538. *The Anodic Behaviour of Copper in Neutral and Alkaline Chloride Solutions.*

By H. Lal and H. R. Thirsk.

The anodic behaviour of copper in neutral and alkaline sodium chloride solutions, in the presence and in the absence of oxygen, has been examined electrochemically by observing changes in the overpotential occurring during constant-current polarization and after the current has been interrupted. Particular attention has been paid to the conditions under which the metal passes freely into solution, to the nature of the oxide or salt deposited on the anode surface, and to the effect of increasing alkalinity on these phenomena. A general discussion of the experimental work has been given which, although omitting a detailed description of the results, presents an overall picture of the behaviour of the system.

UNDER equilibrium conditions a satisfactory description of the corrosion of a copper surface in aqueous chloride solutions over the whole pH range can be made by a theoretical study of the type described by Pourbaix ("Thermodynamics of Dilute Aqueous Solutions," Arnold, London, 1949). This theoretical approach considerably extends the treatment of such systems described some years previously by Gatty and Spooner ("The Electrode Potential Behaviour of Corroding Metals in Aqueous Solution," Oxford, Clarendon Press, 1938), Krueger and Kahlenberg (*Trans. Electrochem. Soc.*, 1930, **58**, 341), and Schmidt and Winkelman (*Helv. Chim. Acta*, 1930, **13**, 304). Thus, by making suitable assumptions concerning the solubility products of cuprous and cupric oxides and limiting assumptions concerning the number and type of complex anions in solution, the nature of the oxide or salt predominating on the copper surface can be calculated. Furthermore, changes in the equilibrium brought about when the electrode potential of the copper is altered by polarization may be deduced by reference to the calculated equilibrium diagrams. It is clear, however, that the kinetics of these changes and the phenomena occurring during the forced dissolution of the metal by the passing of a current are necessarily only accessible by direct experiment.

Hedges (*J.*, 1926, 1533; 1929, 1028) carried out an extensive investigation of the kinetics of the anodic behaviour of copper in hydrochloric acid solutions when polarized by the passage of fairly large currents; he was particularly interested in certain periodic fluctuations of current and voltage which were thus produced and which he related to a periodic change in structure of the layer covering the electrode. Also, Hickling and Taylor (*Trans. Faraday Soc.*, 1948, **44**, 262) studied the behaviour of copper in alkaline solutions.

The present paper is an account of work on the $Cu-H_2O-Cl$ system under neutral and alkaline conditions. Our interest has been centred on the factors controlling the free dissolution of the copper as cuprous ion or cuprous ion complex in neutral salt solutions and the maintaining of this process in alkaline solutions. Some observations have been made on periodic phenomena occurring at higher current densities. The results are discussed in two sections dealing (*A*) with neutral chloride solutions, and (*B*) with the modifications in behaviour brought about by addition of sodium hydroxide to the system.

The same experimental procedure was followed in neutral and alkaline solutions. Copper electrodes were formed from electrolytically pure wire 0·12 cm. in diameter. Areas were left exposed varying from 0·2 to 2 sq. cm., the remainder of the electrode being stopped off by coating with two layers of polystyrene, a process found satisfactory at the lower temperatures, or at higher temperatures by using a commercial thermal-setting plastic, applied in several coats, each cured at 140° for 30 min.

The electrodes were mounted by supporting them in glass tubes of ¼" internal diameter by means of small corks. The exposed metal surface was prepared by two slightly different methods. In the first a preliminary treatment with metal polish on a pad of cotton wool was followed by polishing with magnesium oxide on Selvyt cloth and a final cleaning with alcohol and distilled water. In the second the same procedure was carried out followed by a slight etch in dilute nitric acid. Electrodes thus prepared are referred to as " polished " and " etched " electrodes respectively. The apparent area of the exposed portion was measured by means of a travelling microscope. Current densities quoted refer to the current passed divided by the measured electrode area in cm.^{2}. Solutions were made from " AnalaR " reagents.

The Cells.—The majority of the experiments were performed in a wide-necked bottle of about 400-c.c. capacity fitted with a Perspex lid. The electrode under examination was fixed by means of a plastic-covered clip at one end of a slot machined in the lid. A vertical wide-bore limb of a tube joined to a Luggin capillary could be advanced along the slot by means of a screw of medium pitch working in a bolt to which the limb was attached. The tip of the capillary was thus brought with accuracy adjacent to the working electrode. The other end of the vertical limb was bent round to form a U tube with a three-way tap in the top portion. The liquid junction with a saturated calomel electrode, used as a reference half-cell, was made at the three-way tap. A second U tube was inserted through the lid of the cell and communicated with a separate vessel containing a large platinum cathode. The cell was mounted in a thermostat which could be operated at temperatures up to 60° ± 0·1°.

FIG. 1.

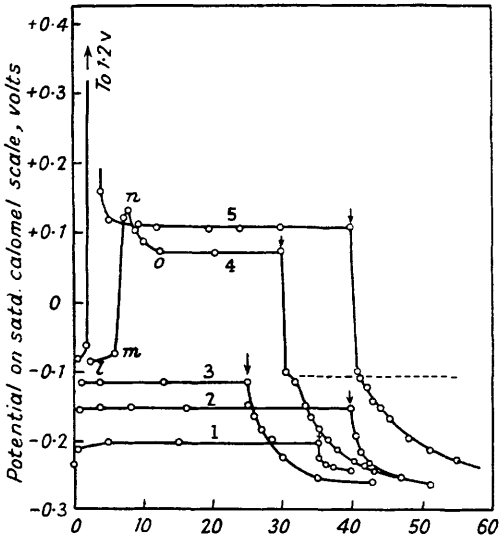

FIG. 2.

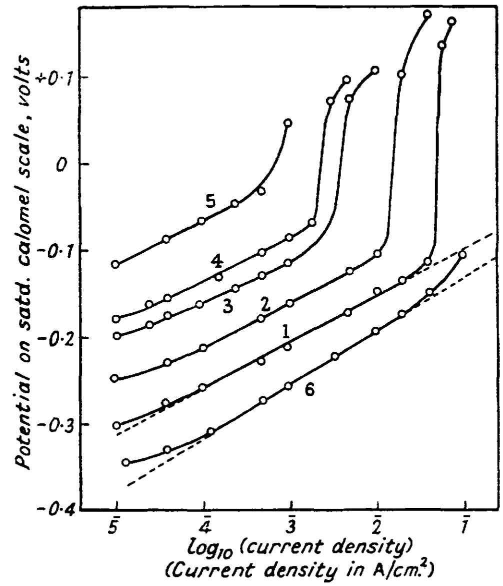

FIG. 1. *Anodic polarization curves for copper in* M-NaCl *together with curves showing the change of potential on stopping the current at the point indicated by the vertical arrow :* (1) 1×10^{-5}; (2) 1×10^{-4}; (3) 1×10^{-3}; (4) 5×10^{-3}; (5) 1×10^{-2} A/cm.^{2}. Dotted horizontal line represents the Cu–CuCl potential.

FIG. 2. *Curves showing the relationship between potential and log (current density) for copper in sodium chloride :* (1) 4M-NaCl; (2) 2·0M-NaCl; (3) 1·0M-NaCl; (4) 0·5M-NaCl; (5) 0·1M-NaCl; (6) 4M-NaCl. *Curves* 1—5 *at* 18°, *curve* 6 *at* 60°.

In experiments for which it was decided to exclude air, a cell was used with the Perspex lid replaced by a rubber bung with extra tubes for bubbling hydrogen or nitrogen through the solution and without the facilities for the lateral movement of the Luggin capillary.

The means of obtaining a constant current supply and of measuring the overvoltage was similar to that described by Lal, Thirsk, and Wynne-Jones (*Trans. Faraday Soc.*, 1951, **47**, 70).

Section A.

Experiments in Neutral Sodium Chloride Solutions.—A range of current densities from 10^{-5} to 0·1 A/cm.^{2} were employed in 0·1, 0·5, 1·0, 2·0, and 4·0M-sodium chloride. Experiments were carried out at 17°, 40°, and 60°. A limited series of runs were made at current densities of the order of 15—80 mA/cm.^{2}.

Fig. 1 gives some typical results, showing the relation between overpotential and time to illustrate the behaviour of the system. The graphs refer to a solution of 1M-sodium chloride at 17°, curves 1, 2, 3, 4, and 5 corresponding to values of the current densities of $0{\cdot}9 \times 10^{-5}$, $1{\cdot}0 \times 10^{-4}$, $1{\cdot}0 \times 10^{-3}$, $5{\cdot}0 \times 10^{-3}$ and $1{\cdot}0 \times 10^{-2}$ A/cm.². The arrow on the right-hand side of the curves shows the point at which the polarising current was interrupted, and the subsequent curve represents the behaviour of the electrode under self-discharge. It will be noted that curves 4 and 5 show an arrest near the Cu–$CuCl_2$ reversible potential, the calculated value being represented by the dotted horizontal line.

Very similar results were obtained at the different concentrations, with the lower range of current densities and at all temperatures noted above, except that in 0·1M-sodium chloride all curves rose steadily to a maximum without showing the peak value and subsequent fall as exhibited, *e.g.*, by curve 4, with a maximum at *n* and a fall to 0. In all the solutions other than 0·1M-sodium chloride the overvoltage oscillated round 1·2—1·5 volts for a few minutes when a polarising current density greater than about $1{\cdot}0 \times 10^{-2}$ A/cm.² was passed. This was a temporary phenomenon and the potential soon fell to a steady value. No evolution of oxygen was observed at the electrode.

Quite a different behaviour was noted with the higher range of current densities. At 25 mA/cm.² in 1·0M-sodium chloride the overpotential rose in 10 min. to a value of 18 v and a continuous oscillation ensued of about 1 v amplitude. Even in this case we did not observe production of oxygen at the electrode. A similar phenomenon was found with current densities of the order of 60 mA/cm.² and above in 2M-sodium chloride and above 80 mA/cm.² in 4M-sodium chloride. At these higher current densities the potential showed no tendency to fall to a steady value as with curves 4 and 5 (Fig. 1).

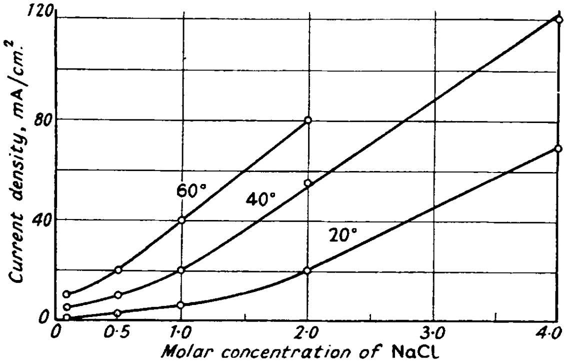

FIG. 3. *The effect of chloride concentration and temperature on the lowest current density at which cuprous chloride is deposited as a film on the electrode surface. (Unstirred solutions.)*

It was realised that when a certain current density was exceeded, dependent on the concentration of the electrolyte and the temperature, a precipitate would be formed on the electrode although the nature of the salt had to be determined. This was done by a consideration of the position of the arrests on the potential–time curves obtained after stopping the polarizing current and by some *X*-ray investigations. In the neutral chloride solutions the precipitate was shown to be cuprous chloride.

The plot of log (current density) against potential gave an almost linear relation up to a critical value of the current density corresponding to the formation of the insoluble deposits. To illustrate this, in Fig. 2 values of $\log_{10}$ (current density) are plotted against overvoltage for five different concentrations of sodium chloride at 17° (curves 1—5) and for 4M-sodium chloride at 60° (curve 6). Similar plots were obtained at 40° and 60°, and the values of the slopes have enabled us to reach some conclusions concerning the cause of the overvoltage during this stage of the dissolution of the metal. Fig. 3 shows the dependence on temperature and chloride concentration of the critical current density at which a deposit is formed on the electrode.

By repeating a selection of the above experiments in the absence of oxygen it was shown that the results in neutral sodium chloride were unaffected by the presence of air above the solution within the experimental accuracy of our potential measurements.

Discussion.—The equilibrium between cuprous and cupric ions in aqueous solution and a copper surface according to Fenwick (*J. Amer. Chem. Soc.*, 1926, **48**, 860) is given by

$$Cu^{++} + Cu = 2Cu^{+}\,;\ K = 1{\cdot}0 \times 10^{-6}$$

favouring the formation of cupric ions. This equilibrium is, however, shifted to the right by the tendency of the cuprous ions to form complexes in chloride solutions (see, *e.g.*, Noyes and Chow, *ibid.*, 1918, **40**, 739; Naray-Szabó and Szabó, *Z. phys. Chem.*, 1933, **166**, *A*, 228), with the result that copper goes into solution mainly as cuprous ions. The electrode potential at a given current density is controlled by the cuprous-ion concentration adjacent to the electrode. This concentration is determined by the difference between the rate of formation of cuprous ions, given initially by the current density and the rate of diffusion of cuprous ions away from the electrode to the bulk of the solution by means of the soluble chloride-ion complex. A dynamic equilibrium is thus established controlling the cuprous-ion concentration at the electrode surface.

The overvoltage, η, which is established along the linear portion of the curves in Fig. 2 may be reduced by stirring. This furnishes evidence that the rise in overpotential over this region is due to concentration polarization. This is not in contradiction to the linear η–log (C.D.) plot although such a relationship is commonly only associated with an activation overpotential. For example, Agar and Bowden (*Proc. Roy. Soc.*, 1938, *A*, **169**, 206) showed that, during electro-solution with the concentration of ions increasing with increasing current density and where the overpotential is determined by concentration changes of only one of the reacting ions, the linear relation $\eta = (\boldsymbol{RT}/n\boldsymbol{F}) \log (-I/I_0)$ holds providing I, the measured current density, exceeds a certain minimal value; I_0 is some limiting value of the current density and in this case $n = 1$.

The estimated value of the slope of the curve given by this simple treatment is 0·058 and 0·066 at 17° and 60°, respectively; the experimental values derived from the linear portion of curves 1—6 (Fig. 3) are $0{\cdot}05_5$ and 0·06 v at 17° and at 60°. These values are much of the same order as the calculated slopes and provide additional evidence for a diffusion-controlled overpotential rather than an activation overpotential.

The points at which cuprous chloride is precipitated are easily observed in Fig. 2 and in Fig. 1. In the latter the conditions are shown by the rapidly reached maxima of curves 4 and 5 (*e.g.*, the portion *lmno* of curve 4). In Fig. 2, a sharply rising overpotential is immediately noted.

For each salt concentration and temperature this sharp change of slope occurs at a reproducible current density, and the relation between the three factors is shown in Fig. 3. Since conditions for exceeding the copper chloride solubility product clearly depend on the temperature, the equilibrium constants for the reactions

$$CuCl + Cl^- \rightleftharpoons CuCl_2^- \text{ and } CuCl + 2Cl^- \rightleftharpoons CuCl_3^{--}$$

and the rate of production of copper ions controlled by the current density, the smooth nature of these curves is not of itself surprising. Fig. 3 is of importance, however, for the discussion of our results on the behaviour of the metal in alkaline solutions since we found difficulty in obtaining a free dissolution of the copper unless the current density over the area of attack was of the order associated in Fig. 3 with each particular temperature and chloride-ion concentration.

It has been shown by many different workers that the stable film in contact with air is cuprous oxide, and Evans (*J.*, 1925, **127**, 2484), Haase (*Chem. Fabr.*, 1934, **7**, 329; *Z. Metallk.*, 1934, **26**, 185), and Bengough *et al.* (*J. Inst. Metals*, 1913, **10**, 13; 1916, **15**, 37; 1919, **21**, 37; 1920, **23**, 97; 1924, **32**, 108) have shown that a similar film in general is formed in aqueous solution. Tourky and El Wakkad (*J.*, 1948, 750), studying the behaviour of copper electrodes in buffer solutions of varying pH and free initially from copper ions, showed that between pH 4·65 and 8·08 the electrode behaves as a well-defined metal oxide electrode. It might be expected, therefore, that the electrodes would attain initially, on open circuit, a potential independent of chloride-ion concentrations. This was not found in practice; some results are shown in the Table on p. 2643, but they agree closely with those obtained in potassium chloride solution by Gatty and Spooner (*loc. cit.*). These authors suggest that the chlorine ions when present in high concentrations cause dissolution of the oxide layer and that the electrode behaves as it would in hydrochloric acid solutions. Reduction of the chloride ion in the salt solution causes the potential to converge to a value corresponding to the presence of a Cu_2O layer. Reference to Pourbaix's discussion (*loc. cit.*) on the system shows quite clearly how the Cu_2O domain is reduced on the addition of chloride ion.

The periodic oscillations at high current densities have been attributed by Hedges (*loc. cit.*) to the formation of a highly resistant oxide film on the electrode. The discontinuity necessary for periodicity was supposed to be provided by the transformation of the stable oxide film into a less resistant variety which is attacked by the electrolyte to form cuprous chloride and then washed away. Hedges's experimental observations of colour changes during the polarization were similar to those recorded by Wilman (*Discuss. Faraday Soc.*, 1947, No. 1, 252), *viz.*, through dark grey, white, light grey, to yellowish-brown. In view of Wilman's observation that at all these stages the electron-diffraction pattern showed only cuprous chloride together with some copper in the early stages of the polarization, it cannot be certain that Hedges's assumption was correct that a particular colour was an indication of the presence of an oxide film. Alternatively, the periodic phenomenon may be due to a compact cuprous chloride film, the discontinuity being provided by cupric ions formed when the chloride deposit reaches a critical thickness. These ions may disrupt or modify the film of cuprous chloride, but at the same time, since the film is also being dissolved away by the electrolyte at the cuprous chloride–solution interface, the film is reduced in thickness and a return to the condition when the electrode dissolves once again as a cuprous ion is brought about; this cycle on being repeated gives rise to the periodic phenomenon. Under these conditions glancing incidence electron diffraction would only provide evidence for the presence of cuprous chloride unless the adhering layer can be stripped off and examined at the metal–salt interface.

Section B.

Experiments in Alkaline Sodium Chloride Solutions.—The effect of making the electrolyte alkaline increased considerably the complexity of the phenomena. They were affected both by the method of preparation of the electrode and by the presence of oxygen in the electrolyte. We limit our account to the range of our experimental conditions and the features of the behaviour for which a general discussion may be given, rather than treat in detail the large variety of overpotential–current density curves obtained.

The results are separated into two groups depending on whether the solutions were in equilibrium (*a*) with oxygen at the partial pressure of the atmosphere or (*b*) with hydrogen.

(a) *Air-saturated solutions.* Solutions used were N, 2N, and 4N with respect to sodium chloride and the pH was changed by the addition of "AnalaR" sodium hydroxide. Addition of 1 g./l. led to measured pH values of 11·79, 11·41, and 11·10, respectively. Experiments were carried out at 18°, 40°, and 60°.

The steady electrode potential reached on open circuit in all solutions before polarization was about $-0{\cdot}15$ v. Similar observations on hydrogen- and oxygen-saturated solutions have been made by other workers. Krueger and Kahlenberg (*loc. cit.*) found that in oxygen-saturated N-potassium hydroxide the open-circuit potential was much more positive than in hydrogen-saturated solutions, the values with respect to a saturated calomel electrode being $-0{\cdot}285$ and $-0{\cdot}548$ v, respectively, and a similar behaviour in alkaline sulphate solution was observed by Gatty and Spooner (*loc. cit.*). In more recent work by Hickling and Taylor (*loc. cit.*) it was suggested that a film of cuprous oxide was first formed on the copper electrode and this was followed by cupric oxide. The Cu_2O–CuO potential in an electrolyte of pH 11 should be about $-0{\cdot}14$ v on the saturated calomel scale. This agrees well with the steady potentials we observed before polarization.

Overpotential–time curves were taken over a range of current densities of 1×10^{-5} to 15×10^{-2} A/cm.². As an example, the behaviour at the lower current densities is described for 4M-sodium chloride containing 1 g. of sodium hydroxide/l. at $3{\cdot}3 \times 10^{-5}$ A/cm.² and at 5×10^{-3} A/cm.² and shown in Fig. 4(*a*) and 4(*b*). On closing of the circuit, at the lower current density, the potential first rises through a few tenths of a volt and then falls to a value, slightly positive to the Cu–CuCl reversible potential, which remains fairly steady. When the circuit is opened, the potential first shows an arrest near the Cu–CuCl potential and then continues to fall before finally rising, in a matter of hours, to the initial open-circuit potential. The extent of this fall of potential depends on the area of attack of the electrode. This area, at $3{\cdot}3 \times 10^{-5}$ A/cm.², was confined to one single red spot, the remainder of the electrode being covered with an adherent grey film. Attack quite clearly was only proceeding at one point, the cuprous chloride formed being converted immediately into the lower oxide. As the current density was increased, the number of points of attack also increased until eventually some change was observed in the shape of the overvoltage curves in that a much more positive value was reached. This is shown by Fig. 4(*b*); the shape resembles that of curve 4 in Fig. 1, but for neutral 4N-sodium chloride in order to obtain an overvoltage curve of this type a current density of 60 mA/cm.^{2} is required. A rough calculation concerning the relative areas attacked in the neutral and alkaline solutions shows that the current densities at the attacked areas are approximately the same in both cases. In the experiment relevant to Fig. 4(*b*) the area attacked was already quite large, and the short arrest at the Cu–CuCl potential on cessation of polarization was followed by a long arrest near the much lower Cu_2O–Cu potential.

Increase in pH produced a displacement of the behaviour in the sense that higher current densities were necessary in order to complete attack on the surface; decrease of pH gave solutions in which the electrode reacted in a manner increasingly similar to that in neutral solutions; *i.e.*, complete attack occurred at lower current densites with a decreasing tendency for the formation of the protective grey film and therefore the reappearance of much more negative prepolarization potentials.

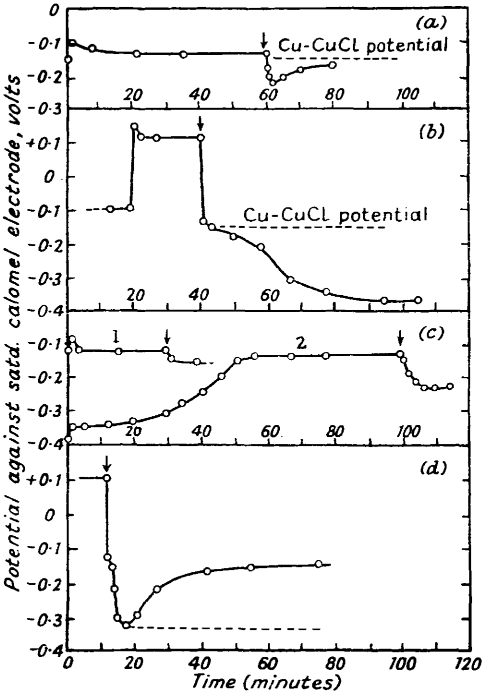

FIG. 4. *Vertical arrows show the point at which the polarizing current was switched off. Curves showing important features in the behaviour of anodically polarized copper in alkaline sodium chloride solutions: (a)* 4N-NaCl *with* 1 *g. of* NaOH/*l.*; *C.D.* $3 \cdot 3 \times 10^{-5}$ A/*cm.*^{2}. *(b) Solution as for (a)*; *C.D.* 5×10^{-3} A/*cm.*^{2}. *(c) Solution as for (a)*: *curve* (1) *polished electrode, curve* (2) *etched electrode. (d) Self-discharge curve after polarization in* 2N-NaCl *with* 1 *g. of* NaOH/*l. at* 1×10^{-2} A/*cm.*^{2}.

(b) *Hydrogen-saturated solutions.* Marked differences were observed with these solutions in the behaviour before and after polarization, but in general terms they can be explained fairly simply.

The polished electrodes showed an initial potential of about −0·15 v independent of chloride-ion concentration; the etched electrodes remained fairly steady at potentials near those found in neutral solutions. This is shown in the table.

Steady potential of etched copper electrodes in neutral and hydrogen-saturated alkaline sodium chloride solutions.

	Neutral sodium chloride:		Alkaline sodium chloride (1 g. NaOH/l.)	
	4M-NaCl	M-NaCl	4M-NaCl	M-NaCl
Potential (v) on the saturated calomel scale	−0·33	−0·23	−0·34 to −0·37	−0·24 to −0·26

It was considered that this difference was due to the presence of a protecting oxide in the case of the polished electrode, and that the etched electrode, in the absence of such a layer. was attacked by chloride ion with subsequent formation of cuprous oxide.

On polarization of these electrodes at similar current densities, the etched electrodes fairly soon reached an overpotential comparable with that given for the polished electrodes, and subsequently the behaviour was the same. This is illustrated in Fig. 4(*c*), curves (1) and (2), again for 4N-sodium chloride with 1 g. of sodium hydroxide/l.; (1) is for the polished and (2) for the etched electrode at a current density of 10^{-5} A/cm.^{2}. The short vertical arrows show the point at which the polarizing current was stopped. At these low current densities the final potential lies near the $CuO-Cu_2O$ potential.

At higher current densities, as in the aerated solutions, the protective layer is destroyed and the effect is shown in Fig. 4(*d*). These results were obtained in 2N-sodium chloride with 1 g. of hydroxide/l. at a current density of 1×10^{-2} A/cm.^{2}. The potential rose rapidly and a considerable area of the electrode showed the presence of red copper oxide. When the current was cut off, the potential fell to a short arrest at the Cu–CuCl potential and then to a steady value at about -0.34 v (the broken horizontal portion). If air was admitted to the solution the potential slowly rose to the steady value for a passivated electrode in the presence of oxygen.

This process is slow and is clearly controlled by the rate of diffusion of oxygen through the solution. The effect of the presence or absence of oxygen during the actual polarization is not marked except at very low current densities, since the diffusion of the gas is slow compared with the other electrochemical processes occurring at the electrode face.

The description of the behaviour in alkaline sodium chloride solutions does not include comments on the sharp and unreproducible fluctuations often observed in the over-potential curves. From a consideration of our data we ascribe these variations to mechanical breakdown in the otherwise continuous areas of oxide or salt on the electrode, so that they are secondary to the general course of the anodic processes described above which are themselves reproducible.

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