Corrosion Properties of Copper in Pure Water

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Copper as a Catalyst

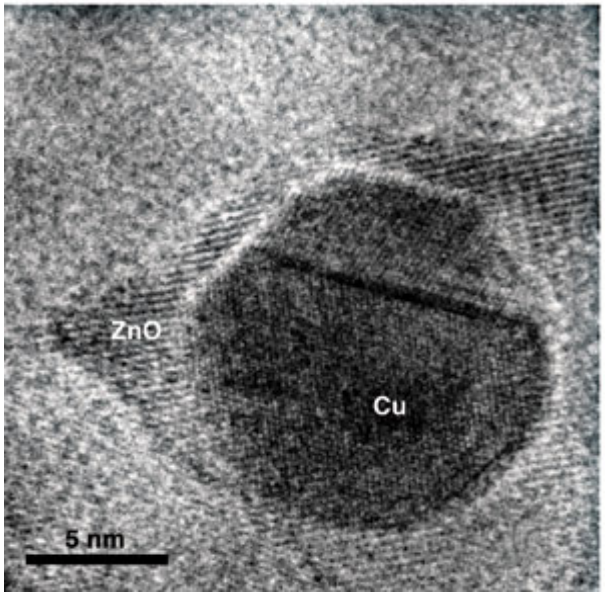
Water gas shift reaction

$$\mathbf{CO + H_2O = CO_2 + H_2} \qquad \Delta H_{298} = -41.2 \text{ kJ/mol}$$

- $CuO/ZnO/Al_2O_3$ is used as a low temperature (gas phase; <250 ^oC) shift catalyst.
- Prior to use, CuO must be reduced to copper by hydrogen. Active species is **copper metal** on which the dissociation of water occurs**.**
- Principal role of zinc oxide is to protect the copper from poisoning by sulfur.

Methanol Synthesis

$$CO + 2H_2 \Leftrightarrow CH_3OH$$



HRTEM image of the Cu/ZnO catalyst during exposure to 1.2 bar hydrogen at 500 °C. The image displays lattice fringes of a twinned Cu nanocrystal and of the ZnO support.

The critical steps including the dissociation of hydrogen occur on copper.

J.F. Creemera et al. Ultramicroscopy, 108 (2008) 993

Surface Science Studies on Adsorption of Water on Copper

On single crystals, adsorption shown to be structure sensitive.

- only molecular adsorption[1],

- surface hydroxylation[2] and even complete dissociation of water.[3]

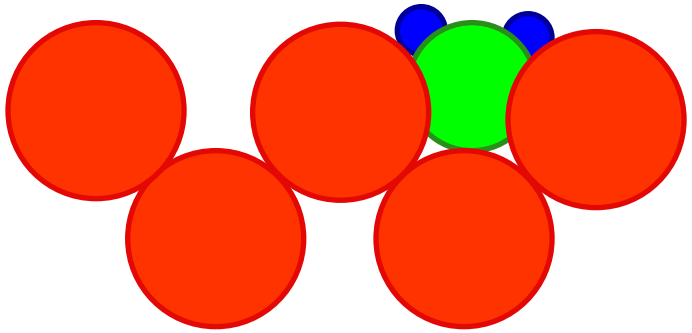
Questions about the role of surface roughness in promoting the decomposition of water– again conflicting evidence.[4,5]

1. A. Spitzer and H. Luth, Surf. Sci. 152/153 (1985) 543.
2. C.T. Au, J. Breza, M.W.Roberts, Chem. Phys. Lett. 66 (1979) 340.
3. A. Spitzer and H. Luth, 120 (1982) 376.
4. K. Bange, D.E. Grider, T.E. Madey, and J.K. Sass, Surf. Sci. 137 (1984) 38.
5. W.D. Clendening, J.A. Rodriguez, J.M. Campbell and C.T. Campbell, Surf. Sci. 216 (1989) 429.

Type of surface

On the Cu(110) surface, water is bonded to a first layer copper atom in a 4-fold hollow site by the oxygen lone-pair electrons.

This surface offers easy interaction between the hydrogen atoms of water and the topmost copper atoms.



Adsorption of a molecular water in the fourfold hollow site on a Cu(110) surface

Adsorption of water on polycrystalline copper

7 – 8 % of polycrystalline copper surface found to readily dissociate chemisorbed water, while the major portion of the surface adsorbs water in a molecular form.

E. Colbourn et al. J. Catal. 130 (1991) 514.

Corrosion properties of copper in pure water

A number of studies by Hultquist and Szakálos on

$$2Cu + H_2O \rightarrow Cu_2O + H_2$$

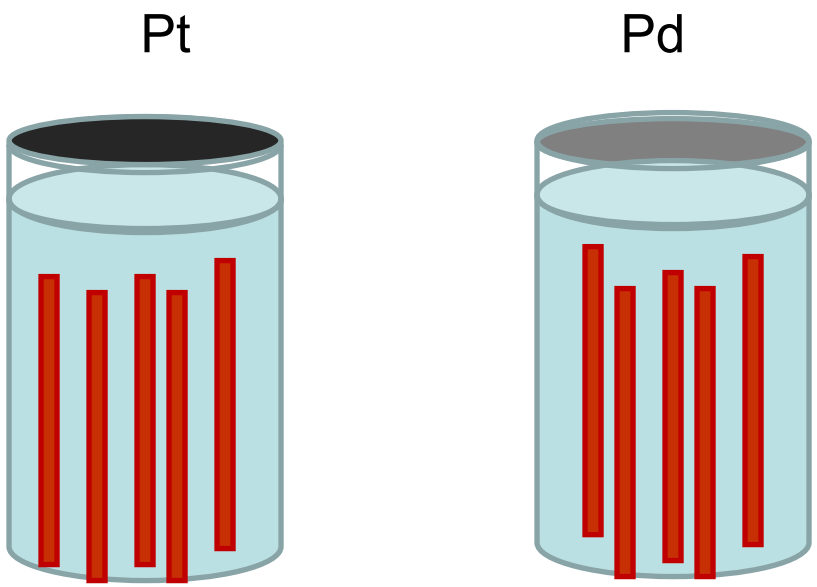
Observation

- Hydrogen is evolved in copper-pure water system.
- If the hydrogen is removed, copper corrosion will continue.

G. Hultquist, Corros. Sci., 26 (1986) 173; G. Hultquist et al. ICC 2008, Paper No. 3884,
P. Szakálos et al. Electrochem. Solid-State Lett. 10 (2007) C63.

Early experiments: – two systems, one is closed with respect to oxygen but open to hydrogen, and the other closed for both oxygen and hydrogen.

Detector – eye.

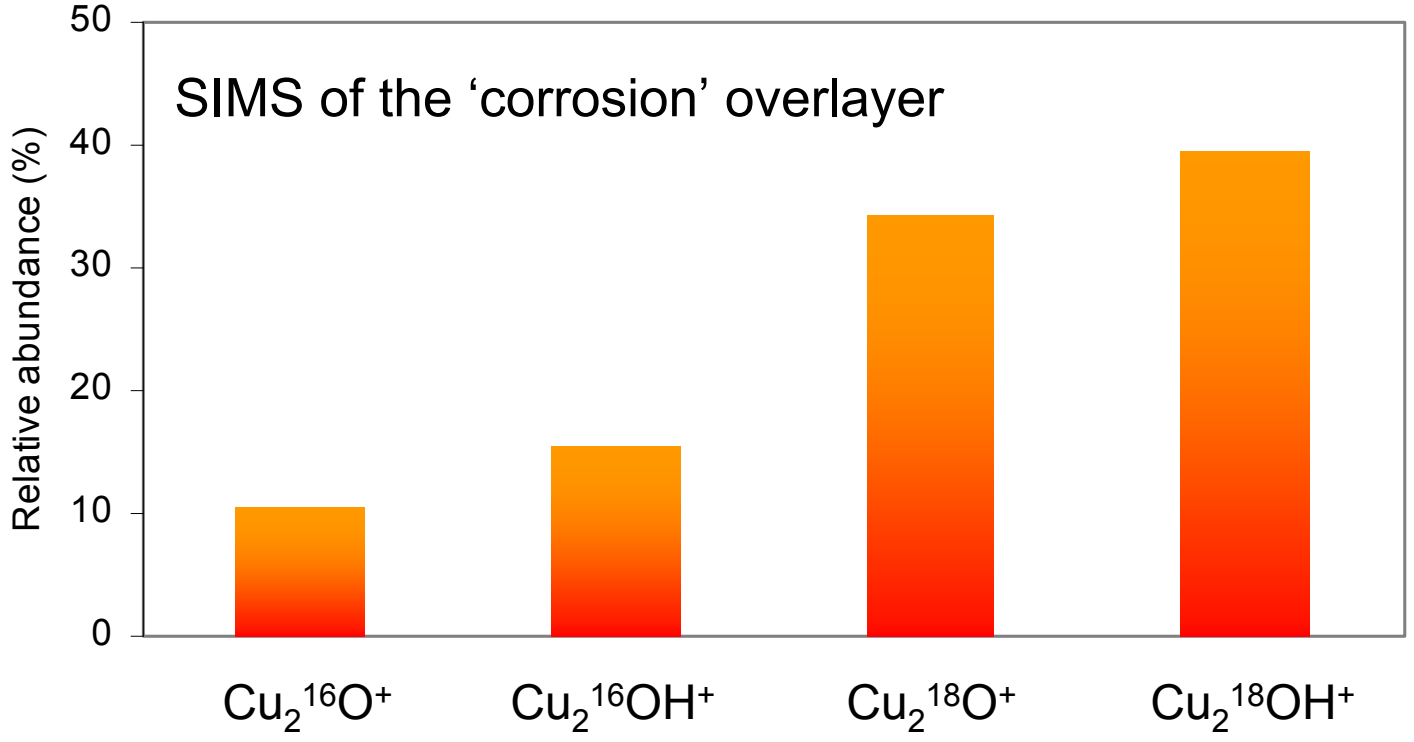


Using XPS with ion etching – binding energy of Cu close to that of Cu_2O with 5-6 times greater depth than those on Pt sealed vial.

G. Hultquist et al, Corros. Sci., 29 (1989) 1371

The incorporated Oxygen comes from Water

Copper exposed to 20 mbar $H_2{}^{18}O$, 2 mbar $H_2{}^{16}O$ and 5 mbar $^{16}O_2$ for 24 h at 150 °C.



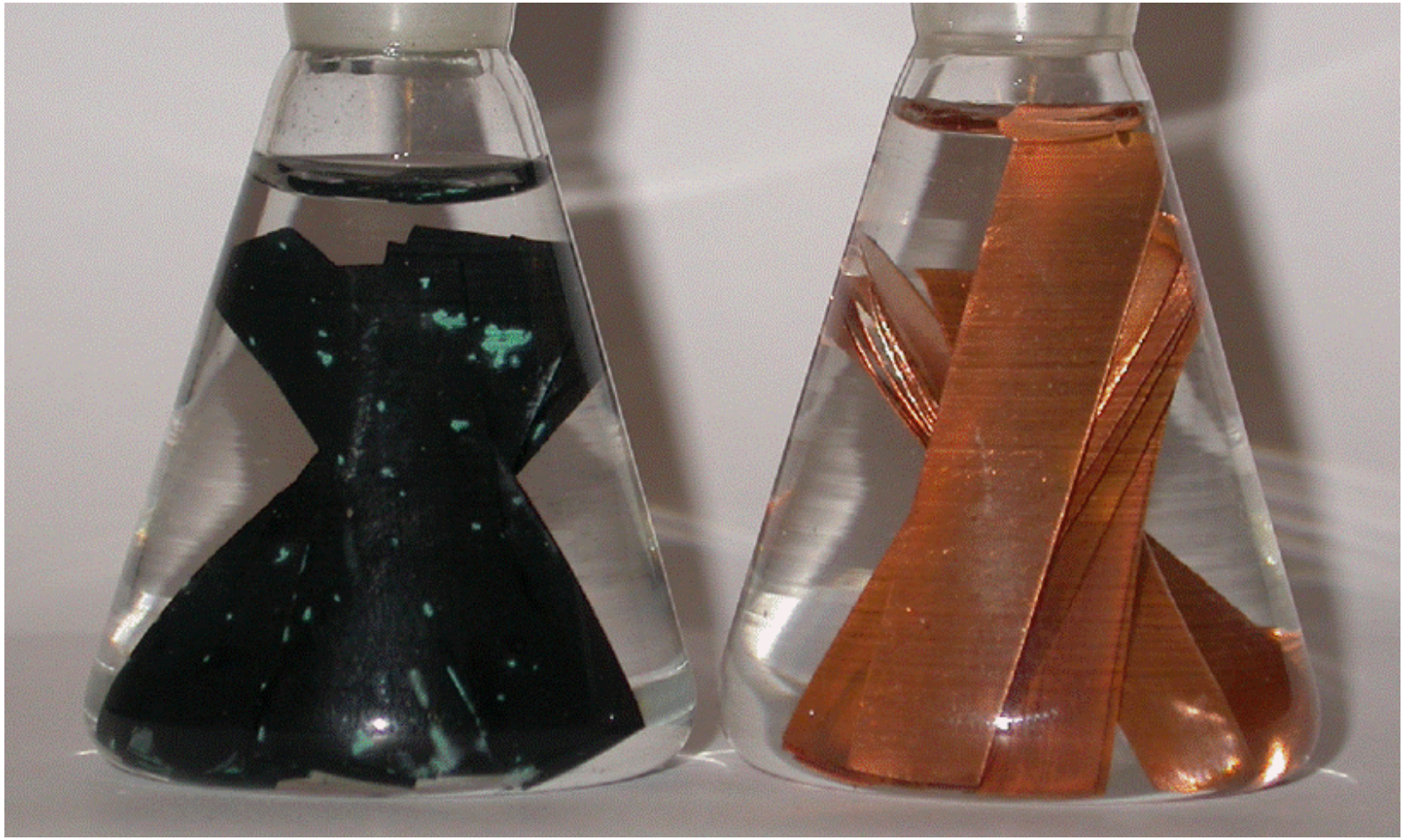
Cu-oxides are significantly enriched in ^{18}O.

G. Hultiquist, L. Gråsjö, G. Lu and T. Åkermark, Corros. Sci. 36 (1994) 1459.

Visually …

Appearance of copper after **15 years** of exposure in distilled water at room temperature. Hydrogen is allowed to escape via the palladium membrane from the lower tube but virtually not from the upper tube which has a platinum membrane. The membranes are sealed with UHV-glue (white).

G. Hultquist et al. ICC 2008, Paper No 3884.

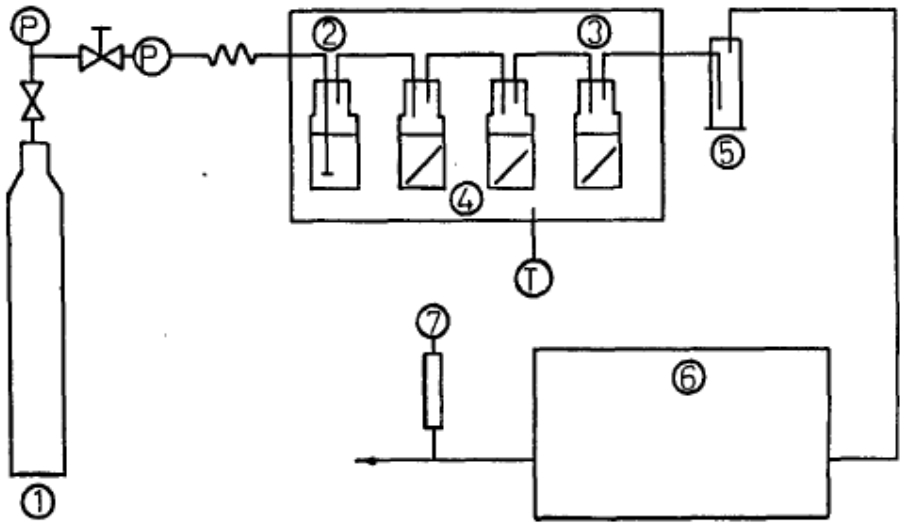


Appearance of copper after 15 years of exposure in distilled water at room temperature. Hydrogen from corrosion can escape from the left container but not from the container to the right. The water volume was equal in the flasks in beginning of the exposure.

G. Hultquist et al. ICC 2008, Paper No 3884.

Other Studies on Copper and Water

Simpson and Schenk (1987)

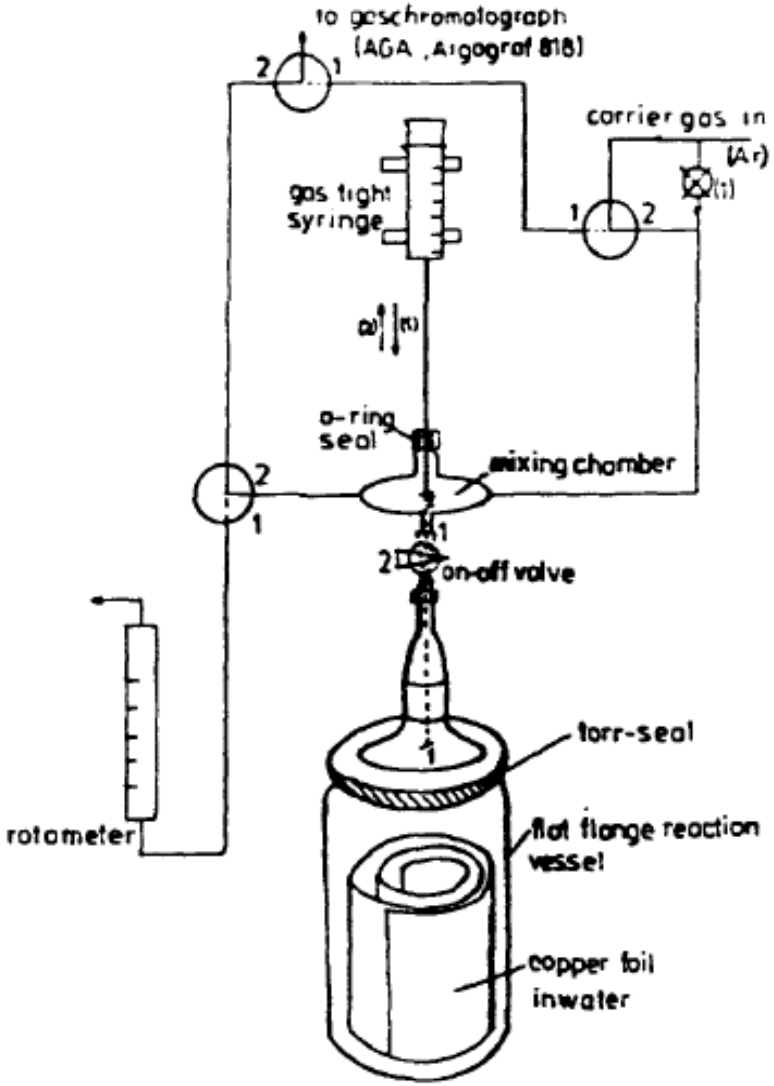


[1] N_2 gas
[2] H_2O to moisten gas
[3] three specimen flasks
[4] water bath
[5] cold trap to remove excess water
[6] gas chromatograph
[7] gas flow rate meter

Copper specimens immersed in 8000 mg/l chloride solutions at 50 °C and 80 °C. A flow of nitrogen passed over samples. Assumed detection limit for GC of 1 vppm H_2.

- No H_2 detected.
- Both weight gains and losses were measured.

J.P. Simpson and R. Schenk, Corrosion Sci. 27 (1987) 1365.



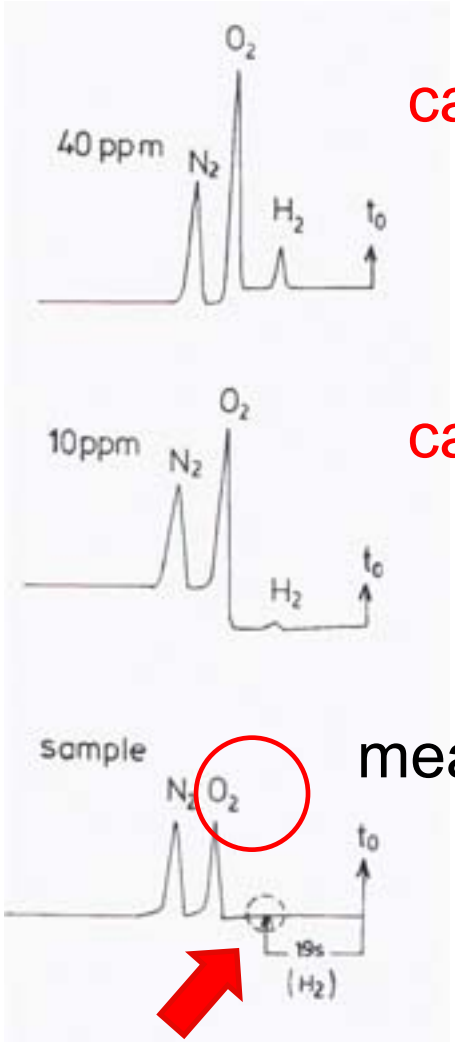
Eriksen et al (1988, 1989) reported that no hydrogen was evolved during exposure of copper in distilled water over a period of 61 days.

T.E. Eriksen, P. Ndalamba and I. Grenthe, Corros. Sci. 29 (1989) 1241.

T.E. Eriksen, P. Ndalamba and I. Grenthe, On the corrosion of copper in pure water, SKB Technical Report 88-17.

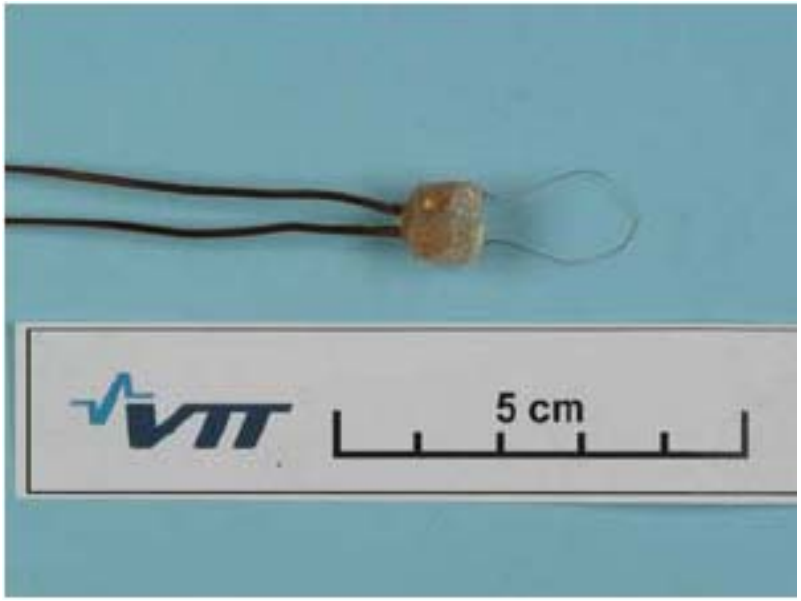
Note: system contained oxygen which would have reacted with any hydrogen formed.

"Surface of exposed copper foils were unevenly corroded with smaller areas clearly discoloured whilst large areas were seemingly unaffected."



no hydrogen

Corrosion of copper in anoxic 1M NaCl solution by VTT Technical Research Centre of Finland (2003)



$$d_{corr} = r_o\left(1 - \sqrt{\frac{R_o}{R}}\right)$$

Corrosion measured by online resistance of a copper wire, weight loss coupons and solution analysis.

M. Bojinov and K. Mäkelä, Working Report 2003-45, Posiva OY;
M. Bojinov, et al, Mat. Res. Soc. Symp. Proc. Vol,. 807 (2004) 1-6.

At 80 °C in 1 M NaCl

Dissolved oxygen removed by N_2 bubbling for 4 – 6 h.

Without Oxisorb, 10 ppb oxygen in solution

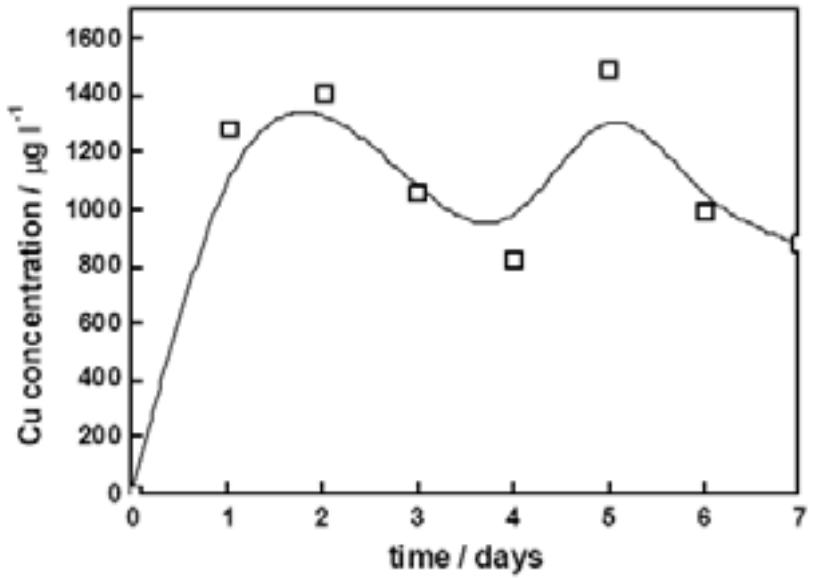
Cu wire probe showed a fast corrosion rate > 100 μm day^{-1} in the first 2 h (oxic period) followed by 1.5 μm day^{-1} thereafter. Cu wire probe broke due to corrosion after 3.5 days.

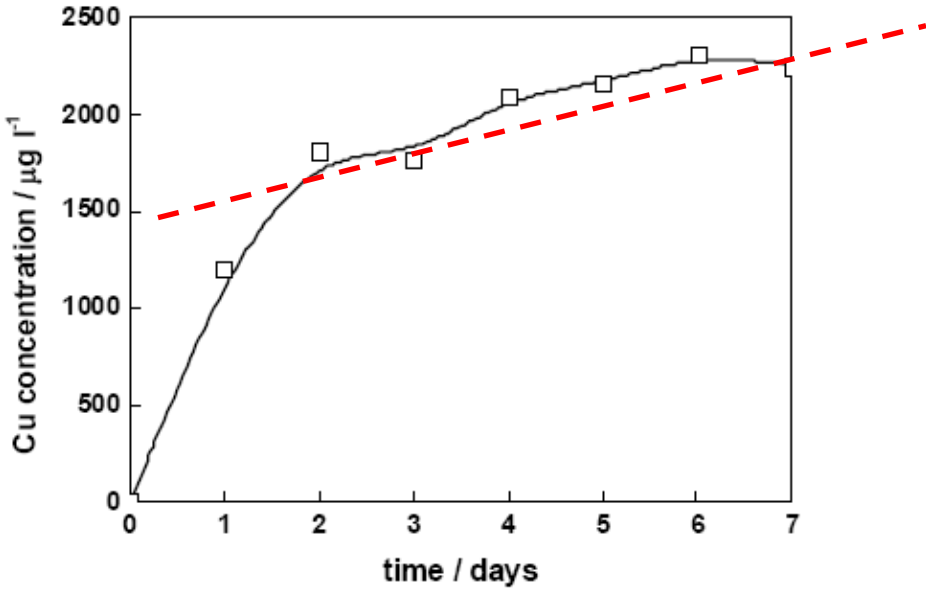
With Oxisorb, 5 ppb oxygen

Initial period of 0.5 h with rapid corrosion rate (> 100 μm day), followed by decreased rate up to 6 h, and finally negligible rate from 6 h to 6 days.

Solution Analyses for Dissolved Copper

Note the change in scale!





Test Nr. 1 (without Oxisorb)

Test Nr. 2 (with Oxisorb)

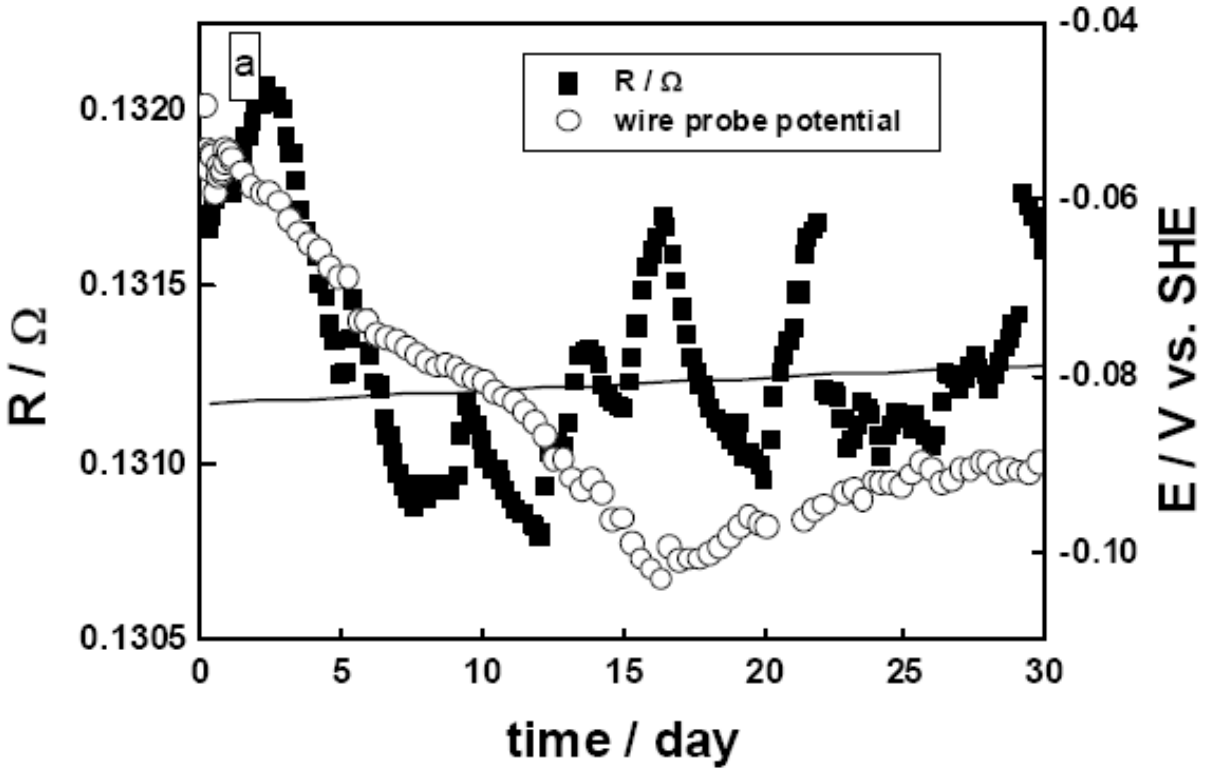
Corrosion rate calculated from weight loss of test coupons

Test Conditions	Corrosion rate[a] ($\mu m\ year^{-1}$)
80 ºC, Without Oxisorb, 6-day test	48
80 ºC, With Oxisorb, 6-day test	11.8
RT, With Oxisorb, 6-day test	7.4
RT, With Oxisorb, 30-day test	3.9

Note: report concludes that corrosion of Cu at RT virtually stops after 60-80 h due to anoxic conditions.

[a]Transient phase of the experiment.

30-day test in 1 M NaCl at room temperature, 1 MPa N_2 (< 5 ppb O_2)



Cyclic behavior - indicates deposition process or temperature fluctuation.

Mean value of resistance – no net corrosion detected by sensor.

Does water corrode copper ?

Some evidence for copper corrosion under anoxic conditions.

- –Hydrogen evolution together with visible signs of corrosion on copper.
- –Posiva working report shows copper dissolution under anoxic conditions at increased rate over oxic conditions.
- –Resistance measurements show oscillations with upward trend.

Appearance of copper coupon in bentonite from retrieved LOT test parcel

B. Rosborg, J. Pan, C. Leygraf, Corrosion Sci. 47 (2005) 3267.

Photo after ultrasonic cleaning in water to remove loose corrosion products and bentonite residues on the surface.

Average corrosion rate calculated from weight loss measurements on copper coupons after 1 or 2 years test duration falls in the range of 2.4 – 3.5 μm/year.

Nature of copper corrosion product

- Anoxic reaction of Cu with water to form hydrogen seems only possible if a thermodynamically stable corrosion product is formed.
- Szakalos and Hultquist proposed the formation of H_xCuO_y.
- Against:[1] no evidence for such a stable H_xCuO_y species unlike Cu_2O and CuO.
- Is it unstable when exposed to oxygen ? Would in-situ techniques be useful ?

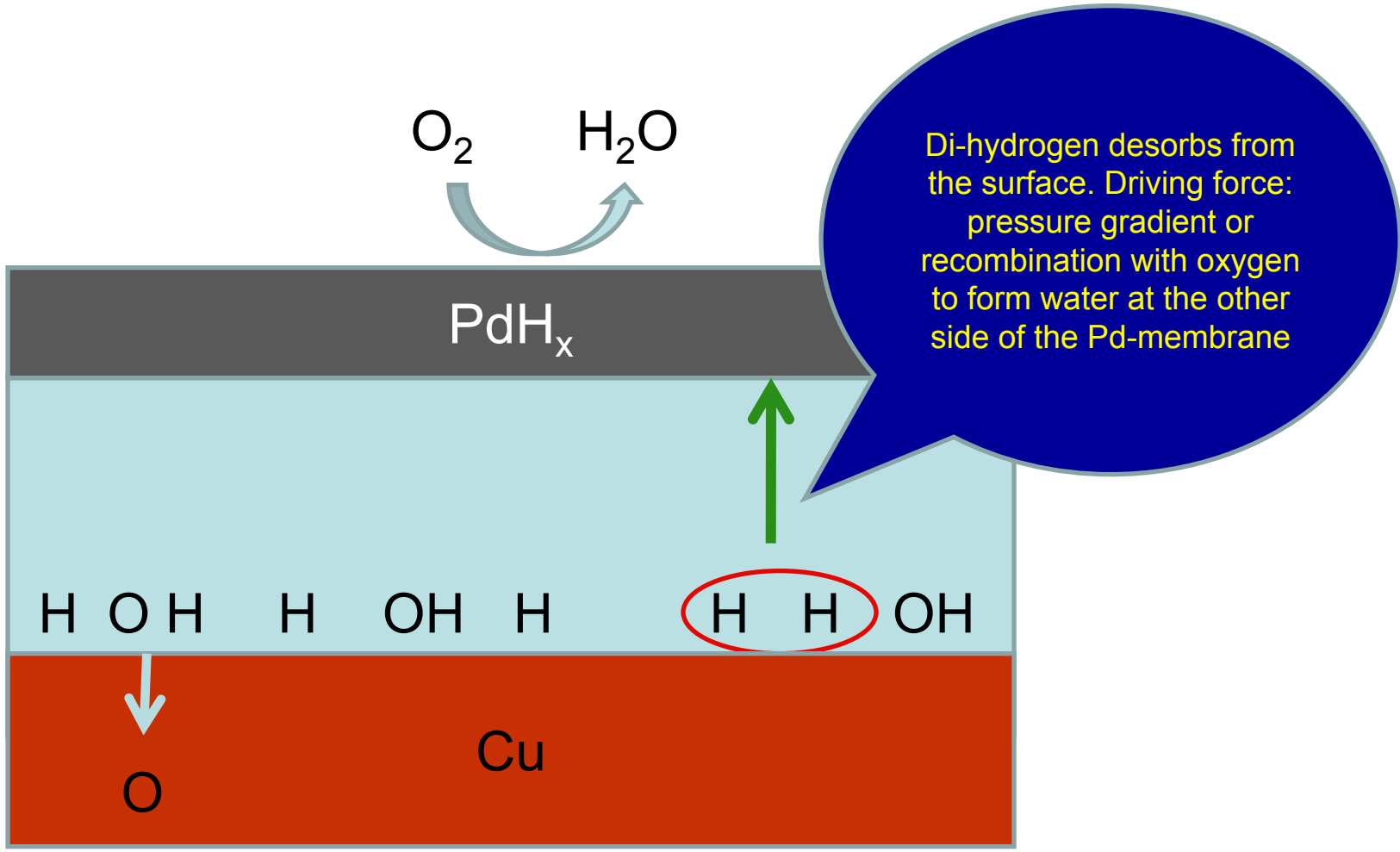
1. L.G. Johansson, Electrochem. Solid-State Lett. 11 (2008) S1

Comments

- The study of copper corrosion by water is one that is of scientific interest as some observations do not fit with our present-day knowledge of thermodynamics for the Cu-H_2O system.
- A good knowledge of the oxidation products of copper and their stability is required. There is room to determine the thermodynamic properties of all these compounds and modifications.
- **Shared experiments designed with input from all interested parties in this study on copper corrosion by water. Primary data be shared for interpretation.**

Thank You
for your attention

Professor Gerhard Ertl (Nobel Prize 2007) – studies of chemical processes on solid surfaces.



Net reaction:

$$Cu + H_2O \rightarrow CuO + 2\,H_{ads} \text{ (or } Cu_2O + 2\,H_{ads})$$

$$2\,H_{ads} \rightarrow H_2$$

$$H_2 + \tfrac{1}{2}\,O_2 \rightarrow H_2O$$

Real-time corrosion monitoring at Äspö Hard Rock Laboratory

(i) Retrieval experiment: Electrically heated full-scale canister emplaced in fall 2000 and retrieved in early 2006. Bentonite next to canister saturated with groundwater.

(ii) Prototype repository: Six full scale canisters deposited in the same manner as the future deep repository. Inner section sealed in 2001, outer in 2003.

(iii) LOT (long term test of buffer material) experiment: 7 test parcels to be run for 1, 5 and 20 years.

Evidences against copper corrosion in water

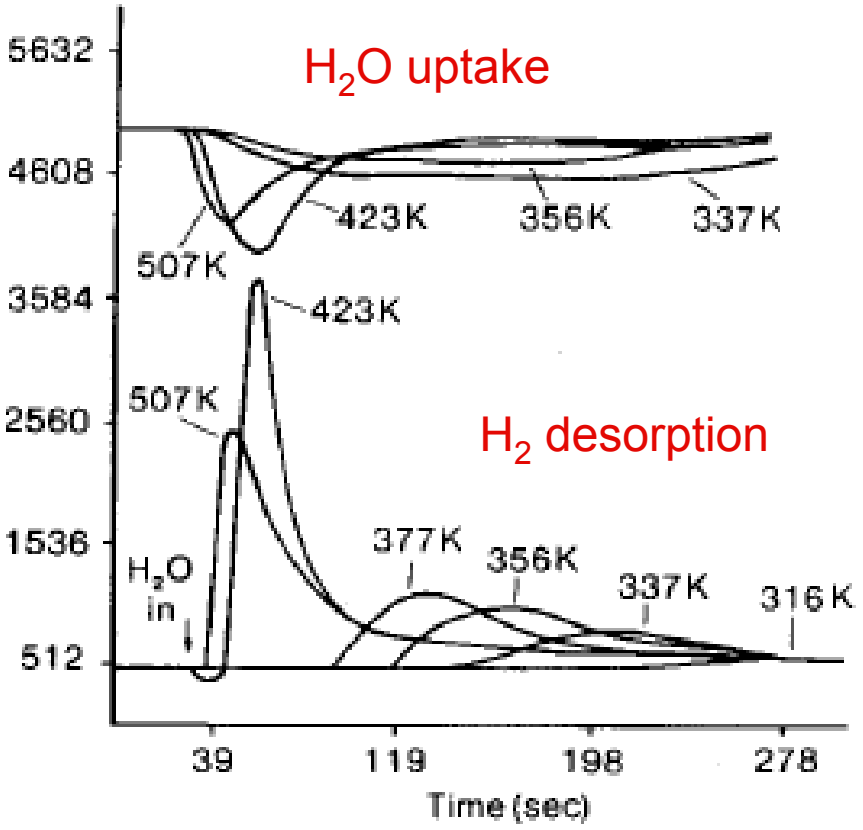
- No hydrogen detected by Simpson and Schenk[1] or Eriksen at al[2] in their studies on copper corrosion in oxygen-free water.
- An attempt by Möller[3] (1995) failed to reproduce the observations of Hultquist et al for Pd-and Pt-sealed glass vessels.
- Note: reported that a significant amount of water "disappeared" from the quartz test tubes during the test.

1. J.P. Simpson and R. Schenk, Corrosion Sci. 27 (1987) 1365.

2. T.E. Eriksen et al, Corros. Sci. 29 (1989) 1241; SKB Technical Report 88-17.

3. Critical review of the literature on the corrosion of copper by water by Fraser King, Integrity Corrosion Consulting Limited, November 2009.

Adsorption of water on polycrystalline Cu from 316 – 507 K is accompanied by H_2 evolution



25 ml/min of 1.5% H_2O in He pass through the catalyst bed at the indicated temperatures.