

Preliminary note

OXYGEN ELECTROSORPTION ON COPPER SINGLE CRYSTAL ELECTRODES IN SODIUM HYDROXIDE SOLUTION

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INTRODUCTION

In a study of the initial stages of anodic oxidation of polycrystalline copper electrodes in alkaline solutions [1], we measured potential sweep voltammetry curves which show that formation of bulk Cu_2O is preceded by electrosorption of oxygen species. The electrosorption occurs in two successive stages, each represented by a current peak, corresponding to a different submonolayer state with a different adsorption energy. We postulated that *a priori* heterogeneity of the surface, e.g. exposure of various crystal planes, could be an explanation for the occurrence of multiple peaks.

In order to test this hypothesis we have investigated the electrosorption of oxygen on carefully prepared copper single crystal surfaces.

Clear evidence is found in our results, that the electrosorption of oxygen is a plane specific reaction. Each peak in the voltammogram on polycrystalline copper can be attributed to exposure of regions with specific adsorption sites as present in majority on different single crystal planes.

EXPERIMENTAL

The working electrodes were disc-shaped crystals, spark-cut to within 2° of the desired orientation from 99.999% pure copper rods purchased from Material Research Corporation. The electrodes were sealed into acrylic resin (Technovite 4071) in such a way that only the top surface of the metal was exposed to the solution. The diameter of the crystals was 6.4 mm. The electrode surfaces were ground with carborundum paper and polished with diamond pastes (6–0.25 μm) and carefully cleaned after each process. Finally, the surfaces were electropolished (see next Section).

All potentials quoted in this paper are against the Ingold "Argenthal" electrode (Ag/AgCl , KCl (3M))//; $E = 207$ mV vs. NHE).

For further experimental details we refer to refs. [1, 2].

RESULTS AND DISCUSSION

Cyclic voltammetry curves were recorded at a sweep rate $s = 20$ mV s^{-1} for copper single crystals in 1 mol dm^{-3} NaOH. The orientations that were studied

were (111), (110) and (100). Meaningful measurements were only obtained with surfaces that had been electropolished by a method described by Kötzt and Lewerenz [3], where electropolishing is done at 0°C in a solution consisting of 2 parts methanol and 1 part HNO₃ (65%). Other polishing procedures [4–6] that were tried resulted in samples of poor quality, as indicated by the ellipsometrically determined optical parameters (*vide infra*) and by the fact that their voltammograms resembled those obtained for polycrystalline surfaces. Kötzt and Lewerenz [3] came to the same conclusion from measurements of the anisotropy in electroreflectance plots.

Figures 1–3 show current–potential curves for Cu(111), Cu(110) and Cu(100) respectively, with increasing reversal potentials in the –700 to –500 mV region. The results obtained were independent of whether the potential scans were single or repetitive. This shows that there is no surface roughening and production of other crystal planes. For the sake of clarity it is noted here that the reversible Cu/Cu₂O potential at a pH = 14 is reported to be –563 mV [7].

From a comparison between the voltammograms in Figs. 1–3 the influence of the atomic geometry of the metal on the oxygen electroadsorption is evident. The Cu(111) face shows little reactivity in the underpotential range. The voltammograms on the Cu(110) face show an adsorption peak at about –610 mV, with the corresponding desorption peak at about –620 mV. From the small peak separation it follows that the adsorption–desorption behaviour is rather reversible.

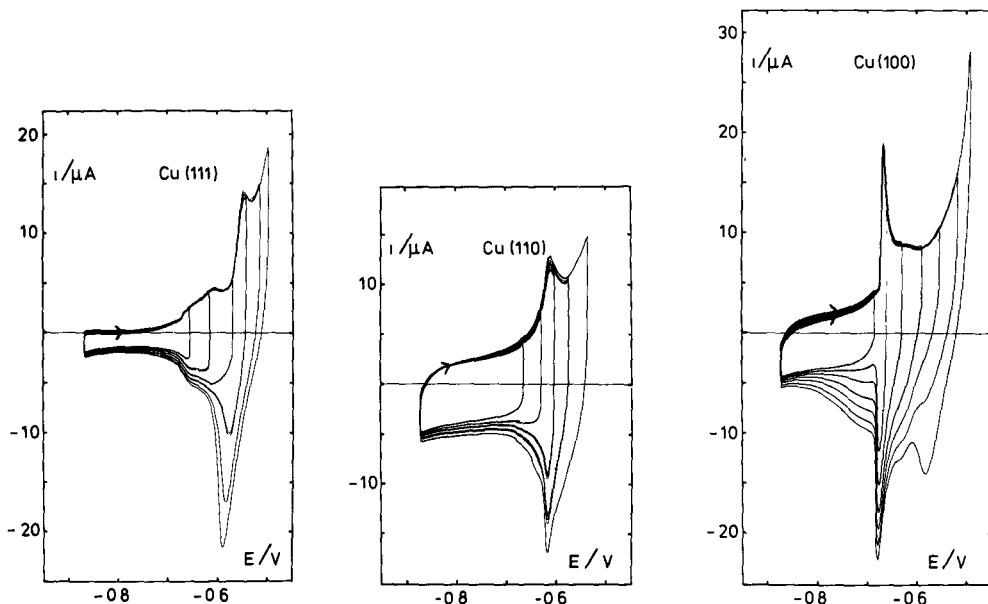


Fig. 1. Potentiodynamic charging curves up to various potentials for Cu(111). 1 mol dm⁻³ NaOH, 22°C, $s = 20 \text{ mV s}^{-1}$.

Fig. 2. Potentiodynamic charging curves for Cu(110). $s = 20 \text{ mV s}^{-1}$.

Fig. 3. Potentiodynamic charging curves for Cu(100). $s = 20 \text{ mV s}^{-1}$.

The voltammogram on Cu(100) is dominated by a very sharp adsorption peak at -670 mV with its counterpart at -680 mV. The sharpness of the peaks indicates the presence of attractive lateral interactions [8–10]. A salient feature of the curve in Fig. 1 is the appearance of the anodic peak at -545 mV. It shows a greater peak separation with its cathodic counterpart than the other peaks, and this effect increases with increasing reversal potential. Evidently on Cu(111) there is a separate step in the beginning of the formation of bulk Cu_2O .

The results with polycrystalline copper [1] (see Fig. 4) can easily be explained now. The Cu(100) plane and the Cu(110) plane make the largest contributions to the adsorption behaviour of polycrystalline copper; the first sharp peak is related with sites on (100) planes, and the second peak is mainly due to sites on (110) planes.

In Fig. 5 optical constants for a number of copper surfaces are given. The samples that gave the best electrochemical results are marked. These samples show the lowest n and the highest k values. This forms further support for the opinion of Albers et al. [12] and Habraken et al. [13], that "defect-free" surfaces show a tendency to lower n and higher k values. No systematic differences were found between the values for the different single crystal planes.

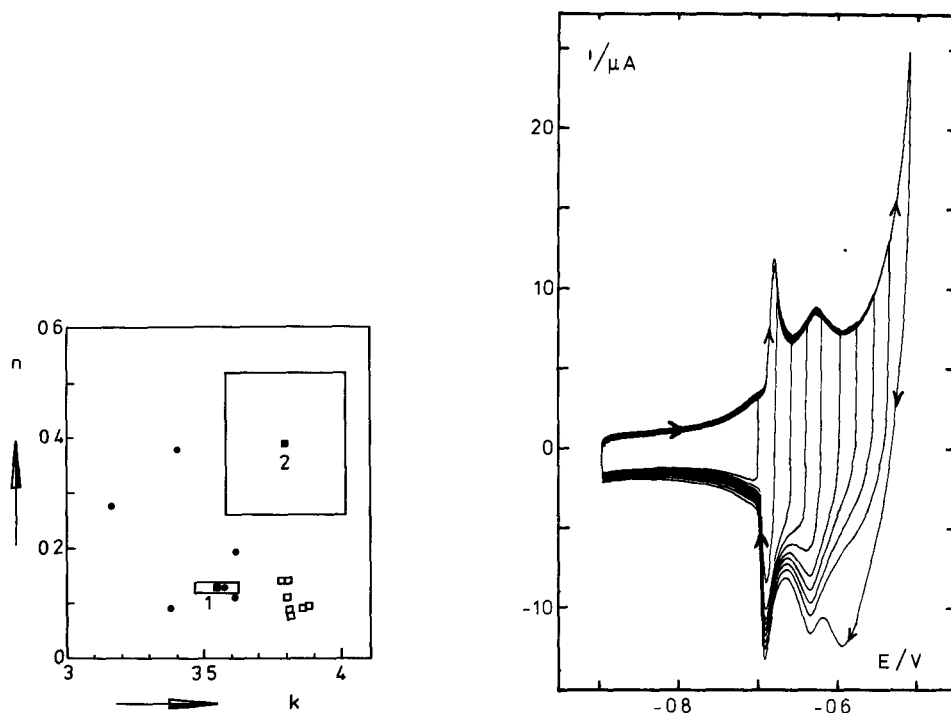


Fig. 4. Potentiodynamic charging curves for polycrystalline copper [1]. $s = 20$ mV s^{-1} .

Fig. 5. Optical constants of Cu at 632.8 nm. (1) single crystal in UHV [11]; (2) polycrystalline in electrolyte [1]; (\square) electropolished single crystals in electrolyte (this work); (\bullet) otherwise prepared single crystals in electrolyte (this work).

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