EXAMINATION OF THE POTENTIAL OF COPPER DURING ITS DISSOLUTION IN SODIUM HYDROXIDE

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Received August 25th, 1980

Parallel to kinetic measurements, the potential of copper was monitored on the (100), (110), and (111) crystallographic planes during its spontaneous reaction in sodium hydroxide in oxygen atmosphere. A quantitative relation was obtained for the potential in dependence on the experimental conditions, indicating that unless a passivating layer of copper(II) oxide is formed on the surface, the metal does not act as an oxygen electrode. The potential change in the given medium was found to depend only on the amount of copper(I) oxide formed, obeying the relation $E = (RT/nF) \ln (m_{Cu_2O}) + K$; use was made of this relation for a quantitative determination of the growth of the copper(I) oxide layer.

The problem of the potential in spontaneous dissolution of metals has not so far received much attention. Among the most extensive works dealing with this topic is that of Butler and coworkers[1], who measured the potentials for common metals in oxygen-containing solutions of $NaHCO_3$ and $NaHCO_3$ + NaCl at the temperatures 20 and 150°C; an increase in the oxygen concentration brought about a shift of the potential in the positive direction, this effect being more pronounced with less noble metals. The authors have suggested that after a passivating oxide layer is formed on the metal, the latter behaves as an oxygen electrode. In our work[2] we examined the potential during the dissolution of polycrystalline copper in sodium hydroxide solution and found it to be determined by the hydroxide activity solely, $E \sim (RT/F) \ln (a_{NaOH})$, the concentration of oxygen having only a negligible effect. Vijh[3] gives for the metal potential in oxygen-containing solutions the relation

$$E = K \ln (i_c/i_a) + K_1 , \quad (1)$$

where i_c and i_a are the cathodic and the anodic exchange currents, respectively, and K and K_1 are constants. The author suggests that the potential is determined by the conjugate cathodic reduction of oxygen, and demonstrates that there is a relation between the potential and the semiconductor properties of oxides on metals.

In the present work, which is a continuation of the paper[4], the effect of medium on the potential of a copper single crystal during its dissolution in sodium hydroxide in oxygen atmosphere is evaluated and the potential is related to the amount of the copper(I) oxide formed on the surface.

EXPERIMENTAL

The potential of copper was monitored during kinetic measurements. The apparatus used and the preliminary sample treatment have been described in the paper[4]. The potential was measured against a saturated calomel electrode, connected with the reacting system by means of a salt bridge of saturated KCl solution and held at a constant temperature of 15°C by using an ultrathermostat. The potentials measured were converted to the hydrogen scale values. A Radiometer Copenhagen pH-meter was employed; the measurement accuracy was ±0·5 mV, the reproducibility was on average ±5 mV.

The oxide detection and determination on the surface was carried out by means of galvanostatic reduction in 0·2M-NH_4Cl, which appeared to be most suitable[5] at current densities of 0·01 to 0·06 mA mm^{-2} under nitrogen. The current was held constant by using a Ple 6 potentiostat, adapted also to galvanostatic measurements. The potential was measured against a saturated calomel electrode, connected with the working electrode by a Luggin's capillary. The potential values in the galvanostatic reduction are given in reference to saturated calomel electrode. The sample for calibration was prepared by anodic dissolution in 4M-NaOH at the temperature

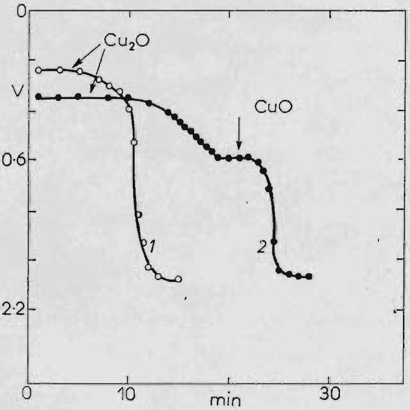

FIG. 1

Calibration measurements for the determination of copper oxides. *1* sample dissolved anodically for 15 min with the current density 0·4 mA mm^{-2}, I_{red} = 0·03 mA mm^{-2}; *2* anodic dissolution for 35 min with I = = 0·4 mA mm^{-2}, I_{red} = 0·06 mA mm^{-2}

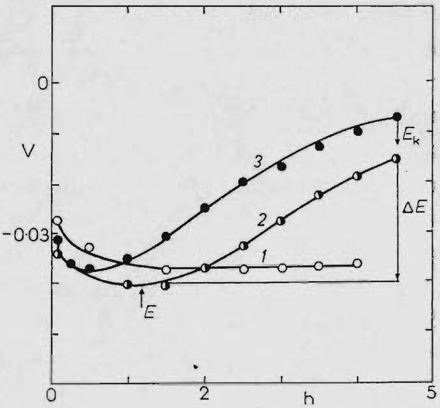

FIG. 2

Time variations of the potential of copper single crystal during its dissolution in 0·5M-NaOH; t = 15°C, P_{O_2} = 0·1 MPa. Planes: *1* (100), *2* (110), *3* (111)

25°C and current density 0·4 mA mm^{-2} for different periods. On a 15 min anodic dissolution, only copper(I) oxide formed on the (111) plane (Fig. 1, curve *1*), whereas both oxides appeared if the dissolution was carried out for 35 min (Fig. 1, curve *2*). The reduction potentials of the oxides depended on the reducing current and on the surface structure, making —0·300 ± 0·070 V for Cu_2O and —0·600 ± 0·030 V for CuO, which is in a good agreement with the data of the papers[5-7]. A platinum electrode served as the auxiliary electrode.

RESULTS AND DISCUSSION

The time variations of the potential are related with the mechanism of dissolution of the various single crystal planes, hence depend on the plane involved (Fig. 2). On the (100) plane, which dissolves with a constant rate from the very beginning of the reaction and on which copper(I) oxide is not observed to form, the potential has a steady value. On the (110) and (111) planes a copper(I) oxide layer is formed during the dissolution; in this process the potential shifts in the positive direction, approaching a limiting value. This indicates that in steady experimental conditions the potential change ($\Delta E = E_k - E$, Fig. 2) depends on the amount of copper(I) oxide formed on the surface. The potential E (the most negative value in the time course) at a constant temperature and stirring rate generally only depends on the pressure (concentration) of oxygen and activity of NaOH.

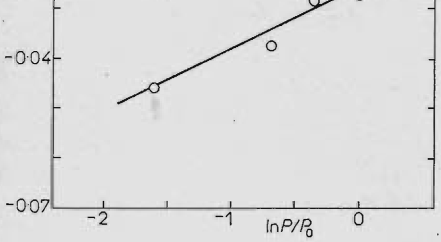

FIG. 3

Effect of the oxygen pressure on the potential of Cu (100) in 0·5M-NaOH at 15°C

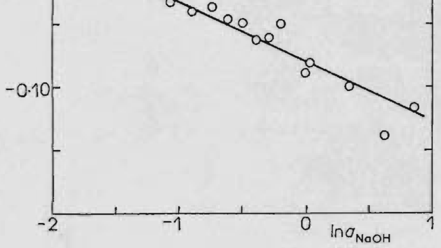

FIG. 4

Dependence of the potential of Cu (100) on the activity of NaOH; t = 15°C, P_{O_2} = = 0·1 MPa

The effect of the oxygen pressure was measured for the three planes in the region of 0·02–0·1 MPa in 0·5 M-NaOH at 15°C; for the (100) crystallographic plane the dependence is plotted in Fig. 3 (relative units are used, for the potential to be independent of the pressure units used). The slope of the plot is 0·012 V, which suggests that the potential in dependence on the pressure can be written as

$$E = E_1^0 + (RT/2F)\ln(P/P_0)\,. \tag{2}$$

The effect of the activity of sodium hydroxide was examined in the hydroxide concentration region of 0·2–4·0 mol l^{-1} at the temperature 15°C and oxygen pressure 0·1 MPa. It must be, however, borne in mind that the oxygen concentrations in the various hydroxide solutions are different, as expressed by the Bunsen absorption coefficient ratio α/α_0, where α_0 refers to the unit activity of NaOH. At a constant oxygen pressure, the potential can be thus written as

$$E = E^0 + (RT/2F)\ln(\alpha/\alpha_0) - A\ln a_{\mathrm{NaOH}}\,, \tag{3a}$$

or

$$E_1 = E^0 - A\ln a_{\mathrm{NaOH}}\,, \tag{3b}$$

where $A = RT/nF$ and $E_1 = E - (RT/2F)\ln(\alpha/\alpha_0)$. The dependence (*3b*) for the (100) plane is plotted in Fig. 4. The A and E^0 values were calculated by the least squares method and are given for the three planes in Table I. Based on the results, numerical values can be inserted in Eq. (*3a*) to obtain

$$E = -0{\cdot}076 + (RT/2F)\ln(\alpha/\alpha_0) - (RT/0{\cdot}5F)\ln a_{\mathrm{NaOH}}\,. \tag{3c}$$

This implies that copper does not behave as an oxygen electrode, because there is no passivating oxide layer on its surface whose potential in alkaline solutions would

TABLE I

Values of the constants in the relation (*3a,b*)

Orientation	$A = RT/nF$ V	n	E^0, V
(100)	0·048 ± 0·003	0·5	—0·079 ± 0·003
(110)	0·040 ± 0·002	0·6	—0·070 ± 0·003
(111)	0·047 ± 0·003	0·5	—0·078 ± 0·003

obey the relation

$$E = E^0 + (RT/4F) \ln P_{O_2} - (RT/F) \ln a_{NaOH} , \qquad (4)$$

obtained by Butler and coworkers[1] and measured by us for polycrystalline copper[2]. In this case the potential will be governed not only by the oxygen reduction, but also by copper oxidation, hence, by the exchange current ratio i_c/i_a (Eq. (*1*)).

TABLE II

Values of the constants in the relation (*5*)

t °C	$B = RT/nF$ V	n	K V
15	0·003	8	0·035
30	0·007	4	0·071
50	0·011	2—3	0·091

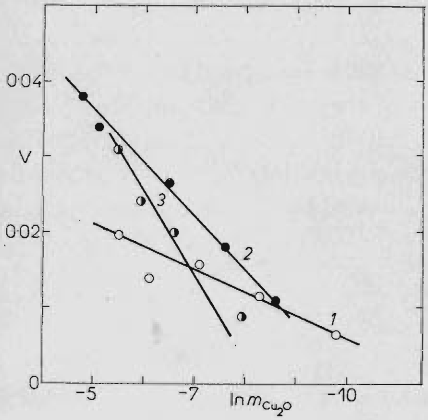

FIG. 5

Dependences of the potential change of Cu (100) on the amount of copper(I) oxide in 0·5M-NaOH for the oxygen pressure 0·1 MPa and temperatures: ○ 15°C, ● 30°C, ◑ 50°C

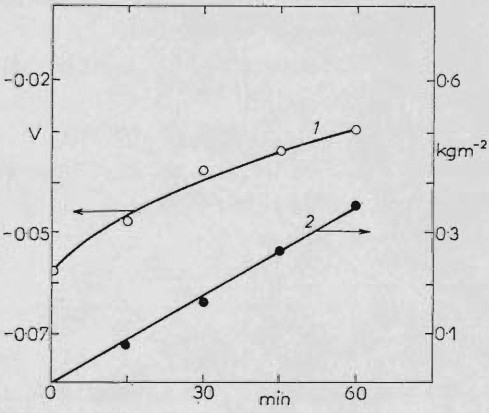

FIG. 6

Monitoring of the growth of copper(I) oxide layer on the (100) plane in 0·5M-NaOH at the temperature 50°C and oxygen pressure 0·1 MPa; *1* potentiometric, *2* coulometric

As mentioned above, the ΔE value in the experimental conditions used depends only on the amount of copper(I) oxide. This is obviously associated with the fact that the source of electrons in the oxygen reduction is the metal oxide rather than the metal itself. For instance,

$$Cu_2O + 2\,OH^- + H_2O = 2\,Cu(OH)_2 + 2\,e \qquad (A)$$

$$Cu_2O + 2\,OH^- = 2\,CuO + H_2O + 2\,e \qquad (B)$$

$$Cu_2O + 4\,OH^- + H_2O = 2\,Cu(OH)_3^- + 2\,e\,. \qquad (C)$$

We have found experimentally that the ΔE value is quantitatively related with the amount of copper(I) oxide through the equation

$$E = B \ln m_{Cu_2O} + K\,, \qquad (5)$$

where $B = (RT/nF)$ and K are constants in the given conditions. This rather unusual dependence probably stems from the tight relation between the amount of copper(I) oxide and the degree of coating of the copper surface by the oxide. The plots of this relation for the (100) plane and three different temperatures are shown in Fig. 5. The B and K values as well as the emerging numbers of electrons n are given in Table II. The number of electrons is seen to decrease with temperature.

Use can be made of Eq. (5) for a quantitative determination of the amount of copper(I) oxide formed, provided that the B and K constant values are known, or else for a qualitative assessment of the layer growth. This has been applied to the rise in the amount of copper(I) oxide during the reaction of the (100) plane in 0·5 M-NaOH at 50°C. The potential measurements revealed that the amount of copper(I) oxide on the surface till the formation of the passivating copper(II) oxide layer obeys the linear relationship (Fig. 6, curve *a*); this was also verified by the galvanostatic method (Fig. 6, curve *b*).

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Translated by P. Adámek.