705. *The Anodic Oxidation of Metals at Very Low Current Density. Part III.* Copper.*

By S. E. S. El Wakkad and (Miss) Sayeda H. Emara.

The anodic oxidation of copper at very low current density is examined primarily in alkaline solutions where passivity takes place more readily. It is shown that when copper is forced from the hydrogen evolution potential to the oxygen evolution value, cuprous oxide is formed as a layer 4—5 molecules thick, and then part of this film is oxidised to cupric oxide or hydroxide. No evidence has been obtained for the formation of Cu_2O_3 as suggested by Müller. In solutions of pH 5·6 the anode never rises to the oxygen evolution potential. The anodic oxidation in such solutions containing copper ions of different concentrations has been studied as well, and the behaviour has been explained.

In continuation of previous work (El Wakkad and Emara, *J.*, 1952, 461), the anodic oxidation of copper at very low current density has been investigated. No work on copper from the present standpoint has been published, but studies under different conditions have yielded relevant information; *e.g.*, copper normally dissolves when made the anode in acid solutions but may become passive if conditions are such that a film of a sparingly soluble salt is formed on the surface, this being followed by production of a more protective oxide film which in general appears to be cuprous oxide, although cupric oxide is also formed under strongly oxidising conditions (Fischer, *Z. Elektrochem.*, 1903, **9**, 507; *Z. phys. Chem.*, 1904, **48**, 177; Shukoff, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1253). Müller (*Z. Elektrochem.*, 1907, **13**, 133) investigated the anodic behaviour of copper in very concentrated sodium hydroxide solutions and suggested that Cu_2O, CuO, and Cu_2O_3 are formed on the copper anode before oxygen evolution (see also Müller and Spitzer, *ibid.*, p. 27).

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* Part II, preceding paper.

The oxide Cu_2O_3 was considered to be unstable and decomposed to give oxygen and cupric oxide. Hickling and Taylor (*Trans. Faraday Soc.*, 1948, **44**, 262) on the other hand, using the oscillographic method, showed that the anodic polarisation at a copper anode in sodium hydroxide solutions was accompanied by formation of an oxide film on the anode. Cuprous oxide was initially formed but was almost at once oxidised to cupric oxide. With buffer solutions of progressively decreasing alkalinity the formation of a sparingly soluble salt preceded or accompanied the formation of the oxide film. In acid solutions giving soluble copper salts a copper anode did not become satisfactorily passive and the anodic process was merely the dissolution of copper.

From measurements on the equilibrium potentials of copper in solutions of different pH values, Tourky and El Wakkad (*J.*, 1948, 740, 749) and El Wakkad (*J.*, 1950, 3563) showed that cuprous oxide is formed on the surface of copper and that this oxide is the stable one on the surface of the metal. Numerous investigations have been made on the nature of the partially protective film formed when a fresh copper surface is exposed to, or heated in, air or oxygen (Hinshelwood, *Proc. Roy. Soc.*, 1923, **102**, 318; Evans, *J.*, 1925, **127**, 2491; Vernon, *J.*, 1926, 2273; Constable, *Proc. Roy. Soc.*, 1927, **115**, 570; Thomson, *ibid.*, 1930, **128**, 654; Murison, *Phil. Mag.*, 1934, **17**, 96; Campbell and Thomas, *Trans. Electrochem. Soc.*, 1939, **76**, 303); the results obtained seem to indicate that the film primarily formed is one of cuprous oxide, although cupric oxide may also be present particularly in films formed at high temperatures or by prolonged heating.

In the present investigation attention has been directed primarily to the behaviour of copper in alkaline solutions where passivity takes place more readily. It is shown that when copper is forced from the hydrogen evolution potential to the oxygen evolution value, cuprous oxide is first formed as a layer 4—5 molecules thick and then part of this film is oxidised to cupric oxide or hydroxide. No evidence has been obtained for the formation of Cu_2O_3 (see above). In comparatively acid solution (pH 5·6) the anode never rises to the oxygen evolution potential. The anodic behaviour in such solutions containing copper ions of different concentrations has also been studied, and it is found that when Cu^{++} ions are present in such acid solutions, oxidation to the cupric oxide stage can take place provided that the concentration of the Cu^{++} ions is not less than 0·0002M. This behaviour is explained by taking into consideration the solubility product of cuprous oxide and the cuprous–cupric equilibrium at the surface of metallic copper.

EXPERIMENTAL

The electrical circuit and the electrolytic cell used were as previously described (El Wakkad and Emara, *loc. cit.*). The copper electrodes were prepared by electrodeposition from acidified copper sulphate solution. The deposition was made on a platinum plate of 1·95 sq. cm. area by a current of 25 mA/electrode for 30 min. The electrode was washed several times in conductivity water and then with the solution under investigation before it was introduced into the electrolytic cell. Each experiment was carried out with a freshly prepared electrode. The anode was placed in such a position with respect to the cathode as to ensure uniform distribution of the polarising current at the anode surface. The cathode was a platinum spiral about 10 cm. long and 0·1 cm. in diameter.

Measurements were carried out mainly in alkaline solutions, *viz.*, 0·1N-sodium hydroxide (pH 13), 1N-sodium carbonate (pH 11·5), and 0·1M-sodium borate pH 9·2), and also in an acetic acid–sodium acetate buffer of pH 5·6. The solution in the cell was boiled before use and cooled in an atmosphere of pure nitrogen to remove dissolved oxygen.

The polarising currents used were 20 μA per electrode for the borate and carbonate solutions and 50 μA per electrode for the sodium hydroxide solution. In each solution three phenomena were investigated for each electrode: anodic polarisation, cathodic polarisation, and anodic decay. The procedure adopted in obtaining the corresponding curves was as described for platinum (El Wakkad and Emara, *loc. cit.*).

The reference half-cell was a saturated calomel electrode prepared as described before (*idem, loc. cit.*). The electrolytic cell and the reference half-cell were kept in an air thermostat at 25° $\pm$ 0·01°. The e.m.f. was measured with a calibrated meter bridge and an Onwood mirror galvanometer having a sensitivity of 190 mm. per microamp. All potentials quoted are on the hydrogen scale.

RESULTS AND DISCUSSION

Curve *A*, Fig. 1, is the characteristic anodic polarisation curve of copper at 25° with a polarising current of 20 μA, in 0·1M-sodium borate (pH 9·2). Curve *A*, Fig. 2, is the same anodic polarisation curve in N-sodium carbonate (pH 11·5), and curve *A*, Fig. 3 is the anodic polarisation curve of copper with a polarising current of 50 μA in 0·1N-sodium hydroxide (pH 13). From these curves, which show the variation in the potential of the copper anode with the quantity of electricity passed, it can be seen that at first there is a rapid initial build-up of potential (ascribable to the charging of the double layer as in previous studies, El Wakkad and Emara, *loc. cit.*) which is followed by two well-defined arrests before oxygen evolution. Measurements from a larger number of polarisation curves in 0·1M-sodium borate gave an average value of double-layer capacity of 900 μF per apparent sq. cm. of our copper electrode; in N-sodium carbonate, this value was also 900 μF, and in 0·1N-sodium hydroxide it was 1300 μF. The standard condition in this case was taken as that in the borate solution, since (see p. 3511) cuprous and cupric oxides are formed over the copper anodes before oxygen evolution, and these oxides are amphoteric. The isoelectric region, *i.e.*, that of minimum solubility, is in the slightly alkaline pH range, represented in this case by the borate buffer solution (Tourky and El Wakkad, *loc. cit.*; McDowell and Johnston, *J. Amer. Chem. Soc.*, 1936, **58**, 2009).

FIG. 1.

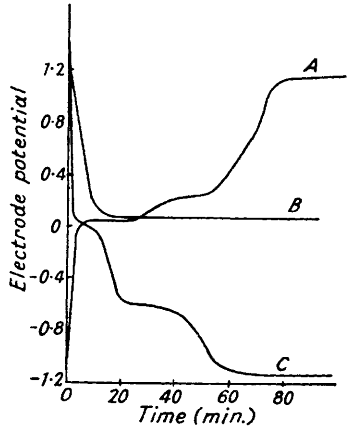


FIG. 2.

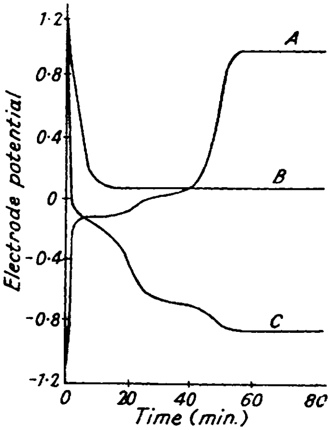
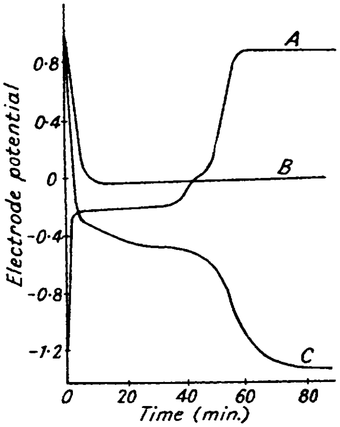


FIG. 3.



The first arrest after the charging of the double layer appears to start at a potential of —0·04 v in 0·1M-sodium borate, at —0·19 v in N-sodium carbonate, and at —0·28 v in 0·1N-sodium hydroxide. The second arrest appears to start at potentials of +0·19, +0·03, and —0·03 v in the three solutions respectively. In the table are shown the starting potentials for these two arrests in various electrolytes compared with the equilibrium potentials of the systems $Cu-Cu_2O$, Cu_2O-CuO, and $Cu_2O-Cu(OH)_2$. These equilibrium potentials were obtained as follows.

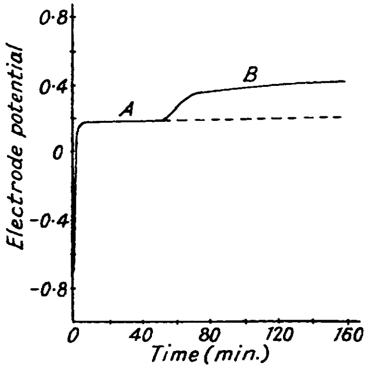
The free energy of cuprous oxide, OH^-, and H_2O being taken as —35,150, —37,585, and —56,690 cal. (Latimer, " The Oxidation States of the Elements and their Potentials in Aqueous Solutions," New York, 1938, p. 35, 170), the free-energy change of the reaction $2OH^- + 2Cu = Cu_2O + H_2O + 2e$ is $\Delta F = -16{,}670$ cal., and hence E_B^0 (the potential value at the extreme alkaline range of pH) is —0·361 v at 25°. By taking the free energy of CuO as —30,400 cal. (Latimer, *op. cit.*) the free-energy change of the rection $Cu_2O + 2OH^- = 2CuO + H_2O + 2e$ is $\Delta F = -7170$ cal., and hence E_B^0 is —0·156 v at 25°. Also by taking the free energy of $Cu(OH)_2$ as —85,500 cal. (*idem, ibid.*), the free energy of the reaction $Cu_2O + 2OH^- + H_2O = 2Cu(OH)_2 + 2e$ is $\Delta F = -3990$ cal., and E_B^0 is —0·087 v. By applying the ordinary equation for the variation of the potential of these systems with pH, the values shown in cols. 4, 5, and 6 of the table were obtained.

The very close agreement between the starting potential of the first and the second arrests and the equilibrium values for the systems Cu–Cu_2O and Cu_2O–$Cu(OH)_2$ leaves little doubt that these two steps in the anodic polarisation in such solutions correspond to the consecutive formation of cuprous oxide and cupric hydroxide. There is no step corresponding to the formation of a higher oxide (Cu_2O_3) as suggested by Müller (*loc. cit.*).

	Starting potential (v) of :		Equilibrium potential (v) of system :		
Solution	first arrest	second arrest	Cu–Cu_2O	Cu_2O–CuO	Cu_2O–$Cu(OH)_2$
0·1N-NaOH	−0·28	−0·03	−0·30	−0·10	−0·03
N-Na_2CO_3	−0·19	+0·03	−0·21	−0·01	+0·05
0·1M-$Na_2B_4O_7$ ...	−0·04	+0·19	−0·07	+0·13	+0·19

The quantity of electricity passed from the beginning of the first step to the end was, in sodium borate and sodium carbonate solutions, about 12,300 microcoulombs per apparent sq. cm. This is sufficient for the liberation of about 3·9 × 10^{16} atoms of oxygen. The specific gravity of copper being taken as 8·9, the diameter of the copper atom may be calculated to be 2·28 × 10^{-8} cm., and hence there would be about 1·93 × 10^{15} atoms per true sq. cm. at a copper surface. A rather rough estimate for the ratio of the real to the apparent area of the copper electrode under investigation can be obtained from the value of the capacity of the double layer at the electrode under the standard conditions. The capacity of the double layer of platinum anodes before oxide formation as obtained from previous studies (Hickling, *Trans. Faraday Soc.*, 1945, **41**, 333; El Wakkad and Emara, *loc. cit.*) can be estimated as 100 μF per true sq. cm. If the difference between the capacity of the copper electrode and platinum electrode is assumed to be due only to the difference in the area, the ratio of the real to the apparent area of our copper electrode will be about 9. This shows that the quantity of electricity passed in the first step corresponds to the formation of a Cu_2O film some 4—5 molecules thick. The quantity of electricity passed from the beginning of the first step to the end in the case of the sodium hydroxide solution was much larger than the above, *viz.*, 46,000 microcoulombs per apparent sq. cm.; this is, however, in harmony with the known fact that the solubilities of both cuprous and cupric oxides increase in such comparatively strongly alkaline solutions The quantity of electricity passed in the second step in the case of the borate solution was 10,300 microcoulombs per apparent sq. cm., but in the carbonate and sodium hydroxide solutions it was 6000 microcoulombs. This suggests that the film of $Cu(OH)_2$ formed was less than the Cu_2O, or that part of Cu_2O film initially present in contact with the metal had been oxidised to $Cu(OH)_2$ before oxygen evolution. This view is further confirmed by both the decay and the cathodic curves (curves *B* and *C*, respectively, in Figs. 1, 2, and 3). The decay curves *B* reveal that on interruption of the polarising current when the copper anode was at the oxygen evolution potential, the potential fell to that of the system Cu_2O–$Cu(OH)_2$, whereat it remained constant and did not fall to that of the Cu–Cu_2O system. It is known that the Cu–CuO or Cu–$Cu(OH)_2$ system is always unstable (specially in alkaline solutions) owing to the reduction of CuO to Cu_2O (Britton, *J.*, 1925, **127**, 2796; Allmand, *J.*, 1909, **95**, 2151). The stability of the electrode potential at the Cu_2O–$Cu(OH)_2$ potential indicates, therefore, that the cupric hydroxide is not in direct contact with the metal.

FIG. 4.



In the cathodic curves there are two distinct steps which are expected to correspond to the reduction of cupric hydroxide and cuprous oxide. The potentials of these steps are, however, displaced to more negative values than the reversible potentials of the Cu_2O–$Cu(OH)_2$ and Cu–Cu_2O systems. The same observations were made also by Hickling and Taylor (*loc. cit.*). This behaviour in the reduction process can be explained by taking into consideration the view expressed before, *viz.*, that in the anodic polarisation most of the cuprous oxide is oxidised to $Cu(OH)_2$. Owing to the comparatively high resistance of both cuprous and cupric oxides or hydroxides, and as the oxide films here are not very protective, it can be imagined that in the cathodic polarisation reduction starts at the metal surface and that the section of the very thin film of Cu_2O in contact with the metal is reduced first. The freshly formed metallic surface will therefore come into contact with the outer thick layer of cupric hydroxide. As this happens, there will be a transient tendency for the more positive potential of Cu_2O–$Cu(OH)_2$ to be restored, but this is rapidly levelled down as reduction proceeds further. The difference in potential between the systems Cu–Cu_2O and Cu–$Cu(OH)_2$ is only about 0·1 v, and it can be expected that, at this stage, the reduction of both Cu_2O and $Cu(OH)_2$ will take place. The second step in the cathodic curves, which occurs at a very negative value and approximately at the same potential in all solutions, may be due to the presence of very small amounts of copper dissolved, probably as cuprite ions (Tourky and El Wakkad, *loc. cit.*).

In the case of more acid solutions, *i.e.*, acetate buffer of pH 5·6 (curve *A*, Fig. 4), the copper anode never rose to the value of oxygen evolution potential but remained constant at 0·19 v. This is the value for Cu–Cu_2O at the corresponding pH, which indicates that the cuprous oxide formed possesses a very high solubility in such a solution. When copper sulphate was added to such a solution, the shape of the curve did not change until the solution became about 0·0002M with respect to Cu^{++} ions, after which it rose to *B* (Fig. 4) starting at the potential +0·35 v, which is the Cu_2O–CuO potential at the corresponding pH value.

These observations can be explained by taking into consideration the solubility product of cuprous oxide and the cuprous and cupric equilibrium at the surface of metallic copper : the solubility product of cuprous oxide being taken as $7{\cdot}18 \times 10^{-14}$ (Tourky and El Wakkad, *loc. cit.*) and the equilibrium constant of the reaction $Cu + Cu^{++} = 2Cu^{+}$ as 1×10^{-5} from El Wakkad's recent work (*loc. cit.*), a solution of pH 5·6 and 0·0002M with respect to Cu^{++} ions will lead directly to the formation of cuprous oxide over metallic copper when this metal is dipped in such a solution. The anodic polarisation under these conditions will lead therefore to the oxidation of Cu_2O to CuO, as has been found experimentally.

CAIRO UNIVERSITY, FACULTY OF SCIENCE, CAIRO, EGYPT. [*Received, April* 13*th*, 1953.]