ART. XXIII.—*The Material and Shape of the Rotating Cathode*; by H. E. MEDWAY.

[Contributions from the Kent Chemical Laboratory of Yale University—CXXX.]

IN a previous article from this laboratory* a method has been described for the rapid, electrolytic precipitation of metals upon a rotating platinum crucible made to serve as a cathode. In the present paper is given the record of experiments with other and cheaper metals, used in place of the more expensive platinum, as well as cathodes in the form of discs.

Experiments were made with a silver crucible of 50^{cm^3} capacity, carefully cleaned, dried at 100° C., weighed and adjusted to the rubber stopper which serves to hold the crucible and press against its inner wall two platinum strips which make the electrical connection.

Into the electrolytic cell was put an acidulated solution of copper sulphate, standardized by deposition of copper upon the rotating crucible of platinum.

Deposition upon Silver.

	Copper taken. grm.	Copper found. grm.	Error. grm.	Current. Amp.	N. D. 100.	Time. min.
(1)	0·1088	0·1086	−0·0002	2·	6·6	15
(2)	0·1088	0·1090	+0·0002	2·	6·6	15
(3)	0·1088	0·1084	−0·0004	1·5	5·	15
(4)	0·1088	0·1085	−0·0003	2·	6·6	15
(5)	0·1088	0·1080	−0·0008	2·	6·6	15
(6)	0·1041	0·1041	+0·0000	2·	6·6	15
(7)	0·1041	0·1046	+0·0005	2·	6·6	15
(8)	0·1041	0·1039	−0·0002	2·	6·6	15

The results of these experiments would seem to indicate that the use of a silver crucible leaves little to be desired so far as accuracy is concerned.

To remove the copper from the crucible, the deposit was rubbed off as much as possible and the rest dissolved in a strong boiling solution of hydrochloric acid, and this was accomplished with but trifling loss of silver, as is shown in the statement below:

	I.	II.
Weight of crucible before treatment	36·0089	36·0062
Weight of crucible after treatment	36·0062	36·0041
Loss of silver	0·0027	0·0021

---

* Gooch and Medway: This Journal, xv, 320, 1903.

Since the crucible should in any event be weighed before each determination, such small loss does not seriously affect the availability of the silver crucible as a substitute for platinum.

Similar experiments were made with a nickel crucible of 50^{cm^3} capacity, under a procedure exactly the same as that described, with the results as recorded.

Deposition upon Nickel.

	Copper taken. grm.	Copper found. grm.	Error. grm.	Current. Amp.	N. D. 100.	Time. Min.
(1)	0·1041	0·1028	−0·0013	1·5	5·	15
(2)	0·1041	0·1054	+0·0013	2·	6·6	12
(3)	0·1041	0·1036	−0·0005	2·	6·6	15

These results show that while nickel may be employed as a cathode, too much reliance must not be placed upon results obtained by its use when the greatest exactness is required. Care must also be taken in drying the crucible, since nickel is very easily oxidized with a consequent increase in weight. The deposit of copper was removed from the crucible with nitric acid, with considerable loss of nickel, as the following will show:

	I.	II.	III.
Weight of nickel crucible before treatment	17·6478	17·6161	17·6091
Weight of nickel crucible after treatment	17·6161	17·6091	17·5932
Loss of nickel	0·0317	0·0070	0·0059

So it appears that, while the silver crucible may with some economy and without sacrifice of accuracy be substituted for the platinum crucible used as a rotating cathode in the electrolytic determination of copper, the ease with which the crucible of nickel is attacked, both during the analytical process and in the subsequent removal of the deposit, is a bar to the use of that metal for the rotating cathode.

Shepherd* recommends the use of the ordinary disc anode of platinum as the rotating cathode, in place of the platinum crucible, while a stiff platinum wire, carried in semi-circular conformity to the edge of the disc cathode, serves as the anode.

According to my experience with this form and adjustment of apparatus, the deposits obtained are not so adherent as might be desired and tend to crumble away from the edge of the disc; and the same thing is true of discs of copper and silver. The probable reason for failure to obtain an adherent

---

* Jour. Phys. Chem., vii, 508, 1903.

deposit is that the edge of the disc, being nearer the anode, receives more current and larger deposit of copper than the central portions, with the consequence that the deposit upon the edge, built out and fragile, tends to break off under the rapid rotation of the disc. To remedy this defect, I have used for an anode a strip of platinum extending across the cell under and parallel to the rotating disc, so that the current may be equalized all over the disc. With the apparatus arranged in this manner, the following very good results were obtained in the precipitation of copper.

Deposition upon the Platinum Disc.

	Copper taken. grm.	Copper found. grm.	Error. grm.	Current. Amp.	N. D. 100.	Time. min.
(1)	0·0670	0·0672	+0·0002	2·	12	15
(2)	0·0670	0·0668	−0·0002	2·	12	15
(3)	0·0670	0·0666	−0·0004	2·	12	15
(4)	0·0670	0·0671	+0·0001	2·5	15	15
(5)	0·0670	0·0670	±0·0000	2·	12	15

The attempt to substitute aluminum for platinum, though the former metal has been recommended by Hough,* as material to receive the deposit, was not successful, owing probably to the film of aluminum oxide always present. Various measures were taken to remove this film—e. g., the aluminum was treated with hydrochloric acid and quickly transferred to the solution, a few drops of hydrofluoric acid added before the current was passed—but all to no avail, the copper falling off as fast as deposited.

From my experience, it seems that the disc is inferior to the crucible for use as a rotating cathode. Not only does the disc fail to hold the deposited copper as well as the crucible, but there are difficulties of manipulation which render the drying and weighing of the deposit upon the disc comparatively inexact.

---

* Jour. Am. Chem. Soc., xx, 302.