Evaluation of evidence for copper corrosion products presented in Hultquist et al. (2013)

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Hultquist et al. (2013) have in a report to SSM presented hydrogen pressure measurements from a long term experiment with copper immersed in oxygen-free water. They also find corrosion products on the copper, which they have examined ex-situ by SEM and characterized by X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). They claim that XPS strongly indicates a corrosion product containing both hydroxide and oxide. In order to conclusively demonstrate corrosion, a copper containing corrosion product needs to be unequivocally identified. Hultquist et al. (2013) suggest CuOH, but deliver, in this author's opinion no solid proof for that. In fact, a closer look at the data leads to a different interpretation.

Korzhavyi et al. (2012) have suggested that solid CuOH is meta- or kinetically stable under certain conditions, but thermodynamically unstable with respect to Cu_2O and water. Thus, it can't be a product of corrosion of copper in water. Following this, Soroka et al. (2013) managed to synthesize hydrated cuprous hydroxide, $CuOH \cdot H_2O$ and characterize it using XPS and FTIR. They also showed that the compound was unstable and decomposed fairly rapidly to copper oxide and water.

In the present report Hultquist (Hultquist et al. 2013) presents a continuation of a previously reported experiment (Hultquist et al. 2009, 2011). The surfaces, when exposed to water, were in 'as received' condition, i.e. they have not been polished before the exposure in the experiment. They must, therefore, have had surface oxides and, most likely, carbon compounds on the surface. These carbon compounds are always present and are sometimes even used for calibration purposes in XPS (adventitious carbon). Ollila (2013) also used 0.1 mm Cu foil and from the same supplier (Goodfellow, UK). Ollila's samples had a surface carbon contamination that may also have included cellulose even after polishing.

Figures 5 and 6 in Hultquist et al. (2013) show SEM pictures of what is stated to be corrosion products. The samples in Fig. 5 are archive samples, analyzed in September 2011 and do not belong to the present study. They have also been exposed (5b, c, and d) for half a year in air before the analysis. As Hultquist et al. (2013) points out: "Corrosion product is evident, but may have changed in composition and structure due to the air exposure."

The SIMS samples were not analyzed immediately after interrupting the experiment; one analysis was performed in Singapore and another in Ottawa. This raises questions about what changes in the surface layers could have occurred while in transit. It would also have been interesting to see some depth profile for some other elements and molecular fragments, such as e.g. C and OH.

Figure 6 is of a sample exposed to air for only 5 minutes. Among what Hultquist et al. (2013) labels as reaction product, there is in addition to micrometer-size crystals a fiber-like material. The crystals are most likely copper containing, but it is very unlikely that any stable copper containing compound should have a fiber-like morphology. It is, however, consistent with cellulose.

The XPS spectrum reported in Hultquist et al. (2013) can be compared with that reported in Ollila (2013). It would have been interesting to see also the Cu 2p spectrum and the C 1s spectrum. Hultquist et al. (2013) refer to the Cu spectrum for their interpretation, but do not show it, unfortunately. Their claim is that the analyses “indicate predominantly copper hydroxide and copper oxide”.

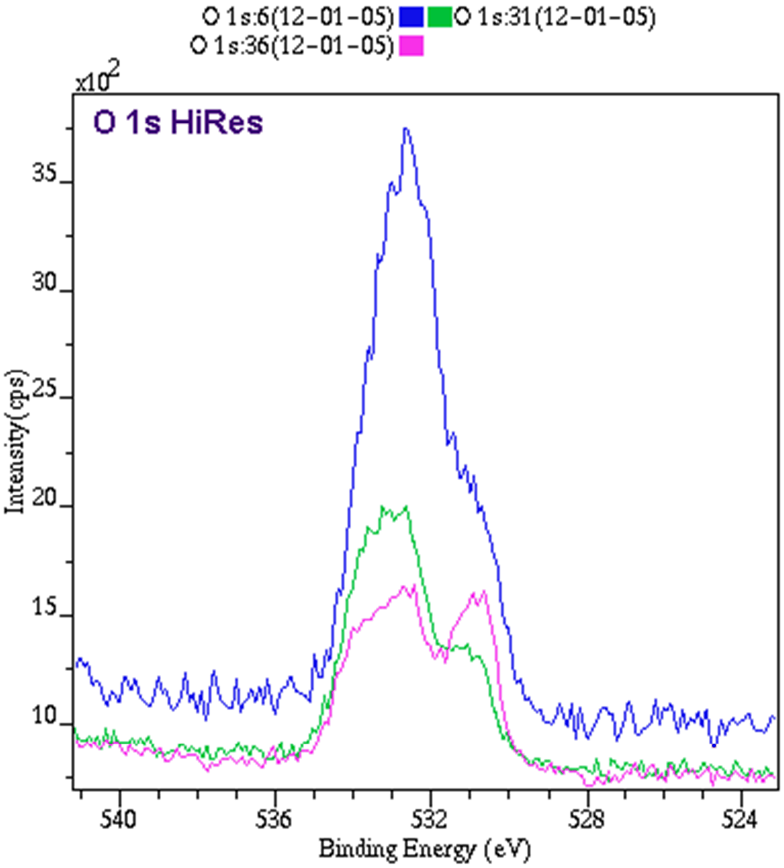

Figure A1-12 from Ollila (2013). O 1s spectra from copper exposed to oxygen-free water for about 700 days; blue is a polished reference sample, red and green are spectra from two locations on the exposed copper foil.

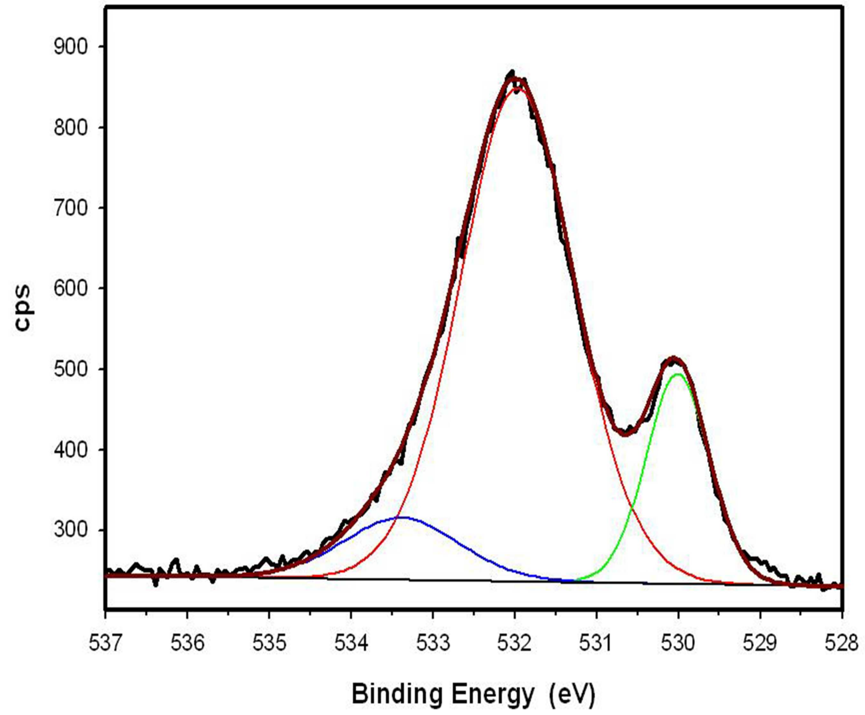

Figure 7 from Hultquist et al. (2013). O1s XPS-spectrum from Cu exposed to distilled water for 18800 hours (783 days).

The same two-peak features are present in both O 1s spectra. There is a slight shift in energy between the two spectra, but, presumably, there has not been an absolute calibration in either case. Ollila's Cu 2p spectra show no signs of Cu(II). The C 1s spectra show that carbon is present, but not only as a hydrocarbon. There are peaks that can be interpreted as C-O bonding carbon. The lower peak at the lower binding energy in both oxygen spectra is most likely from Cu_2O. The dominant peak cannot be copper hydroxide[1]. Based on the data in the NIST database, the higher peak can be adsorbed water, oxygen in C-O bonding, or binding to other atoms. Hultquist et al. (2013) present no complete XPS spectrum. It is, therefore, not possible to determine what else was present on the copper surface. Ollila (2013) concluded that this was oxygen in a cellulose-like compound[2]. The fiber-like reaction products in Fig. 6 in Hultquist et al. (2013) favor that interpretation. It cannot either be

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[1] Hultquist et al. (2013) refer to J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, Handbook of X-Ray photoelectron spectroscopy, Ed. by J. Chastain, Publ. by Perkin-Elmer Corporation, 1992. I don't have access to that database. I use the NIST database, http://srdata.nist.gov/xps/Default.aspx.

[2] Leena-Siska Johansson, who did the XPS is experienced in XPS of cellulose products.

adsorbed OH, since the O 1s binding energy of adsorbed OH is not that high (Andersson et al. 2008).

In Soroka et al. (2013) there are XPS-spectra for solid $CuOH \cdot H_2O$. The resolution is much lower than those in Ollila's and Hultquist et al.'s spectra. A curve deconvolution, however, reveals roughly the same structures. Soroka et al. interpret consistent with Ollila and Hultquist et al. (2013) the peak around 530 eV as a Cu(I) - O bond, while the dominant peak is to a large extent organics or a C - O bond. In other words, it is not possible to unequivocally identify CuOH from an XPS spectrum. Soroka et al. (2013) used FTIR in comparison with calculated phonon density of states to confirm the presence of solid $CuOH \cdot H_2O$.

In conclusion: hydrogen was detected, but no copper-containing corrosion product other than what is most likely Cu_2O was clearly detected. Since the copper was exposed to water in the 'as received' state, it is not possible to determine if the fore-existing oxide layer had been modified or grown during the exposure. Conclusion I in Hultquist et al. (2013), which reads, 'Cu reacts with water producing hydrogen as a by-product', cannot be considered substantiated by the presented data.

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