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W. H. SHYRL
B. T. BELL
R. T. ATANOSOSKI
R. S. GLASS

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COPPER CORROSION IN IRRADIATED ENVIRONMENTS. THE INFLUENCE OF H_2O_2 ON THE ELECTROCHEMISTRY OF COPPER DISSOLUTION IN HC1 ELECTROLYTE

W. H. SMYRL,* B. T. BELL,* R. T. ATANASOSKI** AND R. S. GLASS**
* University of Minnesota, Department of Chemical Engineering and Materials Science and Corrosion Research Center, Minneapolis, MN 55455
** Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94550

ABSTRACT

The anodic dissolution of copper has been examined in deaerated, 0.1 M HC1 aqueous solution in the presence of H_2O_2. Concentrations of H_2O_2 up to 0.2 M were studied at a rotating copper disk-platinum ring electrode. The open circuit potential (OCP) of copper was found to depend on both peroxide concentration and rotation rate. The OCP shifts towards more positive values with increasing H_2O_2 concentration (C) and decreasing rotation rate (n). The dependence of OCP on (C/n^1/2) was the same as for oxygenated solutions reported earlier [1], at small values of (C/n^1/2). At higher values of (C/n^1/2), departure from the expected behavior was observed. The current-voltage curves for anodic dissolution of copper were also influenced by the presence of peroxide. The curves recorded with the potential scanned in the positive direction showed the expected 60 mV slope, but the reverse scans showed significant departures. At a given potential scan rate, hysteresis was observed which was larger for higher H_2O_2 concentrations, lower rotation rates, and more positive anodic potential limits. Monitoring the cuprous ions at the outer Pt ring revealed that there was a complex set of events taking place at the copper surface, including film formation and the appearance of cupric ions.

INTRODUCTION

There were three basic reasons for undertaking the present study of the corrosion of copper in the presence of hydrogen peroxide. The first is a fundamental one, related to the possibility that hydrogen peroxide could act as an oxidant to drive the dissolution and corrosion of copper. Secondly, during the corrosion of copper in the presence of oxygen, hydrogen peroxide would be either an intermediate or an end product of the oxygen reduction reactions. Thirdly, hydrogen peroxide is generated under gamma irradiation as well, which could drive copper corrosion in such environments. While the actual concentration of peroxide due to irradiation could vary, a value of 0.14 mM H_2O_2 had been reported for 35 hours of exposure at a rate of 3.3 Mrad/h [2]. This would be important if copper were to serve as a container material in nuclear waste disposal. It is the latter that is at the heart of the present study, but we note the more fundamental issues as well.

Following the work on Digital Impedance for Faradaic Analysis [3] on copper corrosion in both deaerated [1] and oxygenated [4] 0.1 M HC1, the present research was initiated to substitute H_2O_2 for oxygen. As a first step, open circuit potential measurements and a cyclic voltammetry study of a rotating copper disk (equipped with a platinum ring when appropriate) were undertaken. There were similarities with the behavior of copper found in oxygenated solutions when the concentration of both oxygen and peroxide coincided and departures from that behavior at higher hydrogen peroxide concentra-

† Institute of Electrochemistry ICTM, University of Belgrade, Belgrade, Yugoslavia.
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tent. Hence, these results and their ramifications on understanding the anodic dissolution of copper in chloride environment will be reported in this paper.

There is no report in the literature of a fundamental study of copper corrosion in hydrogen peroxide-chloride solutions. As the most relevant, the work of Molodov et al. [5] on the dissolution of copper in perchloric acid in the presence of hydrogen peroxide could be mentioned. An interesting finding of [5] was that hydrogen peroxide acted as an oxidant in the homogeneous phase rather than through direct electrode reduction at the copper surface.

In chloride solution, copper corrosion will depend on the kinetics of the homogeneous oxidation of copper $\text{Cu}^+1$ state, present as the complex $\text{CuCl}_2^-$ or, at higher chloride content, $\text{CuCl}_3^{2-}$. In 2 M HCl, this problem has been treated by Skinner et al. [6]. It was found that the first step in the oxidation of cuprous ion by hydrogen peroxide in 2 M HCl was slow, with a rate constant $k_1 = 2.6 \text{ M}^{-1}\text{s}^{-1}$. However, the $\text{Cu}^{2+}$ state of copper used as a reactant was generated by reduction of $\text{Cu}^{2+}$ at a platinum electrode, and the authors expressed some uncertainty about the complexation state of the reduced ions during the reaction with hydrogen peroxide. Actually, the problem is of general interest since the number of $\text{Cl}^-$ ions may change in different ranges of current density in the electrochemical step of copper dissolution [see e.g., 7,8].

Hydrogen peroxide was a product of oxygen reduction on copper in sulfuric acid as reported by Ghandehari et al. [9], with no report of further reaction. Molodov et al. [10], in a study where oxygen rather than hydrogen peroxide was used as an oxidant, reported that hydrogen peroxide contributed to the corrosion of copper.

**EXPERIMENTAL**

The copper rotating disk and the experimental procedure associated with it have already been described [1]. A Pine Instrument (Grove City, PA) copper disk (5 mm diameter)-platinum ring (7 mm I.D./8 mm O.D.) has been used as well. The detection of cuprous ions at the ring was performed by holding the ring at a constant potential of 0.3 V vs. SCE. The collection efficiency for the ring disk for the anodic dissolution of copper in 0.1 M HCl was found to be independent of rotation rate (400-4000 rpm), and to have a value of 0.20. The theoretical collection efficiency [11,12] was in agreement with the experimental value.

All the measurements were made in deaerated 0.1 M HCl. The amount of dissolved oxygen introduced in the electrochemical cell with the addition of hydrogen peroxide was negligible. The volume of the added peroxide compared to the total deaerated solution in the cell was less than 1%. Reagent grade chemicals were dissolved in 18 MQ-cm water, additionally purified for organics. The potential was measured vs. a saturated calomel electrode (SCE).

There was no dependence of copper dissolution current on scan rate in deaerated 0.1 M HCl between 10 mV s$^{-1}$ and 1 mV s$^{-1}$. The potential of the copper disk was scanned at 10 mV s$^{-1}$ to minimize the amount of copper dissolved from the disk during any one series of experiments. The surface of the disk was checked after each of these tests under a microscope. It was found that the copper surface was evenly dissolved, with no pits or ridges which could have distorted the hydrodynamics.

Two criteria were adopted to check the electrode and electrolyte preparation. The open circuit potential of copper in deaerated 0.1 M HCl had to be more negative than -260 mV, and the anodic polarization curve had to exhibit a Tafel slope of -50 mV in the current range up to $10^{-4}$ Acm$^{-2}$. 


Particular attention was focussed on the measurement of the open circuit potential (OCP) of copper as a function of hydrogen peroxide concentration and rotation rate. In Fig. 1, the open circuit potential as a function of the rotation rate at different hydrogen peroxide concentrations are presented. The copper potential became more positive with increased concentration of oxidant, but decreased as rotation rate was increased. As shown below, the data may be plotted on a single general curve. An increase of potential represents an increase of copper corrosion, as discussed by Smyrl and Stephenson [4] for oxygen-driven corrosion. There [4], a relationship was derived which predicted that the corrosion potential would change 39 mV for each decade change in \((C/\Omega^{1/2})\). The data presented in Fig. 1 followed this same behavior for \(H_2O_2\) in a certain range, but deviated from it when the hydrogen peroxide concentration was \(~50\) mM and the disk rotation was below \(~1000\) rpm. In this region the potential shifted more than predicted from the previous treatment. The new behavior at large \(H_2O_2\) concentrations suggested that a new corrosion process could be determining the electrode potential. The concentration of cuprous ions at the copper surface was high and may have reacted with \(H_2O_2\) at a significant rate. As a result, the presence of a significant amount of cupric ions could be expected, with consequences which will be discussed later.

Fig. 1. The open circuit potential of a rotating copper disk electrode at different \(H_2O_2\) concentrations in 0.1 M HCl.
The lack of hysteresis during the acquisition of the open circuit potentials indicated no permanent change at the copper surface. It should be pointed out that the reproducibility of the potential measurements in Fig. 1 was extremely good, in the range of 1-3 mV for the higher ranges in hydrogen peroxide concentration. The reproducibility was 10-15 mV at lower H$_2$O$_2$ concentrations.

Anodic dissolution cyclic voltammograms of copper gave two distinct patterns. Copper dissolution in acid solution with no peroxide will be examined first. From -300 mV to -50 mV, the potential sweep in a positive direction produced the usual 60 mV Tafel slope (see Smyrl [1]). Reversing the sweep in this region gave a very small but noticeable hysteresis. The hysteresis

![Cyclic voltammogram of copper disk (A) in 0.1 M HCl and corresponding ring current (B) at E$_{ring}$ = 0.3 V; scan rate 10 mV/s; 500 rpm.](image-url)
was significant only at low rotation rates and high current densities. The same 60 mV slope was obtained at the ring (set at 300 mV) where oxidation of cuprous to cupric was observed. The hysteresis of the ring was more pronounced than the one at the disk, but it was observed only when the disk showed hysteresis as well. However, what appeared to be more interesting were the signs of the hysteresis of the disk and the ring. This yielded a higher apparent collection efficiency for negative-going scans (27%) than for positive-going scans (20%) at 500 rpm. The departure of the collection efficiency from theoretical was more pronounced as the anodic limit of the disk was increased, indicating a second process must occur at the high anodic current densities.

Cuprous chloride film formation during the process of copper dissolution has been reported in the literature. However, before any speculation in this direction is made, the hysteresis in the disk behavior will be examined further. In Figs. 2 and 3 the cyclic voltammograms for copper dissolution for anodic limits at +50 to +60 mV are presented. In the positive direction an expected current response was observed, but in the reverse scan the departure from the Tafel type dissolution was substantial. The hysteresis consisted of a net reduction current in the potential region where a net anodic current was observed in the positive sweep. The voltammograms, including this particular feature, were very reproducible. The reduction process was more pronounced for higher anodic limits. Since no reducible species were present in the bulk solution in the potential region between -50 mV and -200 mV, the species reduced had to originate as a result of the anodic process. Further, the species had to be trapped at the electrode surface in order not

![Fig. 3. Cyclic voltammogram of copper disk (A) in 0.1 M HCl and corresponding ring current (B) at E_{ring} = 0.3 V; scan rate 10 mV/s; 3600 rpm.](image)
to diffuse away. The magnitude of the reduction process was strongly dependent on the rotation rate as well.

As a general observation, it should be noted that, while a cathodic current was recorded at the disk, cuprous ions were still being oxidized at the ring. This required that cuprous ions be continuously supplied to the ring, even though a net cathodic process was observed at the disk. At this stage, the presence of a CuCl film at the surface of copper was necessary in order to explain the results. The cathodic current hysteresis at the disk was ascribed to reduction of the film previously formed. The film was formed more readily at low rotation rates, when the removal of the species from the electrode surface was retarded. Finally an important feature of the results was that the film was completely removed from the surface with each potential cycle. The latter follows from the observation that the voltammograms were reproducible and that both the ring and disk current fell to zero at the same potential. There was no residual film build-up.

The dissolution of copper was studied in the presence of \( \text{H}_2\text{O}_2 \) in HCl solution. Again, two potential regions were distinguished: (i) one with the anodic limit more negative than -50 mV and (ii) one with anodic limit

![Polarization curves](image)

**Fig. 4.** Polarization curves for copper dissolution in the more negative potential region and at low peroxide concentrations.
extended to +50 mV. However, the behavior of copper depended on the concentration of hydrogen peroxide as well. In general, in the more negative potential region, and the lower peroxide concentration (less than 0.01 M), the presence of hydrogen peroxide shifted the polarization curve for copper dissolution in a positive direction (Fig. 4). The curves were shifted so that the potentials at a given current were more positive the higher the concentration of hydrogen peroxide and slower the disk rotation. The Tafel slope was 62-65 mV, and the current density depended on the rotation rate. A linear relation between the dissolution current at a given potential and the square root of the rotation is presented, in agreement with the literature statement that CuCl$_2^-$ diffusion is the limiting step (see e.g. ref. 2).

At more positive anodic potential limits (+50-65 mV), H$_2$O$_2$ affected the cyclic voltammograms as well. In a solution containing 0.03 M hydrogen peroxide (Fig. 5), the cyclic voltammogram at 1000 rpm was recorded. A well-defined plateau in the ring current was observed, but at small currents and with a pronounced reduction peak at the disk. A comparison of the curves taken in 0.03 M hydrogen peroxide at different rates of rotation along with the corresponding curves in HCl solution with no peroxide revealed some interesting features. The hysteresis in the voltammograms was more noticeable in peroxide solutions and the anodic branches were shifted in the region of more positive potentials.

![Fig. 5. Cyclic voltammogram of copper disk (A) in 0.1 M HCl + 0.03 M H$_2$O$_2$ and corresponding ring current (B) at $E_{ring} = 0.3$ V; scan rate 10 mV/s; 1000 rpm.](image-url)

The changes due to the presence of peroxide on the polarization curves are depicted in Fig. 6. As compared to the polarization curves at lower current densities, the linear region was less pronounced and had a slope of over 80 mV. This indicated that the anodic process for copper dissolution
Fig. 6. Polarization curves for copper dissolution in the more positive potential region and at high peroxide concentrations.

was altered. At the highest current densities the polarization curves at different rotation rates merged, in the absence of as well as in the presence of peroxide.

DISCUSSION

For the corrosion of copper in the presence of hydrogen peroxide the results suggest three general areas for discussion:

- low concentration hydrogen peroxide region and low corrosion rates
- high peroxide concentrations
- the fundamentals of copper dissolution at high rates.

The corrosion of copper in an irradiated environment would take place in the region designated as the low concentration region (< 0.01 M \( \text{H}_2\text{O}_2 \) [2]). In solutions of low concentrations of \( \text{H}_2\text{O}_2 \) the dissolution of copper was found to be a rather well behaved system. First of all the open circuit potential obeyed the relation

\[
E = \frac{RT(2.303)}{(a_{aa} + a_{ac} + \chi_{cc})F} \log\left( \frac{C}{\Omega^{1/2}} \right) + \text{const.} \tag{1}
\]
developed for copper corrosion in oxygenated 0.1 N HCl [4]. Here, C is the oxidant concentration, \( \omega \) is the rotation rate, and the \( \alpha \)'s are kinetic transfer coefficients (all equal to 0.5). In Fig. 7, the slope of 39.4 mV was found in the region of low \( \text{H}_2\text{O}_2 \) concentration, which is the same as that found for the oxygenated system. This indicated the same mechanism for copper corrosion was effective in \( \text{H}_2\text{O}_2 \). The small shift of the curve as compared to oxygenated solutions is within the scatter band of the results both here as well as in [4], which suggested similar kinetics. Therefore, one can conclude that up to \( \text{H}_2\text{O}_2 \) concentrations of 0.01 M, and high rotation rates, the corrosion of copper obeyed the model [4] proposed for oxygen as an oxidant: the anodic dissolution reaction was dominated by convective diffusion, and coupled with a kinetically controlled cathodic reaction. The transfer coefficients for both the anodic and the cathodic direction for copper electrode reaction as well as for the reduction of \( \text{H}_2\text{O}_2 \) were 0.5. These findings, derived from the open circuit potentials were in agreement with the polarization data at low current densities (Fig. 4). Here, the 60 mV slope was compatible with the convective diffusion controlled mechanism for copper dissolution, independent of the presence of small quantities of peroxide.

The corrosion of copper under the influence of higher concentrations of \( \text{H}_2\text{O}_2 \) and more positive potentials deviated from the simple process first de-
rived for O₂ solution. However, the interpretation of the data in this re-

gion could be very important, not only from the point of view of under-

standing the fundamentals of copper corrosion, but also for practical reasons as 
well. A build-up of higher concentrations of H₂O₂ in moisture films, or ad-
sorption of it at modified copper surfaces due to corrosion products, could 
make these high concentrations more important. Work is continuing in this 
area.

The initiation of film formation at the electrode surface seems to be of 
crucial importance in the understanding of dissolution of copper at high dis-
solution currents. Thus, the thermodynamic values of the electrode poten-
tials in 0.1 M HCl for reactions involving different copper species [13] sug-
gest that up to -60 mV, the dissolution of copper proceeds to form CuCl₂⁻ 
ions, in a solution containing no copper initially. Above this potential, 
one may form CuCl at the surface, as well as CuCl₂⁻. This value corre-

sponds well with the potential at which the distinction of two regions in the polar-
ization behavior of copper was observed in the present study.

The influence of the rotation rate on the formation of the film required 
that both film formation and film dissolution be considered. The dissolution 
of the film in HCl solutions proceeded most probably through the reaction:

\[
\text{CuCl} + \text{Cl}^- = \text{CuCl}_2^-
\]  

The description given earlier for copper dissolution in pure 0.1 M HCl (Figs. 
2 and 3) fits well with the requirement that a certain surface concentration 
of CuCl₂⁻ ions must be exceeded in order for a stable film to be formed.

What appears to be more important for the purpose of the present study 
is the enhancement of the process of the film formation in the presence of 
peroxide. There are two different ways in which peroxide could contribute 
to the CuCl film formation. The first is to produce CuCl₂⁻ ions through 
copper corrosion by a coupled mechanism. This process would decrease in 
importance as the potential is made more positive, i.e., at higher current 
densities. Thus, for anodic dissolution under imposed polarization, the 
contribution of this process to the total rate at which cuprous species are 
produced is negligible. The other possibility of hydrogen peroxide contri-
bution to the film formation is a rather indirect one and is based on the 
generation of cupric ions by homogeneous oxidation of cuprous species by per-
oxide at the electrode surface. The scheme is similar to the one for auto-
dissolution of copper proposed by Holodov et al. [5]. The cupric ions are 
thermodynamically unstable at the disk potential, and would be reduced at 
the surface to yield a CuCl film. This is an additional reaction to form 
CuCl. As illustrated in Fig. 5, this contributes to film formation so that a 
constant ring current is associated with a constant flux of CuCl₂⁻ to the 
ring in the presence of 0.03 M H₂O₂.

As a conclusion, the proposed mechanism of CuCl film formation in the 
presence of hydrogen peroxide through oxidation of cuprous ions to cupric 
and the subsequent reduction of the latter to CuCl, seems to be able to ex-
plain the shifts in the open circuit potential at both copper and platinum 
surfaces and the behavior of copper under anodic polarization.

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