

## SHORT COMMUNICATION

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### Electrochemical formation and cathodic dissolution of a thin cuprous oxide film on copper in alkaline aqueous solution

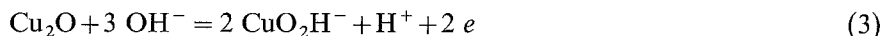
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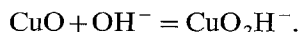
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It is generally agreed that the electrodisolution of copper in alkaline solutions occurs in three successive, one-electron stage reactions. The dissolution as Cu(I) and Cu(III) takes place through a thin oxide film and the Cu(II) stage was interpreted as a dissolution–precipitation process<sup>1</sup>. Cyclic voltammetry *E/I* profiles in 2 *M* aqueous KOH run between  $-1.1$  V to ca. 1.0 V (*vs.* Hg/HgO 1 *M* KOH) exhibits nine current peaks which were assigned with a good degree of certainty by comparison with previously published results, although a few of them were somewhat speculative<sup>2</sup>. Among the latter the current peaks related to Cu<sub>2</sub>O electroformation and electroreduction are included. The electrochemical formation of Cu<sub>2</sub>O on copper was interpreted as a rapid formation of oxide nuclei followed by their lateral growth<sup>3,4</sup>. The current peak related to the formation of Cu(I) in 2 *M* KOH is nearly ten times smaller in both height and area than the one for the formation of Cu(II)<sup>5</sup>. The shape of the capacitance curves run within the potential region limited by hydrogen evolution and oxide film formation was interpreted in terms of adsorption effects<sup>6</sup>.

The present report refers to the potentiodynamic characteristics of the electrochemical formation and cathodic dissolution of the thin Cu<sub>2</sub>O film which participates in the electrodisolution of copper in aqueous alkaline solutions at 25 °C. The principal thermodynamic equilibria to be considered for copper in 10<sup>-2</sup> *M* NaOH are<sup>7</sup>:



and



When a copper disc electrode immersed in a 10<sup>-2</sup> *M* NaOH solution, at 25 °C, is polarized under a linear potential sweep from  $-0.8$  V (*vs.* SCE) upwards, the cathodic *E/I* profiles change with the anodic potential limit reached (Fig. 1). The anodic potential sweep exhibits, then, two current maxima and

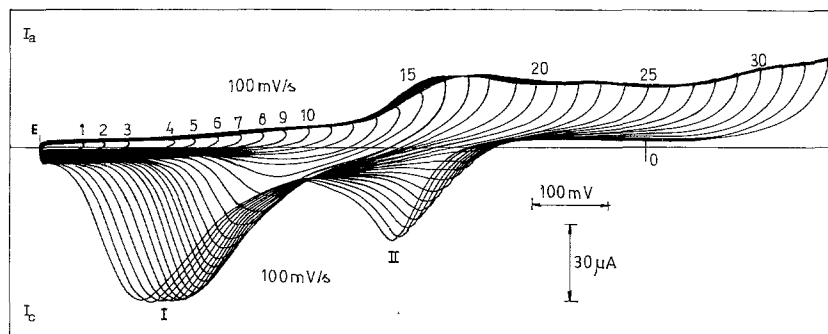


Fig. 1.  $E/I$  profiles obtained with a single triangular potential sweep at  $v_a = v_c = 100 \text{ mV s}^{-1}$  starting from  $E_1$ . The anodic potential limit is increased from the 1st to the 33th potential scan. Each run is made with a new polished copper disc electrode ( $0.07 \text{ cm}^2$ ).

beyond 0 V a continuous current increase is noticed. The cathodic potential sweep presents two main cathodic current peaks, (I) and (II), as indicated in Fig. 1. Current peak (I) has the following features. The corresponding amount of charge increases with the anodic potential limit attaining a maximum value when the anodic potential limit reaches *ca.*  $-0.1 \text{ V}$ . This maximum value is about  $1500 \mu\text{C cm}^{-2}$  and corresponds to a  $\text{Cu}_2\text{O}$  layer thickness of about  $40 \times 10^{-8} \text{ cm}$ . This figure agrees with the conclusion earlier derived concerning the oxide film thickness involved in the anodic dissolution of copper in alkaline solutions<sup>8,9</sup>. The potential corresponding to the current peak becomes more negative when the anodic potential limit increases further. The initial portions of the cathodic  $E/I$  contour are coincident provided the anodic potential limit is lower than  $-0.100 \text{ V}$ . When the latter extends beyond it, then the whole  $E/I$  profile shifts to more negative potentials.

Cathodic current peak (II) appears when the anodic potential limit extends beyond  $-0.050 \text{ V}$ . It should be related to a reduction of  $\text{CuO}$  or  $\text{CuO}_2\text{H}^-$  to  $\text{Cu}$ . The corresponding peak potential shifts also to more negative potentials as the anodic potential limit increases. The occurrence of the cathodic current peak (II) apparently has no appreciable influence on the amount of charge playing part during the cathodic process related to current peak (I). This fact implies that an electrochemical reduction of either  $\text{CuO}$  or  $\text{CuO}_2\text{H}^-$  to  $\text{Cu}_2\text{O}$  should, in principle, be discarded as the main cathodic process associated to current peak (II). The  $E/I$  profiles comprise, too, isopotential points located, respectively, at  $-0.190 \text{ V}$  and  $-0.450 \text{ V}$ .

When the potential amplitude swept is between  $-0.855 \text{ V}$  and  $-0.070 \text{ V}$ , a relatively simple  $E/I$  profile is obtained (Fig. 2). Under these circumstances the amounts of anodic and cathodic charges playing part in both processes are practically equal and then the cathodic current peak (I) increases approximately linearly with the potential sweep rate. The shape of the cathodic  $E/I$  profile, however, should be considered as a complex contour. This is clearly noticed by a systematic increase of the cathodic current at the initial portion of the  $E/I$  curve when the cathodic potential sweep rate increases. This effect apparently reveals the participation of another process at the beginning of the surface oxide electroreduction.

The extent of this contribution depends on the time elapsed from the initiation of the reverse potential sweep to reach the corresponding reduction potential. It should be stressed that the total amount of charge displayed during the cathodic

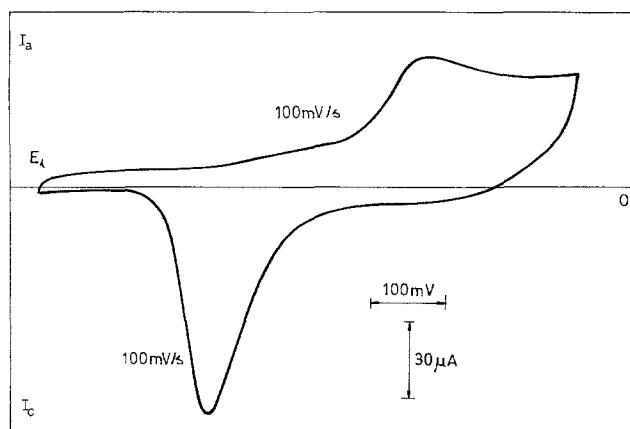


Fig. 2.  $E/I$  profile obtained with a single triangular potential sweep at  $v_a = v_c = 100 \text{ mV s}^{-1}$  starting from  $E_i$ .

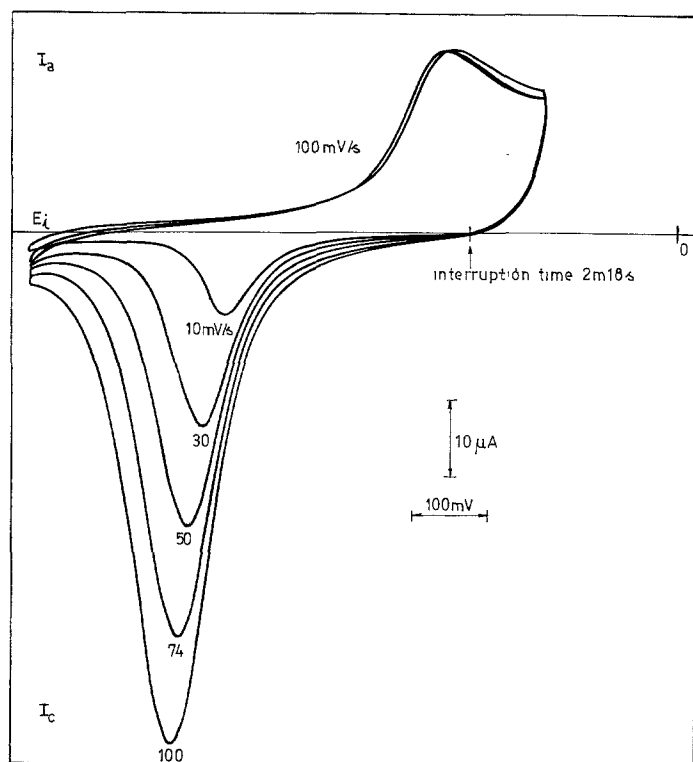


Fig. 3.  $E/I$  profiles obtained with a single triangular potential sweep at  $v_a = 50 \text{ mV s}^{-1}$  and different  $v_c$  with interruption of the potential scan at  $I=0$  for 2 min 18 s.

scan is independent of the relative contribution of the various concurrent processes.

If the cathodic potential scan is interrupted for a certain time at the null net current potential, then the cathodic current peak (I) becomes better defined and the initial cathodic current contribution can be, when the proper time is chosen, practically eliminated (Fig. 3). Under these circumstances, the current peak height (I) increases linearly with the potential sweep rate,  $v$ , and its potential changes linearly with  $\log v$ , involving a slope slightly higher than 60 mV per decade.

The characteristics just described resemble those already seen during the electrochemical formation and electroreduction of thin oxide films on other metals where ageing and chemical dissolution processes have been reported<sup>10,11</sup>. As suspected earlier these processes are inherent to film formation on different substrates, these being either a monolayer thickness film or a thin multilayer film.

The occurrence of isopotential points<sup>12</sup> during  $\text{Cu}_2\text{O}$  film electroreduction indicates that the oxide film is likely to be formed by different solid species whose relative concentration depends on the time elapsed between their formation and electrochemical reduction. These preliminary evidences of complex processes occurring during  $\text{Cu}_2\text{O}$  anodic film formation and electroreduction serve as an approach to the kinetics of the individual processes including the early stages of film formation. A quantitative approach to these processes will be reported in a future extended publication.

#### ACKNOWLEDGEMENT

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