

SHORT COMMUNICATION

HYDROGEN EVOLUTION IN CORROSION OF COPPER IN PURE WATER

G. HULTQUIST

Department of Physical Chemistry, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

Abstract—The corrosion of copper in pure water has been studied. An increase in hydrogen concentration has been found in the gas volume above the water level. When the abundance of oxygen is low the hydrogen evolution rate, monitored above the water, is similar to the corrosion rate, as measured by weight gain of the copper.

INTRODUCTION

THE HYDROGEN electrode $2\text{H}^+/\text{H}_2$ potential is often used in potential–pH diagrams to judge whether hydrogen evolution is possible in a specific corrosion situation. The hydrogen concentration defined in the hydrogen electrode is the hydrogen abundance at a pressure of 10^5 N m^{-2} which is $\approx 0.04 \text{ mol dm}^{-3}$ at 298 K, and this situation is obviously connected to a possible formation of hydrogen gas bubbles in a corroding system. Recently it was pointed out that hydrogen can be transported away from an electrode surface not only via bubbles, but also via diffusion and convection. Furthermore, it was stressed that at a sufficiently low rate only the latter transport mechanisms are operative.¹

In electrochemical corrosion two fundamental cathodic reactions are considered: hydrogen evolution and oxygen reduction. A general opinion is that only oxygen reduction can operate for the corrosion of copper in pure water, but to our knowledge no experimental evidence exists which supports that opinion. Hence, there seems to be a lack of critical experiments which could clarify the role of oxygen in the corrosion of copper in water. There are experimental difficulties involved when separating inlet of oxygen from outlet of hydrogen at the low corrosion rates in question ($< 5 \mu\text{m/y}$). The aim of this short communication is to contribute to the knowledge of mild corrosion, and more specifically, to the understanding of the corrosion of copper in pure water.

EXPERIMENTAL METHOD

The copper used was in the form of 0.1 mm-thick foil ($> 99.7 \text{ wt}\%$). It was mechanically polished with 800 mesh SiC-paper before being immersed in water without stirring at $297 \pm 2 \text{ K}$ under dark conditions. The water used was deionized, and double distilled in a quartz apparatus. Hydrogen was monitored with a recently developed solid electrolyte probe working on the basis of a concentration cell (commercially available from Cormon Ltd, Great Britain). The probe has Pd as a

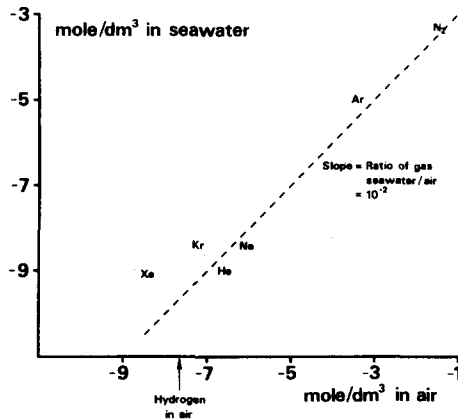


FIG. 1(a). Abundance of different gases (elements) in dry air and sea-water at 298 K.

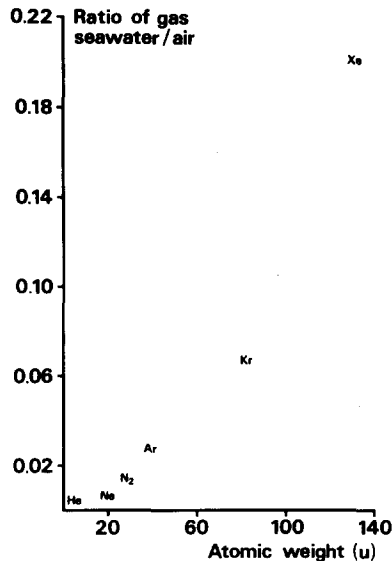


FIG. 1(b). Ratio of gas sea-water/air vs atomic (molecular) weight of gas.

working electrode, WO_3 as a reference, and hydrogen uranyl phosphate as a proton conducting electrolyte.² The potential generated by the probe was measured with a high impedance ($>10^{14} \Omega$) voltmeter. The hydrogen probe was calibrated by exposure to various concentrations of hydrogen in nitrogen (AGA Special Gas AB): 1.2 ± 0.2 , 7.0 ± 0.7 , 52 ± 3 , 496 ± 25 ppm, $4.94 \pm 0.10\%$ and $>99\%$.

EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 1a data from³ show the abundance of different gases (elements) in dry air and sea-water at 298 K. A replot of the same data in Fig. 1b reveals a monotonic increase in 'solubility' in the sea-water vs atomic (molecular) weight of the elements (molecules). From these data we can estimate the concentration of hydrogen in

sea-water to be in the 10^{-11} mol dm $^{-3}$ range. This concentration needs to be taken into account when we judge hydrogen evolution to take place in sea-water corrosion at an infinitesimal rate.

In Fig. 2a the experimental arrangement together with the hydrogen probe output vs time of exposure is presented. The weight gain of the copper was 21.2 ± 0.3 mg as a result of corrosion in the water. Copper found in distilled water was measured by gamma spectrometry in an earlier study⁴ and an upper limit ('solubility') was found at 0.5 mg dm $^{-3}$. If we assume the corroded copper to exist as Cu $_2$ O we can calculate from the measured weight gain the total copper corrosion to be 170 ± 3 mg corresponding to an average corrosion rate of 0.11 μ g cm $^{-2}$ h $^{-1}$. The amount of oxygen initially present in the corroding system (Fig. 2a) was calculated to be 12 ± 3 mg (≈ 6 mg in the water and ≈ 6 mg in the gas volume which had the composition of the air at the time of closure).

Calibration curves for the probe under two different conditions are shown in Fig. 2b. When the Pd-sensor is covered by a film of water the potential is lowered by approximately 150 mV, which is equivalent to a decrease in concentration by a factor of approximately 300. This is natural since the Pd-sensor will monitor the concentration of hydrogen in its immediate vicinity. From Fig. 1a and 1b we could estimate a similar figure for the 'solubility' of hydrogen in seawater. In the experiment presented in Fig. 2a the Pd-sensor is completely covered with a film of water.

From the calibration of the hydrogen probe we find a response of ≈ 60 mV/decade hydrogen concentration. The hydrogen electrode reaction on palladium has been studied previously⁵ and the response of 59 mV/decade hydrogen concentration should correspond to the Volmer step ($H = H^+ + e$) in the Tafel-Volmer route. The calibration in Fig. 2b has been applied to the results in Fig. 2a, and the result is given in Fig. 2c. This linear plot of hydrogen in gas volume vs time of copper immersion shows a very distinct rise in hydrogen concentration after ≈ 650 h immersion of the copper. We can now calculate the total hydrogen evolution rate from the slope in Fig. 2c if we take into account that hydrogen is also present in the water. An evolution rate of $2.2 \cdot 10^{-6}$ g hydrogen h $^{-1}$ is then found.

If we again assume that copper is corroded to Cu $_2$ O we can calculate a corrosion rate for copper based on $2Cu + H_2O \rightarrow Cu_2O + H_2$ to equal 0.10 μ g cm $^{-2}$ h $^{-1}$.

We think that oxygen is consumed mainly during the first 650 h of immersion (Fig. 2c). Probably this takes place predominantly at the copper surface where the hydrogen atoms have previously been formed by discharge of the protons (or H $_3$ O $^+$). By using $H_2 + 1/2 O_2 \rightarrow H_2O$ and the production rate during 650 h calculated previously we find a consumption of 11 mg of oxygen.

The different data from the corrosion experiment, with estimated errors, are summarized in Table 1.

TABLE 1. DEGREE OF COPPER CORROSION IN PURE WATER (SEE FIG. 2)

	From hydrogen production kinetics	From weight gain measurement	From calculation of volume
Initial amount of oxygen present [mg]	11 ± 3	—	12 ± 3
Total copper corrosion [mg]	150 ± 40	170 ± 3	—
Average rate of copper corrosion [μ g cm $^{-2}$, h $^{-1}$]	0.10 ± 0.03	0.11 ± 0.02	—

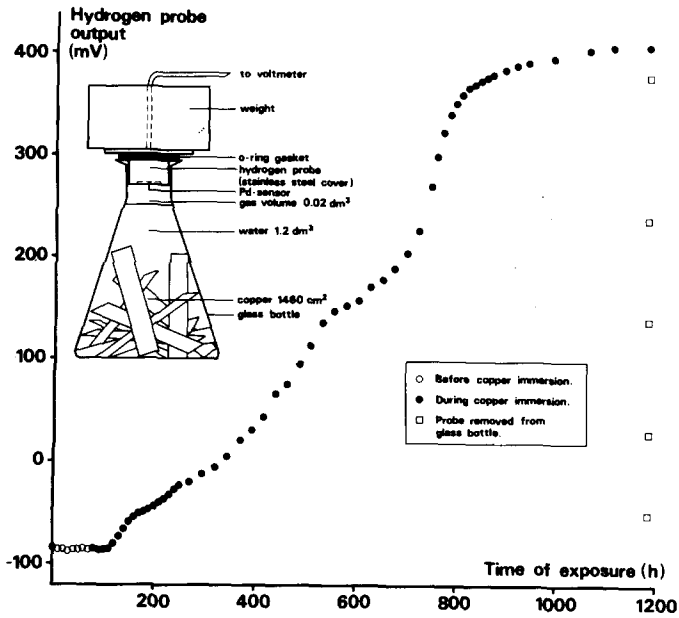


Fig. 2(a). Experimental set up and hydrogen probe output vs time of exposure.

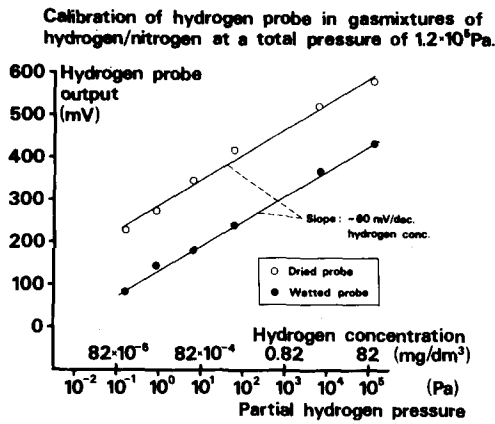


Fig. 2(b). Calibration of hydrogen probe in gas mixtures of hydrogen/nitrogen at a total pressure of $1.2 \cdot 10^5$ Pa.

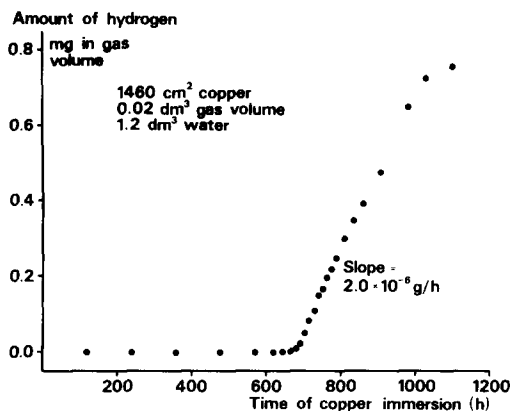


Fig. 2(c). Amount of hydrogen in gas volume vs time of copper immersion.

Water in equilibrium with free air contains $\approx 10^{-11}$ mol dm⁻³ hydrogen while a gas bubble evolved during severe corrosion contains more than $4 \cdot 10^{-2}$ mol dm⁻³. Assuming a one electron process (discharge of protons), and a reversibility $H^+ + e^- = H$, the above concentrations used in the Nernst equation imply that a ≈ 540 mV displacement of the hydrogen electrode in the potential-pH diagram would give hydrogen evolution at an infinitesimal rate. However, if a non-reversible cathodic reaction takes place: $H^+ + e^- \rightarrow H$, $H + H \rightarrow H_2$ we cannot predict an upper hydrogen pressure (in an oxygen-free corroding system). The latter, irreversible situation seems to apply in the present experiment concerning copper corrosion, as indicated by the considerable hydrogen concentration found.

CONCLUSIONS

- (1) Hydrogen is evolved during corrosion of copper in water, i.e. copper is oxidized by water.
- (2) The escape rate of hydrogen from the corroding system is of decisive importance for the corrosion kinetics of copper in water.

Acknowledgement—Financial support from NFR (Swedish Natural Science Research Council) is gratefully acknowledged.

REFERENCES

1. H. VOGT, *Electrochim. Acta* **29**, 167 (1984).
2. S. B. LYON and D. J. FRAY, *Br. Corros. J.* **19**, 23 (1984).
3. R. A. HORNE, *Marine Chemistry*. John Wiley & Sons Inc., New York (1969).
4. G. HULTQUIST, *Dagens Industri*, 19 June (1984). (In Swedish.)
5. M. ENYO and T. MAOHA, *J. Electroanal. Chem.* **108**, 277 (1980).