Monatshefte für Chemie 116, 49—52 (1985)

Monatshefte für Chemie
Chemical Monthly

Dissolution of Copper Foil in Aqueous Solution of $pH = 2$

Short Communication

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(Received 28 August 1984. Accepted 26 September 1984)

The specific dissolution rate, expressed in mol $cm^{-2}\,s^{-1}$, and time-variation of the rest potential of copper foil in an aerated aqueous solution of $pH = 2.0$ were measured.

(Keywords: Copper foil; Cuprite film; Dissolution; Flame AAS; Rest potential)

Die Auflösbarkeit von Kupfer-Folie in wäßriger Lösung von pH 2
(Kurze Mitteilung)

Es wurde die spezifische Auflösungsgeschwindigkeit (in mol $cm^{-2}\,s^{-1}$) und die zeitliche Veränderung des Restpotentials von Kupfer-Folie in einer belüfteten wäßrigen Lösung von pH 2,0 gemessen.

Studies of metal dissolution in acidic solutions and the determination of the respective corrosion rates are part of the extensive field of corrosion science. Such rate measurements become more difficult technically, when studied metals are noble[1]. Here the traditional corrosion-rate measuring techniques, like gravimetry, electric resistance methods, and the kinetic, electrochemical techniques of polarization resistance are not sensitive enough. These techniques had been developed especially for non-noble metals and their alloys, like iron and steels.

The dissolution of metals over short time periods became of interest recently, especially in connection with application of thin, deposited films of metals, like platinum, on semiconductor electrodes forming the base of electrochemical solar cells[2], and in connection with studies of limitations of electrolytic preconcentration techniques of noble and first transition metals applied in modern trace analysis[3–5].

In connection with the second mentioned research field, the present communication describes the results of a study of dissolution of copper metal foil (Merck, 99.7% purity, 0.1 mm thickness) in an aerated standard aqueous solution containing 0.10 M Na_2SO_4 (Merck, Suprapur) and acidified to $pH = 2.0$ with nitric acid (POCH, pro analysis). Solutions of similar composition are typically used in metal traces electrolytic preconcentration experiments.

The copper foil had the geometrical surface area of $S_e = 12.0\,\mathrm{cm}^2$, and it had not been pre-treated before use in the dissolution experiments. The volume of the solution was $V = 150\,\mathrm{ml}$. The solution was magnetically stirred with an arbitrary speed at room temperature of 21 °C. During dissolution experiments, the solution was analyzed for copper using a Perkin-Elmer 503 Flame Atomic Absorption Spectrometer at 324.7 nm.

The analytical results of a typical copper foil dissolution experiment are shown in Fig. 1. The measured dissolution curve is linear, except for a rather short initial period lasting approximately 20 s (it has been determined by visual observation of surface lustre change). In this initial period, cuprite (Cu_2O) formed in air and covering the surface[6], is quickly dissolved. The following, linear dissolution is that of copper metal, according to approximately zero-order heterogeneous metal-solution reaction, in the applied reaction time of 75 min. The zero-order dissolution line is best represented by the following least-squares equation:

$$c\,(\mu\mathrm{g\,Cu/ml}) = 0.0492\,t\,(\mathrm{min}) + 0.281 \tag{1}$$

for which the coefficient of correlation is 0.997.

The slope of the line of Eq. (1) has been used to calculate the specific rate (mass flux) of copper foil dissolution. It is $3.0 \cdot 10^{-11}\,\mathrm{mol\,cm^{-2}\,s^{-1}}$ for the applied arbitrary solution stirring speed.

The intercept of 0.281 μg Cu/ml corresponds approximately to the amount of copper ion in solution due to the fast dissolution of cuprite film covering the surface of the not pre-treated copper foil. This intercept corresponds to a total of $6.64 \cdot 10^{-7}$ mol of copper in the solution, which divided by the surface area of the foil gives $5.54 \cdot 10^{-8}\,\mathrm{mol\,Cu/cm^2}$. As one mol of copper, densely-packed on a plane occupies an area of $3.40 \cdot 10^8\,\mathrm{cm}^2$ [4,7], it follows that approximately 20 atomic layers of copper in the surface layer are present as cuprite. The rate of dissolution of copper from cuprite film is approximately two orders of magnitude higher than that of metallic copper.

Another characteristics of the dissolution process is the variation of the corrosion rest potential of the foil with time, measured against a reference saturated calomel electrode (SCE). The obtained results are shown in Fig. 2. The slow increase of the rest potential, as more of copper finds its way into solution is in a quantitative agreement with a behaviour

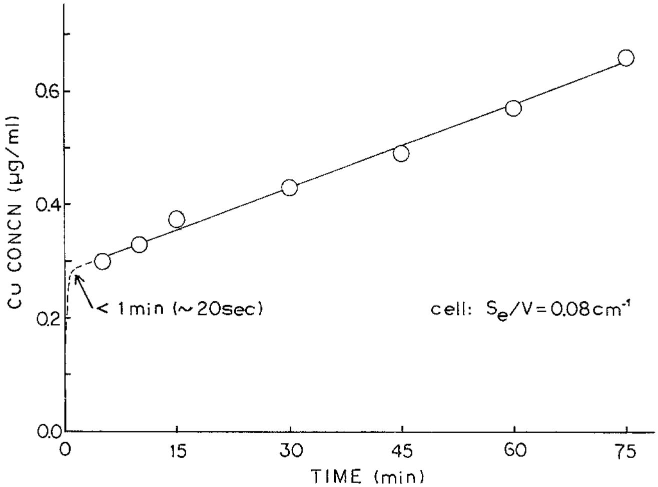

Fig. 1. The increase with time of Cu^{2+} concentration in standard solution of $0.10\,M$ Na_2SO_4, acidified to $pH = 2.0$ with nitric acid, during dissolution of copper foil

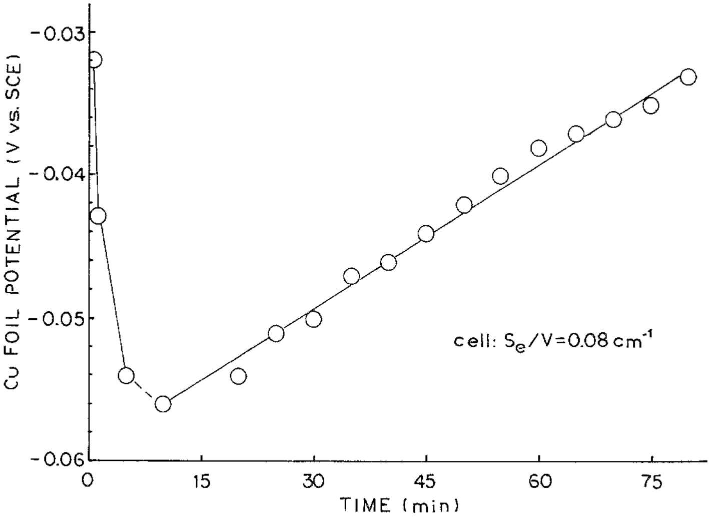

Fig. 2. The time-dependence of copper foil rest potential during dissolution in the standard solution of $0.10\,M$ Na_2SO_4, acidified to $pH = 2.0$ with nitric acid

expected according to the *Nernst* equation. The initially more positive potentials correspond partially to the presence of cuprite on the copper foil surface.

It is believed that similar measurements of dissolution rates can be very useful in determining corrosion properties of metals, in contact with reactive solutions applied, among others, in electrochemical solar cells and in trace analysis samples. A further study of such dissolution rates of especially noble and first transition metals will help to determine optimal experimental conditions for these two important fields of research.

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