THE INFLUENCE OF THE PHYSICAL CONDITION OF METALS ON CATHODIC OVERVOLTAGE.

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The single potential difference necessary to cause the evolution of hydrogen from electrolytes on the surface of cathodes of various metals has been extensively investigated by Caspari,* Coehn and Dannenberg,† Coehn and Osaka,‡ Tafel,§ Kaufler,|| Müller,¶ Nutton and Law,** and others. In some cases the nature of the surface of the cathode, whether smooth or of finely divided metal, has also been observed. Apart from this, however, no systematic measurements seem to have been made on the influence of the physical state of the metal, such as the effect of the degree of hardness and its previous treatment generally.

In the present research determinations were made of the cathodic overvoltage on metals in the different physical conditions that result from electrodeposition, by hardening and annealing, and by drawing into wires. Comparative results only were aimed at, while such factors as temperature and current density were kept constant. The change of overvoltage with time, which is very marked, was also observed.

The overvoltage values are referred to those with a cathode of platinised platinum as zero, and hence denote the excess of voltage necessary for the separation of hydrogen above that in the case of a cathode of platinised platinum under the same experimental conditions.

Method of Determining the Overvoltage.

The anode in all the experiments consisted of a polished platinum electrode of 25 sq. cm. area. The electrolyte consisted of decinormal sulphuric acid, and the measurements were made at room temperature unless otherwise stated. The cell containing the anode and the cathode to be studied was connected in series with two accumulators and a regulating resistance, a milliammeter being inserted to measure the current. The solution behind the cathode was connected through a syphon with that of a normal calomel electrode, and the e.m.f. between the terminal of the latter and that of the cathode of the electrolytic cell was measured by the potentiometer method, a capillary electrometer being used as null instrument. The potentiometer was standardised against a cadmium cell which, on comparison with a standard, was found to give 1.021 volts.

The e.m.f. between the normal electrode and the cathode that was being

* *Z. Physik. Chem.*, **30**, 89 (1899).

† *Ibid.*, **38**, 609 (1901).

‡ *Z. anorg. Chem.*, **34**, 86 (1903).

§ *Z. physik. Chem.*, **50**, 641, 713 (1905).

|| *Z. Elektroch.*, **13**, 635 (1907).

¶ *Ibid.*, **13**, 681 (1907).

** *Trans. Faraday Soc.*, **3**, 50 (1907).

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examined could then be directly evaluated. The difference in the values obtained when using a cathode of platinised platinum and a cathode of any other metal gave directly the overvoltage with that metal.

At the current density usually employed—15 milliamperes for a cathode area of 25 sq. cm.—a visible evolution of hydrogen occurred.

In some experiments abnormally low values were obtained for the cathodic overvoltage on first passing the current, which was probably due to the existence of a film of oxide on the surface of the metal. These cases could be recognised by the rate at which the overvoltage rose with the time, and the results were always rejected.

Except in the case of electro-deposited metals, which were always used as soon as possible after deposition, the surface of the metal was always carefully cleaned by mechanical means to eliminate as far as possible the effect of surface layers of oxides and similar impurities.

Overvoltage on Copper Cathodes.

Electrolyte 0·1N, H_2SO_4 . Current density 15 milliamps. per 25 sq. cm.

1. Copper foil (hard rolled).

Time (Mins.).	Overvoltage.
0	'304
2	'316
5	'362
10	'374
15	'374

2. Same sample of copper after annealing, viz., heating to redness, quenching in water, and removing the surface film of oxide with sandpaper.

Time (Mins.).	Overvoltage.
0	'190
2	'225
5	'272
10	'296
15	'308

3. Same metal after receiving a coating of copper by electro-deposition from a copper sulphate solution using $3\frac{1}{2}$ amps. for the 25 sq. cm. area for 5 minutes. Overvoltage measurements made with same electrolyte and current density as above.

Time (Mins.).	Overvoltage.
0	'327
2	'339
5	'362
10	'374

4. Copper deposited similarly to above, with a current density of 5·2 amps. per 25 sq. cm. for 10 min.

Time (Mins.).	Overvoltage.
0	'339
2	'361
5	'372
10	'384

These results show that electrolytically deposited copper gives higher values for the overvoltage than other forms of this metal, that the overvoltage increases slightly with the current density at which the metal is deposited, and that annealed or soft copper gives a lower value than the hard rolled metal. The overvoltage in all cases increased with time up to 15 or 30 minutes, when it usually remained constant. The above results were confirmed by a number of other measurements.

These changes in the overvoltage on a copper cathode give an explanation of the properties of this metal when used in the electrolytic reduction of nitrates to ammonia. It is known that this reducing action varies considerably with the condition of the metal, and that the reduction to ammonia is most complete when metal with an electro-deposited coating is used.*

Zinc Cathode.

1. Pure cast metal. Current density as above.

Time (Mins.).	Overtoltage.
0	'644
10	'680
20	'680
40	'670

2. Zinc deposited electrolytically, using a current density of 5 amps. per 18 sq. cm.

Time (Mins.).	Overtoltage.
0	'64
20	'60
30	'58
40	'58

Nickel.

1. Rolled sheet metal. Area, 15 sq. cm. Current density used, 15 milli-amps. per 15 sq. cm.

Time (Mins.).	Overtoltage.
1	'277
4	'323
11	'341
24	'362
28	'362
32	'362

2. Nickel, electro-deposited by using a current density of 0.6 amp. per 15 sq. cm. surface. Overtoltage measurements made under same conditions as above.

Time (Mins.).	Overtoltage.
1	'256
7	'277
10	'277
23	'293
37	'293

* *Vide* Ulsch, *Z. Elektroch.*, **3**, 546 (1897); W. Böttger, *ibid.*, **16**, 698 (1910).

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3. Nickel, electro-deposited as above, using a current density of 0.05 amp. per 25 sq. cm.

Time (Mins.).	Overvoltage.
$\frac{1}{2}$	'234
3	'251
7	'255
11	'260

4. Nickel electro-deposited by using a current of 3 amps. per 20 sq. cm.

Time (Mins.).	Overvoltage.
1	'213
2	'255
4	'266
32	'316

5. Nickel deposited by using a current density of 8 amps. per 20 sq. cm.

Time (Mins.).	Overvoltage.
1	'255
4	'266
23	'299

With nickel the overvoltage was thus found to be lower in the case of the electro-deposited metal than with the rolled metal. A small influence also appears to be exerted in the former case by the current density used for the electro-deposition; a low current density apparently giving deposits which show the minimum values for overvoltage. This small effect, however, is largely obscured by the variations of the overvoltage with time.

Iron.

1. Pure soft iron. Conditions of current density and electrolyte as in above cases.

Time (Mins.).	Overvoltage.
1	'357
3	'363
10	'363
15	'363
60	'380

2. Iron deposited electrolytically with a current of 0.1 amp. per 15 sq. cm. for 3 hours from a solution of ferrous ammonium sulphate at 30°.

Time (Mins.).	Overvoltage.
0	'237
5	'288
10	'298
15	'298
20	'298

3. *Steel*.—A piece of hard tempered steel of 15 sq. cm. area was here used as cathode.

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Time (Mins.).	Overvoltage.
0	'231
15	'266
20	'266
25	'308
30	'330

4. *Iron Wires after Drawing*.—A series of pieces of iron wire were taken, of identical composition, but which had been drawn through holes in steel plates to different degrees. The amount of surface used as cathode was in all cases 1·6 sq. cm. and a current of 2 milliamps. was passed.

Sample I.—Annealed wire before drawing. Diameter, 5·2 mm.

Time (Mins.).	Overvoltage.
0	'329
2	'350
5	'370
10	'370

Sample II.—Above wire after drawing once. Diameter, 3·8 mm.

Time (Mins.).	Overvoltage.
0	'309
5	'350
10	'360
15	'370

Sample III.—Above sample after drawing once again. Diameter, 3·0 mm.

Time (Mins.).	Overvoltage.
0	'267
10	'298
15	'329
20	'340

Sample IV.—Above wire after drawing a third time. Diameter, 2·4 mm.

Time (Mins.).	Overvoltage.
0	'226
5	'278
10	'309
15	'309
20	'329

Sample V.—Above wire after drawing a fourth time. Diameter, 1·9 mm.

Time (Mins.).	Overvoltage.
0	'226
2	'247
5	'267
15	'309
20	'350

The hardness of the metal is, of course, very much raised by drawing, and the overvoltage increases concomitantly with the hardness, as was found to be the case with the other samples of iron and steel examined.

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It was found in several of the measurements made with steel that the overvoltage was at first zero, though in the course of 5 or 10 minutes it always assumed the normal value. This discrepancy may have been due to the presence of occluded oxide.

Effect of Temperature on Overvoltage.

The above measurements were all conducted at room temperature. The effect of temperature was, however, ascertained in one experiment by gradually warming the electrolyte, and the following values were obtained.

Cathode, rolled copper. Current density, 15 milliamps. per 15 sq. cm.

Temp.	Overvoltage.
11.5°	.33
20	.31
30	.28
45	.27
60	.25

SUMMARY OF RESULTS.

The overvoltage during the liberation of hydrogen on a metallic cathode was found to be dependent to a considerable degree on the physical condition of the metal. There is no general concordance, however, between the degree of hardness of the different metals and their overvoltage. In the case of copper, for instance, the maximum overvoltage is given with the hard metal, while in the case of iron the reverse is the case, the lowest overvoltage accompanying the hardest condition.

Metals which have been deposited electrolytically in some cases, as with

copper, give the maximum values for those metals; and in other cases, as with nickel and iron, give minimum values.

The general results obtained serve to show that overvoltage measurements

should be of importance in investigations on the properties of metals, and might in many cases become an important factor in ascertaining their physical condition.

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