



Copper in ultrapure water, a scientific issue under debate



M. Ottosson^a, M. Boman^{a,*}, P. Berastegui^a, Y. Andersson^a, M. Hahlin^a, M. Korvela^b, R. Berger^a

^a University of Uppsala, Department of Chemistry—Ångström Laboratory, Box 523, SE-751 20 Uppsala, Sweden

^b University of Uppsala, Department of Chemistry—BMC, Box 576, SE-751 23 Uppsala, Sweden

ARTICLE INFO

Article history:

Received 20 May 2016

Received in revised form 1 February 2017

Accepted 13 March 2017

Available online 16 March 2017

Keywords:

A. Copper

B. XPS

C. AES

D. Oxidation

ABSTRACT

The corrosion properties of copper in ultrapure water have been studied experimentally by submerging copper samples (99.9999%) in pure water for up to 29 months. The surface was first electropolished at ambient temperature, then exposed to hydrogen gas treatment at 300–400 °C, thereby reducing the bulk hydrogen content to 0.03 ppm. These copper samples, the water and the glassware were all then subjected to precise chemical analysis. Great care was taken to avoid contamination. After exposure, only ~6 µg/L copper had accumulated in the water phase. Electron spectroscopy could not detect Cu₂O or any other oxidation products containing copper.

© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

The secure storage of nuclear and radioactive waste by long-term underground deposition is a technique being considered by many countries using nuclear reactor generated electrical power. The practical solution may differ, however in Sweden, Finland and Canada, deposition in copper canisters deep underground has long been considered, on the assumption that copper is essentially inert in an anoxic environment.

After initial claims that copper can undergo substantial oxidation corrosion even in oxygen-free water [1–4], various studies have been made which either corroborate or refute these claims [5–9]. A critical review of the literature on this subject has been made by King [10]. In a recent paper [11], we reported the results of a study conducted under strictly anoxic conditions, using ultrapure copper in ultrapure water in a glovebox environment, which minimised contamination from all other components at all stages of the procedure. To reproduce the experimental setups used as the basis for these earlier claims, we carefully monitored the evolution of the hydrogen gas pressure as a function of time at constant temperature. However, in contrast to earlier studies, we focus here more on the oxidation of copper rather than on the reduction of water in the proposed redox process. It is imperative to monitor the formation of oxidation products (which must contain copper with a positive

oxidation number) to definitively characterise such a corrosion process, especially since it is possible that any hydrogen gas measured could originate from sources other than corrosion. This possibility was deduced from the fact that no rational correlation was found between the measured amounts of copper oxidation products and the detected hydrogen gas [11]. Their relative proportions were strongly at variance with those expected for a chemically stoichiometric redox reaction involving copper and hydrogen. The stainless steel used in the original experiments [2–4] could have been a significant source of hydrogen, which would militate against a valid interpretation.

Detailed experimental features pertaining to the oxidation of copper must be taken into account to derive a realistic picture of the processes that could be involved in the corrosion of copper, for example we must consider what possible products could be formed and whether they would be located on a surface or in solution. We therefore performed chemical analyses not only of the bulk and surface of the copper but also of solute phases in its near environment: the result of the primary contact between copper and water and the secondary contact between water and glass of the test container and an added glass plate. In our previous paper [11], which reported a study of up to 6 months' exposure of copper to water, we described the main technical features of our equipment and measuring procedures. This paper presents new unpublished data from a more extensive study of copper exposed to water for up to 29 months, thereby facilitating a more thorough analysis of the validity of the conclusions drawn earlier. All data expressed in

* Corresponding author.

E-mail address: mats.boman@kemi.uu.se (M. Boman).

ppt, ppb or ppm denote concentrations by weight. In dilute water solutions, ppb corresponds closely to $\mu\text{g/L}$.

2. Experimental

2.1. Materials, treatment and analysis

The copper foil used had a thickness of either 0.25 mm or 0.50 mm and a purity of 99.9999% (Alfa Aesar). The water was ultra-high purity (Merck) and the elements with the largest concentration were: calcium, zinc, boron, sodium and silicon (each ≤ 500 ppt), followed by potassium, iron and aluminum (≤ 300 ppt). Dissolved molecular oxygen was reduced by nitrogen gas purging down to <1 ppb [11]. The beaker holding the copper foils was made from borosilicate glass (Duran type). Furthermore, a small glass plate of the same material was included to allow chemical analysis of the glass used after exposure to the test environment. Glassware was used to reproduce the conditions of earlier work [1–4].

The copper was electropolished in phosphoric acid ($\sim 55\%$ in water; 1.7V for 10 min, followed by 2.0V for 10 min), rinsed in high purity water and transferred to an ultra-high vacuum (UHV) furnace (10^{-8} mbar), where the superficial copper oxides formed during polishing were reduced by hydrogen at 300°C . After purging with argon, it was heated at 400°C under UHV to remove any hydrogen absorbed by the metal, as monitored by Quadrupole Mass Spectrometry (QMS) [11,12]. Fusion analysis (LECO instruments) of copper samples treated in this way showed a strong reduction of the hydrogen content in the metal from 0.1 ppm (concentration in the ‘as received’ material) down to 0.03 ppm. After this treat-

ment, the copper metal was not subsequently exposed to molecular oxygen during transport to and from the glove-box atmosphere ($\geq 99.9999\%$ nitrogen, ≤ 1 ppb oxygen) [11], to ensure the validity of the subsequent surface analysis by electron spectroscopy. The chemical identification of surface species is key to establishing whether copper had actually corroded during the corrosion experiments.

The water phase was also carefully analysed before and after contact with glass and copper. The highly sensitive technique ICP-MS (Inductively Coupled Plasma Mass Spectrometry) can detect whether copper or elements from the glass dissolved on contact with water (detection limit 1 ng/L or better).

The surfaces of the flat glass plates placed in the corrosion cell were also analysed by X-ray electron Spectroscopy (XPS) and X-ray Fluorescence spectrometry (XRF). The total exposed surface area of the glass was 100 cm^2 . The essential element to consider in the composition of the surface of the glass after removal from the exposure test was copper, which was either inherent in the glass from the beginning or had been deposited there through heterogeneous nucleation from dissolved copper in the water.

2.2. Equipment and procedures

The main equipment and procedures used here are described in previous papers [11,12], but a schematic diagram is included here for clarity (Fig. 1). Glass beakers with water were placed into stainless steel vessels. The copper foils (and glass plates) were immersed in the water at 50°C for various periods of time. The metal-sealed steel vessels were covered with a lid of palladium

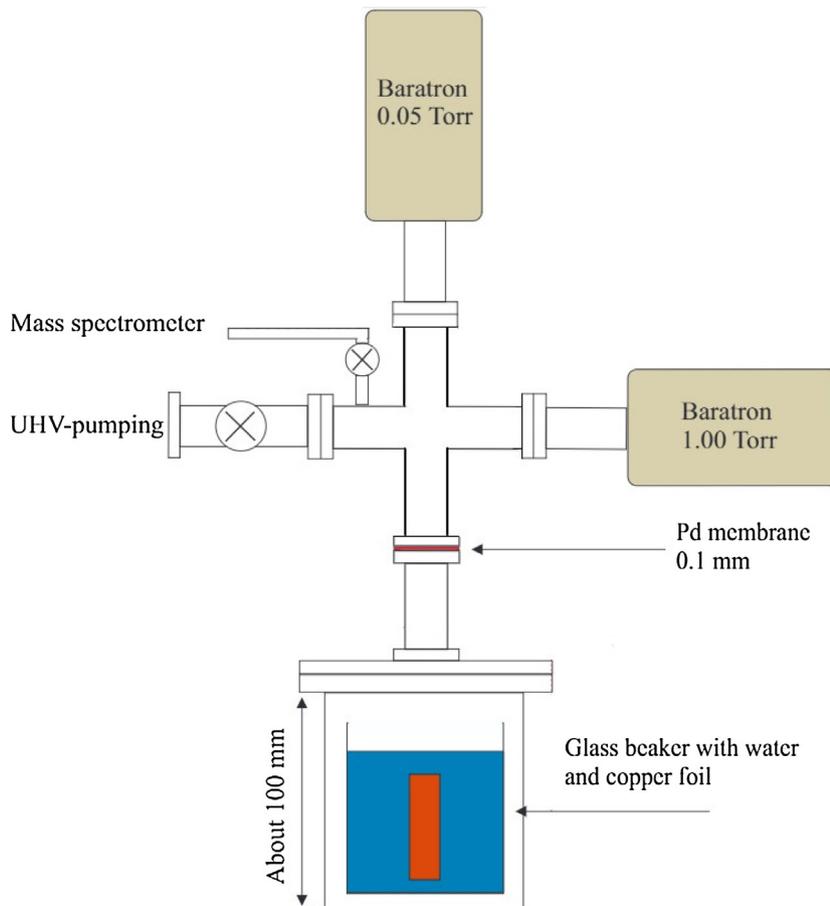


Fig. 1. Schematic illustration of the equipment used in the experiments (from Ref. [11]). Freestanding stainless steel vessels (including membrane but not pressure gauges) were probed for the analyses of copper, glass and water.

(details in Fig. 1), which allowed only hydrogen to pass through [1–4]. The steel vessels were either free-standing or attached to an assembly for monitoring the gas pressure. It should be emphasised that the five free-standing vessels allowed any evolved hydrogen to pass freely into the glove-box; the diffusion was driven by a concentration gradient. Since the materials within the stainless steel vessels were probed for copper oxidation products, they form the basis of a more reliable assessment of the corrosion process than the evolution of hydrogen.

The vessels were opened one by one inside the glove box at various intervals, so that any progression in a possible corrosion process could be followed in discrete steps by successive analyses of the copper surface, the water and the glass. After dismantling a vessel by removing its lid within the glove-box, copper foils were transported to the electron spectrometer for surface analysis within a few minutes, without any contact with air. This was achieved using a small transport vessel of stainless steel, sealed by an O-ring within the glove-box. The transfer time from glove-box to the spectrometer was kept to a minimum.

The water was transported in polymer vials for the ICP-MS analyses. Blank tests were performed. Moreover, analyses on specimens kept for more than a year showed that there was no added contamination from the vials. The glass plates were retrieved, and analysed by XRF. The unattached steel vessels were opened after 1, 3, 6, 15 and 29 months. In our earlier paper [11], the analysis results from 15 and 29 month exposure periods were not yet available.

2.3. Chemical characterisation methods

The analysis method chosen (see below for definitions of the acronyms and instrumental details) depended on the state of matter (i.e. solid, liquid or gas), with the highest accuracy being prioritised when needed.

2.3.1. Electron spectroscopy

The ESCA instrument used for the XPS/AES analysis was a Perkin Elmer Phi 5500 equipped with AlK α radiation. The binding energy (BE) was calibrated against adventitious carbon (C 1s at 285.0 eV). Most Auger spectra were measured using this instrument and the BE was converted to kinetic energy.

A more detailed lateral resolution by AES was obtained using a PHI 660 Scanning Auger Electron Spectroscopy System, where the surface was instead probed by electrons (from a LaB₆ electron gun) rather than X-rays. An SEM image was also obtainable by using the

scanning electron facility. This instrument (AES) was used especially for investigating local homogeneity, a feature possible due to the strongly reduced probed area (a few nm) that permits spot analysis at selected points such as grain boundaries.

2.3.2. X-ray Fluorescence Spectrometry (XRF)

A PAN Epsilon 5 instrument was used with a GdK α primary radiation and a GeK α secondary source. The signals were analysed through energy dispersion and the relative intensities determined by calibration.

2.3.3. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

A Perkin-Elmer NexION 300D instrument was used, calibrated against multi-element solutions from ICP standards. Because of the low concentrations involved, contamination risk from airborne particulates was minimised by performing the preparations in a laminar flow bench (a device working as an inverted fume hood). Special care was taken to avoid interference. Even ⁵⁷Fe, which is usually chosen instead of the more common iron isotopes (e.g. ⁵⁶Fe) to avoid argon oxide ion interference (atomic mass 56 u), would have suffered from interference from ⁴⁰Ar¹⁷O⁺ because the H₂¹⁷O content could not be neglected in view of the excess water present. In this case, ammonia was used as the reaction gas, since it interacts readily with argon oxide ions in a charge transfer reaction that breaks the Ar-O chemical bond. To ensure the ultimate validity of the copper concentration determination, both ⁶³Cu and ⁶⁵Cu were measured and the values scaled according to their relative isotope abundance.

2.3.4. Mass spectrometry (QMS)

A quadrupole MKS Cirrus (LM99) instrument was used to measure gaseous hydrogen concentrations but it was adapted to fit on to a UHV connection, so the base pressure was reduced to $\leq 10^{-9}$ Torr. The sensitivity was estimated to be $\sim 5 \cdot 10^{-5}$ Torr in the pressure logging system (and $\sim 5 \cdot 10^{-10}$ Torr within the spectrometer).

The analysis methods applied to the solid state (copper, glass) were either non-destructive (XPS, AES, XRF) or destructive through heating, melting or leaching (QMS, ICP-MS, fusion analysis). The analyses of all water were made solely by ICP-MS, where liquid is transferred to the gaseous state via an aerosol into a plasma. Gas analysis by QMS was further used for products of the pressure monitoring setup or from the heat treatments of the copper.

The detailed hydrogen content results from fusion analysis are omitted here, but they are reported in reference 12. The main result

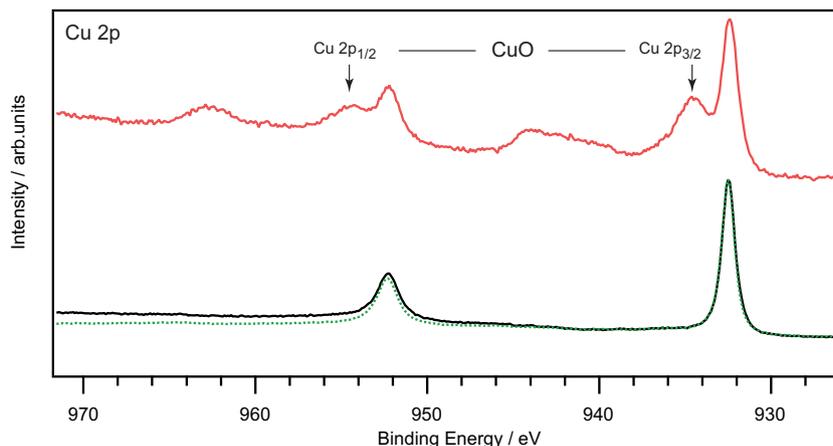


Fig. 2. XPS of copper directly after electropolishing (top, red curve) and after subsequent hydrogen reduction (bottom, black and green curves). The contribution from CuO involves the addition of broad satellite structures to its main 2p peaks (indicated by arrows). The two lower spectra show the Cu 2p states before and after sputtering of the cleaned surface (Cu⁰), not distinctly different from that of Cu₂O (Cu^I) which forms a part of the top spectrum of the oxidised surface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

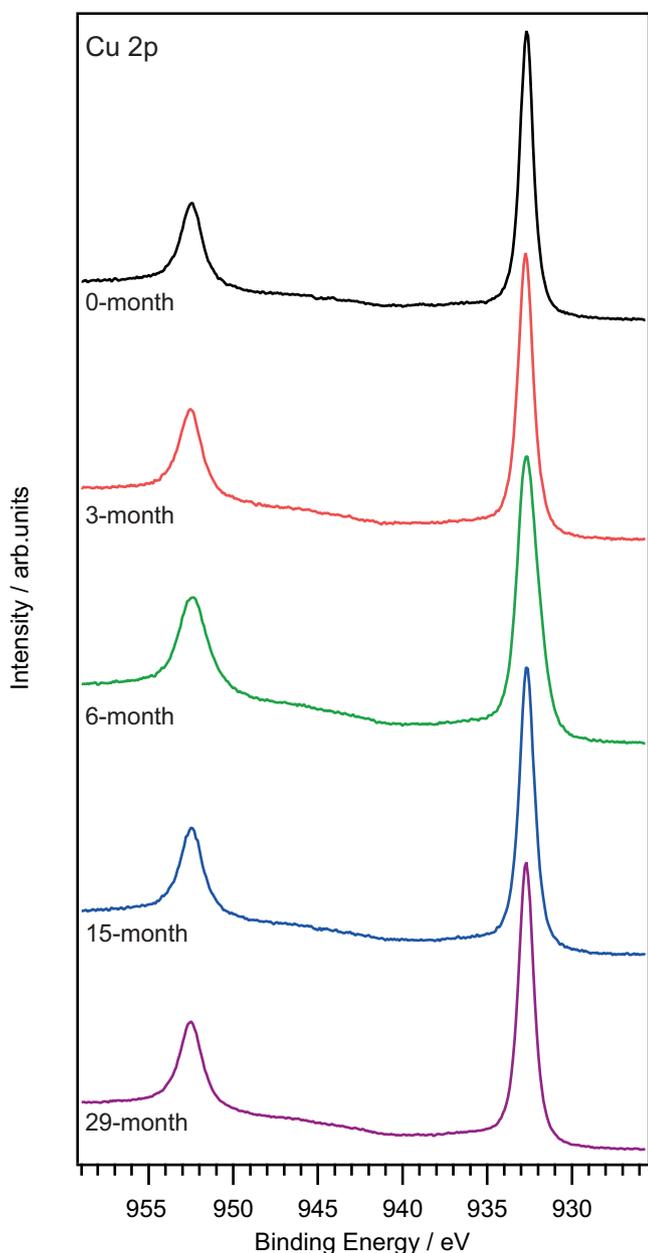


Fig. 3. XPS Cu 2p spectra for copper samples, made just before (0-month) or after immersion in water for extended duration.

is that the hydrogen content of the copper was reduced to 0.03 ppm by heat treatment before the experiment, and that this did not change as a result of immersion in water for up to almost 3 years.

3. Results and comments

3.1. Copper foil

The efficiency of the purification steps (by electropolishing, followed by the hydrogen reduction and purging) was investigated by using XPS [11]. Fig. 2 indicates the presence of oxide coatings from the electropolishing (upper spectrum) as well as the effect of the subsequent hydrogen reduction (lower spectra). The presence of CuO (appearing together with Cu₂O) is shown by the shifts in the positions of the main peaks (Cu 2p_{1/2} and Cu 2p_{3/2}), as well as by the accompanying broad shake-up satellite structures typical of Cu(II) species (at 940–945 and 960–965 eV).

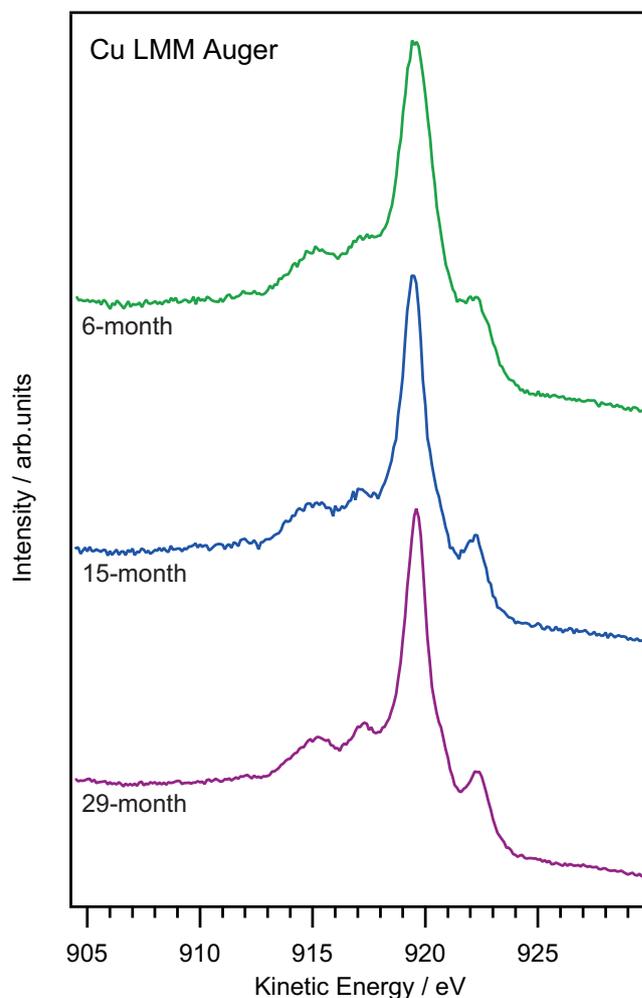


Fig. 4. XPS measurements (cf. Fig. 3) presented as Auger spectra. The binding energies in the XPS spectra have been transformed into kinetic energies. Cu₂O should appear as a broad feature with a maximum near 917 eV [13].

The hydrogen reduction step effectively removed CuO to leave a single Cu 2p spectrum without satellites. Moreover, the hydrogen treatment at high temperature effectively lowered the bulk hydrogen content down to 0.03 ppm from 0.1 ppm in its pristine state. The spectra of the purified copper did not change further on water exposure, as illustrated in Fig. 3 for various immersion times (up to 29 months). However, XPS cannot discriminate between Cu₂O and Cu in such a spectrum. This is illustrated by the spectra in Fig. 2, where at least one of the lower spectra must belong to metallic copper (taken after sputtering). An unambiguous interpretation of the XPS data is crucial to a correct analysis of the surface composition of the copper foils after exposure to water, where any copper(I) oxide deposition must be identified.

Alternative insights into the surface composition were obtained by extracting Auger spectra from the XPS spectra. The Auger electron spectra of Cu and Cu₂O are significantly different, since the electronic levels involved in the production of the Auger electrons are quite different, thereby facilitating separation of metallic copper from an oxide deposit on copper in the spectra. Scanning AES could thus show that samples were homogeneous with no accumulation of oxygen species at the grain boundaries. An overview XPS spectrum is therefore representative. It was clearly demonstrated earlier [11] that the Auger Cu L₃M₄₅M₄₅ spectrum from a pure copper sample exposed to water for 6 months contained no detectable Cu₂O. The spectrum was unchanged after heavy sputtering, during which bulk copper would have been exposed (Ref. [11], Fig. 2). AES

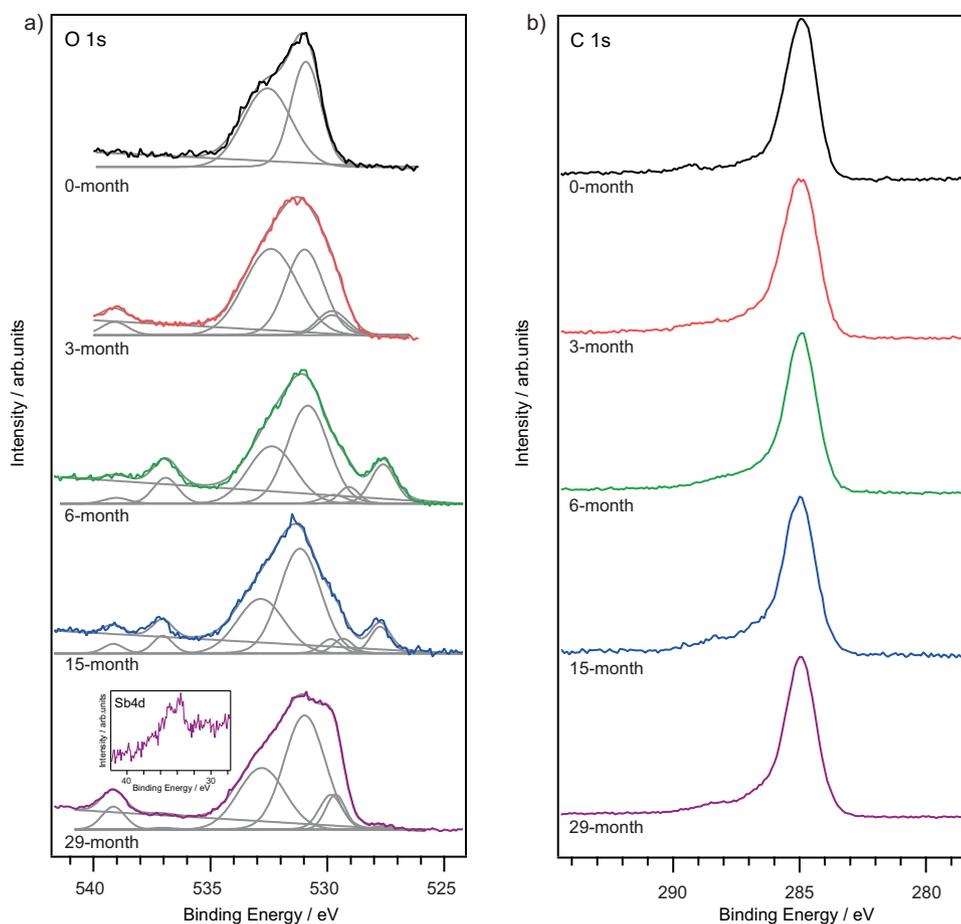


Fig. 5. (a) XPS oxygen spectra with small Sb peaks. Results from the deconvolution are discussed in the text; (b) Spectra of adventitious carbon (C 1s).

results obtained after 15 and 29 months immersion in water show that the initial clean copper surface was still totally intact after almost 2.5 years (Fig. 4). Any copper(I) oxide (Cu_2O) present would have yielded a broad feature with its kinetic energy maximum at 917 eV [13].

Spectra for O 1s were also measured (Fig. 5a). A broad feature can be attributed to two dominating O 1s contributions centered at ca. 531 and 533 eV for all the samples investigated. This indicates that oxygen constitutes an electronegative component in more than one species. The 533 eV contribution can be attributed to superficial adsorbed water, while the 531 eV peak may belong to OH_{ads} [14]. The different relative intensities of these two species may result from different crystal orientations that influence the water adsorption.

The XPS O 1s peaks are flanked by small peaks, which are attributed to antimony ($\text{Sb}3d_{5/2}$ and $3d_{3/2}$). These peaks disappear after sputtering, along with the oxygen peaks. The Sb is probably contamination arising from a water phase adsorbed on the copper surface; the copper foil had just been removed from the water. The antimony appears to have been leached from the glass beaker by the water since the intensity of the antimony peaks increased with immersion time. Weak Sb 4d contributions (binding energy ~ 33.6 eV) can be discerned for the 29 month sample.

The fitting of the small peaks from antimony requires deconvolution constraints concerning theoretical intensity ratios between the Sb 3d peaks and their spin-orbit splitting (see for instance Ref. [15]). With a splitting of 9.3 eV, Sb $3d_{5/2}$ and $3d_{3/2}$ peaks were found at (B.E.) 527.7 eV and 537.0 eV, respectively, for Sb(III), or at 529.9 eV/539.2 eV (assuming the same splitting) for Sb(V). Two overlapping peaks were needed at ca. 530 eV to realise the best fit in

the deconvolution procedure. One belongs to $\text{Sb}3d_{5/2}$ and the other is probably O 1s with a similar intensity. This corresponds rather well to the situation in Sb_2O_3 , where the oxygen contribution to the overlapping Sb peak is of the order of 20% [15] and is expected to be about 30% in Sb_2O_5 with overlap at 531 eV [16]. The fact that the oxygen contribution to the peak intensities for the antimony oxides was so low despite the O:Sb ratios being 3:2 (or 5:2) is a result of the very different electronic cross sections of these two elements [17]. Taking this into consideration, it is clear that the antimony content of the copper surface was very much lower than that of oxygen. The OH_{ads} and $\text{H}_2\text{O}_{\text{ads}}$ species (peaks at 533 eV and 531 eV) can together correspond to only a monolayer under the low-pressure conditions of the spectrometer. Antimony was present in the water in a very low concentration, as verified by ICP-MS results (see below). The sensitivity of XPS is clearly capable of detecting antimony even as a fraction of a monolayer on the surface of the metal.

The amount of carbon detected was very low. It was present as a surface film, as shown by a C 1s peak (Fig. 5b) typical of adventitious carbon, due to hydrocarbons present in the spectrometer.

The smoothness of the foil can be seen qualitatively in Fig. 6. An X-ray diffraction pole figure (not shown) indicates the surface plane of the copper foil was {001} or {110} rather than the close-packed {111}. Interestingly, calculations have shown that copper with a {111} orientation exhibits no water adhesion whatsoever [14].

3.2. Water phase

The high sensitivity of ICP-MS for water phase analysis means that extremely low concentrations of solute can be detected, but

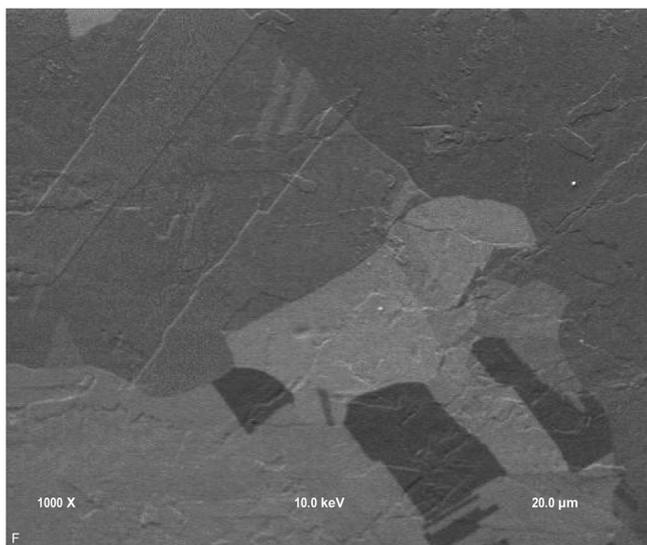


Fig. 6. SEM micrograph of the copper surface of a 6 month sample. The differences in shading reflects different orientations of the copper crystals.

Table 1

A semi-quantitative analysis of the most prominent elements in the water phase, for increasing residence time of copper in water. Concentrations are expressed in $\mu\text{g/L}$.

Element	1 month	3 months	6 months	15 months	29 months
Al	12	73	222	239	275
B	112	341	672	854	1734
Ca	40	103	223	197	241
K	157	431	854	1104	1344
Na	211	446	811	953	1057
Si	1187	6939	9282	12700	12200

also that systematic errors can be difficult to control. The technique does not provide any information about the chemical form of each element present. Moreover, a direct comparison between the concentrations of different elements is only semi-quantitative, because the intensity of the signal depends on how the element is chemically bonded, in particular for molecular ions how efficiently the dissociation occurs in the plasma. Nevertheless, it is possible to identify the dominant elements, and a comparison can be made between different samples for a particular element as time progresses.

The highest concentrations of elements arise from the leaching of the glass [18], as illustrated in Table 1. The results are quite in line with expectations for a borosilicate glass. Charge-compensating cations (Ca^{2+} , K^+ and Na^+) must be present since boron (+III) and aluminium (+III) substitute for silicon (+IV) in a silica network.

Other elements are also leached out, but in much lower concentrations. In this context, it is crucial to differentiate between the leaching of copper from glass and from the metallic copper. A blank glass specimen was therefore also analysed after 41 months in water at the same temperature (50°C) as the copper samples. It was found that the copper concentration was only $0.5\text{--}0.6\ \mu\text{g/L}$. Analyses were also made for a few other important elements. Table 2 shows leaching of selected elements from samples with copper in water. These values are based on three consecutive measurements on each sample, and then checked by control measurements of samples stored (in polymer vessels).

Of the elements listed in Table 2, magnesium and zinc are examples of elements which can easily contaminate samples from the surrounding environment. The presence of antimony ($30\ \mu\text{g/L}$ in the blank sample after 41 months) derives from the deliberate addition of its oxide to glass in order to avoid bubbles [19]. Its presence

Table 2

Results of a semi-quantitative analysis of selected elements in the water phase from various residence times for copper in water (cf. Table 1). Concentrations are given in $\mu\text{g/L}$.

Element	1 month	3 months	6 months	15 months	29 months
^{63}Cu , ^{65}Cu	6.3	5.5	8.3	5.0	19 ^a
^{57}Fe	1.6	0.5	1.4	1.9	1.7
^{24}Mg ^b	4.8	5.3	8.5	7.3	7.6
^{122}Sb	3.3	6.6	5.7	15.9	22.2
^{66}Zn ^b	7.1	7.8	8.0	7.7	8.6

^a The sample is probably unreliable as regards its copper concentration.

^b A blank specimen gave $4\ \mu\text{g/L}$ [12].

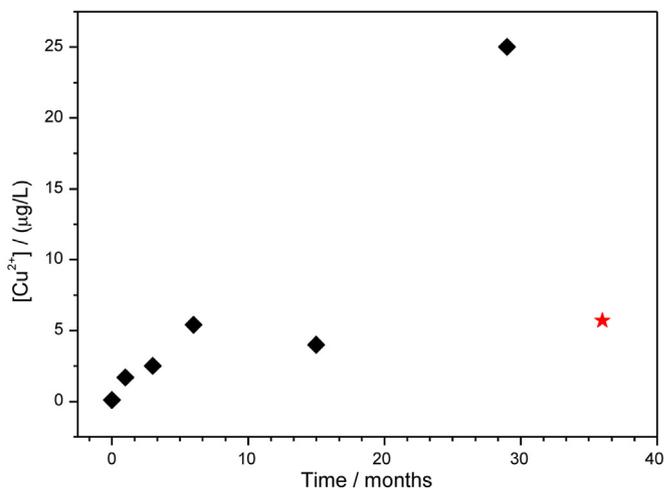


Fig. 7. Time evolution of the copper content in the water phase from quantitative analyses by ICP-MS. The 29-month sample is probably unreliable (see text). The point at 36 month belongs to a setup where the hydrogen pressure was measured and it had a slightly different thermal history.

in the water phase explains why antimony was detected by XPS at the copper surface.

More relevant is the evolution of copper concentration with time. These analyses were therefore performed more quantitatively by calibration against standard samples. The results are shown graphically in Fig. 7. It can be seen that these values deviate to some extent from those given in Table 2 through different levels of accuracy. The copper concentration appears to increase with time, but not in a linear manner. An unsolved problem concerns systematic errors, since the trend is rather erratic for larger times. A reasonable spread based on variations in sample size should be only a few percent, not a factor of 3–4. Control measurements of new samples from start up to 15 or 29 months could not be performed, since that would have cost the same time again of residence in water.

A copper sample used for monitoring pressure was also analysed after 36 months. Although not totally comparable to the other experiments, because it was not maintained at a constant 50°C but kept at temperatures $30\text{--}70^\circ\text{C}$ for various time intervals. It nevertheless showed a copper concentration of only $5\text{--}6\ \mu\text{g/L}$. This would, considering the data of Fig. 7, suggest that the 29 month sample was unreliable with respect to copper content (e.g. extra copper could have entered the system). ICP-MS is such a sensitive technique that it is susceptible to minute disturbances. A small number of nanometer sized copper particles entering the water phase as a colloidal solution would have influenced the result dramatically. If the data from the 29-month sample is discarded and replaced by the data from the 36-month sample, a fair conclusion is that the dissolution of copper is not linear over time but levels off at a constant value (around $6\ \mu\text{g/L}$) after $2\frac{1}{2}$ –3 years.

Table 3

Net copper content^a (expressed as corresponding film thickness) in glass plates exposed to water for various times in a glass beaker containing immersed copper.

Exposure time	3 months	6 months	15 months	29 months
“Thickness” in (nm)	0.00	0.03; 0.05 ^b	0.04	0.03

^a Corrected for blank value corresponding to a 0.02 nm thickness.

^b Measured from both sides.

3.3. Glassware

The copper content in the glass was verified by XPS and ICP-MS (by leaching with nitric acid). The variation in copper content between different glass plates was roughly of the same order as the error in the measurements [12]. A complementary XRF study was made of the glass plates, which accompanied the immersed copper samples. The results are given in Table 3.

The sensitivity to copper in a 360 s XRF measurement is estimated to be $\sim 2 \cdot 10^{-10}$ mol/cm². This corresponds to a significantly lower surface coverage than would correspond to one complete monolayer; rather one tenth of a monolayer. The measurements were normalised against a standard sample in the form of a glass sheet coated with copper deposited under controlled conditions.

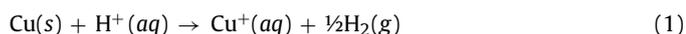
The copper content (in whatever form) can be expressed as the effective thickness (in nm) of a corresponding layer of copper metal, based on the proportionality between quantity and signal intensity (peak area of CuK α at 8.04 keV). This linear relation holds for films thinner than 100 nm, which is certainly the case here. Measurements were performed previously for plates that were exposed to water (together with copper metal) for 1 or 6 months [11]. The spread within one plate ($\sim 30\%$) and between different plates unfortunately creates a large uncertainty in the accuracy of the measurements. No actual copper deposition has been observed; the “thickness” given is only a conversion of the amount of copper to a corresponding metal-layer thickness which would give the same signal intensity. No information can be obtained from these data about how the copper is bonded chemically in the system or whether it occurs in the bulk or at the surface. The general conclusion to be drawn from Table 3 is that the amount of copper on the glass is very low, and that there is no obvious trend in concentration with time to suggest leaching or deposition.

ICP-MS analysis was performed as a complement to XRF on the water phase of a blank sample, involving no metallic copper and in water left for 41 months (see Section 3.2). Minimally low dissolution was observed. In other words, copper contained within the glass was not released significantly on immersion for 3.5 years.

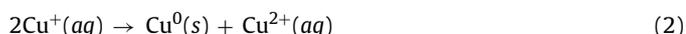
4. Discussion

New experimental data are presented here relating to potential anaerobic copper corrosion in water as has been discussed earlier [11]. Longer exposure times, high copper purity and the creation of an extremely smooth copper surface with a minimum of stress combine to give a set of experimental conditions for a truly controlled study.

Thermodynamic calculations using a program [20] that takes account of species dissolved in the water show that the dominant reaction will be:



Monovalent copper takes part in the disproportionation reaction:



Under equilibrium, where no mass flow takes place in and out, the calculated concentrations of ionic copper species are [Cu⁺

$\sim 10^{-12}$ M and [Cu²⁺] $\sim 10^{-17}$ M. Considering charge balance, OH⁻ is the only counter ion and must be considered, implying that CuOH(s) or Cu₂O(s) could be present. The activity of these species is less than unity. That fact does not prohibit the presence of adsorbed species.

The freestanding test vessels allowed hydrogen to pass out through the palladium membrane, which means that equilibrium of the “corrosion reaction” (Eq. (1)) was not attained but it was continuously perturbed. Not only is hydrogen gas allowed to escape, but there is a constant addition of hydrogen dissolved in the stainless steel itself [21]. Hydrogen atoms at the stainless steel surface can combine and form molecules which leave as gas. Through solid-state diffusion there is a continuous outward migration of hydrogen to compensate for this loss, thereby generating more hydrogen gas. It is therefore difficult to predict the outcome of such experiments based on simple models.

However, if there were any appreciable level of copper corrosion, the presence of species containing oxidized copper would be crucial to such an interpretation. This includes the detection of such species in the water and at the copper surface. Despite it being the most sensitive method for investigating the phase composition at a surface, AES could not detect that Cu₂O had been formed even after 29 months exposure of copper in pure water. If indeed oxide deposition onto copper does occur after this time then it must be at a minimal level (i.e. only a fraction of a monolayer).

It is claimed that copper metal can dissociate water at its surface [22]. Previous experiments were not performed in excess liquid water as they were in the current work. The presence of Cu-H and Cu-OH as adsorbates can be detected by XPS. Indeed, the presence of OH_{ads} was verified. On the basis of thermodynamic stability, Cu₂O could form by surface migration of such species, reaction between them and subsequent water condensation (if their concentration was high enough).

On the assumption that a copper oxide would not adhere to the surfaces, and tend rather to precipitate at the bottom of the beaker, analyses of top and bottom fractions of the water phase should yield different results. This was not seen, however, in the water analysis [12]; nor was there any conclusive evidence that oxidised copper (i.e. Cu^I, Cu^{II}) appears to any appreciable extent in the near-surface environment of the copper. Dissolution of copper from the glassware was found to be negligible along with deposition of copper species onto the glass. After 2½–3 years of copper immersion (28 cm² of copper foil in 100 mL of water), the water had a copper concentration of ~ 6 $\mu\text{g/L}$ and the copper came mainly from the metal samples. This value is higher than that predicted by equilibrium calculations, and is most likely to be a result of copper contamination. For example, 1 ppb of remnant oxygen in the water phase after purging with nitrogen would have been sufficient to create a perturbation due to a small amount of dissolved Cu₂O. Moreover, any accidental addition of a few nanoparticles of metallic copper to the ICP-MS sample would have influenced the measured copper concentration dramatically in a random manner and would have disrupted an otherwise monotonic trend.

Nevertheless, 6 $\mu\text{g/L}$ of copper in solution can be translated into a minimal level of corrosion, even taking in account a possible small deposition of copper onto the glass test vessel (Table 3) and a thin (undetectable) oxide film; in this way a corrosion rate of less than 0.3 nm/year was calculated.

5. Conclusions

Based on new complementary experimental data, we maintain the conclusion drawn in our previous paper [11] that copper corrosion in ultrapure water is very limited, as demonstrated by the minimal detection of oxidation products even after prolonged exposure. From the measurements obtained,

the oxidised copper is estimated to $<2 \cdot 10^{-8}$ mol/year (in the water phase), $<3 \cdot 10^{-8}$ mol/year (deposited on the glass) and $<7 \cdot 10^{-8}$ mol/year (deposited as an oxide). The corrosion reaction described in Eq. (1) thus contributes extremely little to the total amount of hydrogen gas that may be measured. The detection of hydrogen gas (from a corresponding reduction step) and the measurement of its pressure would appear to be a scientifically dubious basis for claiming that copper corrodes appreciably in water when other sources of hydrogen evolution are present; specifically, stainless steel and the components used in the pressure gauges. Even the very best steel quality used today worldwide in UHV work cannot yield such low hydrogen pressures as to allow changes to be unequivocally discerned from the background and be significantly measurable, when considering the obvious fact that oxidation and reduction processes simply have to match. In parallel pressure measurements (not described here), it was found that there was no significant difference in pressure evolution between that of a copper sample in water and of the same steel vessel unloaded (i.e. an empty and dry steel container). Corrosion of the stainless steel by water can therefore be excluded. The hydrogen gas released must therefore derive from the bulk steel (and the attached pressure gauges). Only the additional pressure can be attributed to the alleged redox process. Since there is no difference from the background pressure, the effect is unmeasurable with the current experimental setup. In other words, the oxidation rate of copper corrosion is so small that its pressure effect cannot be recorded.

The only reliable indication that copper undergoes any level of corrosion is the occurrence of copper-containing oxidation species, not a product of some accompanying water reduction. To avoid contamination, the surface of the high-purity copper was cleaned chemically, not by mechanical polishing, which could expose the surface to foreign particles. First electropolishing, followed by treatment in hydrogen and high vacuum yielded a very smooth surface. These two procedures remove dissolved hydrogen from the copper, rendering it extremely pure as shown by electron spectroscopy.

The copper itself, the water phase and the glass were subjected to highly sensitive analysis techniques. No appreciable quantities of corrosion products consistent with extensive copper oxidation were detected. The copper corrosion rate at 50 °C measured over 2.5–3 years under the most stringent of conditions corresponds to the formation of less than a monolayer of oxide. We estimate the corrosion rate to be <0.3 nm/year.

Acknowledgments

This work was financed by the Swedish Nuclear Fuel and Waste Management Co (SKB).

We thank Dr. Jonas Ångström for his skilled help with the purification of the copper samples, and Jan Bohlin and Anders Lund for their fine craftsmanship in the machining of the stainless steel equipment.

References

- [1] G. Hultquist, Hydrogen evolution in corrosion of copper in pure water, *Corros. Sci.* 26 (1986) 173–177.
- [2] P. Szakálos, G. Hultquist, G. Wikmark, Corrosion of copper by water, *Electrochem. Solid-State Lett.* 10 (2007) C63–C67.
- [3] G. Hultquist, P. Szakálos, M.J. Graham, A.B. Belonoshko, G.I. Sproule, L. Gräsjö, P. Dorogokupets, B. Danilov, T. Aastrup, G. Wikmark, G.-K. Chuah, J.-C. Eriksson, A. Rosengren, Water corrodes copper, *Catal. Lett.* 132 (2009) 311–316.
- [4] G. Hultquist, M.J. Graham, P. Szakálos, G.I. Sproule, A. Rosengren, L. Gräsjö, Hydrogen gas production during corrosion of copper by water, *Corros. Sci.* 53 (2011) 310–319.
- [5] J.P. Simpson, R. Schenk, Hydrogen evolution from corrosion of pure copper, *Corros. Sci.* 27 (1987) 1365–1370.
- [6] T.E. Eriksen, N. Ndalamba, I. Grenthe, On the corrosion of copper in pure water, *Corros. Sci.* 29 (1989) 1241–1250.
- [7] R. Becker, H.-P. Hermansson, Evolution of hydrogen by copper in ultrapure water without dissolved oxygen, in: SSM Report 2011:34, Swedish Radiation Safety Authority, 2011.
- [8] L.O. Werme, P.A. Korzhavii, Comments on Hultquist et al. “Water corrodes copper”, *Catal. Lett.* 135 (2010) 165–166.
- [9] L.-G. Johansson, Comment on “Corrosion of copper by water”, *Electrochem. Solid-State Lett.* 11 (2008) S1.
- [10] F. King, Critical review of the literature on the corrosion of copper by water, in: Technical Report SKB TR-10-69, Svensk kärnbränslehantering AB (Swedish Nuclear Fuel and Waste Management Co), 2010, 2017.
- [11] M. Boman, R. Berger, Y. Andersson, M. Hahlin, F. Björefors, T. Gustafsson, M. Ottosson, Corrosion of copper in water free from molecular oxygen, *Corros. Eng. Sci. Technol.* 49 (2014) 431–434.
- [12] M. Boman, M. Ottosson, R. Berger, Y. Andersson, M. Hahlin, F. Björefors, T. Gustafsson, Corrosion of copper in ultrapure water, in: SKB Report R-14-07, Swedish Nuclear Fuel and Waste Management Co, 2014.
- [13] G. Panzner, B. Egert, H.P. Schmidt, The stability of CuO and Cu₂O surfaces during argon sputtering studies by XPS and AES, *Surf. Sci.* 151 (1985) 400–408.
- [14] S. Yamamoto, K. Andersson, H. Bluhm, G. Ketteler, D.E. Starr, T. Schiros, H. Ogasawara, L.G.M. Pettersson, M. Salmeron, A. Nilsson, Hydroxyl-induced wetting of metals at near-ambient conditions, *J. Phys. Chem. Lett.* 111 (2007) 7848–7850.
- [15] F. Garbassi, XPS and AES study of antimony oxides, *Surf. Interface Anal.* 2 (1980) 165–169.
- [16] R.G. Haverkamp, A.T. Marshall, B.C.C. Cowie, Energy resolved XPS depth profile of (IrO₂, RuO₂, Sb₂O₅, SnO₂) electrocatalyst powder to reveal core-shell nanoparticle structure, *Surf. Interface Anal.* 43 (2011) 847–855.
- [17] J.H. Scofield, Hartree-Slater subshell photoionization cross-sections at 1254 and 1487 eV, *J. Electron Spectrosc. Rel. Phenom.* 8 (1976) 129–137.
- [18] W.A. Lanford, K. Davis, P. Lamarche, T. Laursen, R. Groleau, R.H. Doremus, Hydration of soda-lime glass, *J. Non-Cryst. Solids* 33 (1979) 249–266.
- [19] A.B. Atkarskaya, V.N. Bykov, Clarification of glass using arsenic and antimony oxides, *Glass Ceram.* 60 (2003) 389–391.
- [20] D.L. Parkhurst, C.A.J. Appelo, Description of input and examples for PHREEQC Version 3—a computer program for speciation, batch-reaction, one-dimensional transport and inverse geochemical calculations, in: U.S. Geological Survey Techniques and Methods, 2013, Book 6, Chap. A 43, Available only at <https://pubs.usgs.gov/tm/06/a43/>.
- [21] J.K. Fremercy, Residual gas: traditional understanding and new experimental results, *Vacuum* 53 (1999) 197–201.
- [22] K. Andersson, G. Ketteler, H. Bluhm, S. Yamamoto, H. Ogasawara, L.G.M. Pettersson, M. Salmeron, A. Nilsson, Autocatalytic water dissociation on Cu(110) at near ambient conditions, *J. Am. Chem. Soc.* 130 (2008) 2793–2797.