CCCXII.—*The Electrolytic Deposition of Molybdenum at a Mercury Cathode.*

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LITTLE systematic investigation of the conditions under which molybdenum may be deposited electrolytically has been published. It seemed likely, from work on the corresponding but simpler problem, *viz.*, the electrolytic deposition of chromium, that success would depend upon careful choice of current density, nature and concentration of acid, and nature of cathode.

Férée (*Compt. rend.*, 1896, **122**, 733) was the first to effect the reduction of molybdenum in aqueous solution : he used a solution of the trioxide in hydrochloric acid of concentration slightly greater than *N*, a mercury cathode, and a *C.D.* of 5 amp./cm.^{2}, no molybdenum being deposited with *C.D.*'s less than 2·84 amp./cm.^{2}. Chilesotti (*Z. Elektrochem.*, 1906, **12**, 146, 173, 197), working with solutions of molybdenum trioxide in hydrochloric or sulphuric acid, investigated the effect of *C.D.*, acid concentration, cathode material, and temperature, but did not succeed in any circumstances in depositing molybdenum at the cathode. His *C.D.*'s (0·047—0·204 amp./cm.^{2}) were small compared with those of Férée, and his experiments were not continued for more than 9 hours. Myers (*J. Amer.*

Chem. Soc., 1904, **26**, 1129) obtained a quantitative reduction of molybdenum at a mercury cathode from a solution of sodium molybdate in 1·8*N*-sulphuric acid in 14—20 hours with *C.D.*'s of 0·17—0·28 amp./cm.^{2}.

Our preliminary experiments clearly indicated that the most suitable cathode was mercury. The published work also suggested strongly that sulphuric acid would be more effective than hydrochloric, and it has the further advantage over hydrochloric acid of changing little in concentration during a prolonged electrolysis. As a result of varying different factors, we found that molybdenum can be deposited electrolytically on a mercury cathode over a wide range of *C.D.*'s and acid concentrations. The time for completion of the electrolysis was found to be little affected either by altering the temperature of the electrolyte or by rotating the anode.

EXPERIMENTAL.

The apparatus used was essentially that recommended by E. F. Smith ("Electroanalysis," 1919, p. 172), *viz.*, a glass tube, 12 cm. high and of 2·5 cm. internal diameter, containing 2 c.c. of mercury connected by a platinum wire through the glass to a sheet of copper connected to the negative terminal of the cells. The anode was platinum foil, 4 cm.^{2} in area, suspended by a platinum wire sealed into a thistle tube which closed the mouth of the vessel sufficiently to prevent evaporation and contamination of the solution. With high *C.D.*'s the cell required to be cooled, and this was effected by cold water in the ordinary way. Standard solutions of sodium molybdate were prepared by dissolving 3·00 g. of molybdenum trioxide in 40 c.c. of *N*-sodium hydroxide and diluting it to 200 c.c. with water: 10 c.c. portions (containing 0·1 g. of molybdenum) were employed in each of the experiments to be described. The required concentration of acid in each portion was attained by the addition of drops of 33*N*-sulphuric acid, a blank, not electrolysed, being titrated with standard sodium hydroxide. In no case was appreciable change in acid concentration caused by the electrolysis, the titres before and after the electrolysis being the same within the experimental error. The *C.D.* was kept constant within an error of 5%. The temperature at which electrolysis took place varied from 35° at low *C.D.*'s to 90° at high. As preliminary experiments showed that the effect of temperature on the course and duration of the electrolysis was very small, no attempt was made to regulate the temperature beyond the prevention of boiling.

Colour Changes during the Reduction.—Usually immediately after the electrolysis was started the solution next the anode became blue and that near the cathode green. In dilute acid solutions (approx. N) these colours soon merged in a blue-green, changing to green, dark brown, and an increasingly lighter brown as reduction proceeded to completion. In more concentrated acid solutions ($2N$, and upwards) the dark brown colour was reached without apparently going through the green stage; it became increasingly lighter as reduction proceeded to completion, but did not change further when the reduction was incomplete, whereas in dilute acid in the latter case the solution sometimes remained brown, and at other times blue-green. The initial blue colour was identified as being due to molybdenum molybdate, the green to tervalent molybdenum, and the brown to a stage of valency between 4 and 5, being probably raised from the tervalent stage by the action of anodic oxygen. These stages in the reduction, and also the final one when electrolysis was complete, were identified by reducing the solution by zinc amalgam until the green tervalent stage was reached and titrating the reduced solution with standard potassium permanganate solution. Myers (*loc. cit.*) proved that his electrolyses were complete by showing that the weight of the amalgam had increased by that of the molybdenum known to have been present in solution, but our test, in which the solution is shaken with zinc amalgam, is more sensitive, for a quantity of molybdenum (approx. 10^{-4} g.) too small to be identified by ordinary qualitative tests shows itself by its catalytic effect on the reaction $2H \longrightarrow H_2$ initiated by the zinc of the amalgam on very dilute acid, in a manner similar to that found by Russell and Rowell (J., 1926, 1884) for tungsten.

Summary of Results.—Experiments were conducted with variations of *C.D.* over the range 0·10—1·00 amp./cm.^{2}, and of concentration of sulphuric acid over the range 0·66—$10N$. More than 100 separate electrolyses were carried out, and the results are summarised in the table below. In the second column are given the limits of acid concentration for complete reduction within 48 hours, the third column gives the corresponding range of times, and the last gives the concentration of acid effecting the quickest reduction.

C.D., amp./cm.^{2}.	Limits of acid conc., N.	Time, hours.	Normality corresponding to shortest time.
0·25	1·05—2·00	15 —20	1·05
0·30	1·00—3·50	4 —16	1·2
0·40	1·00—3·50	3·5—30	1·25—1·35
0·50	1·00—4·20	1·5—12	1·2
0·60	1·00—5·00	0·7— 6	1·15—1·4
0·75	1·0 —6·0	1·0— 6	1·4
1·00	1·0 —8·0	0·8—15	1·0—1·4

In one case only was an electrolysis complete from a solution of acidity appreciably less than N, namely, with a concentration of

0·8*N* and a *C.D.* of 0·1, and this required 6 days for completion; on the other hand, with the same *C.D.*, the quickest reduction (38 hours) was effected by *N*-acid. Again, whereas with a *C.D.* of 0·6 the electrolysis was complete in 80 minutes at an acid concentration of 1·0*N*, it was incomplete after 5 hours at a concentration of 0·95*N* and after 10 hours at 0·85*N*.

Other results (not shown in the table) also show that as the acidity increases above 2*N*-sulphuric acid the speed of reduction falls off—more slowly at high current densities than at low. Also in solutions of acid concentration between 1·0 and 5·0*N*, a rise in *C.D.* from 0·1 to 0·6 amp./cm.^{2} decreases the time required for complete electrolysis. In this range of acidity, a further increase in *C.D.* up to 1·0 was found to have little effect on the time required for complete electrolysis, but with increase in the strength of the acid the increase of *C.D.* from 0·6 to 1·0 had a marked effect: with 6*N*-acid, the reduction at *C.D.* 0·6 was incomplete after 25 hours, at *C.D.* 0·80 it was complete in 6 hours, and at *C.D.* 1·0 in 4·5 hours.

From the table it is seen that the best conditions for depositing molybdenum from sulphuric acid solution at a mercury cathode are a normality of 1·20—1·40 and a *C.D.* of 0·6—1·0 amp./cm.^{2}; the reduction is then complete in one hour. It is seen also that Myers's results (*loc. cit.*) are in close agreement with ours for similar *C.D.*'s, but his method is slow and inefficient because his acid was too concentrated and his *C.D.* too low. But even in the best conditions which we have found the current efficiency is very small.

The optimum acid concentration for the precipitation of molybdenum is seen to be more than twice that for chromium in corresponding conditions, *viz.*, 0·6*N*-sulphuric acid, as found by Kollock and Smith (*J. Amer. Chem. Soc.*, 1905, **27**, 1265).

Further experiments have confirmed the inference from the results summarised above that acidity and not *C.D.* is the important factor in deciding whether or not the molybdenum will be deposited at the cathode. With 1·25*N*-sulphuric acid, molybdenum can be deposited completely with *C.D.*'s as low as 0·01 amp./cm.^{2}; for the deposition of 0·1 g. of metal about 400 hours are required, and at such low *C.D.*'s the time is roughly inversely proportional to the *C.D.* for the deposition of a given amount of metal. In hydrochloric acid solution, on the other hand, it is clear from the work of Férée (*loc. cit.*) that current density is the important factor; we confirmed his observation that when this is less than 2·84 amp./cm.^{2} no molybdenum is deposited: even after 96 hours at a *C.D.* of 0·25 amp./cm.^{2}, the solution remained blue-green, and the weight of the cathode at the end of the experiment was the same as at the beginning. With this small *C.D.*, however, a very small amount of molybdenum actually was deposited, as was easily ascertained by its catalytic effect on the action between zinc and acids.

Deposition by Use of a Rotating Anode.—It was expected that the time for complete deposition of molybdenum would be materially shortened by the use of a rotating anode, but one of the ordinary type having 400—800 r.p.m. effected no marked diminution in this time or any widening of the ranges of acid concentration and *C.D.* Some comparative experiments, summarised below, show that, except in one case, in which the stationary anode is markedly quicker than the rotating one and gives the shortest time in the series, the times in the different circumstances are not dissimilar, and in view of this result the matter was not investigated further.

C.D., amp./cm.^{2}.	Acid conc., *N*.	Time (hrs.) for complete reduction.	
		Stationary anode.	Rotating anode.
0·50	0·85	(Incomplete)	(Incomplete)
0·50	1·4	2·5	2·0
0·60	1·25	0·7	1·2
0·60	1·5	1·25	1·25
0·60	4·0	6	13
0·75	1·15	1·3	1·0
0·75	1·4	1·0	1·5
1·00	2·0	1·3	1·0

Summary.

The conditions for the electrolytic deposition of molybdenum have been investigated : the most suitable cathode is mercury, the best current densities are 0·6—1·0 amp./cm.^{2}, and the best acidities 1·2—1·4*N*-sulphuric acid.

Under these conditions the time necessary for the deposition of 0·1 g. of molybdenum is about 50 minutes; the use of a rotating anode does not shorten this time.

In effecting the deposition, acidity is a more important factor than current density with sulphuric acid solutions. This result is in contrast with Férée's work with hydrochloric acid solutions, where the opposite holds.

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