ELECTRODEPOSITION UNDER CONDITIONS OF ANAMOLOUS ELECTROLYSIS

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In a series of papers, Palit and his coworkers [1,2] have described the results of their studies on electrolysis using very low concentration electrolytes in the range N/1000 to N/10000 and low currents of the order of 10mA. Certain features not consistent with the usual faraday's laws have been reported, viz, a) the volume ratio of the liberated H_2 and O_2 was not 2:1, b) both the gases are co-liberated at the two electrodes, c) a concurrent migration of neutral molecules like N_2 etc occurs [3] and d) galvanoluminescene occurs as reported earlier. Due to these deviations, this kind of electrolysis has been named as 'non-Faradaic' or 'anamolous'. Similar studies of electrolysis of low concentration of Co, Ni and Cu salts are reported here.

EXPERIMENTAL

Distilled water was vigorously boiled to remove dissolved air, stored in stoppered bottles and used to prepare N/1000, N/750 and N/500 solutions of copper chloride, Nickel chloride or cobaltous sulphate. The solution was taken in a trough of 25 cm dia and 10 cm high. Nickel and Cu cathodes were 2.5 by 2.5 cm plates. In case of Co, wire was used as cathode. Anodes were sheets of metal hung diametrically opposite ends of the electrolysis cell. The current 0.2 mA was injected from a lead acid battery. Because of the low voltage, no cathode glow (galvanoluminicence is not observed at low voltages).

The cathodes were first boiled in KOH solution to remove any greasy material adhering to them and then electropolished, washed by methanol, dried and weighed untouched by hand.

Electrodeposition was carried out for different times and the foils reweighed to determine the mass deposited. The latter was plotted against the deposition time. It is found that in deoxygenated water, the results conform to Faradays laws. Having verified Faraday's laws to hold good for dilute electrolyte solutions of deoxygenated water, we sought to determine the lowest percentage of oxygen which if present causes the deviation from these laws. Small quantities of electrolyte solution was taken in a few beakers separately and pure oxygen was bubled through each at a pressure of 1 Kg/cm² for known times (10 - 20 sec.). Each solution was subjected to Winkler's test [4]. We could go up to 4% oxygen content and found that it was sufficient to cause on erratic behaviour which was by no means reproducible.

RESULTS AND DISCUSSION

Figures 1 a,b,c show results for Ni, Cu and Co respectively. In each case, the plot is a straight line confirming the validity of the faraday laws down to the lowest electrolyte concentration used.

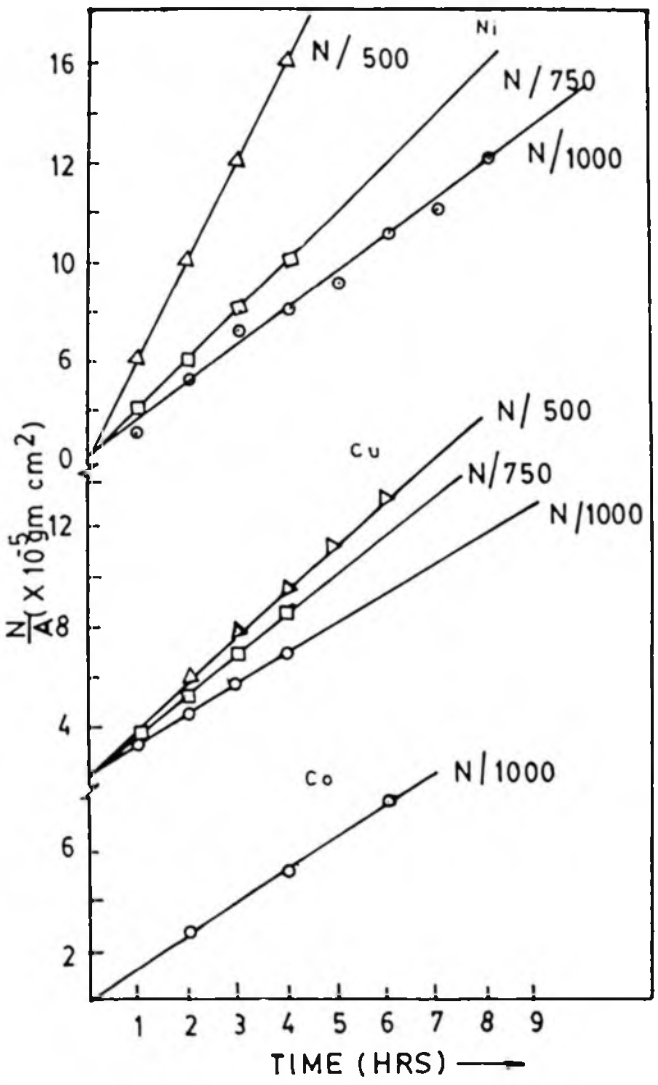


Fig. 1 Mass to metal deposited/unit area after different periods.

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Mass m deposited on area A is given by [5].

$$m/A = J.E.t.\alpha \qquad ...(1)$$

where J is the current density i/A, E the electrochemical equivalent, t the time of deposition and α is the current efficiency factor usually in the range 0.5 to 1.0. In terms of i,

$$m = i.E.t.\alpha \qquad ...(2)$$

The slope of m vs t gives i.E α from which α can be known. Since the factor α depends on the geometry of the electrodes used, we compare below only for Ni and Cu.

TABLE 1

THE CURRENT EFFICIENCY FACTOR α FOR Ni AND Cu AT VARIOUS CONCENTRATIONS

Metal	N/1000	N/750	N/500
Ni	0.34	0.46	0.91
Cu	0.64	0.84	0.95

At low concentrations α has gone below 0.5 for Ni. Thus the effective current used in electrolysis is also less than half the apparant value indicated by the measuring instrument. At higher concentrations α aprroaches 1. In the opinion of Doss [6], one of the probable causes of the observed deviations from the Faraday laws is the erroneous measurements of the current.

Fig. 2 shows the results obtained by deposing Ni on Cu at different electrolyte concentrations. There is an apparent loss in weight. This loss can be due to one of the following reasons. (1) If the Cu foil used as cathode contains Zn as an impurity, the latter present at the surface dissolves out first and Ni deposition takes place thereafter. However, the Cu foils used by us were supplied by Messers Mercke and Co. W. Germany and are free from Zn. They contain Ag, 0.005% Sb and Sn 0.05%. (2) Doss (Private communication) suggested the dissolution of the oxide layer of copper at the surface as the probable cause of the loss in weight: But this oxide layer would be present in both Cu deposition on Cu and Ni deposition on Ni and loss in weight should be observed. The reason behind this loss in weight is not clear.

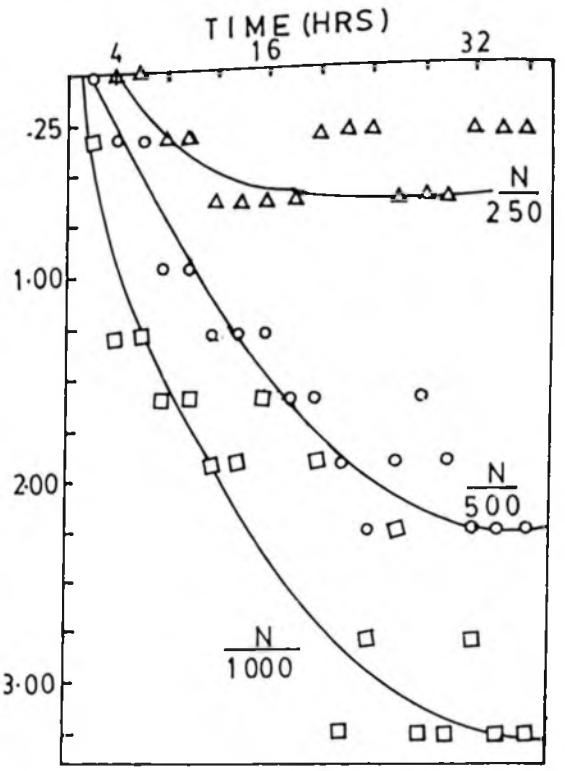


Fig. 2 Deposition of Ni on Copper

We finally conclude:

a) Faraday laws are obeyed even at low concentrations if the electrolyte used is made free of dissolved air and a metal is deposited on its own substrate. During electrodeposition, O_2 is evolved at the anode and gets dissolved in the electrolyte. In our case the volume of the electrolyte is large and hence the small quantities of dissolved O_2 have not been felt. However, we see that the electrolyte can not be used for more than 4-5 hours and has to be replaced by fresh solution. The reason lies in dissolved O_2 or N_2.

b) If the substrate is of a metal different from the anode metal, the electrodeposition is hindered. The reason might lie in the flow of a Galvanic current* between the two electrodes which are of different metals.

c) 4% oxygen present in electrolyte solution can cause deviations from Faraday's laws.

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