, Collenberg and Backer (*Z. Elektrochem.*, 1924, **30**, 230), using cathodes of mercury and platinum, solutions of hydrochloric acid, and *C. D.*'s of 0·008—0·096 amp./cm.^{2}, and Neumann and Richter (*ibid.*, p. 474), using solutions of double cyanides and oxalates of tungsten at a mercury cathode, all failed to obtain deposits of the metal. Also, Collenberg and Nilsson (*ibid.*, 1925, **31**, 555) were unsuccessful with solutions of oxalic acid, cathodes of lead, platinum, tin, or mercury, and *C.D.*'s of 0·0044—0·035 amp./cm.^{2}.

The general similarity between metallic tungsten and molybdenum, and the ease with which chromium and molybdenum may be deposited from sulphuric acid solutions at a mercury cathode, led us to suppose that the deposition of tungsten should be easily effected once the right acid concentration and *C.D.* had been found. On the other hand, Russell and Rowell (J., 1926, 1884) found that, with conditions suitable for the deposition of molybdenum, only sufficient tungsten to show its catalytic effect was deposited; the amount obtained was less than could be weighed on an ordinary balance.

The failure of the foregoing attempts is ascribed to the feebly basic character of the oxides. Tungsten salts in aqueous solution are almost completely hydrolysed, so that tungsten ions can exist in appreciable amount only in presence of high concentration of acids; in such solutions, however, the whole of the current is devoted to producing hydrogen and no metallic deposit is obtained. Another difficulty in the use of solutions of sulphuric acid is that the tungsten compound is only apparently in solution in them; sooner or later, according to the acid concentration, tungsten trioxide is precipitated; moreover, most of the tungsten is probably in the colloidal form and would not therefore be deposited at a cathode as the metal. Férée probably used hydrofluoric acid because of the comparatively great solubility of tungsten trioxide therein: 100 g. of the ordinary concentrated acid at 50° dissolve 53·7 g. of the oxide, whereas 100 g. of concentrated hydrochloric acid at 50° dissolve only 0·36 g., and in concentrated sulphuric acid the oxide is insoluble.

We have therefore confined our work to solutions in hydrofluoric acid. We confirmed Férée's statement that tungsten may be deposited at a mercury cathode from hydrofluoric acid solution, and find that the most favourable conditions are as follows: acid concentration 4·6*N*, temperature 95°, *C.D.* 0·65—1·0 amp./cm.^{2}. A second acid must not be present.

EXPERIMENTAL.

Satisfactory vessels resistant to the action of hydrofluoric acid and ozone up to the temperatures used in the electrolysis were obtained either by machining a block of " Bakelite " or by soaking an ordinary Soxhlet extractor in " Bakelite " varnish and then stoving it at a suitable temperature. The former, a cylinder 10 cm. high, with outside and inside diameters of 4·1 and 2·3 cm., respectively, was mechanically stronger than the latter, but its thickness made the cooling of its contents during an experiment more difficult. Near the bottom of either vessel, a small hole sealed with " Bakelite " varnish admitted without leak the platinum wire connected to the cathode, which was formed by 2 c.c. of mercury, at the bottom of the vessel. Vertically above the cathode was fixed the anode of platinum (4 cm.^{2} in area, and either plain or coated as described below), at various distances depending upon the temperature at which it was required to carry out the electrolysis. Loosely fitting stoppers of platinum prevented undue evaporation of electrolyte during the experiment.

Before using the "Bakelite" vessels, we tried lining ordinary vessels with various waxes and with acetyl cellulose, but none of these was satisfactory in use. We also tried various carbon and graphite anodes, but they disintegrated too rapidly to be suitable. Platinum anodes usually lost 0·01—0·02 g. in an 8-hour experiment according to the concentration of acid employed (1—6*N*-hydrofluoric acid), the electrolyte being at about 90°, but a coherent film of lead dioxide deposited on the platinum made it much more resistant to corrosion for concentrations of the acid up to 3*N*, the loss of weight during an 8-hour experiment being then only 0·002 g.; for higher concentrations of acid, however, the uncoated platinum was the more resistant. In the experiments to be described, the anode was chosen so as to sustain the minimum loss under the conditions.

During the electrolysis, the solution tended to become more concentrated owing to loss of water as hydrogen and oxygen, but its volume was kept constant by the addition of water three or four times during an 8-hour experiment, and its acidity, determined by titration with standard sodium hydroxide, was then approximately the same at the end as at the beginning. The electrolyte in the experiments to be described was prepared from sodium tungstate and hydrofluoric acid and contained 0·47 g. of tungsten in 25 c.c.; it was kept at a constant temperature by a water jacket.

The deposition of tungsten in the most favourable circumstances was markedly slower than that of molybdenum, which itself is a very inefficient process. In no case did we succeed in depositing more than 20% of the dissolved tungsten on the mercury during a period of 8 hours.

It was found impracticable to determine the amount of tungsten deposited by means of volumetric estimation in the electrolyte at the conclusion of the experiment. Moreover, as the cathode was sometimes contaminated with platinum, resulting from corrosion of the anode, the tungsten could not be determined by weighing the cathode before and after the experiment or by weighing the residue left after the mercury had been distilled off. It was found simplest to filter the cathode amalgam through chamois leather or through a ground-glass Gooch filter; owing to its inappreciable solubility in mercury, tungsten remains quantitatively as a paste. This was treated with aqua regia, and the resulting yellow tungsten trioxide was separated by filtration from the solution of mercury salts, and then either (i) carefully washed, dissolved in a known volume of standard sodium hydroxide solution, and the excess of alkali determined by titration, or (ii) dissolved in alkali, acidified with dilute sulphuric acid, reduced by zinc amalgam, and titrated with standard potassium permanganate. Both methods gave very similar results.

Colour Changes during the Reduction.—In contrast to the reduction of molybdenum electrolytically (see preceding paper), no colour changes were noticed as the reduction proceeded. In these experiments there was always a large excess of hydrofluoric acid, and such solutions, even when shaken with zinc amalgam, did not show any colour change. If, however, the hydrofluoric acid is not in excess, the reduction of tungsten solutions shows the following sequence of colours : blue, dark blue, blue-black, purple-blue, and dark purple. The presence of colour is obviously connected with the relative amounts of tungsten salt and hydrofluoric acid.

Experiments were conducted over the following ranges of conditions : hydrofluoric acid, 1·8—5·7*N* ; temperature, 30—95° ; *C.D.*, 0·58—1·7 amp./cm.^{2}. Typical results are given below, the tungsten deposited being stated as a percentage of the total (0·47 g.).

Effect of Acid Concentration.—Time 8 hrs.; temp. 90° ; *C.D.* 0·58 amp./cm.^{2}.

Conc. of acid, *N*	1·8	2·6	3·3	4·0	4·6	5·2	5·7
Tungsten deposited, %	2·8	4·4	15·4	18·8	19·4	16·6	15·4

It is seen that in these circumstances the optimum acidity is approximately 4·6*N*. Rosenheim and Bernhardi Grisson (*loc. cit.*), with a similar current density but in 50% acid, obtained no deposit of tungsten.

Effect of Temperature.—Time 8 hrs.; conc. of acid 4*N* ; *C.D.* 0·63 amp./cm.^{2}.

Temp.	30°	40°	60°	85°	95°
Tungsten deposited, %	3·5	5·6	10·5	16·8	19·5

It is clear that under these conditions the yield is greater the higher the temperature.

Effect of Current Density.—A few experiments only have been done on the relation between the yield of tungsten in a period of 8 hours and the *C.D.* These show that the former is little affected by the latter over the range investigated, *viz.*, 0·58—1·7 amp./cm.^{2}, the maximum variation being 30%, and the best range about 0·65—1·0 amp./cm.^{2}.

Effect of a Second Acid.—A second acid in the electrolyte totally inhibited the deposition of tungsten if it had a concentration of the same order as that of the hydrofluoric acid. For instance, at 90°, and with a *C.D.* of 0·63 amp./cm.^{2}, no tungsten was deposited in 8 hours from a solution of 1·8*N*-hydrofluoric and 2*N*-hydrochloric acids, or of 2·6*N*-hydrofluoric and 2*N*-sulphuric acids. The effect of smaller quantities of second acids has not yet been investigated.

This negative result is in agreement with that of McCay and Furman (*loc. cit.*).

Summary.

The conditions for the electrolytic deposition of tungsten have been investigated. In view of the failure of all previous workers, except Férée, to effect deposition of tungsten from aqueous solution, experiments have been confined to a cathode of mercury and solutions of hydrofluoric acid. Férée's general result is confirmed. The best conditions for depositing tungsten are a temperature of 95°, an acid concentration of approx. 4·6*N*, and a range of current densities of 0·65—1·0 amp./cm.^{2}. Hydrochloric or sulphuric acid must not be present in the electrolyte.

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