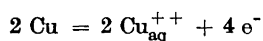


On the Kinetics of the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ Electrode

TOR HURLEN

Central Institute for Industrial Research, Blindern, Oslo, Norway

Investigations have been made on the anodic dissolution and cathodic deposition of copper in acid sulphate solution at 20 and 25°C by means of a slow amperostatic technique. The reactions have been found to obey the Tafel relationship, except for the occurrence of a cathodic limiting current, to have mutually symmetric Tafel lines with slopes of numerically $2.303 RT/2F$, and to be little dependent on the pH and the sulphate concentration. The rate of deposition (in the Tafel region) is moreover found to be proportional to the square of the cupric ion activity, and the rate of dissolution to be independent of this activity. This indicates a mechanism covered by the equation:



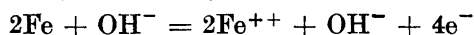
For the exchange current (i_0) of the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode in 0.1 N sulphuric acid solutions of cupric sulphate at 20 and 25°C, respectively, it is found:

$$\begin{aligned} i_0 &= 2.4 a \cdot 10^{-2} \text{ A/cm}^2 \\ i_0 &= 3.4 a \cdot 10^{-2} \text{ A/cm}^2 \end{aligned}$$

where a is the cupric sulphate activity. The standard exchange current is by definition $J_0 = i_0/a$.

1.0 INTRODUCTION

In a previous paper¹, it has been shown that the reactions of the $\text{Fe}/\text{Fe}_{\text{aq}}^{++}$ electrode seem best represented by the "kinetic unit equation":



indicating that two metal ions are transferred for each rate determining step in the electrode process, and that there is an interaction of one hydroxyl ion for every second metal ion reacting. It has further been suggested that the double metal ion mechanism might be a consequence of the steric relationship between water and metal, which for an iron/water interface of closest packing gives a relationship of very nearly 2:1 between the number of metal atoms and that of water molecules at this interface. However, it may be shown that this relationship does not suffice in explaining the occurrence of *two* metal ions in the kinetic unit equation.

Before attempting any further theoretical approach to this problem, it was assumed desirable to carry out the same type of slow amperostatic polarization measurements on other metals as those previously¹ performed on iron. The desirability of this is first of all due to the fact that (to our knowledge) no previous investigators in the field of metal/metal-ion electrode reactions have concluded on a kinetic unit equation involving *two* metal ions. This also necessitates a relatively thorough discussion of previous work.

The present work is confined to the behaviour of copper in sulphate solutions of various sulphuric acid and cupric sulphate concentrations. In these solutions, the cuprous ion is unstable² and can mainly be formed as a possible intermediate in the copper electrode reactions. The behaviour of copper in the presence of cuprous ion stabilizing anions (especially chloride ions) will be the subject of a subsequent paper.

2.0 PREVIOUS WORK

The anodic behaviour of metals in general has been reviewed by Hoar³, and the cathodic deposition of metals by Fischer⁴ and Bockris⁵. All these surveys include references to copper, but do not reveal any really good polarization data for anodic dissolution nor cathodic deposition of this metal.

More recently, however, these reactions have been studied by several investigators. Sroka and Fischer⁶ found a Tafel slope of $b_c = -0.029$ V for the deposition of copper at low current densities (up to about 5×10^{-3} A/cm²) from 1 N cupric sulphate + 1 N sulphuric acid at 22°C. At higher current densities, the polarization curve was steeper ($b_c = -0.232$ and -0.116 V), and they correlate this with changes in the crystallization habit (pyramidal to cubic to finely polycrystalline deposits with increasing current density). Analogous results are further reported by Seiter and Fischer⁷, by Seiter, Fischer and Albert⁸, and by Barnes, Storey and Pick⁹. Barnes¹⁰ has moreover shown that the deposits formed at low current densities (up to about 15×10^{-3} A/cm²) are extensions of the base, whereas twinning occurs at higher current densities (the twinning possibly initiating polycrystallinity). The low current density range seems thus to be of greatest interest for correlating studies on the mutually reverse reactions of the Cu/Cu_{aq}⁺⁺ electrode. In the present work, therefore, special attention is paid to data obtained in this range (especially as far as the cathodic reaction is concerned). The polarization measurements of the above mentioned authors⁶⁻⁹ do thus indicate that the proper cathodic Tafel slope is given by:

$$b_c = -2.303 (RT/2F)$$

which is the same as previously obtained for iron¹. These measurements have mainly been performed on polycrystalline cube-texture copper sheets of high purity.

Mattsson and Bockris¹¹, from galvanostatic short-pulse measurements on copper electrodes produced through electrodeposition (15×10^{-3} A/cm²), found a linear V/\dot{i} -relationship for both the anodic and the cathodic reaction at very low overpotentials (up to about 0.01 V) in acidified cupric sulphate solutions. This is in agreement with the theory of activation-controlled electrode reactions^{5,13}, but not with that of slow surface diffusion of adions¹⁴ (which predicts a proportionality between the rate and the square of the overpotential at low overpotentials). Mainly from the relation between overpotential and time, Mattsson and Bockris nevertheless conclude that a surface diffusion is rate-controlling at low current densities, but also the assumptions on which this evaluation is based¹⁵, have recently been criticised by Fleischmann and Thirsk¹⁴.

At high current densities (above 15×10^{-3} A/cm²), Mattsson and Bockris¹¹ (see also Mattsson and Lindström¹²) found the Tafel relationship to be obeyed and report $b_c = -0.12$ V and $b_a = 0.04$ V under steady state conditions at 30°C. They interpret this as indicating that the reactions under these conditions are controlled by the redox process between cupric and cuprous ions, whilst the latter ions exist in reversible equilibrium

with copper at the electrode surface. The correctness of this conclusion very much depends on the significance of the observed cathodic Tafel lines. All the above mentioned authors⁶⁻⁹ (see especially Ref.⁹) observed a much stronger variation of potential with cathodic current density from about 15×10^{-3} A/cm² and upwards than did Mattsson and Bockris. The inconsistency in the results obtained by the various authors in this current density range (with nearly the same electrolyte composition), could perhaps mean that the conditions of stirring here are important, and that these conditions have been different in the various investigations. The limiting current to be expected for copper deposition from an unstirred 1 N cupric sulphate solution lies namely in the lower part of this current density range (see *e.g.* Ref.¹⁶).

The anodic Tafel slope value of about 0.04 V at 30°C reported by Mattsson and Bockris, may probably be somewhat too high. In drawing at least the two anodic Tafel lines shown in their paper (Figs. 7 and 8 in Ref.¹¹), they have apparently ignored the appreciably lower-lying polarization points at high current densities. Gerischer and Rickert¹⁷ have moreover given an anodic polarization curve for copper in an acidified cupric sulphate solution, and Piontelli *et al.*¹⁸ some curves for copper single crystals in an acidified cupric perchlorate solution, all of which seem to indicate an anodic Tafel slope of about 0.03 V at 25°C. It may thus be that for the Cu/Cu_{aq}⁺⁺ electrode we have:

$$b_a = -b_c = 2.303(RT/2F)$$

just as previously found for the Fe/Fe_{aq}⁺⁺ electrode¹. A symmetric behaviour of the Cu/Cu_{aq}⁺⁺ electrode, when under activation control, is in accordance with the early results of Juza and Kopyl¹⁹.

The exchange current (i_0) of the Cu/Cu_{aq}⁺⁺ electrode has been determined by several investigators: Juza and Kopyl¹⁹ (referred to by Bockris⁵) found $i_0 = 2 \times 10^{-5}$ A/cm² from charging curves in 1 M cupric sulphate at room temperature. The cathodic Tafel lines given by Sroka and Fischer⁶ in the low current density range (see above) indicate $i_0 = 2 - 3 \times 10^{-4}$ A/cm² in 1 N cupric sulphate + 1 N sulphuric acid at 22°C. Seiter and Fischer⁷, by calculations from cathodic $V - i$ slopes at low overpotentials in 0.1 to 1 N cupric sulphate + 1 N sulphuric acid at 25°C, found $i_0 = 2 \times 10^{-3} \times c^{0.45}$ A/cm² (where c is the concentration of cupric ions in mole/l). Seiter, Fischer, and Albert⁸ found in the same way $i_0 = 1.6 \times 10^{-3}$ A/cm² and from morphologic data $i_0 = 2.1 \times 10^{-3}$ A/cm² in 1 N cupric sulphate + 1 N sulphuric acid at 25°C. However, a Tafel extrapolation of their low current density polarization data (assuming $b_c = -2.303(RT/2F)$) indicates a value slightly below 1×10^{-3} A/cm². For the same temperature and electrolyte composition, Barnes, Storey, and Pick⁹ also found $i_0 = 1 \times 10^{-3}$ A/cm² by extrapolation of the cathodic Tafel line obtained at relatively low current densities. This value of i_0 is also in good agreement with the data given by Piontelli *et al.*¹⁸ for a corresponding perchlorate solution at 25°C. Mattsson and Bockris¹¹, from $V - i$ slopes at low overpotentials in 1 N sulphuric acid + 1 N, 0.15 N, and 0.022 N cupric sulphate at 30°C, give as mean values $i_0 = 2.1 \times 10^{-3}$, 1.4×10^{-3} , and 0.9×10^{-3} A/cm² for helium prepared copper electrodes and, in the two strongest solutions, $i_0 = 5.4 \times 10^{-3}$ and 2.7×10^{-3} A/cm² for electrodeposited copper electrodes. From impedance measurements on copper electrodes in 10^{-3} to 10^{-1} N cupric sulphate + 1 N sulphuric acid presumably at room temperature (not specified), Bockris and Conway²⁰ report $i_0 = 0.6 \times c^{0.75}$ A/cm² (where c is the cupric sulphate concentration in mole/l). This is very much higher than the above quoted values. Similar impedance measurements have been made in 0.05 M cupric sulphate + 1 M H₂SO₄ by Lorenz²¹, who reports an exchange between ad-atoms and cupric ions of $i_0 = 3 \times 10^{-2}$ A/cm² and assumes a lower rate of exchange for lattice atoms. It does seem, however, that Lorenz in the evaluation of his results has ignored the possibility of a direct dissolution and deposition at lattice building sites (see Ref.¹⁴).

Neglecting the mutually and from the other data widely diverging i_0 -values obtained from impedance measurements, and also the early results of Juza and Kopyl, the above results seem to agree relatively well in showing

$$i_0 = 1 - 2 \times 10^{-3} \text{ A/cm}^2$$

in 1 N cupric sulphate (or perchlorate) + 1 N sulphuric (or perchloric) acid at 25°C. It further seems that the i_0 -values obtained by extrapolation of Tafel lines at relatively low current densities generally are lower than those obtained from $V - i$ slopes at very low overpotentials. The former values do not depend on any assumption as to the stoichiometry of the exchange reactions, whereas the latter do^{5,13}. The above quoted determinations assume first order reactions. If these reactions should be second order (as has been found for the $\text{Fe}/\text{Fe}_{\text{aq}}^{++}$ electrode reactions¹), the above quoted i_0 -values from $V - i$ slopes should be halved. This would give an even better agreement between the results.

The effect of cupric ion concentration on the rate of the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode reactions has been little studied. As mentioned above, Seiter and Fischer⁷ report

$$d \log i_0 / d \log c = 0.45$$

and Bockris and Conway²⁰:

$$d \log i_0 / d \log c = 0.75$$

in 1 N sulphuric acid solutions of cupric sulphate.

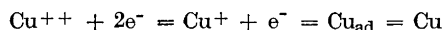
The data of Mattsson and Bockris¹¹ indicate an exponent lower than any of these. Such data, however, do not directly give the specific effect of the cupric ion concentration on any of the two mutually reverse reactions of the electrode, but only a possible combination of these effects.

The effect of pH on the rate of these reactions does not seem to have been studied systematically. Seiter, Fischer, and Albert⁸, however, have reported on the effect of pH on the electrocrystallization habit.

The crystallographic orientation of the copper surface has by several authors been shown to affect both the dissolution and the deposition reaction. Piontelli, Poli, and Paganini¹⁸, Leidheiser and Gwathmey²², and Glauner and Glocker²³ have all found the (111) plane to dissolve faster than the (100) plane. The differences in dissolution rate of these faces, however, seem to be relatively small (not more than some 20 %). Leidheiser and Gwathmey even found that the behaviour could be reversed by a hydrogen atmosphere anneal of the copper single crystals. The rate of deposition (at least at low overpotentials) has also been found^{18,22} to be faster on (111) faces than on (100) faces, but the differences are here even smaller than on the anodic side. In accordance with these rate data, Tragert and Robertson²⁴ have shown that the (111) plane is in fact the only copper surface giving a stable, reversible $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ half-cell. The exposure of other faces ((100), (110), and (210) to a cupric sulphate solution gives a slightly unstable potential which approaches that of the (111) face with time, the initial differences being approximately 0.005 V.

The effect of the crystallographic orientation of the base metal on the structure of electrodeposited copper has recently been studied by Pick *et al.*^{9,25,26} (see also Wranglén²⁷), and the role of dislocations in the electrocrystallization of copper by Vaughan and Pick²⁶ and by Economou, Fischer, and Trivich²⁸.

The reaction mechanism of the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode is apparently far from clear as several distinctly different opinions exist on this matter. Mattsson and Bockris¹¹ arrived at the following consecutive reaction steps:



from left to right in deposition and oppositely in dissolution. They further conclude that the $\text{Cu}^{++}/\text{Cu}^+$ redox step is rate controlling at high current densities and the $\text{Cu}_{\text{ad}}/\text{Cu}$ step at low current densities. As discussed above, however, these conclusions seem open to some criticism. Moreover, from impedance measurements on copper in acidified cupric sulphate solutions, Lorenz²¹ could find no evidence for an intermediate formation of cuprous ions.

Bockris *et al.*^{11,20,29}, Fischer *et al.*⁸, Lorenz²¹, and Gerischer³⁰ seem otherwise to agree in suggesting the surface diffusion and crystallization process to be slower than the transfer reaction in cathodic deposition of copper. Gerischer³⁰ give a relationship of approximately 1:10 between these rates at equilibrium. Fleischmann and Thirsk¹⁴, however, have shown that many of the kinetic data on copper deposition are in disagreement with the model of lattice growth being controlled by slow surface dissolution (see also the above

discussion of the *linear* V/i -relationship found by Mattsson and Bockris¹¹ at low overpotentials). The available anodic polarization data are moreover in disagreement with the anodic limiting current to be expected from the reverse of this model (Mattsson and Bockris¹¹).

3.0 EXPERIMENTAL

Electrodes of high purity copper (2 ppm Fe, 2 ppm Ag, 1 ppm Pb, 1 ppm Ni, 1 ppm Si, 1 ppm Na, and less than 1 ppm each of Ca and Mg, other metallic elements and the elements O, S, Se, Te, and P either being not present or being below the limits of detection by the spectrographic, chemical, and metallographic methods applied) have been used in the form of circular sheets (about 4.5 cm diameter) punched from a cold-rolled strip (about 0.6 mm thick). Prior to use, the electrodes were vacuum annealed for about one hour at about 700°C, mechanically polished, etched in dilute nitric acid, washed in running water, distilled water, and acetone, dried and weighed. Each electrode was only used once in determining a single potential-time curve at constant applied current (see below).

The solutions were prepared from A. R. quality cupric sulphate and sulphuric acid in water distilled from a "pure" and soft fresh water. The solutions were presaturated with hydrogen which first was purified by passage through a palladium catalyst at about 250°C. The solutions were also stored under purified hydrogen and were further transferred to the test cell by hydrogen pressure. A sketch of the electrolyte preparation and storage unit is shown in Ref.¹.

The test cell was a cylindrical Pyrex glass cell (about 10 cm² internal cross section and about 15 cm long) carrying tubes for the ingress and egress of liquid and gas. The test electrodes are placed so as to form the two end walls of the cell. After having been clamped in position, the electrodes were covered around their outer edge with polystyrene (dissolved in chloroform) and paraffine wax. The cell further has two Haber-Luggin capillaries for electrolytic connections to two external reference electrodes, and copper wires for metallic connections to the potentiometer and to the current source. In this cell, a sketch of which is shown in Ref.¹, the electrolyte is exposed to the atmosphere in two capillaries of one millimeter diameter only.

The experiments were performed galvanostatically. The current was supplied from an assembly of four 12 V accumulators connected in series. It was read on a calibrated Avometer and controlled by a number of variable resistances in series with the cell. The electrode potential of each electrode as a function of time was measured against a saturated calomel electrode by means of a Cambridge pH-meter. Convection and diffusion between the test cell and the two reference electrodes were hindered by a closed stopcock in each of the connecting tubes.

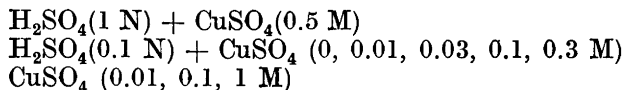
The partial current density of the reactions was determined from the weight change of the electrodes over a considerable time at a constant applied current. A Mettler semi-micro balance was used for these weighings. The duration of the runs varied from two days to one hour depending on the current applied, 10^{-5} – 10^{-2} A/cm² (apparent).

The experiments were carried out partly in a water thermostat at $25 \pm 0.1^\circ\text{C}$ and partly in a thermostated room at $20 \pm 0.5^\circ\text{C}$. Except for one series of experiments with magnetic stirring in the cell, no stirring was applied.

The saturated calomel electrode has been ascribed the potentials 0.242 V and 0.245 V on the normal hydrogen scale (NHS) at 25 and 20°C, respectively.

4.0 RESULTS AND INTERPRETATIONS

Experiments of the above described type have been performed with the following nine electrolyte solutions:



These solutions have various pH-values in the range 0 to 5.

4.1 Reversible potentials, activities, and liquid junctions

In the not acidified cupric sulphate solutions at 25°C, the observed zero current potentials averaged to 0.268, 0.291, and 0.311 V (NHS) in the 0.01, 0.1 and 1 M solution, respectively. The values to be expected from the accepted^{2,31} standard potential of 0.337 V and the activity coefficients (0.438, 0.154, and 0.043) tabulated by Parsons³¹ are 0.267, 0.283, and 0.297 V. There may be several reasons for the discrepancies between these two sets of values, but they are easily accounted for by assuming the liquid junction potential between the saturated potassium chloride solution in the reference half-cell and the three cupric sulphate solutions to be 0.001, 0.008, and 0.014 V (+ CuSO₄/KCl-), respectively. This interpretation has here been accepted and corrections accordingly made in all the potential measurements in these solutions. The fact that these corrections bring the respective anodic Tafel lines (in a $V(\text{NHS})-\log i$ diagram) to coincide mutually (see below), lends confidence to the above interpretation.

The potential measurements in the 0.1 N sulphuric acid solution have been corrected for a liquid junction potential of 0.004 V (-H₂SO₄/KCl +), a value tabulated by Milazzo³².

The anodic Tafel lines obtained in the 0.1 N sulphuric acid solutions of cupric sulphate at 20°C coincide without corrections with the one obtained in pure 0.1 N sulphuric acid at the same temperature. This indicates that the liquid junction potential is negligible in these cases. The observed zero current potentials, which averaged to 0.263, 0.274, 0.285, and 0.296 V (NHS) at the cupric concentrations 0.01, 0.03, 0.1 and 0.3 M, respectively, may thus be regarded as the reversible potentials of copper in these solutions. According to de Bethune *et al.*³³ the isothermal temperature coefficient of the standard copper sulphate electrode is 8×10^{-6} V per degree centigrade, giving a standard potential of 0.337 V (NHS) also at 20°C. On this basis, the following activity coefficients of cupric sulphate in 0.1 N H₂SO₄ at 20°C are arrived at: 0.280 at 0.01 M, 0.224 at 0.03 M, 0.161 at 0.1 M and 0.129 at 0.3 M. The relationship between these and the corresponding coefficients in water seem to be in accordance (at least qualitatively) with what is to be expected from the dissociation constants of cupric sulphate and sulphuric acid³⁴.

In 1 N sulphuric acid + 0.5 M cupric sulphate, the average zero current potential was 0.306 V (NHS) at 25°C. No attempts have been made neither to evaluate the liquid junction potential encountered in these measurements, nor to determine the reversible potential and the cupric activity in this solution. Only overvoltage values (in which the liquid junction potential cancels out by difference) have been used in the below described kinetic studies in this solution.

The average deviation in the observed zero current potentials was generally about ± 0.002 V. The above evaluations moreover involve the approximation associated with the potential difference between the standard copper sulphate electrode and the saturated calomel electrode having been regarded the same on the *molar* as on the *molar* scale.

4.2 Current efficiencies

The weight change measurements on anodes used in 0.1 N sulphuric acid gave as an average of eighteen runs a current efficiency of $100.6 \pm 1.8 \%$ for the formation of cupric ions. There was no distinct trend in the results to indicate any variation in the efficiency with current density (10^{-5} to 10^{-2} A/cm²).

In the acidified cupric sulphate solutions, a corresponding dissolution efficiency of $100.4 \pm 2.3 \%$ (34 runs) and a deposition efficiency of $100.8 \pm 2.4 \%$ (28 runs) were obtained. At the highest current densities applied under conditions of no stirring, loosely adhering powdery deposits were formed on the cathodes. This gave rise to highly erratic (too low) cathodic efficiency values which have been neglected. This also applies to the not acidified cupric sulphate solutions. Except for its effect on the formation of powdery deposits, the stirring could not be found to have any effect on the current efficiency.

In the not acidified cupric sulphate solutions, the experimental efficiency values were far from 100 % (below for anodes and above for cathodes) at low current densities, approaching this value with increasing current density (except for the formation of powdery deposits). These results were found to be due to the formation of some solid compound on the copper surface. No attempts were made to identify this compound. According to the work of Miller and Lawless³⁵, however, it probably is cuprous oxide.

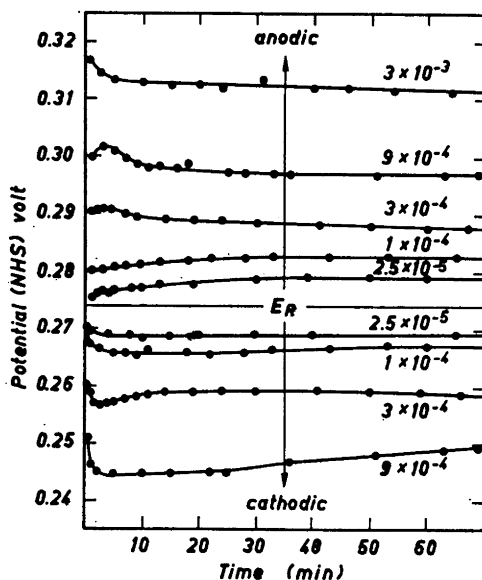


Fig. 1. Potential-time curves for copper at various anodic and cathodic current densities (A/cm²) in 0.03 M cupric sulphate + 0.1 N sulphuric acid at 20°C.

4.3 Potential-time curves

Some examples of the potential-time curves obtained are shown in Fig. 1. These curves apply to 0.03 M cupric sulphate + 0.1 N sulphuric acid at 20°C, but are relatively representative for the time dependence generally found also in the other solutions. In some cases (especially in stirred solutions), the curves were almost straight horizontal all through the experimental time period, indicating a nearly time-independent potential. However, at those relatively high cathodic current densities at which powdery deposits were formed, the potential was always low (sometimes lower than the reversible hydrogen potential in the applied solution) and usually rather unstable. The current density above which this occurred, varied with the electrolyte composition and the stirring conditions just as is to be expected for a limiting current. The poorly adhering powdery deposits and the relatively low and rather unstable cathodic potentials appear thus to be due to the applied current exceeding the limiting current. This is further discussed below.

4.4 Polarization curves

In constructing polarization curves from the above described potential-time curves, it has in the case of time dependence been assumed that the potentials giving the lowest numerical overvoltage values are the most representative ones. This has most usually been the stationary potentials reached after some time of electrolysis (see Fig. 1).

The polarization data obtained in this way are given by the points in the Tafel diagrams presented in Figs. 2–5. The Tafel lines shown there have all been drawn with slopes of:

$$b_a = -b_c = 2.303(RT/2F) \quad (1)$$

per logarithmic unit in current density. The corresponding anodic and cathodic lines have moreover been drawn in such a way as to intersect at the reversible potential (which has been determined as described above).

The symmetric deviation from these Tafel lines in the vicinity of the reversible potential, is at least qualitatively in accordance with what is to be expected from the reverse reaction being appreciable. At higher overpotentials and especially in the 0.1 N sulphuric acid solution, the experimental *anodic* polarization points exhibit a reasonable fit to the lines drawn. Also the *cathodic* points mostly show a reasonable fit to the respective Tafel lines at medium current densities, but break relatively sharply away from the lines above a certain current density strongly dependent on electrolyte composition and stirring. This type of deviation is shown by the dashed curves in Figs. 4 and 5.

In unstirred 0.5 M cupric sulphate + 1 N sulphuric acid at 25°C, the unsymmetric deviation from the cathodic Tafel line seems to start even before the reverse anodic reaction has become negligible, whereby the polarization points do not even reach the line. This is shown in Fig. 2, where present results in an *unstirred* solution are compared with some previous results of Barnes, Storey, and Pick⁹ in a *stirred* solution of the same composition and temperature. This comparison gives the first indication that the deviations observed from

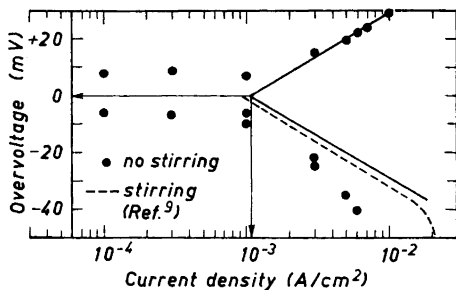


Fig. 2. Tafel diagram for the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode in 0.5 M cupric sulphate + 1 N sulphuric acid at 25°C.

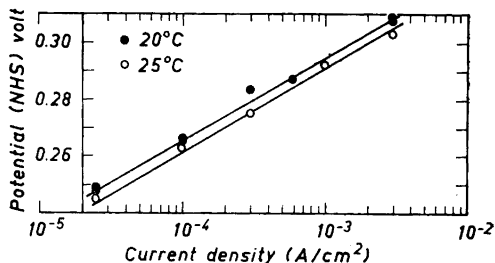


Fig. 3. Tafel curves for anodic dissolution of copper in 0.1 N sulphuric acid at 20 and 25°C.

the symmetrically drawn cathodic Tafel lines, are due to the deposition reaction becoming influenced by the rate of transport of cupric ions to the electrode surface.

This interpretation is further strongly supported by the effect of stirring shown in Fig. 4 (B), and the effect of increasing cupric sulphate concentration shown in Fig. 4 (A to D) and Fig. 5 (A to C), in counteracting the deviation by

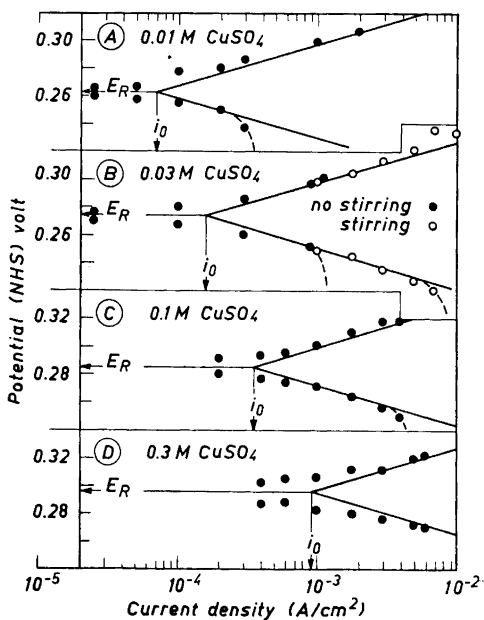


Fig. 4. Tafel diagrams for the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode in 0.1 N sulphuric acid solutions of cupric sulphate at 20°C.

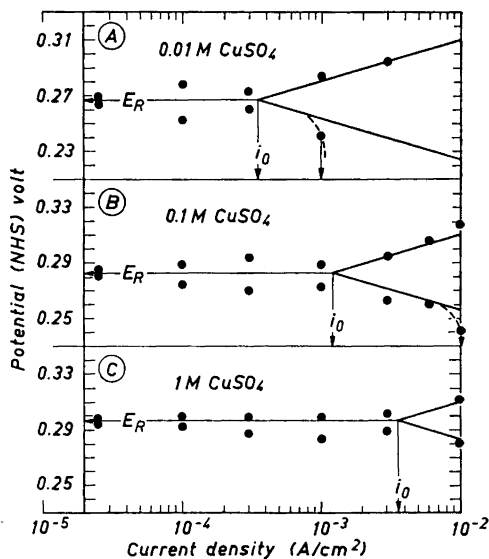


Fig. 5. Tafel diagrams for the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode in solutions of cupric sulphate in water at 25°C.

transferring it to higher current densities. It is also of interest to note that analogous deviations occur at very nearly the same current densities in the deposition of iron from solutions of corresponding ferrous ion concentrations¹, and that these current densities coincide reasonably well with calculated approximate values of the limiting current¹⁶.

It thus appears that the deviation from symmetry, as indicated by the dashed curves in Figs. 4 and 5, represents a transition from activation control to diffusion control in deposition, and that the symmetrically drawn Tafel lines are representative for the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode reactions when under activation control. This is in agreement with the suggestions made in the above discussion of previous work, and indicates a symmetry factor (α) and a stoichiometric number (ν) of:

$$\alpha = 1/2 \quad (2)$$

$$\nu = 1/2 \quad (3)$$

for the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode, just as has previously been found for the $\text{Fe}/\text{Fe}_{\text{aq}}^{++}$ electrode¹.

4.5 Exchange currents

The exchange current (i_0) of the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode in the various solutions applied (as given by the intersection of the Tafel lines at the reversible potential) is indicated by the vertical arrows in Figs. 2, 4, and 5. The values found at the various cupric sulphate concentrations and activities (as given above) in water at 25°C and in 0.1 N sulphuric acid at 20°C are moreover plotted in Fig. 6.

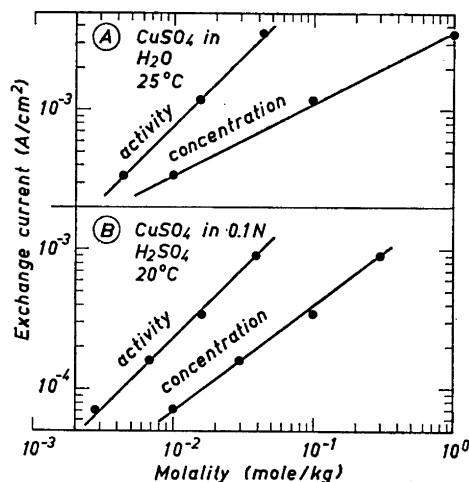


Fig. 6. Effect of cupric sulphate concentration and activity on the exchange current of the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode in pure water solutions (25°C) and in 0.1 N sulphuric acid solutions (20°C) of cupric sulphate.

The straight lines drawn in Fig. 6 correspond to $d \log i_o/d \log c = 0.51$ (in water at 25°C) and 0.73 (in 0.1 N sulphuric acid at 20°C) and to:

$$d \log i_o/d \log a = 1 \quad (4)$$

in both cases. The results more explicitly give:

$$i_o = a(23.6 \pm 0.9)10^{-3} \text{ A/cm}^2 \quad (5)$$

$$i_o = a(80.5 \pm 2.1)10^{-3} \text{ A/cm}^2 \quad (6)$$

at 20 and 25°C, respectively. The values in the parentheses represent thus the *standard* exchange current in mA/cm² at the respective temperatures, provided the experimental data do not include any possible effects of the changes in pH and sulphate ion concentration accompanying the changes in the cupric sulphate concentration (see below).

In 0.5 M cupric sulphate + 1 N sulphuric acid at 25°C, the present results (Fig. 2) indicate an exchange current near to $1 \times 10^{-3} \text{ A/cm}^2$. This is in excellent agreement with previous results (see above).

4.6 Effect of electrolyte composition

The effects to be discussed here, will only be those possibly exhibited by the components of pure and mixed solutions of cupric sulphate and sulphuric acid on the rate of copper dissolution and deposition when these reactions are under activation control. It has already been somewhat considered how the transition from activation control to diffusion control in deposition is affected by the composition of such solutions.

From Figs. 3 and 4 is seen that the anodic Tafel line has very nearly the same position in the Tafel diagram for the 0.1 N sulphuric acid solution as for any of its mixed solutions with cupric sulphate at 20°C. From Fig. 5 is further seen that the anodic Tafel lines obtained in the pure water solutions of cupric sulphate at 25°C, also have mutually the same position. This obviously means that neither the sulphate ions nor the cupric ions present in these solutions have any measureable effect on the dissolution reaction. As the sulphate ions are not components of the thermodynamic reaction equation of the Cu/Cu_{aq}⁺⁺ electrode ($\text{Cu} = \text{Cu}^{++} + 2e^-$), it is thereby clear that they cannot directly interact in the deposition process either.

A comparison of the anodic data in Fig. 3–5 further indicates that the reactions also are very nearly pH independent in the pH-range concerned (approximately 0 to 5), but that there possibly is a slight tendency for the reaction rates to increase with increasing pH in the upper part of this pH-range (the anodic curves in Fig. 5 showing an approximately 2.2 times faster rate than the 25°C curve in Fig. 3 at corresponding potentials). This may be the reason for the relatively large difference shown by eqns. (5) and (6) in the standard exchange current for copper/cupric sulphate in water at 25°C and in 0.1 N sulphuric acid at 20°C, respectively.

As the cupric sulphate activity has not been found to have any effect on the rate of dissolution, the observed effect of this activity on the exchange current

(eqn. (4)) must be entirely due to its effect on the rate of deposition. On the basis of (1), (4), and the Nernst equation for the reversible potential, it is easily seen that this means:

$$(d \log i_c / d \log a)_{v,T} = 2 \quad (7)$$

saying that the rate of deposition is proportional to the square of the cupric ion activity. According to the theory of activation controlled electrode reactions^{5,13}, the inverse of this exponent is equal to the stoichiometric number. The observed effect of activity is thereby in agreement with the observed effect of electrode potential in indicating this number to be 1/2 for the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode reactions (see eqn. (3)).

Except for the absence of any pH-effect, this is quite analogous to what has previously been found for the $\text{Fe}/\text{Fe}_{\text{aq}}^{++}$ electrode¹.

5.0 DISCUSSION

The results obtained in the present work, give the Tafel diagram shown in Fig. 7 (A) for the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode at 25°C. For comparison, some representative Tafel diagrams for the $\text{Fe}/\text{Fe}_{\text{aq}}^{++}$ electrode at the same temperature (constructed from the results discussed in Ref. 1) are shown in Fig. 7 (B) and (C). The symbols pCu and pFe used there, mean the negative logarithm of the activity of cupric and ferrous ions, respectively. All these diagrams only apply as far as the reactions are under activation control and the metal surface is sufficiently active.

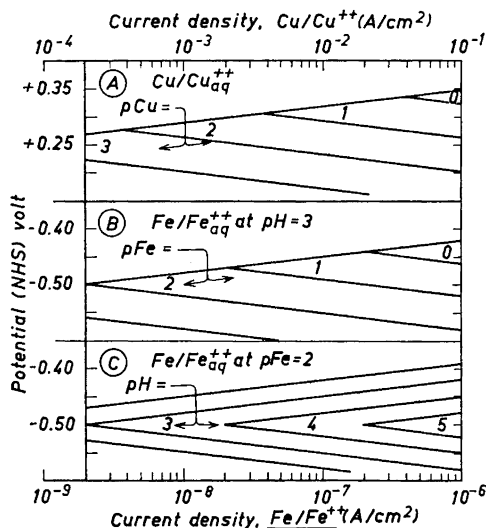


Fig. 7. Tafel diagrams for the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ and the $\text{Fe}/\text{Fe}_{\text{aq}}^{++}$ electrode at 25°C when under activation control (effect of potential, metal ion activity, and pH on reaction rate).

The results clearly indicate that the kinetic unit reaction (the smallest repeating reaction unit) of the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode in acid solution is:

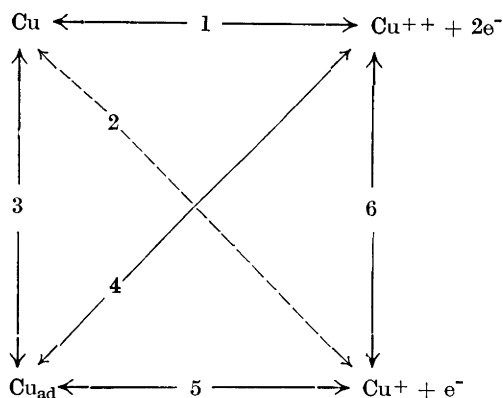


as compared to:



for the $\text{Fe}/\text{Fe}_{\text{aq}}^{++}$ electrode (see Ref.¹). These reaction equations directly reflect the observed effects of metal ion activity, pH, and potential (the Tafel slope being numerically $1/4$ of $2.303RT/\alpha F$) on the rate of the reactions in either direction.

The present results are not in agreement with the model of slow surface diffusion of ad-atoms, nor with the mechanism proposed by Mattsson and Bockris¹¹ of an intermediate formation of cuprous ions (see the above discussion of previous work). Both these models do namely seem to predict an unsymmetric behaviour of the electrode. Nevertheless, there obviously are several reasons to believe in the formation both of ad-atoms (see especially the work of Gerischer³⁰) and of cuprous ions (see especially the work of Miller and Lawless³⁵). A possible explanation of these apparent contradictions may be that the ad-atoms and the cuprous ions not are intermediates in the main reaction occurring under stationary conditions, but rather are components of some side reactions. As the reaction possibilities of the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode are:



the above suggestion is equivalent to saying that the reactions 2 and 3 (or 4 and 6) are negligibly slow as compared to reaction 1, making the reactions 4, 5, and 6 (or 2, 3, and 5) an almost independent, non-interfering circuit of side reactions (the formal possibility mentioned in parenthesis being less likely). The present experiments do not reveal anything else as to the relative rates of these possible side reactions, nor anything about their kinetics. It is possible, however, that the available impedance data^{20,21,36} and potentiostatic short-time transient data³⁰ may contain some clue to this question, when the model has been properly worked out.

A few remarks will finally be given to the crystallization habit by electro-deposition of copper. Both Fischer *et al.*⁶⁻⁸ and Pick *et al.*^{9,25,26} have shown that the crystal form of the deposit depends on either the current density (Fischer) or the overpotential (Pick) at which the deposition occurs. The main change is from a coherent pyramidal or ridged structure to an incoherent finely polycrystalline structure with increasing departure from equilibrium. In solutions rich enough in sulphuric acid, there appears an intermediate range in which a cubic or platelet type of structure is formed.

In the present work, poorly adhering powdery deposits (partly falling off the cathodes and thereby interfering with the cathodic current efficiency measurements) were obtained at current densities exceeding a limiting current dependent on both electrolyte composition and stirring. The limiting current is indicated by a steep deviation from the cathodic Tafel line (see Figs. 2, 4, and 5). These observations are essentially in accordance with those of Fischer *et al.* and Pick *et al.* However, with the additional information obtained in the present work through the observed effect of stirring (see especially Fig. 4B) it seems likely that the changes in crystallization habit simply are connected with the transition from activation control to diffusion control in deposition. All factors affecting this transition (*e.g.* electrolyte composition, temperature, stirring, inhibitors) must therefore be expected to be co-determining for the current densities (or overvoltages) at which the changes in crystallization habit occur. In the solutions of cupric sulphate in water (Fig. 5) and in 0.1 N sulphuric acid (Fig. 4), the transition seems to be distinctly sharper than in 1 N cupric sulphate + 1 N sulphuric acid (Fig. 2). It will at the present stage be refrained from going into the possible reasons for this, but only be pointed out that this trend is parallel to that of the occurrence of the cubic or platelet type of structure at intermediate current densities or overvoltages⁸.

Acknowledgement. The author is much indebted to Miss E. Huseby and Miss T. Tønnderum for technical assistance, to various members of the staff at the Central Institute for Industrial Research for valuable discussions and other help, and to the *Royal Norwegian Council for Scientific and Industrial Research* and the *U.S. Department of Army, European Research Office*, for financial support.

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Received November 16, 1960.