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Experimental in situ studies of copper exposed to humidified air

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Abstract

Three complementary experimental techniques for in situ surface analysis have been combined for the first time in order to explore the chemistry and physics of a copper surface exposed to humidified air. Infrared reflection absorption spectroscopy, quartz crystal microbalance and atomic force microscopy provide a congruent picture of the processes occurring at the surface. At a given relative humidity, cuprous oxide forms according to an approximately logarithmic rate law. In addition, an aqueous adlayer of constant mass physisorbs on the surface. Increased relative humidity stimulates the physisorption of water and enhances the nucleation rate of oxide grains, thereby increasing the formation rate of cuprous oxide. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The interaction between a metal and the surrounding atmospheric environment is a vital part in many naturally occurring or technically important processes. In

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order to understand the course of events of e.g. atmospheric corrosion there is an obvious need to characterise the metal/atmosphere interface. While this interface is of profound importance, it still represents a system with a large number of experimental and theoretical challenges. The interface involves chemical, physical and electrochemical processes occurring in three different phases: the metal, the aqueous adlayer and the atmosphere [1]. The interaction of water with metal surfaces in vacuum has been studied with, for instance Low Energy Electron Diffraction (LEED) [2] and Electron Energy Loss Spectroscopy (EELS) [3] where the structure of the adsorbed water was investigated. An extensive review of the interaction of water with solid surfaces was completed by Thiel and Madey [4]. However, studies under atmospheric conditions are necessary as a bridge to relate vacuum studies with field studies, such as copper exposed in rural atmosphere [5]. Phipps and Rice [6] have investigated the role of water in atmospheric corrosion, especially with pollutants in the atmosphere, and others have studied the adsorption of water on metal surfaces with quartz crystal microbalance (QCM) [7–9]. These among other studies have resulted in an improved understanding of e.g. the corrosion kinetics and the importance of humidity. However, there are remaining questions, such as the influence of the aqueous adlayer on the metal oxide growth.

This work aim at a deeper molecular understanding of the metal/atmosphere interface through a combination of three experimental techniques for in situ studies of any metal exposed to an atmospheric environment. This unique approach is based on information from a combination of a recently developed set-up for simultaneous infrared reflection absorption spectroscopy (IRAS) and QCM [10] and on a set up for tapping mode atomic force microscopy (TM-AFM) [11]. Thus, chemical (IRAS), kinetic (QCM) and morphological (TM-AFM) in situ information can be obtained under atmospheric conditions.

As a first example of this novel approach, the techniques have been used to obtain a deeper understanding of the most important reactions taking place on a copper surface exposed to clean humidified air. Studies of the initial atmospheric corrosion stages obtained at different relative humidities are presented. The kinetics of cuprous oxide growth and of the aqueous adlayer on the oxide surface has been followed and the results of the three different techniques have been compared, resulting in a detailed description of the copper/atmosphere interface.

2. Experimental

2.1. Combined IRAS/QCM set-up

A previously developed set-up was used that enables simultaneous in situ studies of the metal/atmosphere interface by means of IRAS and quartz crystal microbalance, IRAS/QCM [10]. The set-up consists of a chamber, in which the samples were exposed to a well-controlled atmosphere. Three external devices are connected to the chamber: a Fourier transform infrared spectrometer (BIORAD

FTS 60A) with external optical compartments, a QCM sensor probe with a frequency counter (Maxtek 740), and a system for generation and analysis of corrosive air. The corrosive air is generated from compressed air, which is cleaned and dried, before entering a temperature stabilised bath. The air stream is divided into different streams, one being humidified to 100% relative humidity (RH) and then mixed with a dry air stream to obtain the desired humidity.

The samples used in the IRAS/QCM experiments were purchased from Maxtek. They consist of AT-cut quartz crystals with a resonance frequency of approximately 5 MHz. The diameter of the quartz crystal is 25.4 mm into which a film of chromium (thickness 500 Å, for better adhesion between quartz and copper) and of copper (thickness 3500 Å, purity 99.99%) is evaporated. The diameter of the copper film is 10 mm on the crystal side facing the atmosphere. The samples were pickled for 30 s in 5% amidosulfonic acid, rinsed three times in ethanol (Kemetyl AB, 99.5%) and, finally, dried in nitrogen before being placed in the chamber. This cleaning procedure results in a surface with cuprous oxide and some hydrocarbon contamination as the main species [10].

Each copper-coated quartz crystal was exposed to dry as well as humidified cleaned air at atmospheric pressure. The flow rate of the air was 44 cm s^{-1} (80 l/h) at the entrance of the chamber, in a direction perpendicular to the sample surface. Three levels of relative humidity were used, 40, 60, and 80%, and the exposure times varied from 3 to 24 h. Two different exposure schemes were used. In the first scheme samples were continuously exposed to humid air and in the second scheme, alternately exposed to humid and dry air. All experiments were concluded by at least one hour in dry air. IRAS spectra were obtained by averaging 1024 scans at a resolution of 8 and 4000 cm^{-1}, corresponding to a measuring time of approximately 9 min. All spectra were recorded in absorbance units ($-\log R/R_0$), where R is the reflectance of the exposed sample and R_0 is the background reflectance obtained after one hour of exposure in dry atmosphere. The resonance frequency of the copper coated quartz crystal was recorded with the frequency counter at least every 10 s.

2.2. AFM set-up

Fig. 1 depicts the AFM set-up. It consists of a NanoScopeIII® MultiMode AFM from Digital Instruments, an acrylic glass plate with gas inlet, and a system for generating corrosive air [11]. The optical head of the AFM was used as exposure chamber and was covered by the acrylic glass plate. The AFM measurements were performed in tapping mode (TM-AFM) at constant amplitude combined with phase detection imaging (PDI) [12]. Commercial silicon cantilevers (Digital Instrument) were used.

The sample used in the AFM experiments was a $10 \times 10 \times 2$ mm^3 copper sheet (Johnson Matthey, maximum 25 ppm trace metal impurities). The copper sheet was polished down to 0.25 μm, cleaned in ethanol, dried with a fuss-free tissue to remove polishing particles and immediately transferred to the exposure chamber.

By mixing either dry nitrogen (Messer Griesheim, Austria, $N_2 > 99.999\%$) or synthetic air (Messer Griesheim, Austria, O_2 20.5%, rest N_2) with the same gas humidified to 100% the desired level of relative humidity was obtained. The stream entered the exposure chamber through the gas inlet of the acrylic plate with a flow of 10 l/h and the exposures lasted for 28 h.

3. Results

3.1. Simultaneous IRAS/QCM in situ measurements

Upon exposure of copper to humidified air, surface related changes could be followed simultaneously with QCM and IRAS under in situ conditions. QCM registered a mass change and absorbance bands were visible in the IRAS spectra. These bands were located around 3600, 1600 and 645 cm^{-1}, where the first bands are attributed to water and the latter to cuprous oxide. These assignments are in agreement with other IRAS studies [13,14]. In Fig. 2, the mass change (QCM) is plotted together with the corresponding intensity of the cuprous oxide absorbance band (IRAS), for an exposure at alternately humidified (80%) and dry air. As seen in Fig. 2, the mass change consisted of at least two different parts. One reversibly mass change, with species leaving the surface when the humid air was

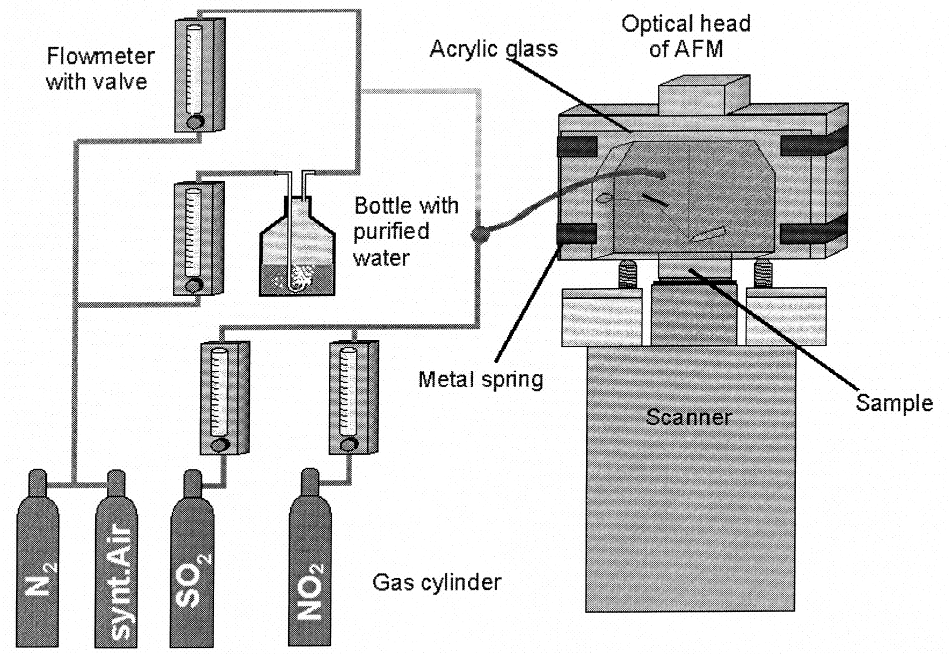

Fig. 1. AFM set-up, showing the gas mixing system and the exposure chamber situated inside the AFM optical head.

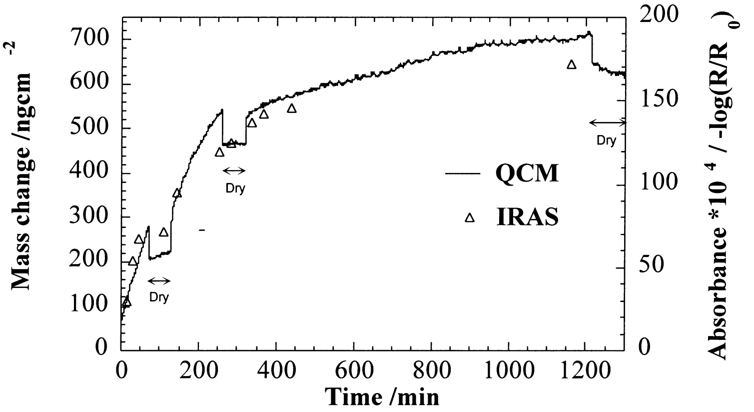

Fig. 2. Copper alternately exposed to humidified air at 80% relative humidity and dry air. The solid line represents the mass change measured by QCM (left axis). Under dry conditions the physisorbed water leaves the surface, which is shown as a mass decrease. The triangles represents the intensity of the IRAS absorbance band at 645 cm^{-1} (right axis) corresponding to cuprous oxide formed and assumed to be Cu_2O.

changed to dry air, and one irreversibly mass change, with species remaining on the surface also under dry conditions. The water absorbance bands in the IRAS spectra also disappeared under dry conditions whereas the intensity of the cuprous oxide band remained essentially constant. Hence, the reversibly mass change was associated with physisorbed water, the aqueous adlayer, and consequently, the remaining mass change was mainly due to the formation of cuprous oxide. In the figure, it can also be seen that the amount of physisorbed water remained approximately constant with exposure time by comparing the reversible mass

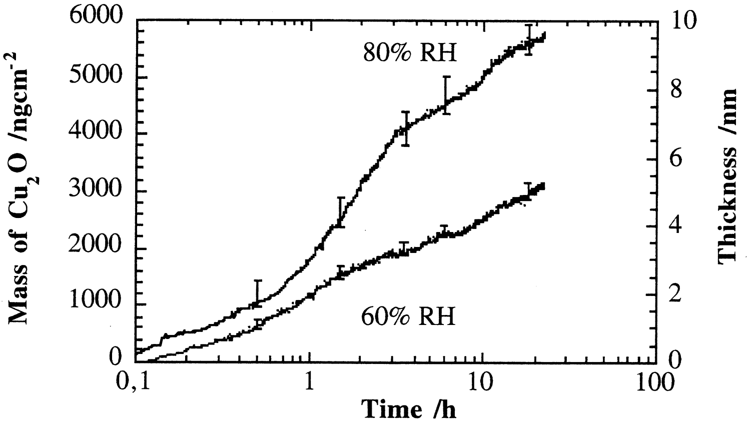

Fig. 3. Growth of Cu_2O estimated by QCM. The error bars show the scatter of at least three different exposures.

change during the three dry periods. In Fig. 3, the kinetics of the cuprous oxide growth is plotted for exposures at 60 and 80% RH. The growth, based on the QCM measurements, is plotted versus the logarithm of time. For simplicity, the cuprous oxide formed is hereafter referred to as Cu_2O, although its properties may deviate from crystalline Cu_2O. The total Cu_2O mass was estimated from the QCM measurements, assuming that the mass change only accounts for the oxygen adsorbed. The reversibly adsorbed mass of the physisorbed water was subtracted and the remaining mass change was multiplied by the molecular weight of Cu_2O divided by the atomic weight of oxygen. The thickness of the Cu_2O layer was then obtained by dividing the mass change by the density of Cu_2O, 6.0 g cm^{-3} [15]. In addition, the intensity of the Cu_2O absorbance band was used to estimate the thickness, which is linearly proportional to the thickness of the Cu_2O layer for a thin homogeneous film [10]. As seen in Fig. 3, the formation rate of Cu_2O at 80% is between 1.5 and 2 times higher than at 60% RH. At 40% RH, no Cu_2O is detected with IRAS, but a minor irreversible mass change is measured with QCM. Table 1 summarises the results obtained after 24 h of exposure to 40, 60, and 80% RH. In the table, the amount of the Cu_2O formed and of the aqueous adlayer is presented as an average thickness in nanometers (nm). From Table 1, it is seen that the formation rate of Cu_2O was enhanced, and more water was physisorbed on the surface with an increasing relative humidity. To summarise, copper exposed to humidified air forms a cuprous oxide, Cu_2O, with an aqueous adlayer adsorbed on the surface. The growth of Cu_2O follows approximately a logarithmic rate law and is enhanced by an increased relative humidity. Higher relative humidity results in increased amount of physisorbed water, but the amount is approximately independent of exposure time. Since IRAS/QCM provide average information from the area of interest, two obvious questions arise from these results: The laterally distribution of the Cu_2O formed and the effect of the adsorbed aqueous adlayer on the corrosion rate?

3.2. TM-AFM in situ measurements

TM-AFM was used to investigate the lateral distribution of the Cu_2O formed on copper exposed to humidified air. At this moment, it is important to emphasise that the AFM studies were made on polished copper sheets, whereas the IRAS/QCM studies were made on pickled evaporated copper. The reason for this was that it was very difficult to observe change occurring on the pickled surface. Fig. 4 depicts a freshly polished copper sample. Scratches originating from the polishing

Table 1
Average Cu_2O and aqueous adlayer thickness obtained from both IRAS and QCM measurements after 24 h of exposure at 40, 60 and 80% RH

Humidity (% relative humidity)	40	60	80
Thickness of Cu_2O layer (nm)	0.2 ± 0.1	5.5 ± 0.3	9.6 ± 0.4
Thickness of aqueous adlayer (nm)	0.3 ± 0.1	0.8 ± 0.2	1.1 ± 0.2

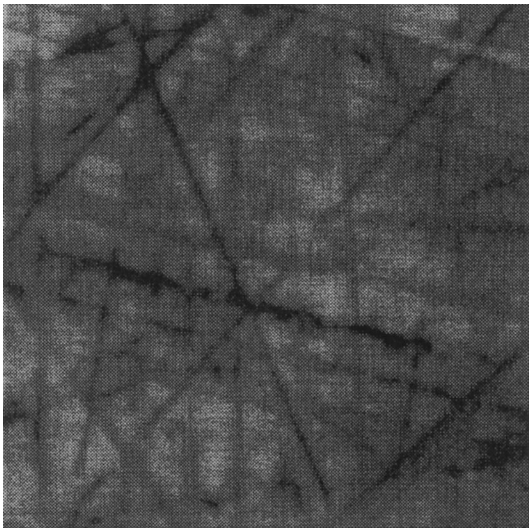

Fig. 4. Freshly polished copper surface imaged by TM-AFM. Scratches from the polishing procedure are visible. The scan size is 1 × 1 μm^2 and the black to white height range is 25 nm.

treatment can clearly be seen. The roughness, expressed as the root mean square, of the freshly polished copper samples was 4 ± 2 nm and remained essentially constant upon exposure. As 80% RH was introduced, the formation of round features, without any preferred site of formation, could be observed. After 80 min (see Fig. 5(a)) the surface was already completely covered by these features being

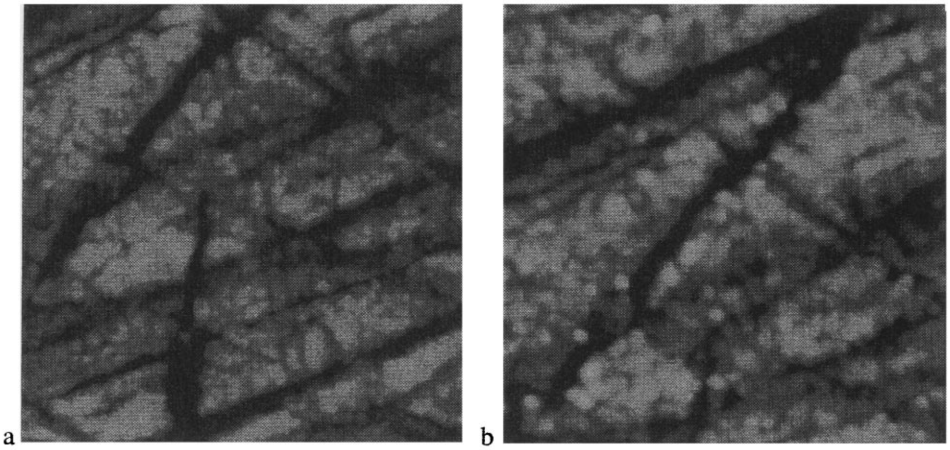

Fig. 5. Polished copper surface after (a) 80 min, (b) 1400 min exposure to synthetic air with 80% RH. Scratches are still visible and the round features are completely covering the surface. The scan size is 1 × 1 μm^2 and the black to white height range is 25 nm.

as an average 20 nm in diameter. In the PDI mode, the features were clearly in the valleys of the scratches. The features typically continued to grow to a diameter of 50 nm after 250 min, after which the diameter remained more or less constant up to 1400 min (Fig. 5(b)). No significant change in surface morphology could be seen when the experiments were concluded in dry air. Combining information from IRAS/QCM, the features were attributed to the formation of Cu_2O grains. At 60% RH, the process was much slower. After 300 min (see Fig. 6(a)) Cu_2O grains with a diameter of typically 15 nm were visible. Initially there were few grains but they increased in number with exposure time. After 1300 min there had been a significant change of the surface as shown in Fig. 6(b). The grains still had similar shape and height but their number had increased substantially, although they did not completely cover the surface. Complementary exposures to humidified nitrogen were also carried out at 80% RH in order to investigate whether adsorbed water had affected the experiments. However, no morphological change on the surface was observed within 24 h, supporting the assignment of the round features seen above to Cu_2O. To summarise the IRAS/QCM and TM-AFM experiments, cuprous oxide (referred to as Cu_2O) was formed upon exposure of copper to humidified air. The formation rate of Cu_2O followed an approximately logarithmic rate law and increased with relative humidity. The Cu_2O formed as grains with a diameter of around a few tens of nannometer and with a nucleation rate enhanced by relative humidity.

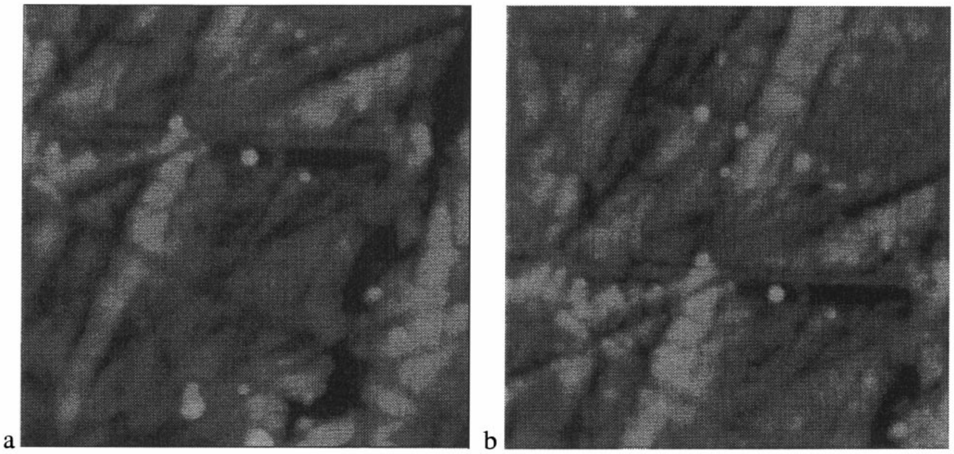

Fig. 6. Polished copper surface after (a) 300 and (b) 1300 min exposure to synthetic air with 60% RH. Scratches are still visible and round features are appearing, but not completely covering the surface. The scan size is $1 \times 1\ \mu m^2$ and the black to white height range is 25 nm.

4. Discussion

Under present conditions, IRAS/QCM can provide in situ chemical and kinetic information during the formation of Cu_2O on a copper surface in the presence of an aqueous adlayer. The oxidation of the copper surface followed approximately a logarithmic rate law. This observation is in good agreement with other laboratory studies of copper exposed to humidified air [13,16,17] and with field studies of copper exposed to a rural atmosphere [5]. The observed enhanced oxidation rate at higher relative humidity might be connected to the increased amount of physisorbed water as discussed below. The present results of the amount of physisorbed water are in the lower region of what is presented in reports by others [6–9,16]. An explanation for the discrepancy in results can be different flow conditions during the experiments and/or different surface conditions. According to the AFM studies, Cu_2O forms as small grains on the surface, with an enhanced nucleation rate at higher relative humidity. Thus, the enhanced nucleation rate is one reason for the increased oxidation rate at higher relative humidity. Remaining to explain is the effect of relative humidity on the nucleation rate and a possible effect on the growth rate of each grain. It is obvious that the physisorbed water layer occupies a prominent role in the oxidation course of copper. At least three important effects of increased relative humidity can be identified.

1. The increase in number of physisorbed water clusters with relative humidity.
2. A gradual change with relative humidity towards more bulk-like properties of the physisorbed water layer.
3. The effect of relative humidity on the mechanism of Cu_2O growth.

Firstly, the lateral distribution of the physisorbed water is probably of profound importance. According to Thiel and Madey [4] and references therein, water generally adsorbs in clusters on clean metal surfaces. This minimises the surface energy, because of the approximately equal binding energies between the water molecule and the surface and the hydrogen bonding between water molecules. However, on metal oxides the tendency to cluster is less pronounced at low coverage. Nevertheless, a heterogeneous aqueous adlayer is more probable than a homogeneous. Heterogeneously adsorbed water clusters may act as nucleation sites for Cu_2O grains, which implies that the number of nucleation sites increases with relative humidity.

Secondly, the properties of the physisorbed water layer change with thickness. The more bulk-like water facilitates mobility of surface species in the aqueous adlayer and affects the solubility of gases, in this case O_2. According to Franks [18], a water molecule is affected by other water molecules closer than three molecule diameters. This suggests that between five and ten monolayers of water are necessary to obtain bulk properties. In all, increased relative humidity results in more bulk-like water properties from which follows an increased oxidation rate.

Thirdly, the physisorbed water is known to interact with Cu_2O [19] whereby so called hydrogen defects may be introduced [20]. These defects may influence the transport properties of the oxide. Evidence of a highly defect rich Cu_2O was found by Lenglet et al. [21] who revealed that the Cu_2O layer may be non-stoichiometric. Oxygen in the aqueous adlayer and defects in the oxide promote the dissociation of water. Furthermore, oxygen from dissociated water has been shown to contribute more than 50% of all oxygen in Cu_2O [19]. To summarise the third effect, the transport properties of the oxide can vary depending on the relative humidity. A more defect-rich oxide is obtained at higher relative humidity, which enhances the copper transport in the oxide.

To conclude, water may adsorb heterogeneously in clusters, the number of which increases with relative humidity and, hence, also the number of nucleation sites of Cu_2O grains. The oxidation rate may be further stimulated by relative humidity through formation of a more defect-rich oxide containing oxygen both from dissociated water and dissolved oxygen gas.

5. Conclusions

Copper interaction with humidified air has been studied in situ by combining IRAS/QCM and TM-AFM. The formation of an aqueous adlayer and of a cuprous oxide layer was followed and quantified for exposure times up to 24 h. The average thickness of the aqueous adlayer increased with relative humidity, but was approximately independent of exposure time. The growth of cuprous oxide followed approximately a logarithmic rate law and occurred through nucleation of cuprous oxide grains on the surface. The overall oxidation rate as well as nucleation rate and grain size increased with relative humidity. Thus, the increased cuprous oxide growth can be attributed to an increased nucleation rate at higher relative humidity. However, an additional effect of increased relative humidity might be a more defect-rich oxide resulting in enhanced transport properties of each cuprous oxide grain.

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