586. *Hydrogen Overpotential at Electrodeposited Copper in Hydrochloric Acid.*

By (the late) S. E. El Wakkad, I. A. Ammar, and H. Sabry.

Hydrogen overpotential, η, is measured on copper cathodes, deposited from a cyanide bath on a platinum substrate, in N-hydrochloric acid, at 30°. Two Tafel line slopes are observed in the current density range 3×10^{-2} to 10^{-5} A/cm.². Below 10^{-5} A/cm.² dissolution of copper interferes with the overpotential results. The results are statistically analysed and the mean Tafel line is given. This line is characterised by a lower slope of 0·060 v and a higher slope of 0·130 v. The effect of potassium cyanide on the overpotential at copper, deposited from copper sulphate, is also studied. The effect of the nature of the substrate on the overpotential at copper, deposited from a cyanide bath, is studied by measuring Tafel lines on copper deposited on nickel and copper substrates.

Though no definite theory can be given, attempts are, however, made to explain the break in the Tafel line by assuming that hydrogen is evolved on a non-uniform surface containing two main kinds of sites of adsorption.

A LIMITED amount of work is reported on the overpotential characteristics of copper. Early investigators [1] used experimental techniques which are now known to be unsatisfactory. More recent work [2] on electrodeposited copper indicated that copper electrodes vary among themselves with respect to their overpotential–current-density relations. Further, each electrode varies in its own behaviour from day to day. No individual Tafel line occurs for all electrodes studied. The values of the slope, b, as well as the values of the over-potential, η, at a fixed current density, vary from one electrode to another in the same solution and at the same temperature.

Recent advances in overpotential studies [3] indicated the importance of b as a criterion for distinguishing between the possible rate-determining mechanisms for cathodic hydrogen evolution. Evaluation of b is therefore made by statistical methods. For each electrode–solution combination a mean value of b is computed, for a constant temperature.

The aim of the present work is to establish, with the help of statistics, the mean parameters of the cathodic hydrogen evolution on copper deposited from a cyanide bath.

EXPERIMENTAL

Electrolytic Cell.—The cell used (Fig. 1) was similar to that used by Bockris and Potter.[3] It was constructed of arsenic-free glass (" Hysil "). The anode compartment, *A*, was separated from the cathode compartment, *B*, by a sintered-glass disc, *C*, and a tap. The barrels, *E*, of two hypodermic syringes were joined to a ground-glass joint, *D*, to the top of *B*. The pistons of the two syringes carried two electrodes. One of these electrodes was used for pre-electrolysis, and the other as a test electrode. With the use of such an arrangement it was possible to lower the test electrode to touch the tip of the Luggin capillary *F* (of 1 mm. internal diameter). The Luggin capillary was connected to the hydrogen-electrode compartment *G*. Purified hydrogen was introduced into the cell through *H*. The anode, *I*, was in the form of a platinum disc, with an apparent area of 1 cm.². Hydrochloric acid was introduced into the cell through the side-arm *J*. To hinder the diffusion of air inside the cell, three bubblers, *K*, filled with conductivity water, were used as outlets for hydrogen. An exit, *L*, in the bottom of the cathode compartment, was used for washing. The taps, as well as the ground-glass joints, were of the solution-sealed type.

Preparation of Solutions.—Hydrochloric acid solutions were prepared from the constant-boiling acid and conductivity water ($\kappa = 8 \times 10^{-7}$ ohm^{-1} cm.$^{-1}$). The constant-boiling acid was prepared from " AnalaR " acid and conductivity water by a three-stage distillation process

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[1] Knobel, Caplan, and Eiseman, *Trans. Electrochem. Soc.*, 1923, **43**, 55; Wirtz, *Z. phys. Chem.*, 1937, **36**, *B*, 435.

[2] Senett and Hiskey, *J. Amer. Chem. Soc.*, 1952, **74**, 3754.

[3] Bockris, *Chem. Rev.*, 1948, **43**, 525; Bockris and Potter, *J. Chem. Phys.*, 1952, **20**, 614.

in all-glass apparatus. The distillation apparatus was subjected to the same process of cleaning as the electrolytic cell (see below).

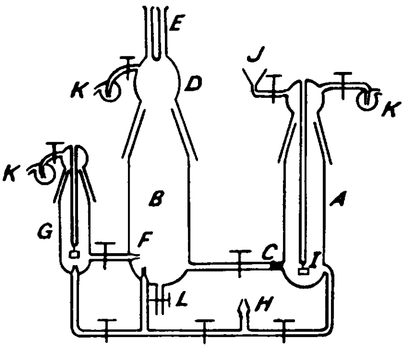
Purification of Hydrogen.—Cylinder hydrogen was purified from oxygen by passing it over copper at 450°. Traces of carbon monoxide were oxidised to dioxide by a mixture of manganese dioxide and copper oxide ("Hopcalite"). Carbon dioxide was then removed by soda-lime. The purification system was made of "Hysil" glass and was joined to the electrolytic cell by a movable glass bridge.

Preparation of the Electrodes.—Copper was electrodeposited from a cyanide bath[4] on a platinum substrate (apparent area, 0·32 cm.^{2}) with a current density of 60 mA/cm.^{2}, for 20 min. at 70°. The plating bath was prepared from "AnalaR" materials. After deposition, the electrode was washed 8—10 times with conductivity water and immediately fixed in position in the previously cleaned electrolytic cell.

Electrodeposition was also carried out from an acidified copper sulphate bath (15 g./l.) at a current density of 70 mA/cm.^{2}, a coarse deposit being obtained.

Pre-electrolysis.—Conditions for satisfactory pre-electrolysis[5] were reached when further increase in the extent of pre-electrolysis did not cause more than ± 10 mv difference in η at a given current density. The electrolytic purification of the solution (1·0N-hydrochloric acid) was carried out on a subsidiary pre-electrolysis electrode, of the same material as the test electrode, at a current density of 40 mA/cm.^{2}, for 20 hr.

Fig. 1.



Procedure and Measurements.—Before each experiment, the cell was cleaned with "AnalaR" chromic–sulphuric acid, and washed 8—10 times with equilibrium water and 10 times with conductivity water. The electrodes, previously washed with conductivity water, were introduced into the cell. The cell was then completely filled with conductivity water, and this water was replaced by purified hydrogen. The anode compartment, *A* (Fig. 1), was then separated from the other compartments by closing the adjacent taps. The hydrochloric acid solution was introduced through *J* to fill the compartment *A* completely. Purified hydrogen was then passed into *A* for several hours, to minimise the amount of oxygen dissolved in the solution (when this method was used, no oxygen depolarisation was detected in the results). The solution was then divided between *A* and *B*, and the pre-electrolysis electrode (with a potential difference corresponding to a current density of 40 mA/cm.^{2} imposed on it) was lowered into the solution. Pre-electrolysis was continued for 20 hr., with hydrogen passing in the two compartments, *A* and *B*, and the tap between *A* and *B* closed. At the end of the pre-electrolysis period, the pre-electrolysis electrode was drawn out of the solution with the current still on. Part of the pre-electrolysed solution from the cathode compartment was introduced into the hydrogen-electrode compartment, *G*, and hydrogen was passed into this compartment for 20—30 min. The test electrode (with a potential difference corresponding to a current density of 40 mA/cm.^{2} imposed on it) was then lowered into the solution and was adjusted to touch the tip of the Luggin capillary, *F*.

The direct method of measurements and the rapid technique were employed. The Tafel line was rapidly traced between 3×10^{-2} and 10^{-6} A/cm.^{2}. Measurements were carried out in unstirred 1·0N-hydrochloric acid at 30°. The potential was measured with a valve pH meter-millivoltmeter, and the current with a multirange micro-milliammeter. The current density was calculated from the apparent surface area.

RESULTS

Two Tafel line slopes, b_1 at the low current density range and b_2 at the high current density range, are observed in the linear logarithmic section of the Tafel lines for copper deposited from cyanide baths. The values of b_1, b_2 and the corresponding values of the exchange current, *i.e.*, $(i_0)_1$ and $(i_0)_2$ are given in Table 1 for 15 experiments (different electrodes and solutions) in N-acid at 30°. Below 10^{-5} A/cm.^{2}, dissolution of copper interferes with the overpotential results.

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[4] Blum and Hogaboom, "Principles of Electroplating and Electroforming," McGraw-Hill Co., New York, 1949, p. 297.

[5] Azzam, Bockris, Conway, and Rosenberg, *Trans. Faraday Soc.*, 1950, **46**, 918.

Fig. 2.

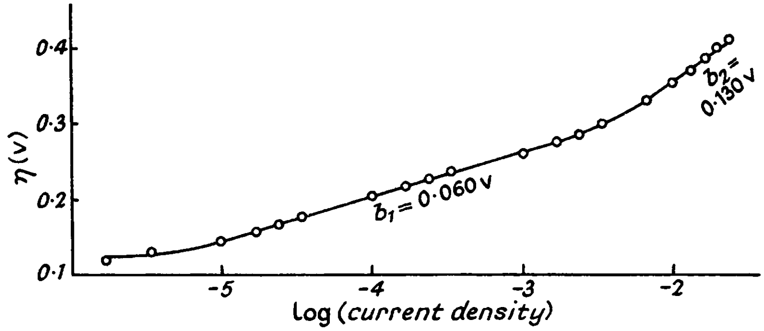
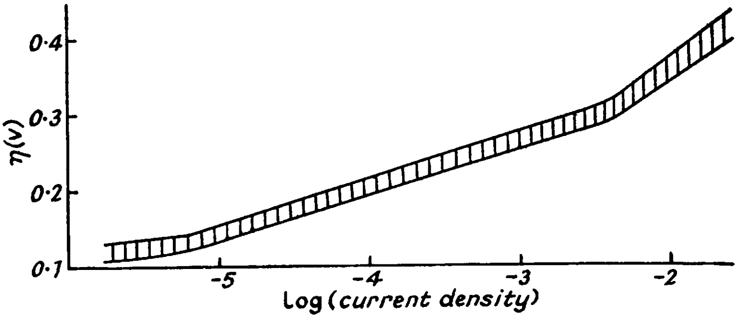


Fig. 3.



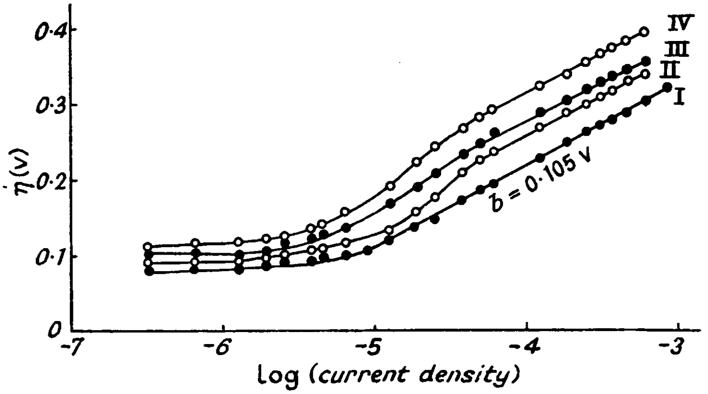
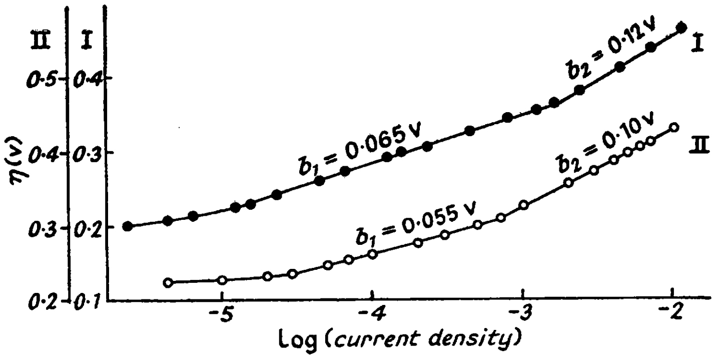


Fig. 4.
I, *No* KCN.
II, 0·01M-KCN.
III, 0·02M-KCN.
IV, 0·04M-KCN.

Fig. 5.
I, Cu *on* Cu.
II, Cu *on* Ni.



The results for copper, deposited from a cyanide bath, were treated statistically.[6] The mean Tafel line is shown in Fig. 2. It is characterised by the parameters : b_1 = 0·060 v, b_2 = 0·130 v, $(i_0)_1$ = 4·0 × 10^{-8} A/cm.^{2}, and $(i_0)_2$ = 3·2 × 10^{-5} A/cm.^{2}. The results of the statistical analysis are given in Table 2. Fig. 3 gives the upper and the lower confidence limit for the experimental Tafel line.

TABLE 1.

Run	b_1 (mv)	$(i_0)_1$ (10^{-8} A/cm.^{2})	b_2 (mv)	$(i_0)_2$ 10^{-5} A/cm.^{2})	Run	b_1 (mv)	$(i_0)_1$ (10^{-8} A/cm.^{2})	b_2 (mv)	$(i_0)_2$ (10^{-5} A/cm.^{2})
1	50	5·0	125	6·3	9	55	1·6	130	1·1
2	55	5·6	125	3·2	10	65	8·9	120	1·1
3	50	3·2	130	4·5	11	60	7·1	130	2·6
4	55	2·2	120	1·2	12	60	7·0	120	1·3
5	60	5·6	120	1·0	13	65	7·9	120	1·0
6	55	1·7	130	1·3	14	65	7·9	125	1·1
7	60	2·5	130	1·0	15	65	10	130	1·1
8	55	3·2	120	1·0					

TABLE 2.*

C.d. (A/cm.^{2})	Mean η (mv)	Standard error (mv)	95% confidence limits (mv)	C.d. (A/cm.^{2})	Mean η (mv)	Standard error (mv)	95% confidence limits (mv)
2·3 × 10^{-2}	411	8	±17	3·3 × 10^{-4}	233	5	±11
2·0 × 10^{-2}	399	8	±17	2·3 × 10^{-4}	225	5	±11
1·7 × 10^{-2}	386	9	±19	1·7 × 10^{-4}	217	5	±11
1·3 × 10^{-2}	372	8	±17	1·0 × 10^{-4}	203	5	±11
1·0 × 10^{-2}	355	8	±17	3·3 × 10^{-5}	176	5	±11
6·6 × 10^{-3}	332	8	±17	2·3 × 10^{-5}	165	5	±11
3·3 × 10^{-3}	299	7	±15	1·7 × 10^{-5}	156	4	± 9
2·3 × 10^{-3}	286	6	±13	1·0 × 10^{-5}	144	5	±11
1·7 × 10^{-3}	276	7	±15	3·3 × 10^{-6}	128	6	±13
1·0 × 10^{-3}	261	6	±13	1·7 × 10^{-6}	120	6	±13

* The mean, standard error and 95% limits are given to the nearest mv.

It is observed that, when copper cathodes are deposited from an acidified copper sulphate bath, Tafel lines with one slope in the linear logarithmic section are obtained (cf. Fig. 4). The effect of potassium cyanide * on the overpotential at copper deposited from copper sulphate is also studied. The results are shown in Fig. 4. It is clear that addition of the cyanide causes a numerical increase in the values of η, more pronouncedly at high current densities.

The effect of the nature of the substrate on η is studied by measuring Tafel lines for copper, deposited from a cyanide bath, on copper and nickel substrates. The Tafel lines obtained (Fig. 5) are also characterised by the occurrence of two slopes in the linear logarithmic section.

DISCUSSION

Comparison with Previous Work on Electrodeposited Copper.—Senett and Hiskey[2] observed that the overpotential results on electrodeposited copper are irreproducible in the sense that η (at a constant current density), as well as b, varies from one electrode to another in the same solution and at the same temperature. Thus, for electrodes deposited from a cyanide bath, the above authors observe that η at 0·96 A/cm.^{2} varies from 533 to 218 mv, and b varies from 91 to 53 mv, at 22°. Different Tafel equations are fitted to individual measurements between 10^{-6} and 5 × 10^{-4} A/cm.^{2}. The present investigation, on the other hand, indicates that two Tafel equations may be fitted to all measurements on copper deposited from a cyanide bath (cf. Fig. 2).

The difference between the present and Senett and Hiskey's results may be attributed to the difference in the techniques of measuring overpotential. Senett and Hiskey kept their electrodes polarised, at a current of 4 × 10^{-6} A, between measurements. This process of ageing is dispensed with in the present investigation. Ageing the electrode may have various results : (i) Contamination of the electrode surface by trace impurities from the solution over the period of ageing which may last for several days (traces of impurities are known to affect values of both η and b) ; and (ii) variation of the electrode surface with time of ageing. On the above basis, different periods of ageing may produce different values

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* These KCN solutions were de-oxygenated and pre-electrolysed in a separate cell attached to the cathode compartment of the electrolytic cell (cf. Bockris [3]).

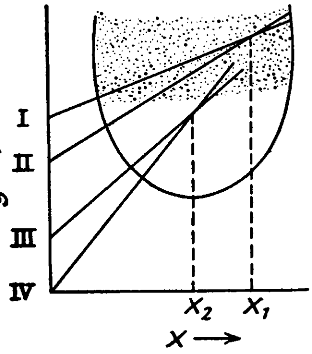
[6] Davies, " Statistical Methods in Research and Production," Oliver and Boyd, London, 1949

of η (at a constant apparent current density) and b even for the same electrode, in the same solution and at the same temperature, as observed by Senett and Hiskey.

Significance of the Change of Slope of the Tafel Line with Cathodic Polarisation.—The occurrence of two Tafel-line slopes has been reported in the literature. *E.g.*, Bockris and Conway [7] observed two slopes for silver cathodes in 0·1—7·0N-hydrochloric acid in the current-density range 10^{-6}—10^{-2} A/cm.^{2}. They attribute the break in the Tafel line to specific adsorption of H_3O^+ ions. Schuldiner [8] also observed an increase in the slope, from 0·027 to 0·12 v for bright platinum in 0·1N-sulphuric acid, with increase of cathodic polarisation. He attributes the break in the Tafel line to the change of mechanism from a rate-determining catalytic desorption at low cathodic polarisation to a rate-determining slow discharge from water molecules at high cathodic polarisation. Similar observations have been reported for tungsten [9] and tellurium [10] in hydrochloric acid. A theoretical study by Parsons [11] on dual and coupled mechanisms indicates the possibility of change of mechanism, and consequent change of slope, with increase of cathodic polarisation.

The results of the present investigation may be attributed to the heterogeneity of the surface of deposited copper. Most deposits are known to be heterogeneous in nature. In a study of the electrochemical behaviour of non-uniform surfaces, Busing and Kauzmann [12] indicated that different currents are carried by different parts of the electrode surface. The Tafel equation, $V = a - b \ln I$, is written as: $y = VX + \ln I$, where $y = a/b$ and $X = 1/b$. Each elementary area of the electrode surface is characterised by certain values for X and y. According to the above authors, the steady-state potential is related to the macroscopic current density by the Tafel equation only when the macroscopic current lines (represented by $y = VX + \ln I$) intersect at a common point on the distribution representing the electrode surface.

FIG. 6.



It is possible to explain the occurrence of two Tafel-line slopes for copper deposited from a cyanide bath if the assumption is made that hydrogen is evolved on two main kinds of site of adsorption on the electrode surface. In this case the plot of y against X for different currents (macroscopic) may be represented by Fig. 6. At low currents (represented by I and II) the intersection of the current lines may take place on a point represented by (X_1, y_1) on the first kind of sites of adsorption. At high current densities (represented by III and IV) the intersection may take place on a point (X_2, y_2) in the region of the second kind of adsorption sites. Since $X_1 > X_2$ and $b = 1/X$, b_2 is greater than b_1, indicating that the Tafel line slope at high current densities is greater than that at low current densities.

The fact that the Tafel line for copper deposited from copper sulphate is characterised by a single slope may be due to the occurrence of only one kind of site of adsorption for hydrogen evolution. The fact that the overpotential for copper deposited from a cyanide bath is numerically greater than that for copper deposited from copper sulphate (cf. Figs. 2 and 4) may be attributed to the de-activation of active centres by cyanide ions. The activity for hydrogen evolution is, therefore, greater (and η is smaller) in the case of a deposit from copper sulphate than in the case of a deposit from a cyanide bath. This is supported by the fact that addition of potassium cyanide numerically increases η on copper deposited from $CuSO_4$.

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[7] Bockris and Conway, *Trans. Faraday Soc.*, 1952, **48**, 724.
[8] Schuldiner, *J. Electrochem. Soc.*, 1952, **99**, 488.
[9] Ammar, Ph.D. Thesis, London, 1953.
[10] Ammar and Awad, *J. Electrochem. Soc.*, 1956, 103, 182.
[11] Parsons, *J. Chim. phys.*, 1952, **49**, C 82.
[12] Busing and Kauzmann, *J. Chem. Phys.*, 1952, **20**, 1129.