



# Corrosion of copper in distilled water without O<sub>2</sub> and the detection of produced hydrogen



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## ABSTRACT

This paper reports on hydrogen pressures measured during ~19,000 h immersion of copper in oxygen-free liquid distilled water. Copper corrosion products have been examined *ex-situ* by SEM and characterized by XPS and SIMS. XPS strongly indicates a corrosion product containing both oxygen and hydrogen. SIMS shows that oxygen is mainly present in the outer 0.3 μm surface region and that hydrogen penetrates to depths well below the corrosion product. Thermal desorption spectroscopy shows that the reaction product formed near room-temperature is less stable than that formed in air at 350 °C.

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## 1. Introduction

Release of hydrogen upon immersion of a metal in liquid water is evidence for reaction between the metal and the water [1]. A summary of ultrahigh vacuum (UHV) experiments and considerations of stabilities of various products in metal–water reactions has been presented in [2]. However, a printing error in [2] (–30 should be +30 kJ mole<sup>–1</sup>) concerning the stability of a hydrogen-free reaction product means that a hydrogen-containing reaction product (CuOH) is favoured over a hydrogen-free reaction product (CuO and Cu<sub>2</sub>O) in the Cu–water reaction. This fact is not generally known and emphasizes the need for characterization of hydrogen in the reaction product.

The first report of hydrogen gas evolution from Cu-corrosion at room temperature in liquid distilled water in the absence of any applied potential and in the absence of O<sub>2</sub> was made almost 30 years ago [3]. This has been followed by relatively recent work [4–6]. The measured hydrogen gas pressure will ultimately be in the mbar (10<sup>2</sup> N m<sup>–2</sup>) range. This pressure is of the order of a thousand times higher than the hydrogen gas pressure in ambient air [7].

It has been argued, however, that this detection of H<sub>2</sub> must be the result of something other than reaction of Cu with water.

These arguments are mainly based on that the second law of thermodynamics is violated and consequently other reactions than copper corrosion have been suggested [8,9]. Due to the importance of the application of final storage of nuclear waste in Cu-canisters, a serious attempt was recently made to repeat the experiments in [4,5]. Results confirming the detection of hydrogen gas are reported in [10]. These previous experiments were performed with copper contained in leached glass within a 316 stainless steel system. Here we also report hydrogen gas measurements where the stainless steel container is replaced by titanium to exclude that the measured hydrogen originates from the container material as was suggested in [9].

Previously [4,5], it was found that the formed product contains hydrogen and in this work we also present *ex-situ* characterization of the reaction product in O<sub>2</sub>-free liquid water and O<sub>2</sub>-free water-vapor. The products formed in liquid water are from an approximately total two years exposure (19,000 h) of Cu in distilled water in the 21–55 °C temperature range. The *ex-situ* characterization is performed by field emission gun scanning electron microscopy (FEG-SEM), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and thermal desorption spectroscopy (TDS). TDS-data from outgassing of copper after exposure in water-vapor at 350 °C is also presented.

Finally a model is presented for the corrosion of copper in oxygen-free water which summarizes some factors overlooked in a

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prediction based on traditional thermodynamics of copper in water.

## 2. Experimental

The ultra-high vacuum (UHV) experimental setup has been described in detail in previous publications [4,5]. Briefly, hydrogen gas pressures are measured with an absolute pressure meter and a mass spectrometer is employed for verification of the hydrogen gas. An example of a mass spectrum is shown in [5] where also a schematic of the equipment is found. All experiments are with a palladium membrane of a thickness 0.1–0.2 mm through which only hydrogen will be transported. The fastening of the palladium membrane is crucial for the measurements of hydrogen. It is essential to apply the right pressure in forcing the edge of stainless steel into the thin membrane. An initial evacuation of the compartment placed on one side of the membrane will enable the detection of hydrogen gas with the absolute pressure meter. This evacuation must be thorough and made with a UHV pump for at least 24 h near room temperature. The other side of the membrane is in direct contact with the volume where hydrogen gas is generated during corrosion. Also this volume was evacuated to obtain O<sub>2</sub>-free conditions as described earlier in detail [5]. Any possible residual O<sub>2</sub> after the evacuation is consumed in the early stage of corrosion in the closed system. The UHV system is air-tight and no leaks are detected during the experiments. Before any exposure of copper in glass vessels placed in stainless steel or titanium below the palladium membrane, these containers were filled with boiling distilled water to remove any easily dissolved surface debris. Also the glass was “leached” in boiling water before the copper immersion. Depending on the detection limit of the pressure meter, H<sub>2</sub> can be measured down to  $\sim 2 \times 10^{-7}$  bar.

Copper of purity 99.95+ wt.%, 0.1 mm thick rolled sheet supplied by Goodfellow was used in the “as received” condition. A typical impurity analysis in ppm is: Ag, 100; As, 200; Cr, 50; Fe, 5; Pb, 2; B, Bi, Mg, Mn and Si, <1. The grain size was  $\sim 20$   $\mu$ m. This copper was used in all exposures except for some in Figs. 9a and 9b where a 2 mm thick Cu-sample (part of UHV-copper gasket in the as received condition) was used.

Analysis of the previously exposed Cu-sheets was performed with FEG-SEM, XPS and SIMS. In the FEG-SEM micrographs an accelerating voltage of 20 kV was used. XPS-analysis was performed in a PHI 5500 spectrometer with a monochromated Al K <sub>$\alpha$</sub>  source, SIMS in an PHI Adept 1010 with a primary 4 keV Cs ion beam, and secondary ions from approximately 0.1  $\times$  0.1 mm were detected (in Ottawa) and in a Cameca spectrometer with a primary 10 keV Cs source with detected secondary ions from 30  $\mu$ m diameter and raster area of 200  $\mu$ m  $\times$  200  $\mu$ m (in Singapore).

Thermal desorption spectroscopy (TDS) was used to assess outgassing after different exposures of Cu, including the  $\sim 19,000$  h exposed Cu. This characterization was preceded by a thorough evacuation of a quartz tube (background) up to 900 °C. The sample was inserted and this was followed by an initial evacuation with a turbo molecular pump at room-temperature. Measurements were taken with a mass spectrometer pumped with an ion-pump. The pump-element of titanium was outgassed in a separate ion pump to remove hydrogen in order to obtain a low detection limit for hydrogen. In TDS the sample temperature was increased 50 °C in a stepwise fashion every 12 h.

## 3. Results and discussion

### 3.1. Detection and measurement of H<sub>2</sub>

Fig. 1 shows detected hydrogen gas pressures during the last 5000 h of the almost 19,000 h exposure of 140 cm<sup>2</sup> copper sheets

in 90 ml distilled water in a glass container within a stainless steel vessel. The detected hydrogen gas pressures at shorter exposure times in the same experiment are found in [4,5]. The hydrogen pressure increase due to copper corrosion is clearly observed in Fig. 1, where the same rate of H<sub>2</sub>-increase due to copper corrosion is pointed out at 14,500 and 17,800 h. It is also seen that temperature increases produce rapid increases in measured hydrogen pressure due to decreases in the amount of hydrogen in the palladium and vice-versa. At 17,000 h there is almost no change of pressure due to a steady state between formation (oxidation) and reduction of the corrosion product. This steady state does not depend on the hydrogen content in the palladium membrane.

It is possible to estimate the corrosion rate from the increase of H<sub>2</sub>-pressure at a certain temperature in Fig. 1. This estimate is based on the volume where the pressure is measured and the area of Cu exposed. In this estimate we neglect a small part of hydrogen present in the palladium membrane. We find a hydrogen gas production rate of  $\sim 4 \times 10^{-10}$  moles per hour both at 14,500 and 17,800 h in Fig. 1. With this measured generation rate of hydrogen, assuming a density of a reaction product of 4 g cm<sup>-3</sup> and the simplified reaction  $\text{Me} + \text{H}_2\text{O} \rightarrow \text{MeO} + \text{H}_2$  (measured) we can calculate a metal corrosion rate. This means that the assumed simplified reaction product does not contain any hydrogen. This calculation will result in an underestimation of the thickness of the corrosion product, in that hydrogen contained in the corrosion product, in the copper metal and in the palladium membrane is not taken into account. The extent of underestimation depends on the thickness of the corroding sample and the palladium membrane and the true corrosion rate may be at least a factor of three higher than that calculated from hydrogen gas release rates. With this factor taken into account the corrosion rate for the copper sheets is estimated to be 0.01–0.1  $\mu$ m per year at room temperature.

Fig. 2 shows hydrogen gas measurements of 20 cm<sup>2</sup> copper sheets in 15 ml of distilled water in a glass container within a titanium vessel. An almost time independent hydrogen gas pressure in the mbar range ( $10^2$  N m<sup>2</sup>) is also found in the figure and this takes place at  $\sim 7800$  h.

A steady-state of hydrogen gas generation (constant measured H<sub>2</sub>) in Cu-corrosion is clearly not dependent on either stainless steel or titanium as the background (container) material. This is illustrated in Fig. 3 where the same steady state is obtained with these two materials. The experimental data (solid points and one

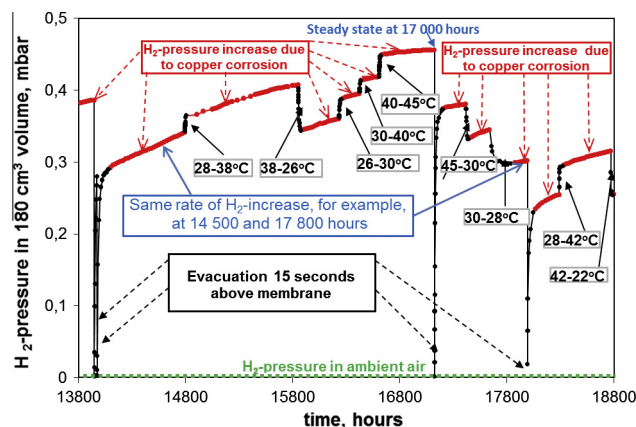


Fig. 1. Measured H<sub>2</sub>-pressure in exposure of 140 cm<sup>2</sup> Cu in 90 ml distilled water at 21–26 °C at pH near 7. Evacuation of hydrogen gas above the Pd-membrane and temperature influence of the Pd-membrane in the 22–45 °C range (shown within squared boxes) on measured H<sub>2</sub>-pressure. Almost no change of pressure at approximately 17,000 h due to a steady state between formation (oxidation) and reduction of a corrosion product. Same rate of increase of H<sub>2</sub>-pressure indicated at 14,500 and 17,800 h.

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