



UdeA
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**ATMOSPHERIC CORROSION OF COPPER INDUCED
BY LOW CONCENTRATION OF CARBOXYLIC ACIDS**

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Doctoral Thesis

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Abstract

The interaction of carboxylic acids with copper is a phenomenon found in both outdoors and, more commonly, indoors. The influence on copper of some carboxylic acids (formic, acetic, propionic, and butyric) have so far been studied at concentrations levels at least three or four orders of magnitude higher than actual indoor conditions (< 20 ppb, volume parts per billion), and with only limited emphasis on any mechanistic approach. In this doctoral study a unique analytical setup has been successfully applied for in situ characterization and quantification of corrosion products formed during initial atmospheric corrosion of copper in the presence of acetic, formic or propionic acid. The setup is based on monitoring mass changes by the quartz crystal microbalance (QCM) and simultaneously identifying the chemical species by infrared reflection-absorption spectroscopy (IRAS). Post-analysis of corrosion products was performed by coulometric reduction (mass of copper (I) oxide formed), grazing incidence x-ray diffraction (phase identification) and atomic force microscopy (surface topography).

The absolute amounts of mass of individual constituents in the corrosion products, mainly copper (I) oxide or cuprite, copper (II) carboxylate and water or hydroxyl groups, have been deduced in situ during exposure in 120 ppb of carboxylic acid concentration, 95% relative humidity and 20°C. An overall result is the consistency of analytical information obtained. For copper (I) oxide the quantified data estimated from IRAS, QCM or coulometric reduction agrees with a relative accuracy of 12 % or better.

Likewise, an electrochemical reduction mechanism is proposed to describe how copper oxides formed in presence of acetic acid are reduced in potassium chloride. These types of reduction curves for copper have been studied before without intention to find a model that explains the experimental results. The simulation is based on copper oxides obtained in climatic chamber experiments with 0, 500 and 800 ppb of acetic acid at 95% RH. The experimental results were compared with electrochemically produced oxide films imposing anodic potentials to copper specimens in several concentrations of pure acetic acid, of 1, 0.1, 0.01 and 0.001 M. The reduction model includes the electrochemical reduction of copper (II) oxide (CuO), amorphous cuprite $(\text{Cu}_2\text{O})_{\text{am}}$, intermediate cuprite $(\text{Cu}_2\text{O})_{\text{in}}$, crystalline cuprite $(\text{Cu}_2\text{O})_{\text{cr}}$ and hydrogen. These oxides have been previously detected in similar conditions and are considered to follow the Langmuir isotherm. The result shows a relative accuracy of 0.98 or better in R^2 coefficient.

In conclusion, the interaction of copper with the carboxylic acids seems to follow two spatially separated main pathways. A proton-induced dissolution of cuprous ions followed by the formation of copper (I) oxide, and a carboxylate-induced dissolution followed by the formation of copper (II) carboxylate. The first pathway is initially very fast but levels off with a more uniform growth over the surface. This pathway dominates in acetic acid. The second pathway exhibits a more constant growth rate and localized growth, and dominates in formic acid. Propionic acid exhibits low rates for both pathways. The difference between the carboxylic acids with respect to both

total corrosion rate and carboxylate-induced dissolution can be attributed to differences in acid dissociation constant and deposition velocity.

Keywords: Atmospheric corrosion, carboxylic acids, copper, in situ, IRAS, QCM, coulometric reduction, potentiodynamic reduction.

Resumen

La interacción entre los ácidos carboxílicos y el cobre es un fenómeno que ha sido encontrado en ambientes exteriores y más comúnmente en interiores. La influencia de algunos ácidos carboxílicos (fórmico, acético, propiónico, y butírico) en el cobre ha sido estudiada en niveles de concentración de al menos tres o cuatro ordenes de magnitud más grandes que las verdaderas condiciones en interiores (< 20 ppb, partes por billón en volumen), ay con un énfasis limitado solamente en una aproximación mecanística. En este estudio doctoral, una configuración analítica ha sido exitosamente aplicada para la caracterización y cuantificación in situ de los productos de corrosión formados durante la corrosión atmosférica inicial del cobre en presencia de ácido acético, fórmico o propiónico. La configuración es basada en el monitoreo de cambios de masa mediante una Microbalanza de Cristal de Cuarzo (QCM) y mediante la identificación simultánea de especies químicas mediante Espectroscopia de Absorción-Reflexión Infrarroja (IRAS). Análisis posteriores de los productos de corrosión fueron desempeñados mediante el uso de Reducción Coulométrica (masa del óxido de cobre (I) formado), Difracción de Rayos-X con Angulo Rasante (identificación de fases) y Microscopía de Fuerza Atómica (Topografía superficial).

Las cantidades absolutas de masa de los constituyentes individuales en los productos de corrosión, principalmente óxido de cobre (I) o cuprita, carboxylato de cobre (II) y agua o grupos hidroxilo, han sido deducidos in situ durante la exposición en una concentración de 120 ppb de ácido

carboxílico a una humedad relativa de 95% y una temperatura de 20°C. Un resultado global es la consistencia de la información analítica obtenida. Para óxido de cobre (I) la estimación de los datos cuantificados desde IRAS, QCM o reducción coulométrica están de acuerdo con una precisión relativa de 12 % o más.

Así mismo, un mecanismo de reducción electroquímico es propuesto para describir cómo óxidos de cobre formados en presencia de ácido acético son reducidos en cloruro de potasio. Estos tipos de curvas de reducción para el cobre han sido estudiadas anteriormente sin ninguna intención de encontrar un modelo que explique los resultados experimentales. La simulación es basada en óxidos de cobre obtenidos en experimentos en cámara climática con 0, 500 y 800 ppb de ácido acético a 95% HR. Los resultados experimentales fueron comparados con películas de óxidos producidas electroquímicamente imponiendo potenciales anódicos a muestras de cobre en varias concentraciones de ácido acético puro, de 1, 0.1, 0.01 y 0.001 M. El modelo de reducción incluye la reducción electroquímica del óxido de cobre (II) (CuO), cuprita amorfa $(\text{Cu}_2\text{O})_{\text{am}}$, cuprita intermedia $(\text{Cu}_2\text{O})_{\text{in}}$, cuprita cristalina $(\text{Cu}_2\text{O})_{\text{cr}}$ e hidrógeno. Estos óxidos han sido previamente detectados en condiciones similares y se consideran que siguen la isoterma Langmuir. Los resultados muestran una precisión relativa de 0.98 o mejor en el coeficiente R^2 .

En conclusión, la interacción del cobre con los ácidos carboxílicos parece

seguir dos rutas espacialmente separadas. Una disolución de iones cuprosos inducida por protones seguida por la formación de óxido de cobre (I), y una disolución inducida por el carboxylato seguida por la formación de un carboxylato de cobre (II). La primera ruta es inicialmente muy rápida pero luego se estabiliza con un crecimiento más uniforme sobre la superficie. Esta ruta domina en el caso de ácido acético. La segunda ruta exhibe una velocidad de crecimiento más constante y de forma localizada, la cuál domina en el caso del ácido fórmico. En el caso del ácido propiónico, éste exhibe bajas velocidades para ambas rutas. La diferencia entre los ácidos carboxílicos con respecto a la velocidad total de corrosión y a la disolución inducida por el carboxylato puede ser atribuida a las diferencias en las constantes de disociación y a las velocidades de deposición.

Palabras Claves: Corrosión atmosférica, ácidos carboxílicos, cobre, in situ, IRAS, QCM, reducción coulométrica, reducción potenciodinámica.

Preface

The thesis is based on experimental work carried out at the Division of Corrosion Science, KTH, in Stockholm and Corrosion and Protection Group laboratory at University of Antioquia, in Medellín.

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I have performed most of the experimental work related to infrared reflection absorption spectroscopy, quartz crystal microbalance, electrochemical measurements and data modelling. I have taken active part in the analysis of results, and in the discussion. I also contributed to the outline and writing of the papers.

Papers included in the thesis:

This thesis is based on the following papers, which will be referred to in the text by their roman numerals.

I. Quantitative *In Situ* Analysis of Initial Atmospheric Corrosion of Copper Induced by Acetic Acid.

H. Gil and C. Leygraf.

Journal of Electrochemical Society, 154, C272 (2007).

II. Initial Atmospheric Corrosion of Copper Induced by Carboxylic Acids- A Comparative Study.

H. Gil and C. Leygraf.

Journal of Electrochemical Society, 154, C611 (2007).

III. “W.R. Whitney Award Lecture: Molecular *In Situ* Studies of Atmospheric Corrosion”.

C. Leygraf, J. Hedberg, P. Qiu, H. Gil, J. Henriquez and C.M. Johnson.

Corrosion (NACE), 63, 715 (2007).

IV. Cathodic Reduction Model of Copper Oxides Films Formed in Presence of Acetic Acid.

H. Gil, A. Echavarría and F. Echeverría.

17th International Corrosion Congress (October 6-10, 2008), Las Vegas.

**V. Electrochemical Reduction Modeling of Copper Oxides Obtained
During In Situ and Ex Situ Conditions in Presence of Acetic Acid.**

H. Gil, A. Echavarría and F. Echeverría.

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Papers not included in the thesis:

VI. Mechanism of Interaction Between Copper and Propionic Acid Vapors.

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Journal of the Brazilian Chemical Society.

Submitted.

VII. Influence of Environmental Factors in the Atmospheric Corrosion of Copper in Presence of Propionic acid.

A. Echavarría, F. Echeverría, H. Gil and C. Arroyave.

Journal of the Chilean Chemical Society.

Submitted.

VIII. Indoor Atmospheric Corrosion of Electronic Materials in Tropical Environments.

J. A. Calderón, H. Gil. C.P. Buitrago, and R. Mira.

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1. Introduction

Atmospheric corrosion induced by organic constituents is a phenomenon found both outdoors, and more commonly indoors. This is important issue due to accumulation of atmospheric pollutants that can accelerate the degradation process of metallic surfaces. This effect has been observed on copper, material of wide use in electronic devices, where is necessary to avoid any formation of corrosion products in order to prolong its service life. Moreover it is important to preserve cultural heritage that could be affected by volatile organic compounds.

1.1 Carboxylic acids

Carboxylic acids are ubiquitous and important components of the troposphere; they are currently measured in different environments^[1]. They have been found in fog water^[2-4], in cloud water^[5-7], in rain water^[8-16], in snow and ice water^[17-20], in the gas phase^[12,21-31] and in aerosol particles^[12,13,32-35]. Dominant organic pollutants include formic acid (HCOOH) and acetic acid

(CH₃COOH), both playing a major role in the precipitation acidity. The acidification effect is observed in both urban and more rural areas of the world^[9,23,31,36-39]. Smaller quantities of propionic acid (CH₃CH₂COOH), butyric acid (CH₃(CH₂)₂COOH), and oxalic acid (H₂C₂O₄) are also found in the atmosphere^[9,10,12,29,40,41].

In aqueous atmospheric systems, aldehydes are readily transformed to acids by transition metals and other catalysts^[42]. Field and experimental measurements of carboxylic acids produced by O₃ reactions with biogenic terpenes point to their key role in secondary aerosol formation^[43]. Several possible sources have been suggested for organic acids in the atmosphere. The largest of these sources include direct anthropogenic emissions^[44-46], biogenic emissions^[14,47], biomass burning^[48], and homogeneous oxidation of hydrocarbons^[49,50]. Photochemical oxidation of precursor organic species in the gas phase or aqueous phase are also typical sources of organic acids^[43]. The contribution of each source remain very uncertain and location dependent.

Organic acids are also formed as a result of industrial activity, e.g., vinegar from the food processing industry and from decomposition of raw materials in the paper industry. They are also released by woods^[51] and certain paints, plastics, rubbers, and resins^[52-57]. In the atmosphere, these acids can be form by reactions as: a) O₃ reaction with alkenes^[29,58], b) aldehyde reaction (HCHO) with the radical ·HO₂^[21,59,60], c) reaction through phenols with the free radical

$\cdot(\text{OH})^{[29]}$ and d) aldehyde oxidation in cloud water^[29].

1.2 Atmospheric corrosion of copper influenced by carboxylic acids

The effects of organic acids on copper surfaces have been observed in a broad range of situations. For instance, early failures of heat exchanger copper tubes have been recognized, not only during service time but also during storage^[61,62]. From these results was concluded that the corrosion attack occurs more frequently on samples treated and rinsed in deteriorated organochlorine solvents. Moreover, it is known that the decomposition products of these solvents are organic acids^[63]. This kind of corrosion attack has been referred to as “ant-nest” corrosion because of its characteristic morphological appearance^[64]. The pinholes penetrating the copper walls are generally difficult to detect by the naked eye. However, when observed with an optical microscope, cross-sections of corroded parts are characterized by complicated microscopic caverns connected by a network of tunnels containing porous copper oxide (Cu_2O) in directional pits^[65]. It has been reported that the same effect can be reproduced in wet atmosphere containing formic or acetic acid^[65]. Likewise, it has been found that the presence of organic acids (formic, acetic and propionic acid) formed on heat exchanger copper tubes may originate from the hydrolysis of self-evaporating lubricant oils^[66].

Atmospheric corrosion of copper originated by organic acid can occur in

both outdoor and indoor atmospheres. In outdoor atmosphere it is characterised by a high aggressive ion concentration and the presence of solid particles, associated with an alternating sequence of dry and wet periods, seasonal variations, variable winds hitting the metallic surface, the important influence of extreme temperature, radiation and RH conditions, drop deposition from dew, or the depositions of foreign bodies, such as bird droppings. This is the characteristic environment of sculptural works or exposed outdoor structures^[67]. The effect of organic acids is enhanced during indoor conditions, because some type of woods or materials can emit carboxylic acids and organic molecules can be also be deposited on the metallic surfaces from particles and aerosols in the atmosphere. Therefore, indoor metallic corrosion products can be expected to contain important amounts of organic compounds. Consequently, organic acids can cause corrosion on several metals, especially zinc, nickel, lead, iron, cadmium and copper. Typical concentrations of acetic and formic acid of about 20 ppb (volume part per billion) have been reported^[42]. Microbiological degradation of manure is an important source of butyric acid. For this reason, in livestock sheds the butyric acid concentration can reach very high levels, up to 0.2 ppm^[68].

Vernon^[69] reported the deterioration of copper structures exposed in urban atmospheres to the presence of organic acids for long periods and concluded that the attack in the presence of acetic acid was more vigorous than in the presence of formic acid. Fukuda *et al*^[70] confirms the existence of copper

carboxylates in specimens exposed to indoor environments in cities of south-east Asia. On the other hand, copper acetates have been detected as part of the corrosion products on surfaces exposed to indoor atmospheres. Metal carboxylate formation has been followed on copper, zinc and nickel exposed in indoor environments, such as in museums and churches of Europe^[71].

1.3 Experimental and theoretical methods for studies of atmospheric corrosion of copper

Attempts to understand the corrosion effects of organic acids on metal surfaces have been performed using highly accelerated corrosion tests, characterized by enhanced levels of relative humidity and organic acids (acetic^[72,73], formic^[74,75], propionic^[76] and butyric acids vapours^[68]) in the ppm (volume part per million) range. According to these results for copper specimens exposed to organic vapours at 100% RH and a contaminant level in the range of 10 to 300 ppm, the relative aggressiveness of these acids is (from high to low): acetic > formic > butyric > propionic.

The aggressiveness of organic acids has been followed by several experimental methods to follow copper corrosion studies in the presence of carboxylic acids. Gravimetric analysis has been performed to obtain the corrosion rate, and characterization of the solid phases by means of various *ex situ* techniques. According to infrared and x-ray diffraction measurements, copper (I) oxide (Cu_2O), copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$) and copper hydroxy acetate ($\text{Cu}(\text{OH})_4(\text{CH}_3\text{COO})_2$) have been detected as main corrosion products in

the patina on copper formed in acetic acid exposures in the range from tens to hundreds of ppm^[72]. Similarly, on copper exposed to a formic acid-containing atmosphere, cuprite, copper (II) hydroxide monohydrate ($\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$), as an intermediate compound, and copper formate tetrahydrate ($\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$) were detected. The copper formate quantity was observed to increase with acid concentration, whereas the opposite occurred with cuprite and the hydroxide^[74]. Copper exposed in propionic acid vapour ranging from 10 to 300 ppm produced cuprite and copper hydroxide. Copper propionate ($\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2$) was detected after 21 days at concentrations higher than 50 ppm of exposure^[76]. Under similar exposure conditions cuprite and copper butyrate ($\text{Cu}\{\text{CH}_3(\text{CH}_2)_2\text{COO}\}_2$) was identified as the main corrosion products on copper exposed to between 10 and 100 ppm of butyric acid^[68]. The literature review shows that the atmospheric corrosion studies on copper influenced by carboxylic acids so far have been carried at concentration levels far above what is observed in ambient environments (< 20 ppb), with only a small probability to capture the processes that operate under more realistic conditions.

More recently, highly surface sensitive techniques with *in situ* capability, mainly infrared reflection-absorption spectroscopy (IRAS) and sum frequency generation (SFG) have been applied for studies of the atmospheric corrosion of zinc induced by acetic and formic acid and also by acet- and formaldehyde. The data have resulted in new insight into the physico-chemical processes involved in the initial stages of atmospheric corrosion

induced by acids and aldehydes at only slightly increased levels (80-120 ppbv, parts per billion in volume) of concentration ^[77-80].

The so-called GILDES model^[81] includes computer-based calculations to simulate atmospheric corrosion. The model recognize that there are six distinct regimes that may need to be treated theoretically, as shown in Fig. 1^[81]: G (gas), I (interface), L (liquid), D (deposition layer), E (electrode regime) and S (solid), so models treating such systems may be designated GILDES models. Within the regimes chemical reactions can occur to change the constituents. Transport of chemical species of interest between regimes can occur, as in condensation and dissolution, and must be assessed. The products of the chemical reactions are susceptible to transport and deposition or volatilization just as are the reactants. It has been successfully applied to zinc^[82] and to copper and nickel exposed to gaseous SO₂ alone or in combination with either NO₂ or O₃^[83-85]. The GILDES model requires quantitative and qualitative data on patina formation as an experimental counterpart. Hence, for future applications of GILDES on copper in the presence of carboxylic acids it is necessary to generate quantified data of the different species involved in the corrosion products obtained under *in situ* conditions.

In the Fig 1, the circles indicate initial reactants and the squares indicate reaction products. Solid lines connecting reactants and/or products denote processes that can be readily described by formulations based on first

principles. Dashed lines indicate processes whose details are less straightforward and which are described by parameterized coefficients based on experimental data. The dotted line indicates that liquid phase chemistry can be described by first principles at low ionic strength but must be parameterized at high ionic strength. The dashed-dotted line indicates that chemical transformations in the solid state are not included in the current GILDES formulation, as they are thought not relevant to the problems of interest.

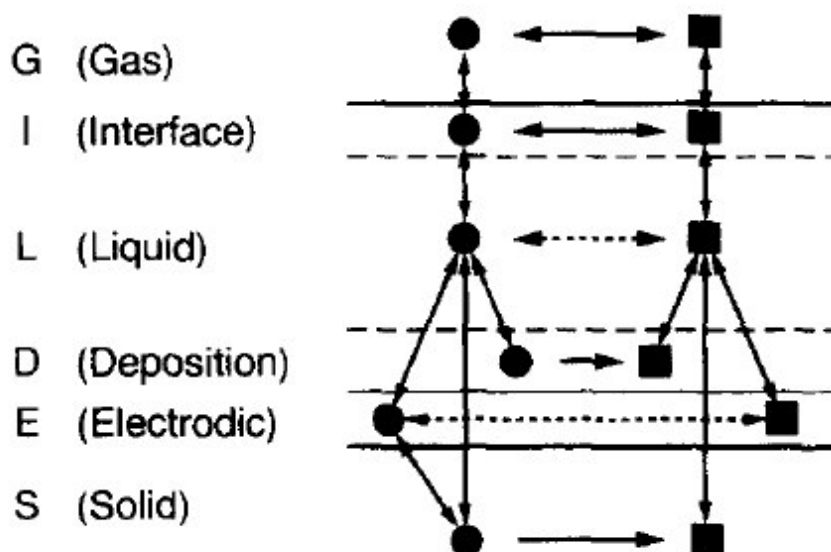


Figure 1. Schematic representation of the six regimes and the transitions and transformations that make up the GILDES model of aqueous environmental chemistry.

1.4 Evolution and characterization of the copper patina

During natural weathering, copper goes through a number of stages. Salmon-

pink is the colour for clean copper with essentially no surface oxide as for example after acid cleaning. After exposure to the atmosphere, copper rapidly turns to the more familiar “copper” colour due to a thin surface oxide. This causes the copper surface to turn dull brown after a few days, weeks or months, and later almost black. These changes in colour are all due to the oxide, cuprite which has the chemical formula Cu_2O wherein the copper is in the +1 oxidation state^[86]. Subsequently, a green layer forms on top of the oxide layer by further reaction with trace atmospheric impurities so that the copper is in the +2 oxidation state. This green upper layer provides the typical patinated appearance^[86]. Once formed, the patina layer is relatively stable and acts as a protective barrier of the copper object under many exposure conditions^[87].

On copper roofs, the green patina is usually thought to be aesthetically pleasing and is a major reason why copper is used extensively throughout the world as a prestige roofing material. The time scale for patina formation varies with local environmental conditions^[88]. Copper patinas are spatially heterogeneous containing voids and discontinuities. The porosity can be readily demonstrated by the ability of patinas to absorb significant amounts of water^[86]. The thickness of the outer layer varied from 10 to 84 μm , but on average did not exceed 45–50 μm . The average thickness of the inner cuprite layer was 17 μm ^[88].

From the thermodynamic point of view, it is possible to observe the reactions

of the atmospheric corrosion in a metallic surface and the different product formation from the work developed by Pourbaix^[89]. Metallic copper is a very stable species in a wide dominion of the stability area of water. According to the diagram (see Fig. 2) the native copper oxidizes to Cu^{2+} under acid pH, then goes through to Cu_2O (cuprite) to higher pH. Cuprite oxidizes to CuO (tenorite) to higher potentials. For very high pH, CuO dissolves to form CuO_2^{2-} , and the Cu_2O also oxidizes to this species.

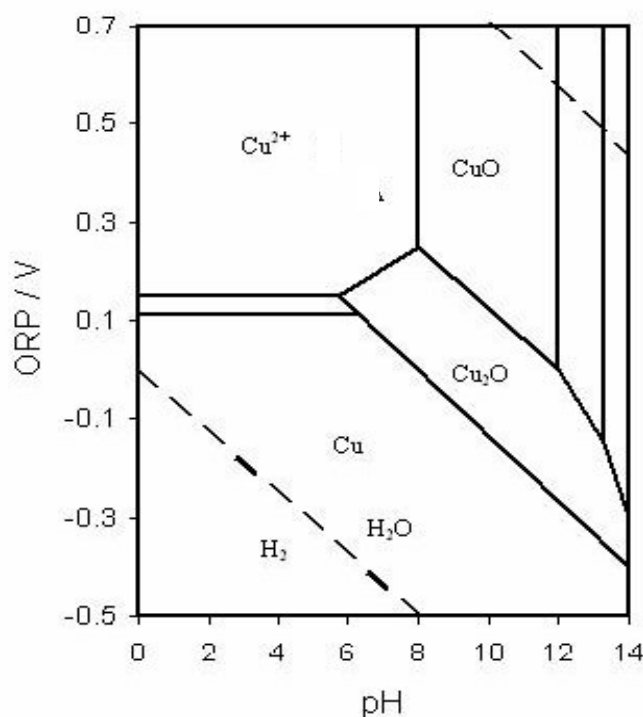
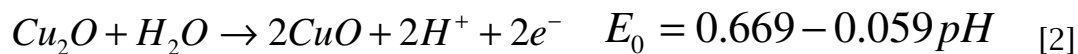
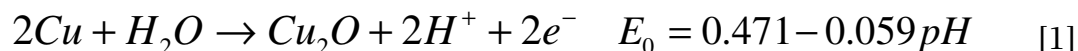


Figure 2. Potential-pH diagram $\text{Cu-H}_2\text{O}$; 25°C, 10^{-6}M Cu, established considering as solid species Cu, Cu_2O , and CuO .

Taking into account the patina thermodynamics, from the Pourbaix diagram is possible to conclude that the two main reactions happening during the

patination processes of copper are:



Numerous field exposures have been carried out over the years, to determine copper corrosion rate and characterize the corrosion products. Thus, the most popular techniques used to characterize the copper compounds are the electrochemical methods. However, there are two different views regarding correct interpretation of measurement data^[91,92]. Different types of copper oxides formed at the copper surface have been recognized depending of the conditions^[93-96], and so its reduction potential. As early reported by Miley^[97], the oxide layers are composed of cuprous oxide (Cu₂O) and cupric oxide (CuO). Other authors have reported three kind of copper (I) oxide, namely “precursor”, intermediate and “bulk” cuprite^[98,99]. The initial or “precursor” oxide (Cu₂O)_p is spontaneously formed in the air after polishing. According to some authors, its composition is Cu_xO with x>4^[100,101] and it shows a mixed valency character containing interstitial metallic copper in the Cu(I) oxide phase. Since its reduction potential is close to the reversible potential (-0.30 V_{SCE} at pH 9) for the process



It has been called “reversible” copper (I) oxide^[93]. Other authors represented this initial oxide as Cu_2^*O in which Cu^* is an “activated” copper atom distributed among “ordinary” copper atoms^[96].

The second copper (I) oxide named “intermediate” cuprite has a reduction peak slightly negative than $(\text{Cu}_2\text{O})_p$. It could form through transformation of the precursor oxide and that it has a limited life time^[98]. Deutscher and Woods^[93] described this oxide as “restructured” form of $(\text{Cu}_2\text{O})_p$, but the difference in the reduction potentials have not been clearly exposed. XPS did not evidence any difference in their composition, Cu_2O being the only phase identified on copper. The only difference lies in their electrochemical properties. Some authors point out that the origin of the peak displacement towards more negative values is rather thermodynamic attributing the shift to the decrease of the activity of Cu(I) in the oxide lattice^[102]. For other authors^[93], the origin of the difference in the reduction peaks is rather kinetic, a higher overpotential being necessary for reducing a more stable compound. Conductivity changes in the oxide layer during its growth have sometimes been suggested^[103] as responsible for the shift of the reduction peak, considering that Cu_2O has a cation deficiency structure with p-type conductivity and its ionic and electronic conductivity depend on the concentration of the holes^[104].

On the other hand, Tran *et al* suggested^[98] that the high overpotential

observed for the reduction of thick copper (I) oxide layer is mostly due to the activation energy required for the extraction of electrons from the copper substrate into the oxide layer^[105]. Finally, the $(\text{Cu}_2\text{O})_c$ is the more stable form and corresponds to the “bulk” copper (I) oxide. Table I summarizes the main values given to the cathodic reduction of copper compounds referred to calomel saturated electrode used as a reference.

Table I. Potential values of the reduction peaks for different copper species

Compound	Reference data V/SCE	References
CuO	-0.25 to -0.35	[106]
	-0.77 to -0.90	[107]
$(\text{Cu}_2\text{O})_p$	-0.4 to -0.6	[93,108-111]
	-0.45 to -0.71	[108]
$(\text{Cu}_2\text{O})_i$	-0.6	[93,94]
$(\text{Cu}_2\text{O})_c$	-0.8 to -1.0	[93,94,100,109-112]
CuOH	-0.77	[74]

2. Theory

2.1 Infrared reflection absorption spectroscopy (IRAS)

Infrared radiation, like all electromagnetic radiation, is a sinusoidal electromagnetic wave consisting of an electric and magnetic field which always are perpendicular to each other and in phase. It is the electric field that causes interaction with molecules. The radiation travels in a direction perpendicular to the two fields, and can be characterized by its wavelength λ (m), which is the distance between two consecutive maxima, its frequency ν (Hz), which is the number of waves per unit time, and its velocity c (m.sec⁻¹), which is the speed of the light in vacuum ($=2.9997925 \times 10^8$ m.sec⁻¹).

Because the wavelength of the IR radiation is much longer than the length of a molecule, it is in order to assume that the whole molecule experiences the same electric field. IR spectroscopy is mostly performed in the mid-IR region^[113], in which qualitative analysis are common, but this region enables quantitative studies. In the group frequency region, it is possible to

determine what functional groups are present in the molecule, such as C-H, C=O, and O-H. Affected by the surroundings, the group frequencies will not be found at exactly the same wavenumber for all different compounds, but instead in a certain wavenumber range characteristic of that bond^[113]. IR radiation has energy enough to cause rotational and vibrational excitations in molecules, but the energy is not energetic enough to cause electronic excitations. Absorption of IR is restricted to compounds with small energy differences in the possible vibrational and rotational states. For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule. The alternating electrical field of the radiation interacts with fluctuations in the dipole moment of the molecule. If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of molecular vibration.

IRAS can be described as a double transmission process, where the IR beam passes twice through the thin surface layer next to a substrate (see Fig. 3). To avoid losses it is important that the substrate has highly reflecting properties, and therefore metals are suitable substrates^[113].

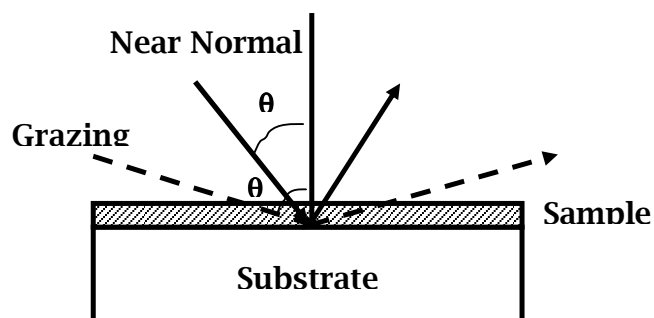


Figure 3. Experimental set-up used for reflection- absorption (IRAS).

Depending of the angle of incidence θ_i (measured from the surface normal), the technique is either classified as near-normal incidence when θ_i is small, or grazing angle incidence when θ_i is large. Grazing incidence is often used in the studies of thin films and their interaction with the incident infrared (IR) light depends on the polarization of the light. Unpolarized IR radiation consists of two perpendicular electrical vectors, s-polarized light, which is perpendicular to the plane of incidence, and p-polarized light, which is parallel to the plane of incidence (the plane of incidence is the plane containing the surface normal and the incident IR ray). S-polarized light undergoes a phase shift close to 180° upon reflection for all angles of incidence. This leads to destructive interference between the incident and the reflected rays at the surface, and a cancellation of the electric field, thereby disabling any interaction with dipoles in the surface film. The phase shift of p-polarized light depends on the angle of incidence. At high angles of incidence, the incidence and the reflected waves will be in phase at the surface, resulting in an enhancement of the amplitude of the electric field in

the direction normal to the surface. The optimum angle of incidence, which is slightly depending of the kind of metal used and the wavenumber, is reported to be around 88° ^[114,115]. As a consequence of the different behaviour of s- and p-polarized light, only adsorbates on the metal surfaces having a vibrating dipole component along the surface normal will absorb IR radiation^[113]. This is referred to as the *surface selection rule* which makes it possible to determine the orientation of adsorbates on metal surfaces^[116].

IRAS (also denoted IRRAS) studies are of great importance in corrosion science, both experiments performed ex situ and in situ. By integrating IRAS into electrochemical measurements, it became possible to obtain atomic and molecular information of adsorbates or films of reaction products on electrode surfaces in electrochemical environments. Another important application of IRAS is related to corrosion inhibition mechanisms. IR-spectroscopy-based techniques in combination with electrochemistry have been used in a large number of studies to help elucidate the actual role of molecules that can act as corrosion inhibitors. Moreover, could be used in surface treatments for corrosion protection or corrosion product formation in atmospheric environments ^[71,117-119].

2.2 Quartz crystal microbalance (QCM)

QCM is a mass-sensitive device with a resolution equivalent to less than one monolayer of water or corrosion products. The use of quartz crystals for this purpose was suggested by Sauerbrey^[120]. The method for mass-change

monitoring is based on the inverse piezoelectric effect in which a voltage applied to an ionic crystalline solid, such as quartz, will produce physical distortions of the crystal^[121]. Piezoelectric materials have long been used as stable oscillators and it was soon recognised that the addition of mass to an oscillator would change its frequency. The dominance of the quartz crystal for all kind of frequency control applications started in 1934 when the AT-cut quartz crystal was introduced. The advantage with the AT-cut quartz crystal is that it has nearly zero frequency drift with temperature around room temperature. From the very beginning of using quartz crystal resonators as frequency control elements it was common to increase the frequency of the resonator by drawing pencil marks on the electrodes, or decreasing the frequency by rubbing of some electrode material with an eraser. AT-cut quartz crystals consist on a quartz piece in which two electrodes of gold are deposited in both sides of the crystal. The electrodes are connected to a frequency counter that monitors the variation of the resonance frequency with time. A scheme can be seeing in Fig. 4.

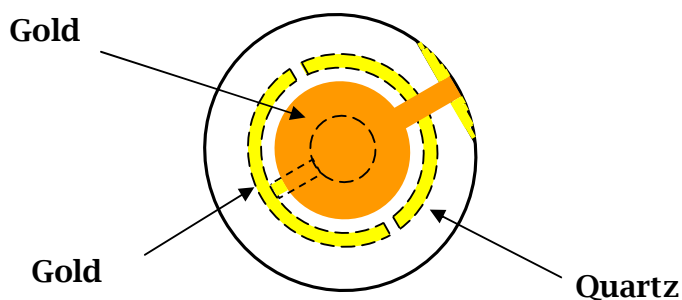


Figure 4. Scheme of an AT-cut quartz crystal.

The QCM can be used to monitor mass changes in the nanogram range with a millisecond time resolution, and can provide valuable information on atmospheric corrosion kinetics, during laboratory as well as field exposure conditions ^[118,122,123]. When combined with techniques giving chemical information on the surface properties, the QCM becomes a powerful method for *in situ* measurements of desorption, adsorption, and film growth^[113]. For a shear wave at the base oscillatory mode, the quartz thickness equals half the wavelength. The eigenfrequency for this mode is given by

$$\Delta f = -2f_0^2 (\Delta m)(\rho_q \nu_q)^{-0.5} \quad [4]$$

Where Δf is the frequency shift; f_0 the frequency at the starting point; ρ_q the density of quartz (2.648 g cm⁻³); ν_q the shear wave velocity (2.947 x 10¹¹ g cm⁻¹ s⁻²); and Δm the mass change per unit area (g cm⁻²). For a quartz crystal oscillating at a fundamental frequency of 5 MHz, the sensitivity is about 18 ng cm⁻² Hz⁻¹, corresponding to approximately 2/3 of a monolayer of water. This equation is commonly referred to as the Sauerbrey equation^[120]. It is valid for small changes. During the last decades the QCM method has undergone rapid progress and has found numerous applications in scientific and technical fields, such as surface science, analytical chemistry, and thin film deposition processing. Moreover, QCM method can be used for atmospheric corrosion studies of metals.

Exposure of a metal to humid atmosphere leads to the formation of corrosion products, which usually stay on the surface. The corresponding mass increase of the sample can be monitored with a QCM. The method has been used by different groups for the investigation of the atmospheric corrosion of copper under laboratory conditions ^[117,118,123,124]. In such studies, the method has been successfully applied in simulated environments containing SO₂ and/or NO₂ with humidified air, proving that is a reliably technique to get information on atmospheric corrosion kinetics under both laboratory exposures and field exposures.

2.3 Coulometric reduction (CR)

With the aim to check the validity of quantitative data obtained with IRAS/QCM, coulometric reduction was used to estimate the thickness of copper (I) oxide. The technique has been widely used for copper specimens exposed to both field and controlled laboratory conditions ^[97,125-128]. With this technique is possible to resolve the complex total film into its major individual chemical constituents, so that the detailed correlations can be made. This resolving power can provide a “fingerprint” capability for identifying significant deviations from intended test conditions, as well as in comparing the corrosive characteristics of different environmental exposures.

Coulometric reduction is a galvanostatic technique in which a constant cathodic current density is applied to a metallic specimen immersed in an

ionic conductive solution. The response is measured in terms of potential variation (against some reference electrode) as a function of reduction time. When a homogeneous film is present on the surface, the potential remains relatively constant with time, with a number of horizontal portions, or steps, each corresponding to a specific reduction of a given constituent of the film^[127]. After complete reduction, the cathodic potential decreases suddenly to more negative values until it reaches the reduction potential of hydrogen ions to hydrogen gas, indicating the end of the reduction. This potential represents the limiting potential, below which no other reduction process can be detected. For each constituent of the film there is a specific reduction potential, which makes it possible to identify the constituent by comparing the obtained potential value with that of films of well-known composition. From the elapsed times at the various steps, one can often draw conclusions regarding the corrosion and tarnishing processes that have occurred in the environmental chamber. One can also calculate from the time at each voltage step the number of coulombs of electrical charge required to complete the reduction process at that particular voltage.

There are some conditions that have to do in every reduction curve in order to secure a good practical experiment. The elimination of the dissolved oxygen is important because if any oxygen gas is present in the working electrode, it will tend to interfere with the coulometric determinations, since O_2 is easily reduced in the same voltage range as many oxides or tarnish film components. It is eliminated by deaerating the electrolyte solution prior to

use and by running the reduction in a closed cell under an inert atmosphere. Moreover, a minimum solution volume is necessary to be large enough to reduce the effect of soluble reaction products to an insignificant level. According to Krumbein^[127], the cell must be sufficient size to hold 200 to 400 mL of solution.

The results of the constant-current coulometric procedure can be expressed directly as the elapsed time (in seconds) required to complete the reduction of a particular film component at its observed voltage step, as well as the total time needed to complete the reduction of all the reducible components of the film. The elapsed time can be also multiplied by the total applied current to give the number of coulombs of electrical charge required to complete the reduction processes at various respective voltages. If the chemical identity of the reducible components is known or strongly referred, one can also calculate both the mass of the substance and its thickness (assuming that it is present as an homogeneous layer in the film). So, the equivalent thickness of copper (I) oxide was obtained from Faraday's law:

$$e = 10000 (t \times I \times M) / (A \times n \times d \times F) \quad [5]$$

Here e is the thickness (nm); t is the required time to reduce the oxide (s); I is the galvanostatic current (mA); A is the exposed copper area (cm²); M is the molecular weight of the copper oxide (g mol⁻¹); F is the Faraday constant (9.65 x 10⁴ C mol⁻¹), n is the number of Faradays required to reduce one unit

of molecular weight of the copper (I) oxide, and d is the specific weight of the reduced oxide (g cm^{-3}). The derivative of each reduction curve gave a better precision when defining the inflection point representing the onset or finish of reduction of copper (I) oxide species^[90].

The total mass of all the components and the apparent thickness of the entire film can be obtained by adding the respective values for these known or inferred constituents. If weight gains have been determined previously for the samples, these can be compared with the total mass values of the respective samples, and appropriate correlations can be made.

2.4 Cathodic scan (CS)

Cathodic scan is a potentiodynamic reduction technique scanning the electrode potential with a specific scan rate with the electrode immersed in a non stirred solution. Analysis of the current response can give information about the thermodynamics and kinetics of electron transfer at the electrode-solution interface, as well as the kinetics and mechanisms of solution chemical reactions initiated by the heterogeneous electron transfer^[129]. The electrode response to the potential disturb is the current associated to an electrochemical process in the electrode/electrolyte interface. A potentiostat system sets the control parameters of the experiment. Its purpose is to impose on an electrode (the working electrode) a linear potential sweep and to output the resulting current-potential curve. This sweep is described in general by its initial (E_i), and sweep (or scan) rate (v , in $\text{V}\cdot\text{sec}^{-1}$). The potential

as a function of time is:

$$E = E_i - \nu t \quad [6]$$

The electrochemical reduction takes place at the working electrode (WE). Electrical current at the WE due to electron transfer is termed *faradaic current*. An auxiliary or “counter” electrode (AE) is driven by the potentiostatic circuit to balance the faradaic process at the WE with an electron transfer of opposite direction (oxidation taking place on it). The process at the AE is typically not of interest, and in most experiments the small currents observed mean that the electrolytic products at the AE have no influence on the processes at the WE.

The potential-current curve is lately analysed and in similar way as with coulometric reduction technique, each reduction peak having a potential range is associated to some identifiable species by comparing compounds reported in literature. But different studies, leads to different interpretation regarding the sequence of copper oxides reduction as are observed in Table I. However, the technique has been successfully applied to atmospheric corrosion of copper in different environment including organic polluted exposures^[68,72-74,76]. One can also calculate from the integration of current peak the number of coulombs of electrical charge required to complete the reduction process at that particular voltage range. This can be done by using the following equation:

$$Q = -\frac{1}{\nu} \int_{E_1}^{E_2} i^* dE \quad [7]$$

where, Q , is the charge per unit area (Coul.cm⁻²), i is the current density (μA.cm⁻²), ν is the scan rate (1mV.sec⁻¹), E_1 represents the initial potential of the reduction curve, and E_2 represents the end of the reduction for each particular compound.

2.5 Atomic force microscope (AFM)

Scanning probe microscopes (SPM) define a broad group of instruments used to image and measure properties of material, chemical, and biological surfaces. SPM images are obtained by scanning a sharp probe across a surface while monitoring and compiling the tip-sample interactions to provide an image. The two primary forms of SPM are scanning tunnelling microscopy (STM) and atomic force microscopy (AFM). STM was first developed in 1982 at IBM in Zurich by Binnig, et al ^[130]. The invention of the scanning tunnelling microscope (for which Binnig and Rohrer were awarded the Nobel Prize in Physics in 1986) has had a great impact on the technical community by providing a new and unique tool to advance fundamental science and technology. Although the ability of the STM to image and measure material surface morphology with atomic resolution has been well documented, only good electrical conductors are candidates for this technique. This significantly limits the materials that can be studied using

STM and led to the development, in 1986, of the atomic force microscope by Binnig, Quate, and Gerber^[131].

With SPM techniques it is possible to study single atoms on conducting materials at atmospheric pressure. AFM provides a number of advantages over conventional microscopy techniques. AFMs probe the sample and make measurements in three dimensions, x, y, and z (normal to the sample surface), thus enabling the presentation of three-dimensional images of a sample surface. This provides a great advantage over any microscope available previously. With good samples (clean, with no excessively large surface features), resolution in the x-y plane ranges from 0.1 to 1.0 nm and in the z direction is 0.01 nm (atomic resolution). AFMs require neither a vacuum environment nor any special sample preparation, and they can be used in either an ambient or liquid environment.

The AFM uses a small tip at the end of a cantilever, which bends because of the force between the tip and the sample^[131]. The tip is maintained at constant contact when scanning the surface. This type of measurements is referred to as contact mode imaging, which easily can reveal, e.g., steps and other defects on surfaces. Typical forces used are some tenths of nN, which are limited by adhesive forces. These forces are low enough to obtain reproducible, non-destructive, imaging of many surfaces^[132].

2.6 Grazing incidence X-Ray diffraction (GI-XRD)

It is sometimes very difficult to analyze thin films due to their small diffracting volumes, which result in low diffracted intensities compared to the substrate and background. This combination of low diffracted signal and high background make it very difficult to identify the phases present. Accordingly, special techniques must be used when analyzing thin films. X-ray diffraction is the most common method for phase identification of solid bulk materials. X-rays are scattered by the charge distributed in and around atoms. Because x-ray scattering is relatively weak, x-rays can penetrate deep into materials and the bulk structure can be probed. The intensity of x-rays diffracted by atoms in a surface layer is small compared to that diffracted by the bulk. Nevertheless it is possible to obtain surface crystallographic information with x-ray diffraction. For this to happen, the sample needs to be illuminated with a narrow beam of monochromatic x-rays, whereby the angle between the incident wave vector and the surface needs to be very small in order to enhance the surface sensitivity in the diffraction experiment. The intensity of the x-ray beam is made as high as possible without damaging the sample during the radiation^[133].

The grazing incidence geometry is surface selective, *i.e.* largely avoids scattering from the substrate, and does not require a transparent substrate. This technique is based on the fact that at X-ray energies, the refractive index for most materials is slightly less than 1.0. One can therefore have total

external reflection from a surface if the incident angle is small enough (typically 1–25 milliradians or 0.05–1.5°, depending on the substrate electron density and the X-ray energy). At this point the substrate is not entirely invisible to X-rays, but only an evanescent wave penetrates into and scatters from it. The X-ray intensity is therefore highest at the surface, as desired. It is possible to increase the surface selectivity further by reducing the incident angle and thus causing the evanescent wave to damp out faster. Of course, this technique has some limitations. The first is that it works well only with very smooth surfaces, and not all surfaces can be made sufficiently smooth. Second, at grazing angles, most of the incoming X-ray beam is wasted. The need is therefore for a beam that is intrinsically both compact and collimated. This is provided by synchrotron sources^[134].

3. Aim of the study

The aim of this doctoral study is to provide a better understanding of the initial atmospheric corrosion of copper in the presence of three important organic acids, formic, acetic and propionic, at concentration levels reasonable representative of ambient indoor or outdoor conditions. The aim is also to provide quantitative data of corrosion product formation, for comparison with future GILDES model studies.

The work has been carried out primarily by mean of two integrated *in situ* techniques, namely IRAS (to provide chemical characterization of species present in the corrosion products) and QCM (to monitor absolute mass changes) during exposure. Complementary *ex situ* analyses have been performed with electrochemical reduction (to validate the copper (I) oxide growth and find a reduction model), atomic force microscopy (to obtain morphological information after exposure) and grazing incidence x-ray diffraction (to possibly identify phases in the minute amounts of corrosion

products formed). Finally, potentiodynamic reduction curves were performed and electrochemical reduction model was proposed to understand and simulate such curves.

4. Experimental part

4.1 Sample preparation

Two kinds of samples were used. AT-cut quartz crystals of 99.99% purity and with a resonance frequency of 5 MHz were purchased from Maxtec Inc. They consist of a chromium film evaporated on the quartz crystal with a thickness of approximately 50 nm ($\text{nm} = 10^{-9} \text{ m}$), used to improve the adhesion between the quartz and copper, and on top a copper film of approximately 350 nm thickness. The copper-covered crystal facing the corrosive atmosphere has a diameter of 13 mm. Each copper film on quartz was polished using two different series of diamond paste; 1 and 0.25 μm , cleaned with ethanol during and between each polish, and then immersed for 30 seconds in 5% of amidosulfonic acid (H_3SNO_3). This acid was used with the purpose of removing any of the previous oxide left. The samples were thereafter rinsed three times in ethanol (99.5% purity) and finally dried in nitrogen before exposure. These samples were used for IRAS/QCM analysis.

The second kind of copper samples consists of solid pieces sized 20 x 20 x 0.5 mm³ and with 99.5 % of purity. They were cut and polished with silicon carbide paper down to 1200 mesh, and cleaned with the same procedure as before. These samples were used for polarization curves, electrochemical reduction, AFM and GI-XRD analysis.

4.2 Laboratory exposures for *in situ* measurements

4.2.1 Corrosive air and relative humidity control

The air used as carrier gas is prepared from compressed air passing through charcoal and particle filters. It is reduced with respect to water and carbon dioxide in an adsorption drier, before it passes through a second particle filter^[117]. The dried air is separated into three different streams, the first going to a humidifier, and the second to a container with the permeation tube containing the acid, and the third remaining as dry air. All three streams are regulated with needle flow meters, and are later recombined in a mixing chamber before entering the exposure chamber. The mixing chamber and the container with the acid are submerged in a thermostatic bath (see schematic description in Fig. 5). The ratio between the humid and dried air gives the intended relative humidity (RH), which can be controlled from 0.5 to 100%. Permeation tubes were purchased from VICI Metronics containing either acetic, formic or propionic acid in equilibrium with the liquid/vapour phase. The temperature is controlled at 19.5 ± 0.5 °C.

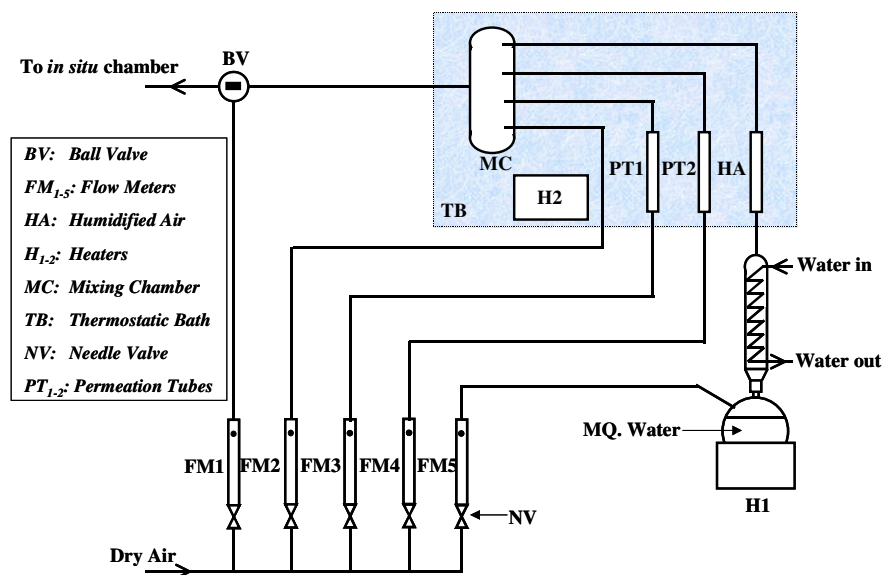


Figure 5. Schematic representation of relative humidity control and production of polluted air.

4.2.2 In situ exposure chamber

The exposure chamber is made of stainless steel covered inside with Teflon. The air enters from above through a ball valve that allows quick changes between dried and acid-containing humid air. The air had a flux of 1.3 lt min⁻¹, corresponding to a velocity of 3.5 cm s⁻¹ over the sample, which is in the lower range of normal indoor air-flow conditions^[78]. The chamber has been built to integrate IRAS and QCM for *in situ* measurements, using a Teflon holder located below the chamber (see Fig. 6). Likewise, a copper plate sample can be located in the chamber by using a Teflon holder to fasten the sample with the exposed side facing up towards the corrosive air.

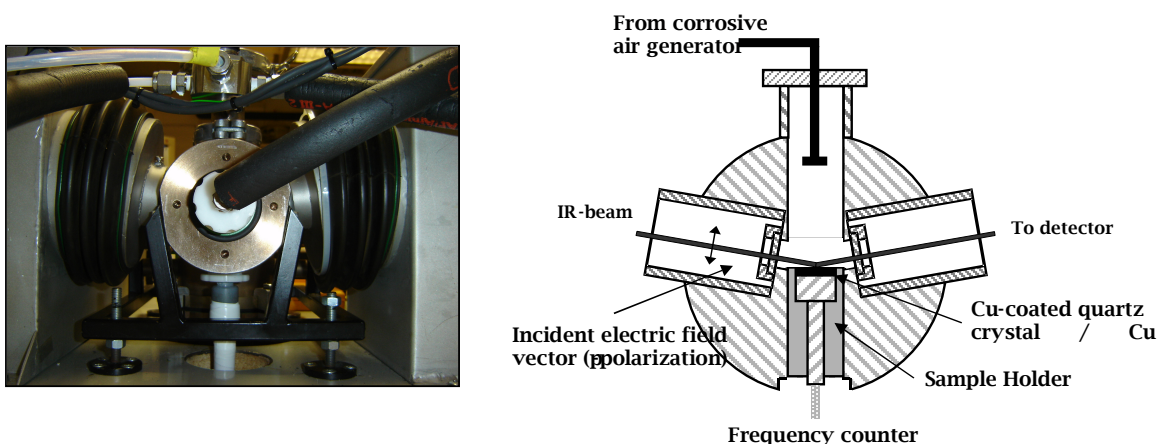


Figure 6. Lateral view and cross-section of the *in situ* chamber.

4.3 Laboratory exposures for *ex situ* measurements

Measurements in synthetic atmosphere were performed during 21 days, in an exposure chamber, at constant temperature of 25°C (see Fig. 7). A relative humidity of 95% was obtained by mixing water saturated air flow with dry air flow. The samples were located vertically inside a glass vessel. The experiments were done with 0, 500 and 800 ppb of acetic acid by using a permeation tube filled with pure acetic acid. The acid concentration was validated with mass gain measurements.



Figure 7. Outside and inside view of the exposure chamber.

4.4 *In situ* measurements

4.4.1 Infrared reflection-absorption spectroscopy (IRAS)

In this study were used p-polarized light which is parallel to the plane of incidence. The incidence angle used is around 88 degrees. IRAS spectra were obtained using p-polarized light, with 1024 scans at a resolution of 8 cm^{-1} . Absorbance units ($-\log(R/R_0)$) were used as a measure of intensity, with R being the reflectance of the sample and R_0 the reflectance of the background. All samples were initially left 40 min in dry conditions, and a background spectrum was collected. Then the air was changed to humid and reached 95% RH after 20 min. At this point a new background spectrum was collected, which was used as a start spectrum when following the formation of surface species. Because of similar wavenumber of some vibrations of water and

carboxylate species, the measured background spectrum was subtracted from all later spectra in order to eliminate any contribution from physisorbed water, gas phase water and other contributions^[94,117].

4.4.2 Quartz crystal microbalance (QCM)

The QCM sensor probe is a modified commercial (Maxtec MPS 550) probe in a sample holder made of Teflon and Viton. The sensor probe attached to the exposure chamber is connected to a commercial frequency counter (Maxtec PM 740), taking data point every minute. Once the frequency was collected, the data were subsequently transformed to mass according to the Sauerbrey Equation^[120].

4.4.3 Coulometric reduction (CR)

Coulometric measurements were performed at the exposed side of copper plates, while the other side was covered with adhesive tape used in electrochemical analysis. A platinum mesh was used as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The solution was 0,1M of KCl and, following the procedure in an ASTM standard^[90]; it was purged with pure nitrogen 20 min before and during the measurements. A potentiostat/galvanostat EG & G model 273 A was used with a current density of 0.05 mA cm⁻². All the experiments were done by triplicate.

4.4.4 Atomic force microscope (AFM)

Copper sheet samples for the AFM measurements were of dimension 20 x 20

x 0.5 mm³ and polished down to 0.25 µm, cleaned in ethanol for 20 min, dried with a fuss-free tissue to remove polishing particles and then transferred to the exposure chamber. The AFM measurements (Quesant Instrument Ltd) were carried out in contact mode operation on copper exposed to 0, 1, 10, 40, and 90 hours in 120 ppb of acetic, formic or propionic acid with the same exposure conditions as with the *in situ* measurements.

4.4.5 Grazing incidence x-ray diffraction (GI-XRD)

GI-XRD was performed on copper plates after four and eight days of exposure. The diffractograms were obtained with a Philips MRD Instrument (Department of Materials Chemistry, Uppsala University) using a parallel plate from 10 to 70°, and going in steps of 0.1°.

4.5 *Ex situ* measurements

4.5.1 Cathodic Scan (CS)

Potentiodynamic reduction measurements were performed on the copper plates to characterize corrosion products produced by synthetic air and anodic polarizations. All the experiments were done by triplicate. The reductions were made by using an electrochemical cell with a platinum plate used as counter electrode and a saturated calomel electrode (SCE) as reference electrode (see Fig. 8). The working electrode was the copper sample with a small hole by which it was hanging in a platinum wire. The support solution was 0.1M of KCl. The solution was purged with pure nitrogen 20

min before and during the measurements. A potentiostat/galvanostat Bas Zahner was used with scanning rate of $1\text{mV}\cdot\text{sec}^{-1}$, from the corrosion potential until -1.4V to secure the complete reduction of the species.



Figure 8. *Electrochemical cell used for the potentiodynamic reductions.*

4.5.2 Polarization curves (PC)

Copper samples sized 2×2 cm were polarized after 15 minutes of stabilization, until 1 V in several concentrations of pure acetic acid. The concentrations were of 1, 0.1, 0.01 and 0.001 M. This was performed in order to produce electrochemically corrosion products present at the copper surface comparable with the atmospheric produced ones. After each polarization, the samples were washed with deionized water and put in the electrochemical cell to proceed with the electrochemical reduction in 0.1M of KCl. All the experiments were done by triplicate.

5. Results and discussion

A quantification method for individual species formed during in situ conditions was developed and applied for copper exposed in humidified air with acetic acid during up to 96 hours. First the method is described in some detail, followed by the application of the method to copper exposed to all three carboxylic acids. This leads to a proposal mechanism of atmospheric corrosion of copper in this type of environment. Finally, a reduction mechanism that explains potentiodynamic reduction curves of copper in acetic acid is proposed.

5.1 Quantification method for individual species in the corrosion products

To begin with, the quantification of the water/OH groups was made by using gold-coated quartz crystals, exposed to pure humidified air at different relative humidity corresponding to different amounts of physisorbed water.

By plotting the intensity of the absorbance band at $\sim 3400\text{ cm}^{-1}$ (corresponding to the stretching vibration of the water and OH groups^[135]) against the mass changes measured by QCM, a linear relation was established. Using this relationship, and the intensities for the same region found on copper exposed to acetic acid, an estimate of the amount of water/OH groups could be calculated. Fig. 9 displays the broad band of the water/OH groups around 3400 cm^{-1} after 96 hours of exposure of copper in 120 ppb of acetic acid. The absorbance of this band formed in the corrosive air contains various forms of water and hydroxyl groups; both firmly attached and more loosely bonded, physisorbed, water. Simultaneously, the total mass could be followed by QCM using copper-coated quartz crystals exposed to pure humidified air. By varying the relative humidity it is possible to vary the amounts of both copper (I) oxide and of physisorbed water, whereby the total mass measured by QCM corresponds to both constituents. Once steady-state was achieved, the air was changed from humid to dry, and the observed decrease in mass (QCM) was assumed to correspond to the amount of physisorbed water. By subtracting the physisorbed water mass from the total mass gain, it was possible to obtain the mass of copper (I) oxide (QCM).

By plotting the intensity of the copper (I) oxide band at $\sim 645\text{ cm}^{-1}$ (IRAS) against the corresponding copper (I) oxide mass (QCM), a linear relation was obtained. Since QCM only measures mass changes, the mass gain due to copper (I) oxide must be multiplied by 8.94 (the molar weight of Cu_2O divided

by the molar weight of O) to obtain the actual mass of copper (I) oxide^[122]. Similar relationships involving water and copper (I) oxide or cuprite have been found before^[136]. The validity of this procedure has previously found further support through independent data from coulometric reduction^[94].

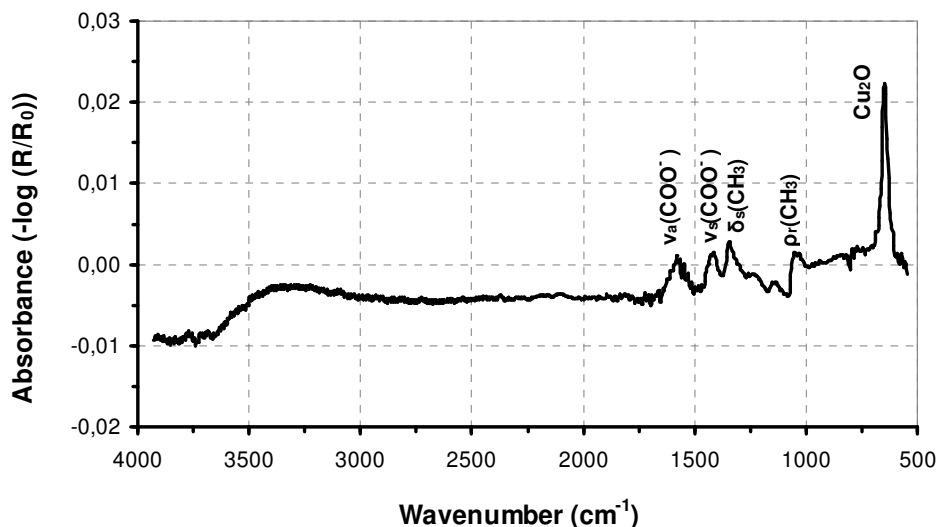


Figure 9. *In situ IRAS spectrum of copper-coated quartz crystal at 95% RH and 120 ppb of acetic acid after 96 hours.*

To finalize the quantification procedure, an estimate of the copper acetate mass was obtained by subtracting the water and copper (I) oxide mass from the total mass gain, under the assumption of only three individual species formed on the exposed surface, Cu_2O , H_2O and $\text{Cu}(\text{CH}_3\text{COO})_2$. Fig. 10 presents the total mass gain together with the mass of the individual constituents as a function of copper exposure in humidified air with 120 ppb of acetic acid.

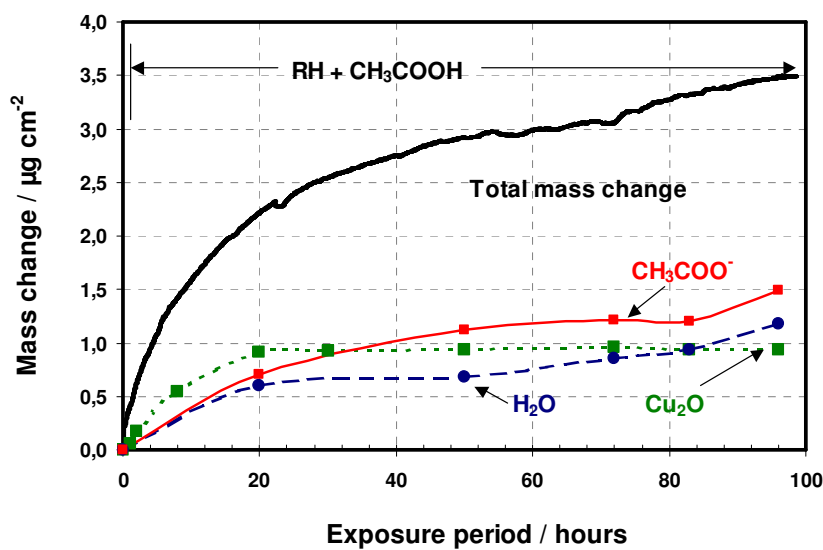


Figure 10. Total mass gain (in $\mu\text{g cm}^{-2}$), measured by QCM, and corresponding mass gain due to Cu_2O , H_2O and $\text{Cu}(\text{CH}_3\text{COO})_2$, deduced from IRAS as a function of exposure time in 120 ppb of acetic acid at 95% RH.

The method could be successfully applied to all three acids with results that turned out to be consistent with each other (see further in section 5.2). However, in the case of formic acid, one more species, copper (II) hydroxide, had to be considered. To estimate the copper (II) hydroxide mass gain, a further relation between IRAS absorbance and mass had to be added. It involves the absorbance of a sharp peak around 3572 cm^{-1} (corresponding to the vibration of free hydroxyl groups in $\text{Cu}(\text{OH})_2$ without involvement of any hydrogen bonds^[137], Fig. 11a) and the equivalent mass obtained by coulometric reduction (with a plateau around -0.720 V vs. SCE, Fig 11b). The

individual masses of water/OH, copper (I) oxide and copper (II) hydroxide was finally subtracted from the total mass gain, in order to obtain the mass gain due to formation of copper formate.

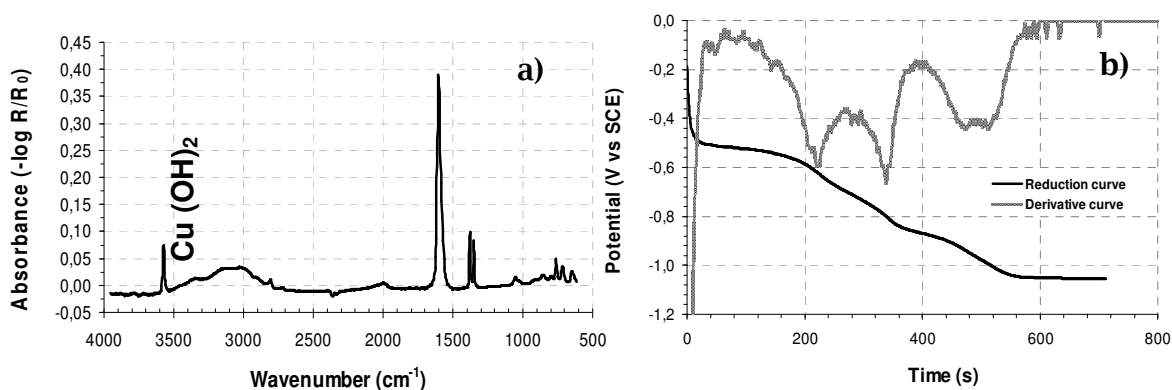


Figure 11. Infrared spectrum a) and coulometric reduction curve b) for copper plate exposed to 120 ppb of formic acid during 96 hours.

5.2 Comparison of corrosion effects induced by the carboxylic acids

5.2.1 Quantitative and qualitative differences for copper (I) oxide based on IRAS/QCM and coulometric reduction

The IRAS spectra of copper exposed in 120 ppb of acetic, formic and propionic acid exhibit both similarities and differences. Firstly, in all spectra the copper (I) oxide band appears in the range 645-648 cm^{-1} , together with a broad band at $\sim 3400 \text{ cm}^{-1}$ attributed to the stretching vibration of water/OH, as discussed above. The highest intensity for the cuprite band was found in acetic acid exposures, and the lowest in propionic exposures. Fig. 12 presents

the kinetics of copper (I) oxide growth for all three organic acids.

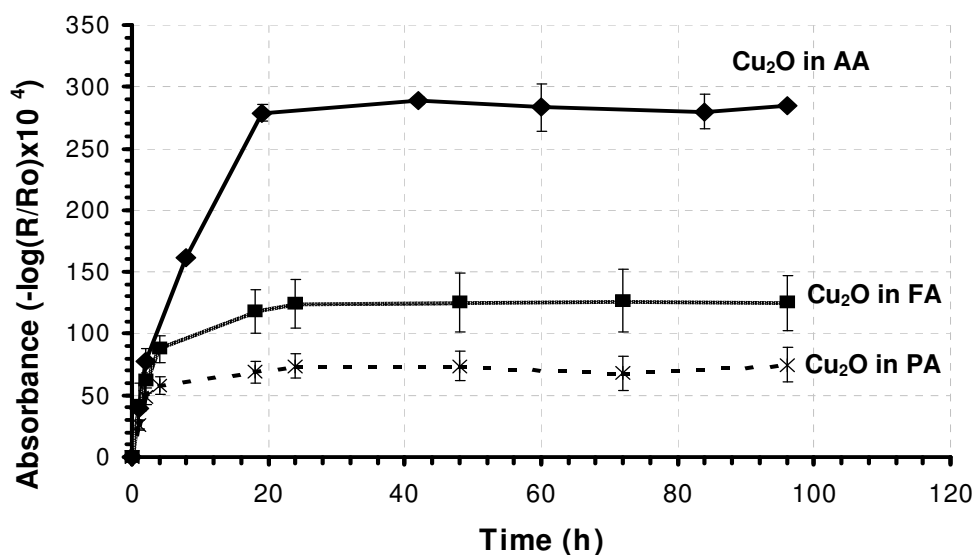


Figure 12. Intensity of the copper (I) oxide band at 648 cm⁻¹ as a function of exposure time for copper exposed at 95% RH, in 120 ppb of acetic (AA), formic (FA) and propionic acid (PA).

Coulometric reductions of copper plates were performed to follow the copper (I) oxide growths, and the results turned out to be consistent with the corresponding quantified data from IRAS/QCM, see Fig. 13 below. In this figure, the thickness of the copper (I) oxide was calculated as the summary of two kinds of copper (I) oxides, a precursor (Cu_xO) with the same crystallographic structure as Cu₂O but with a mixed valence due to interstitial metallic copper in the Cu (I) oxide phase (at ~ -500 mV vs. SCE), and crystalline and stoichiometric Cu₂O (at ~ -850 mV vs. SCE)^[95,100]. The total

calculated thickness of both phases was obtained by assuming homogeneous layers, a complete reduction of both oxides, and a density of 6.0 g cm^{-3} for both oxides. The summary of all results for the three acids is presented in Fig. 13, where error bars are based on three independent experiments. Based on a regression analysis the quantified data seen in the figure obtained with IRAS, QCM or coulometric reduction agree with each other with a relative accuracy of 12% or better.

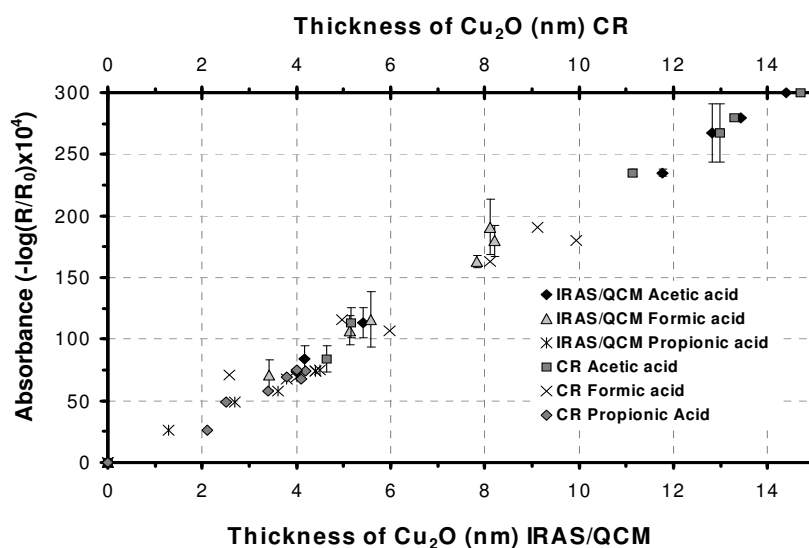


Figure 13. Relation between the absorbance of the cuprite band at 648 cm^{-1} measured by IRAS, cuprite thickness obtained by IRAS/QCM (lower x-axis) and cuprite thickness obtained by coulometric reduction (upper x-axis) for copper exposed at 95% RH, in 120 ppb of acetic, formic or propionic acid.

5.2.2 Quantitative and qualitative differences for copper carboxylate based on IRAS / QCM

Peaks due to CH₃ bending and rocking vibration, CH bending, stretching and deformations are seen in the spectra obtained upon exposure to all three carboxylic acids^[138]. The symmetric and antisymmetric stretching vibrations of the carboxylate ion are observed between 1420 and 1427 cm⁻¹ and between 1573 and 1589 cm⁻¹ for acetic acid^[138]; at 1354 cm⁻¹ and between 1597 and 1604 cm⁻¹ for formic acid^[138] and at 1419 cm⁻¹ and 1600 cm⁻¹ for propionic acid^[76]. The intensity of these peaks versus time provides information on growth rates of copper carboxylates formed, as presented in Fig. 14. The fact that the asymmetric and symmetric stretching vibration intensities are similar for both acetic and propionic acid indicates a more random orientation of the C-O-O axis in the acetate or propionate groups^[71]. For formic acid a non-uniform distribution of intensities exists, with the asymmetric peak more intensive than the symmetric. This difference suggests the C-O-O axis in the formate ion to be orientated preferentially perpendicular to the copper substrate^[139]. Regarding the difference in wavenumber between the symmetric and asymmetric stretching vibration, the observed values in this study are between 155-162 cm⁻¹; 247-254 cm⁻¹; and 174-181 cm⁻¹ for acetic, formic and propionic acid, respectively. The values are in agreement with those found in the literature ^[72,74,76].

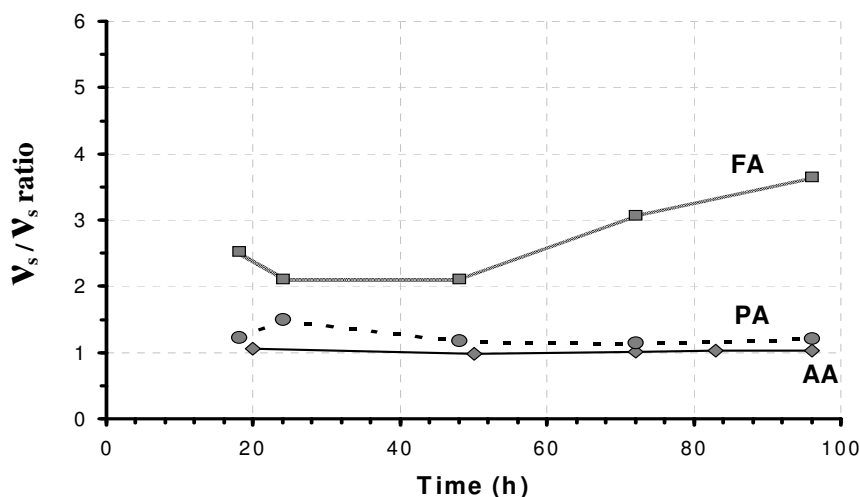


Figure 14. Intensity ratio of the antisymmetric and symmetric stretching vibration (v_a / v_s) as a function of time for copper exposed at 95% RH, 20°C in 120 ppb of acetic (AA), formic (FA) and propionic acid (PA).

5.2.3 Topography images and phase identification based on AFM and GI-XRD analysis

Comparison between AFM-images after 96 hours of exposure in the three acid environments also gave different results. Fig. 15 shows an unexposed sample with scratches of very low topography due to the polishing procedure. Acetic acid produced more copper (I) oxide than formic and propionic acid, and are seen as cubic-shaped crystallites. In addition, rounded features are also seen which can be associated with copper (II) acetate formation (Fig. 15b). Formic acid exposures result in more homogeneous features and more elongated forms (Fig. 15c). A more closed view of the effect of formic acid on copper can be seen in Fig. 16. Copper exposed in propionic acid represented the lowest variation in topography

(Fig. 15d). The shape of the copper (I) oxides is enlarge in Fig.17 for a copper sample exposed during 10 hours in acetic acid, where the crystallites cover the scratches due to polishing. The growth of the corrosion products can be quantified by the increase in height range compared to the unexposed sample. The range is around 800 nm for acetic acid, 570 nm for formic acid and 140 nm for propionic acid after 96 hours of exposure.

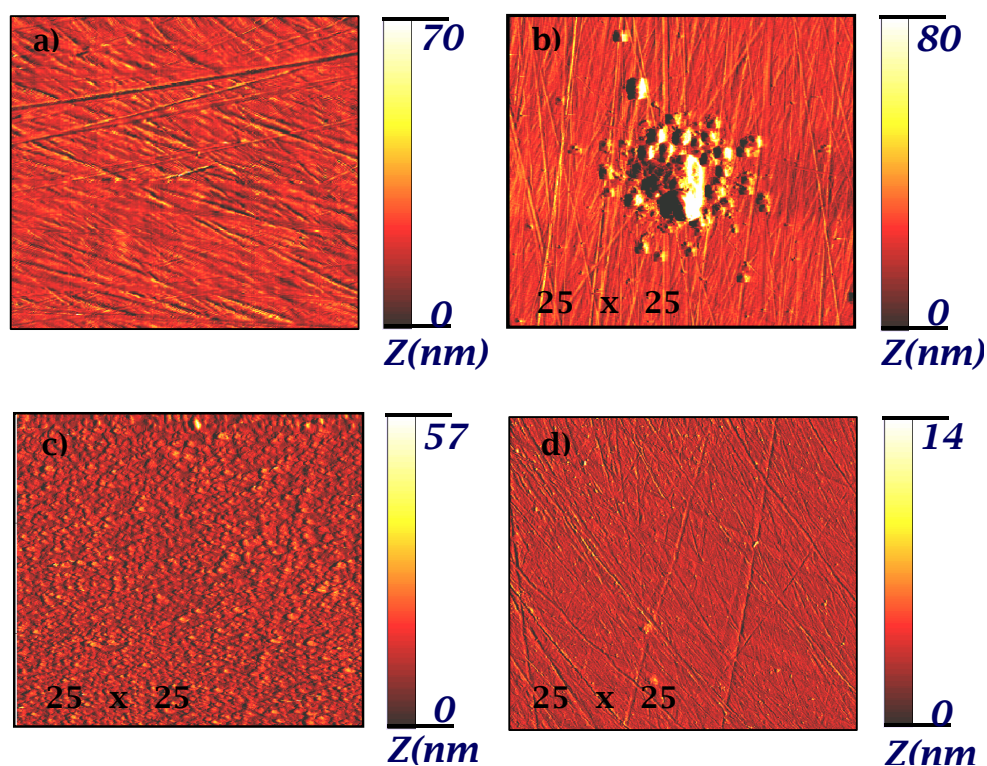


Figure 15. AFM images of copper before exposure a) and after 96 hours of exposure at 95% RH, 20 °C and 120 ppb of b) acetic acid, c) formic, and d) propionic acid. Scan size $25 \times 25 \mu\text{m}^2$.

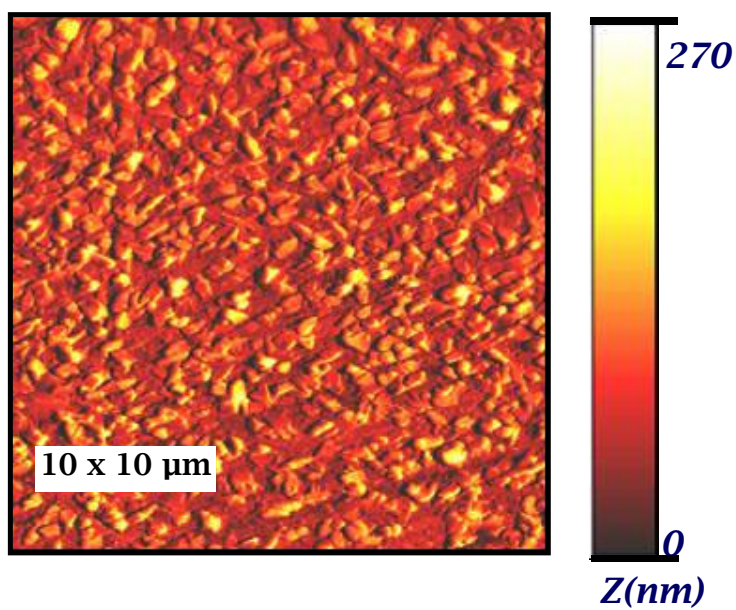


Figure 16. AFM images of copper after 10 hours of exposure at 95% RH, 20 °C and 120 ppb of formic acid. Scan size 10 x 10 μm^2 .

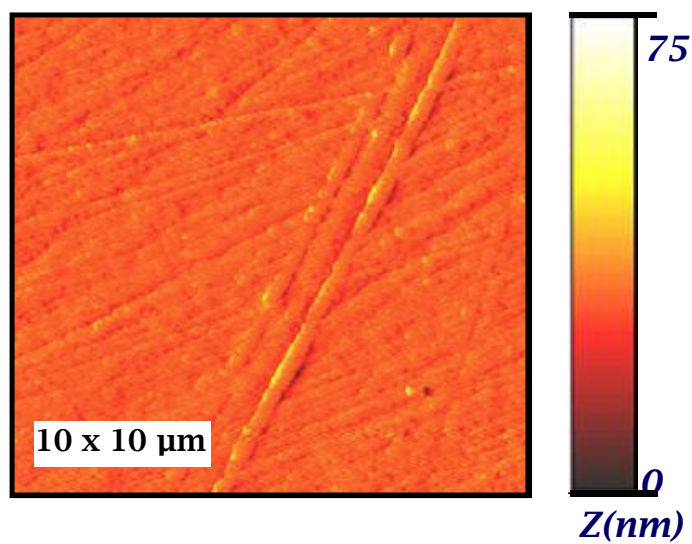


Figure 17. AFM images of copper after 10 hours of exposure at 95% RH, 20 °C and 120 ppb of acetic acid. Scan size 10 x 10 μm^2 .

Phase analysis by GI-XRD of copper surfaces after exposures times of up to four days in acetic and formic acid showed copper (I) oxide (Cu_2O), some copper (II) hydroxide ($\text{Cu}(\text{OH})_2$) but no copper carboxylate. This suggested that the amount of copper carboxylate formed upon carboxylate acid exposure either was too small to be detected, or that copper carboxylate formed an amorphous phase during shorter exposure times. However, after eight days of exposure, Cu_2O , CuO and hydrated copper hydroxy acetate ($\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\text{H}_2\text{O}$) was identified after acetic acid exposures and Cu_2O , CuO and copper hydroxy formate ($\text{Cu}(\text{OH})(\text{HCOO})$) after formic acid exposures.

When comparing the ratio (Δm carboxylate/ Δm H_2O -OH) from the quantitative results obtained by IRAS/QCM and the corresponding ratio from the phase analysis obtained with GI-XRD, an excellent general agreement could be obtained, in particular when considering the many assumptions made.

5.2.4 General remarks

In all the results suggest that the corrosion behaviour of copper in acetic, formic and propionic acid can be said to follow the GILDES model^[140] with proton- and ligand (carboxylate)-induced dissolution processes governing the anodic reaction:



and with the cathodic reaction written as:



Fig. 18 is a schematic picture of possible pathways for copper dissolution and copper carboxylate production, taking acetic acid as example. After dissociation of the organic acid (step 1 in Fig. 18) both protons and carboxylate ions may interact with the hydroxylated surface formed upon exposure with the aqueous adlayer. Two reaction pathways can be discerned. The first involves proton-induced dissolution of cuprous ions (steps 2-4), subsequent reaction of cuprous ions with hydroxyl ions produced in the cathodic reaction (step 5) ^[141], followed by the formation and precipitation of cuprite (step 6). The second involves ligand-induced dissolution of the cuprous ions, release of an aqueous copper carboxylate species from the surface (steps 7-9), and subsequent precipitation of copper (II) carboxylate (step 10) into which water and hydroxyl groups may have been incorporated.

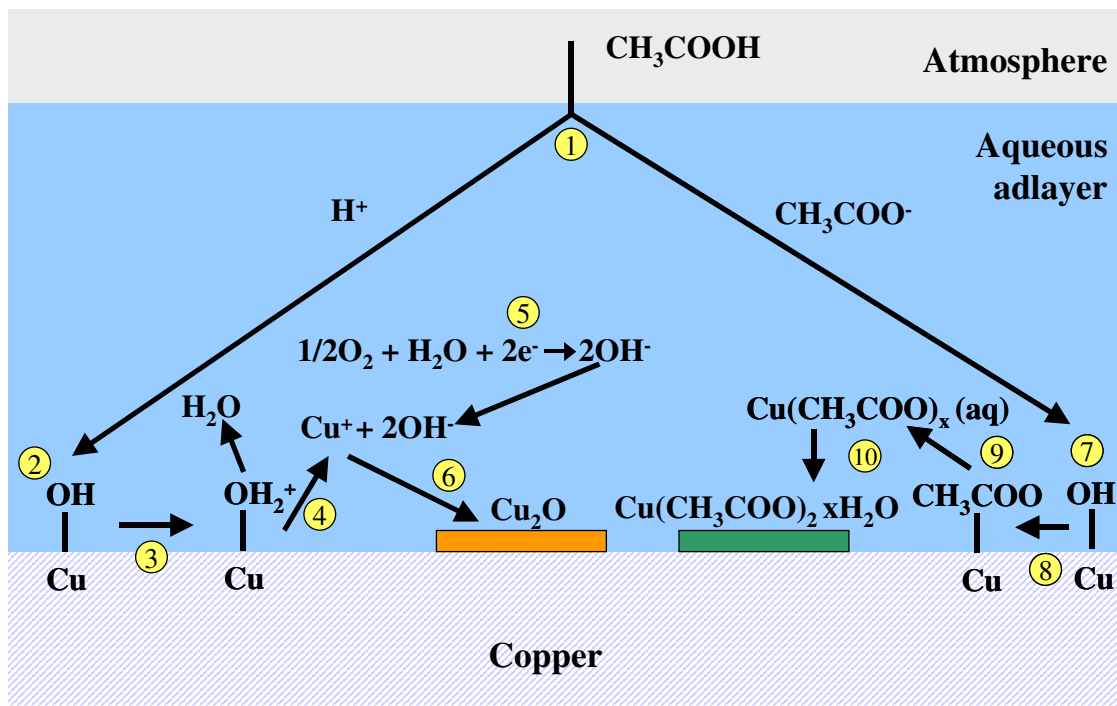


Figure 18. Schematic description of reaction pathways for copper (I) oxide and copper (II) carboxylate formation in acetic acid.

Depending on acid, one route seems to dominate over the other. Acetic acid triggers copper (I) oxide formation, as is evidenced from the IRAS/QCM measurements, demonstrating that the pathway with proton-induced dissolution is dominating. Formic acid, on the other hand, stimulates carboxylate-induced dissolution, whereas propionic acid represents the lowest stimulant for both pathways. The differences in acid dissociation constant between the acids decreases in the order^[142]: formic acid (1.77×10^{-4}) > acetic acid (1.76×10^{-5}) > propionic acid (1.34×10^{-5}).

The deposition velocity of each acid, calculated from the quantified IRAS/QCM data, follows the same order: formic acid (0.014 cm s^{-1}) > acetic acid (0.007 cm s^{-1}) > propionic acid (0.003 cm s^{-1}), in good agreement with data reported in the literature^[143]. Hence, higher acid strength and also higher deposition velocity seem to favour the overall corrosion rate, and also the second pathway with carboxylate-induced dissolution of copper.

5.3 Cathodic reduction model of oxide films formed in presence of acetic and propionic acid

5.3.1 Exposures of copper in an unpolluted environment

The reduction curves of copper samples exposed in synthetic air at 95%RH without any acetic acid concentration were obtained, during 10, 30, 60, 120 and 150 minutes (see Fig 19). After 10 min of exposure, a peak around -0.56V vs. SCE was found, corresponding to the amorphous cuprite, referred here as $(\text{Cu}_2\text{O})_{\text{am}}$ present at the surface before any exposure time^[98]. This oxide is present in all exposures times and the amount remains approximately constant according with the reduction charge, calculated as the integration of the area between the experimental curve and the background line, both taken between two selected potential values (see Fig. 20).

After 30 min of exposure, a second copper (I) oxide is found close to -0.8V, that could be associated with the intermediate cuprite, referred here as $(\text{Cu}_2\text{O})_{\text{in}}$ having a reduction potential more negative than the amorphous one.

In our case, the intermediate oxide grows after 30 min of exposures and then decrease until disappear it for longer exposures (Fig. 17). Finally, a third copper (I) oxide, referred here as crystalline oxide $(\text{Cu}_2\text{O})_{\text{cr}}$ was found after 60 min of exposure, and grows until the end of the experiment. There is no presence of cupric oxide (CuO) in these measurements.

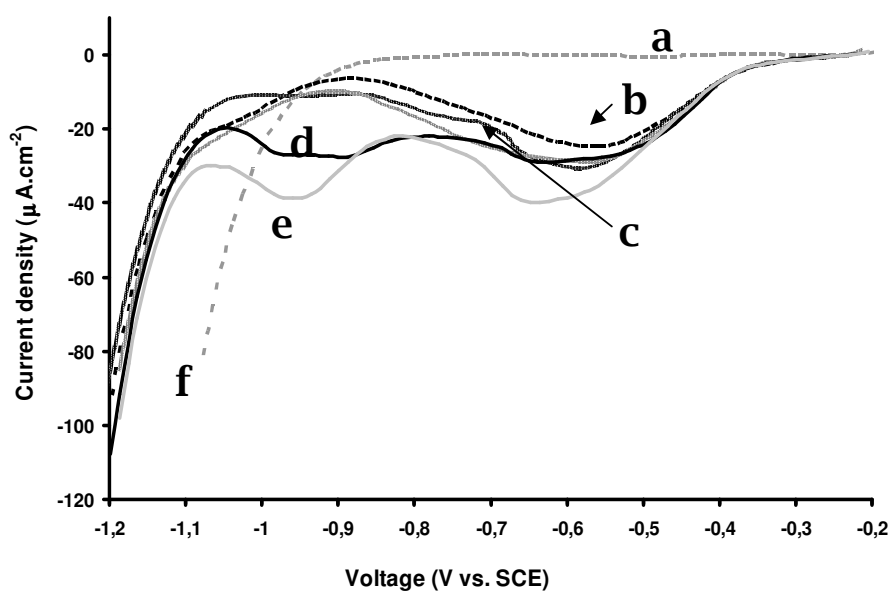


Figure 19. Potentiodynamic reduction curves of copper in deaerated 0.1M KCl solution ($v = 1 \text{ mV} \cdot \text{sec}^{-1}$) of unexposed sample (a), exposed sample in pure air during 10 min (b), 30 min (c), 60 min (d), 120 min (e) and 150 min (f).

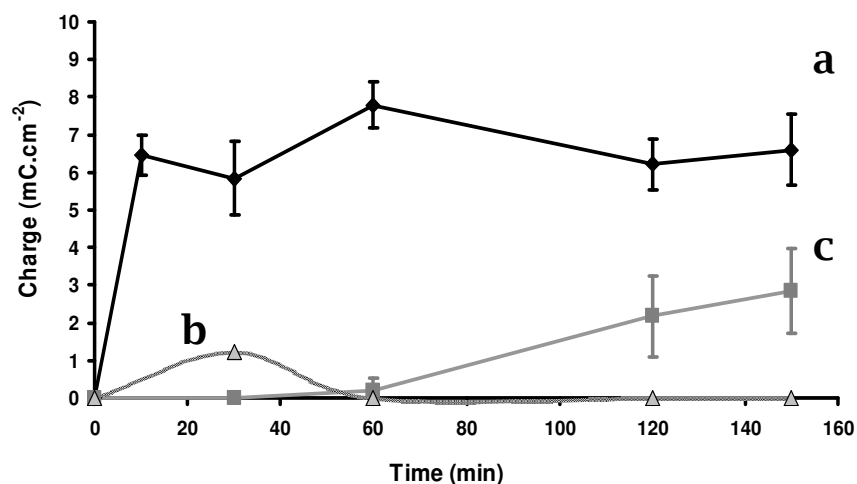


Figure 20. Variation of oxides reduction charge amount with time of (a) amorphous cuprite $(\text{Cu}_2\text{O})_{\text{am}}$, (b) intermediate cuprite $(\text{Cu}_2\text{O})_{\text{in}}$ and (c) crystalline cuprite $(\text{Cu}_2\text{O})_{\text{cr}}$.

5.3.2 Electrochemical reduction of copper compounds produced in acetic acid atmospheres and with anodic polarizations

Potentiodynamyc reduction curves of copper exposed to 500 and 800 ppb of acetic acid at 95% RH were performed. With 500 ppb, is possible to see an increment in the current density with time, indicating increasing of corrosion rate. Similar peaks as when exposures in pure air are found. The peaks are located close to -0.65, -0.81 and -1V vs. SCE during the whole experiment. Thus, we can conclude that these exposures produces three kind of copper (I) oxides at the copper surface. When comparing the two concentrations of acetic acids we found that after 21 days of exposures, the dominant reduction peak is the “bulk” or crystalline cuprite. Fig. 21 displays the reduction charge amount corresponding to exposures in 800 ppb of acetic acid.

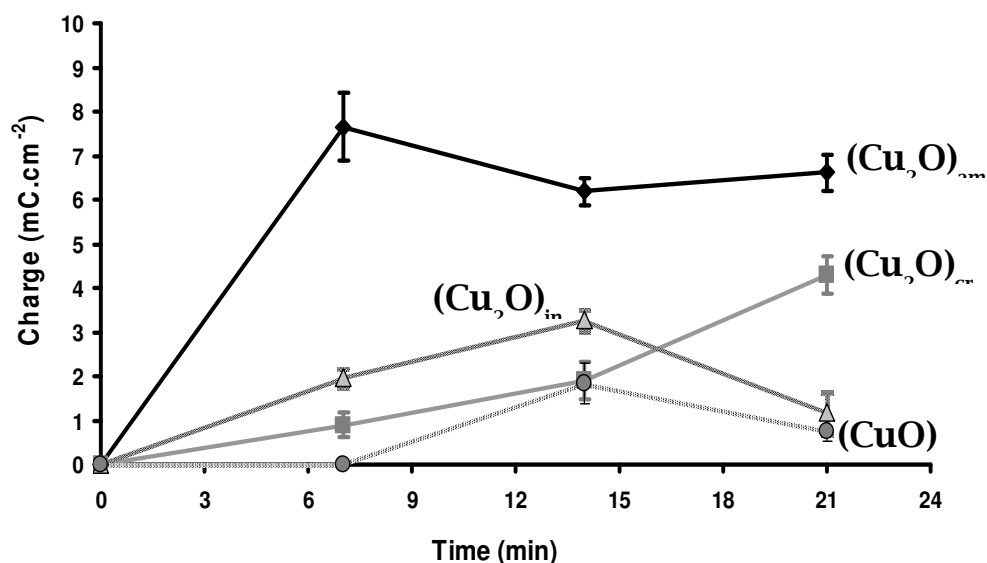


Figure 21. Variation of oxides reduction charge amount with time of copper samples exposed to 800 ppb of acetic acid.

One can see that the amount of the oxides increases as increase the exposure time. The amorphous cuprite amount after 21 days is almost 5 times larger in 500ppb and 2 times in 800ppb of acetic acid. A new peak around -0.42V vs. SCE is seen for exposures of copper in 800ppb of acetic acid. This peak could be related to the presence of copper (II) oxide, named tenorite, with a reduction potential range referred as -0.25 to -0.38 V vs. SCE according with literature^[98].

Fig. 22 displays the reduction curves of electrochemically produced oxides in different concentrations of acetic acid. The first reduction curve shows a broad peak around -0.5V vs. SCE which could be associated with the amorphous oxide. The diminishing of the concentration results in more

oxide amount, reaching a maximum at 0.1M, and then slightly decreases until concentration of 1M. There was not detected the presence of an intermediate oxide. Moreover, crystalline cuprite appears after polarization in 0.01M with a large reduction current density which increases when copper is polarized in 0.001M. This can be interpreted as follows, when decreases the acid concentration to produce the oxides, the pH level increases making a more thermodynamically stable oxides according with the Pourbaix diagram of copper in water^[89].

Likewise, the oxide seems to be more stable, taking into account the small displacement of the reduction peak to more negative potential for the crystalline cuprite. When comparing the electrochemically produced oxides with the atmospheric produced ones, it is possible to see that with concentration exposure of 800ppb of acetic acid could produce similar corrosion levels that with polarization at 0.01M of acetic acid. Like in the case of atmospheric exposures, no evidence of copper acetate was found according with the potentiodynamic reduction curves.

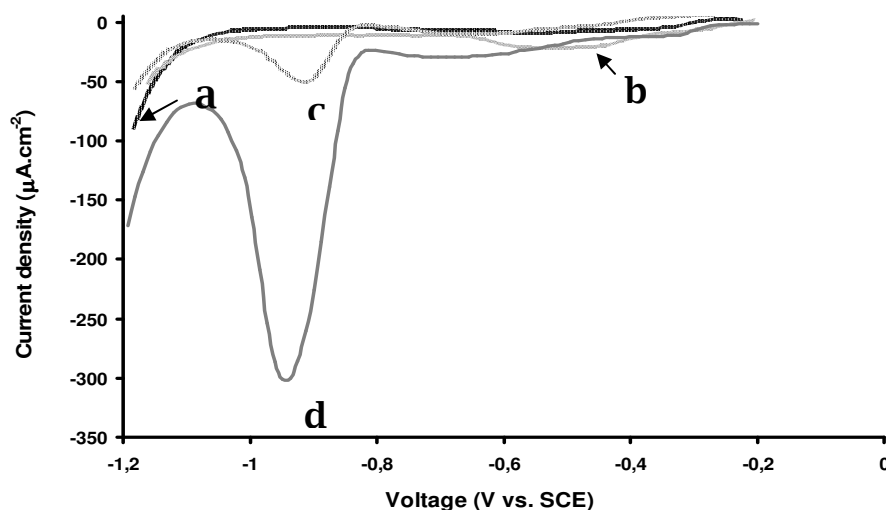


Figure 22. Potentiodynamic reduction curves of copper in deaerated 0.1M KCl solution ($v = 1 \text{ mV} \cdot \text{sec}^{-1}$) after polarization in 1M (a), 0.1M (b), 0.01M (c) and 0.001M (d) of acetic acid solutions.

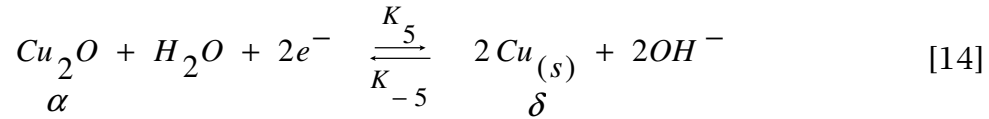
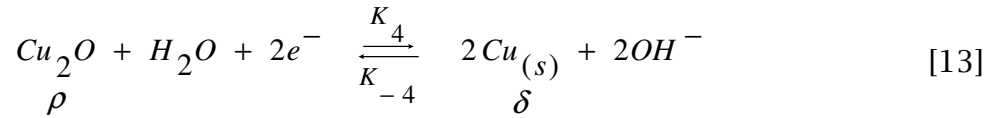
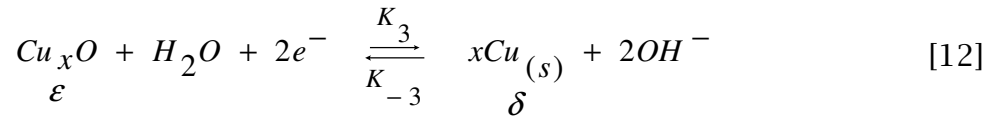
5.3.3 Cathodic reduction model of copper oxides

The cathodic reduction of copper oxides have two reduction sequences, but, in concordance with the pH-E diagram for copper^[89] and previous work with potentiodynamic curves performed in similar conditions ^[68,76,92,98,144-146], we proposed that the reduction of the copper oxides begins with a reduction of the copper (II) oxide in two steps as follows:



where θ , γ and α are the surface coverage of the species Cu(II), Cu*(I) and Cu(I) respectively.

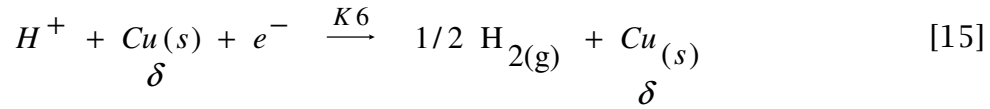
The reduction of the cupric oxide goes with the K_1 reaction to produce adsorbate specie named Cu*(I). The Cu*(I) specie is an intermediate, that lately reduces to copper (I) oxide. Then we have the reduction of the three copper (I) oxides present at the surface, according to:



where ε , ρ and α are the surface coverage of the amorphous cuprite $(Cu_2O)_p$, intermediate cuprite $(Cu_2O)_i$ and crystalline cuprite $(Cu_2O)_c$ and δ is the coverage of the remaining copper surface.

Finally, we have the hydrogen evolution over the copper surface following

the equation:



where K is the potential dependent parameter being $K_i = K_{oi} \cdot \exp(-b_i E)$; $K_{-i} = K_{oi} \cdot \exp(b_i E)$ and $b_i = F/RT$.

No overlapping of this coverages is considered, thus $\delta = 1 - \theta - \gamma - \alpha - \varepsilon - \rho$. We assume that all of the adsorption-desorption follows the Langmuir-type isotherm. Base on this hypothesis, the charge balance gives the total reduction current flowing through the electrode interface:

$$I_{Total-red} = I_{Cu(II)} + I_{Cu_xO} + I_{(Cu_2O)_i} + I_{Cu_2O} + I_{H_2} \quad [16]$$

$$I_{Total-red} = F * [(-K_1\theta) + (-2K_3\varepsilon + (2/x)K_{-3}\delta) + (-2K_4\rho + K_{-4}\delta) + (-2K_5\alpha + K_{-5}\delta) - (K_6\delta)] \quad [17]$$

K_2 does not intervene in the charge balance because the related reaction neither produces nor consumes electrons. The surface coverages are potential- and time dependent parameters. Since I is expressed in A.cm², K implies the concentration expressed in mole.cm⁻². The mass balance of the

species allows one to express the time dependence of the coverages through differential equations:

$$\beta_1 \frac{d\theta}{dt} = \beta v \frac{d\theta}{dE} = -K_1 \theta \quad [18]$$

$$\beta_2 \frac{d\gamma}{dt} = \beta v \frac{d\gamma}{dE} = K_1 \theta + K_{-2} \alpha - K_2 \gamma \quad [19]$$

$$\beta_3 \frac{d\varepsilon}{dt} = \beta v \frac{d\varepsilon}{dE} = -K_3 \varepsilon + K_{-3} \delta \quad [20]$$

$$\beta_4 \frac{d\rho}{dt} = \beta v \frac{d\rho}{dE} = -K_4 \rho + K_{-4} \delta \quad [21]$$

$$\beta_5 \frac{d\alpha}{dt} = \beta v \frac{d\alpha}{dE} = -K_5 \alpha + K_{-5} \delta \quad [22]$$

β is the constant linking the fraction of the coverage and the surface concentration of adsorbed species expressed in mole.cm². β_i values are considered to be equal to 10⁻⁸ (mole.cm²) which corresponds to about one monolayer. The scanning rate v is set to 0.001V.sec⁻¹ according with the experimental setup. The constant K values are computer simulated to give satisfactory fitting results. To perform this, one attempts to reproduce the experimental results by modifying the least number of $K_{0,i}$ values. A calculated potentiodynamic reduction curve corresponding to copper exposed during 14 days in 800 ppb of acetic acid is presented in Fig. 23 compared with the real reduction curve. We found a correlation coefficient of 0.98.

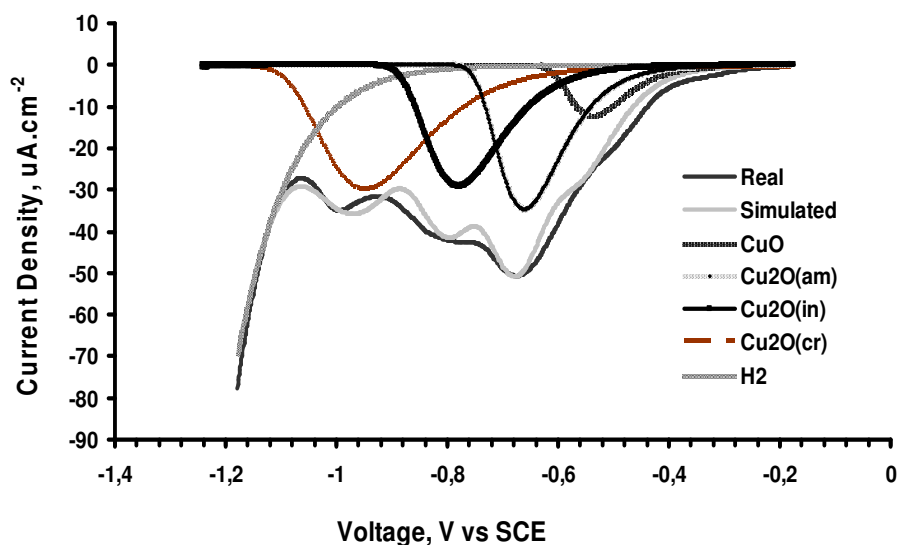


Figure 23. Real and simulated potentiodynamic reduction curves of copper exposed in acetic acid during 14 days.

The evolution of surface coverage with potential corresponding to Fig.23 is presented in Fig. 24. All the oxides present at the copper surface begins with high coverage close to the open circuit potential and then decreases with more negative potential values. The intermediate and amorphous cuprite present coverage of almost zero after -0.9V, meanwhile the crystalline cuprite decreases his coverage after 1V, as we stated before. On the contrary, coverage associated with the hydrogen reduction begins with a value of zero to high potential values, and increases when decreases the potential. At the end of the reduction, close to -1.2V the surface coverage belongs just to the hydrogen evolution as we expected. These means that the proposed model is able to describe the potentiodynamic changes when the electrochemically or

atmospheric produced copper oxides are reduced.

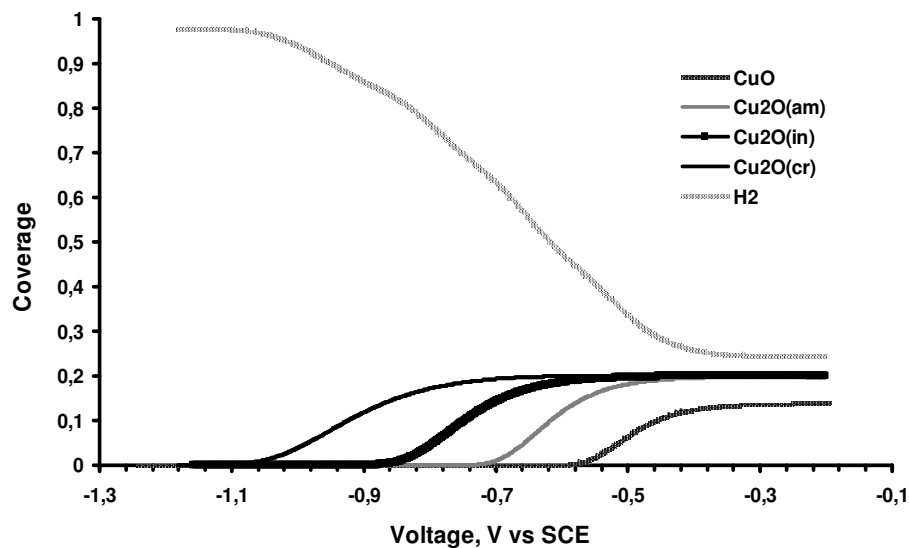


Figure 24. Evolution of the calculated surface coverage with the potential for copper reduction in deaerated 0.1M KCl solution ($v = 1\text{mV}\cdot\text{sec}^{-1}$) after exposure during 14 days in 800 ppb of acetic acid.

The kinetic constant values used for the simulation calculation are summarized in Table II. For almost all experiments the correlation was 0.985 or better except for exposure after 21 days in 800ppb where the correlation was 0.92. This could be explained by the fact that the copper surface has more than one monolayer of corrosion products, in all cases causing that the amount of crystalline cuprite exceeds the simulated amount done with the assumption of one monolayer. The proposed reduction mechanism provides a tentative explanation of the potendynamic reduction curves, however there

is not evidence of the species $\text{Cu}^*(\text{I})$. In this paper we proposed a model that could explain the curves by making several assumptions, but an accurate model is necessary for the entire comprehension of the reduction curves and further pH-local measurements and spectroscopic methods are needed to verify the reaction mechanism.

Table II. Kinetic parameters used to simulate the experimental curves

Time (days)	Concentration (ppbv)	k_{01}	k_{03}	b_3	k_{04}	k_{-04}
7	500	6.9E-14	2E-14	17.6	1.5E-14	8E-13
14	500	7.3E-14	2E-14	17.6	1.4E-14	8E-13
21	500	4.4E-14	2E-14	17.6	1E-14	8E-13
7	800	5.7E-14	2E-14	17.6	2E-14	1E-12
14	800	4.4E-14	2E-14	17.6	1.2E-14	8E-13
21	800	7E-14	3E-14	17.7	3.2E-14	8E-13

Time (days)	Concentration (ppbv)	k_{05}	k_{-05}	b_{-5}	k_{06}
7	500	3.6E-14	2E-11	1.6	4E-15
14	500	3.6E-14	1E-11	1.6	4E-15
21	500	3.1E-14	1E-11	1.6	6E-15
7	800	5.6E-14	3E-11	1.6	4E-15
14	800	3.6E-14	1E-11	1.6	4E-15
21	800	2.7E-14	6E-11	2.2	5E-15

For all experiments, the following parameters were kept constant: $b_1=19.9$;

$k_{-01}=9.1\text{e-}6$; $b_{-1}=1.2$; $k_{-03}=3.2\text{e-}14$; $b_{-3}=2.7$; $b_4=15$; $b_{-4}=1.5$; $b_5=10.9$ and $b_6=10.4$.

6. Concluding remarks

In situ infrared reflection absorption spectroscopy (IRAS), integrated with the quartz crystal microbalance (QCM), was applied to study the initial atmospheric corrosion of copper exposed to humidified air with 120 ppb of acetic, formic or propionic acid. Formic acid resulted in a total corrosion-induced mass gain rate of $6.0 \mu\text{g cm}^{-2}$ after 4 days of exposure, followed by $1.5 \mu\text{g cm}^{-2}$ for acetic acid and $0.5 \mu\text{g cm}^{-2}$ for propionic acid.

A main result is the quantification procedure based on IRAS/QCM and the data reported for absolute values of mass changes of individual species in the corrosion products formed. Copper (I) oxide was identified and quantified with IRAS, QCM and coulometric reduction, giving consistent results that agreed with a relatively accuracy of 12% or better.

The absolute mass gain per surface area of copper carboxylate formed can be used to estimate the deposition velocity for all acids which decreased as

follows: formic acid (0.014 cm s^{-1}) > acetic acid (0.007 cm s^{-1}) > propionic acid (0.003 cm s^{-1}). This difference is what qualitatively would be expected from the amount of non-polar groups of each acid, and their inherent property to decrease the water solubility and kinetically constrain the deposition rate and deposition velocity of the acids into the aqueous adlayer. The difference in total corrosion rate and in rate of carboxylate formation follows the same order as their acid dissociation constant and deposition velocity: formic > acetic > propionic acid.

Other important achievement of this work is the proposal of an electrochemical reduction model. There is no evidence in the literature survey to such model, that it can be used to fit potentiodynamic curves of copper exposed to acetic acid atmosphere. The model was applied to reduction of these compounds in 0.1M KCl, which involves copper (II) oxide [CuO], and three kind of copper (I) oxides [(Cu₂O)_p, (Cu₂O)_i and Cu₂O]. The good agreement of the model with the experimental data allow us to support the idea of the reduction sequence involving the copper oxides, from copper (II) type oxides and then the reduction of three copper (I) oxides.

The results were interpreted using the GILDES model for initial atmospheric corrosion, whereby two spatially separated main pathways could be identified: proton-induced dissolution of cuprous ions followed by the formation of copper (I) oxide, and carboxylate-induced dissolution followed by the formation of copper (II) carboxylate. The first pathway is initially very

fast but levels off, grows more uniformly over the surface and dominates in acetic acid. The second pathway exhibits a more constant growth rate and localized growth of copper (II) carboxylate, and dominates in formic acid. Propionic acid exhibits low rates for both pathways.

7. Future work

The work presented herein describes quantitative *in situ* analysis of the initial atmospheric corrosion of copper induced by three important carboxylic acids. A serious limitation is the lack of chemical characterization of corrosion products with any spatial resolution. Neither IRAS/QCM nor coulometric reduction has any inherent lateral spatial resolution. To reach further, it is proposed to use infrared microscopy based on synchrotron radiation. Such studies have recently been implemented in collaboration with the national synchrotron radiation facility Maxlab in Lund (Prof. Per Uvdal). The results generated so far are only preliminary but they show that a lateral spatial resolution of around one micrometer can be achieved.

The quantified data obtained within this study could furthermore be used for future GILDES computer studies in order to simulate the atmospheric corrosion of copper in carboxylic acid environments.

More experimental studies could also be undertaken with the same quantitative method by exposing copper to other organic constituents, in particular acetaldehyde and formaldehyde, because of their potential accelerating effect on the atmospheric corrosion of copper. Likewise more experimental studies could be performed with local pH measurements to clarify the conditions in which the copper oxide reduction takes place.

Finally, more detailed molecular information of the interface between the copper oxide and the carboxylate overlayers can be obtained with sum frequency generation combined with *ab initio* calculations. Such studies are already underway, and could be of fundamental importance not only in the field of atmospheric corrosion, but also for a better understanding of the important interfacial region between any inorganic substrate and organic overlayer.

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PAPER I



Quantitative In Situ Analysis of Initial Atmospheric Corrosion of Copper Induced by Acetic Acid

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The initial atmospheric corrosion of copper was investigated by means of a quantitative in situ analysis in an atmosphere containing 120 ppb of acetic acid and 95% relative humidity using a quartz crystal microbalance (QCM) integrated with infrared reflection absorption spectroscopy (IRAS). Crystalline cuprous oxide (various structural forms of Cu₂O) and hydrated copper acetate were detected as corrosion products during up to 100 h of exposure. The quantification of data was made possible through an observed linear relationship between the absorbance of vibrations (IRAS) of both phases and the corresponding mass (QCM). The quantification of cuprous oxide was further supported by ex situ coulometric reduction of the corrosion products. The growth rate of cuprous oxide was initially very fast but almost zero after 20 h exposure where it reached an average thickness of 13 ± 1 nm. Copper acetate exhibited a more constant growth rate. Atomic force microscopy showed a uniform growth of cuprous oxide with surface roughness that increased with time and localized formation of copper acetate. The quantified data are consistent with a previously proposed model that involves proton- and acetate-induced dissolution of copper and subsequent precipitation of cuprous oxide and copper acetate.

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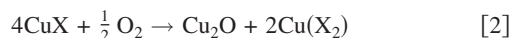
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Organic acids have a noticeable influence on the atmospheric corrosion of copper surfaces, and this has generated several investigations with the purpose of clarifying the mechanisms of patina formation in outdoor or indoor atmospheres induced by organic acids. Graedel found that the anions of organic acids (acetates and, in smaller amounts, formates) constitute between 0.1 and 1% of the total ion concentration in the copper patina exposed in outdoor atmospheres during extended periods of time.¹ Muller and McCrory found that the most abundant organic compound in copper patina is the acetate species.² Fukuda et al. detected carboxylate ions on copper patina formed indoors.³ Persson and Leygraf found corrosion products composed of mixtures of different carboxylates, such as acetates and formates, on samples of copper, zinc, and nickel exposed 1 year in different indoor sites located in Sweden.⁴ Studies made by López-Delgado et al. on the corrosion of copper in the presence of acetic acid at high concentrations (10–300 ppm) and 100% relative humidity (RH) showed the formation of cuprite (Cu₂O), copper acetate hydrate [Cu(CH₃COO)₂·2H₂O], and copper hydroxy acetate [Cu₄(OH)(CH₃COO)₇·2H₂O].⁵ Furthermore, Vilca-Melendez found that the corrosion products, formed on copper samples after 1 year of exposure in a highly contaminated urban atmosphere, consisted of 4.7 mmol/cm² of acetate.⁶ Corbett studied indoor corrosion failures of finned aluminium and copper evaporator tubes and concluded that organic acids produce premature failures on the copper tubes resulting from a very localized form of corrosion known as “ant nest corrosion.”⁷

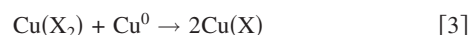
A more detailed mechanism for the interaction between copper and organic acids was proposed by Notoya et al.⁸ It involves the oxidation of copper at surface discontinuities according to



A copper complex [formed between the carboxylate (X) anions and copper cations] is oxidized to form cuprous oxide (Cu₂O) and copper carboxylate as follows



In a final stage of the proposed mechanism, the copper carboxylate complex attacks the cracked surfaces and the cuprous complex reforms. These reactions repeat according to



The cathodic reaction in the acidic solution is



Cano et al. proposed a similar mechanism in acetic acid at high levels of concentration (of the order of 10–300 ppm) based on Notoya's mechanism with the addition of the formation of copper acetate hydrates.⁹

The aim of this paper is to further contribute to the understanding of the initial atmospheric corrosion phenomena by exposing copper to lower levels of acetic acid (120 ppb) at 95% RH and dynamic conditions. This concentration corresponds more closely to actual outdoor or indoor concentrations, which typically range from zero to some tens of ppb. Few corrosion studies have been reported at such low levels of concentration. The study was carried out with infrared reflection/absorption spectroscopy (IRAS) and quartz crystal microbalance (QCM) as in situ techniques in order to identify and possibly quantify the different compounds present on the surface. IRAS is commonly used for identification of chemical species in the surface region, while QCM provides quantitative information on mass changes. One of the main results of this paper is that the final results from both techniques correlate and together provide quantitative in situ identification of corrosion products formed. To check the validity of the quantification procedure, the quantified data have been compared with data obtained from coulometric reduction, this time under ex situ conditions. Finally, the morphology and lateral distribution of corrosion products was studied by ex situ atomic force microscopy (AFM) and grazing incidence X-ray diffraction was performed to obtain structural information of the corrosion products.

Experimental

Copper samples and exposure conditions.— Copper-coated quartz crystals were polished with 1 and 0.25 μm diamond paste, pickled during 30 s in 5% amidosulfonic acid to remove the previous oxide, rinsed three times for 30 s in 99.5% ethanol, and finally dried in nitrogen. The AT-cut quartz crystals have a resonance frequency of 5 MHz and a diameter of 25.4 mm, with a copper film thickness of approximately 350 nm. Copper foils (99.5% purity) of 20 × 20 × 0.5 mm³ were polished by silicon carbide papers down to 1200 mesh, rinsed in ethanol, abraded with 1 and 0.25 μm of diamond paste, and cleaned with ethanol.

The corrosive air was produced from compressed air, which is passed through particle and charcoal filters, and dried using an Adsorption drier Zander KEA 400. The purified air is separated in different streams that go to the humidifier or to the permeation tube

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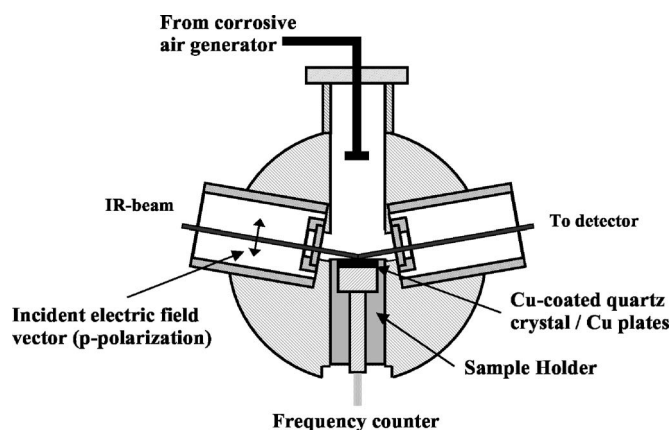


Figure 1. Cross section of the in situ chamber.

(Vici Metronics) containing acetic acid, or directly to the chamber for further air mixing. The different ratios of dry/humid air are regulated by needle valves to get the desired RH and the mixing is performed in a chamber, which is temperature-controlled through a thermostatic bath. The concentration of the acid was verified by weight analysis before and after the exposures. The experiments were carried out at $95 \pm 3\%$ RH with a laminar flow of velocity 3.5 cm/s along the sample surface and a temperature of $19.5 \pm 0.5^\circ$.

Combined IRAS/QCM measurements.—The samples were exposed in a cylindrical in situ chamber integrated with an infrared spectrometer for IRAS measurements and a QCM sensor (see Fig. 1). The IRAS/QCM setup has been described in detail in previous work.¹⁰ The corrosive air enters the chamber from above through a ball valve that allows rapid changes from pure dry air and humidified polluted air. The exposure chamber is made of stainless steel covered inside with Teflon. The QCM sensor is a modified commercial probe in a sample holder made of Teflon and Viton seals located on the bottom of the chamber, with the copper side facing the in situ chamber. Copper plates were positioned with a Teflon holder and an RH and temperature sensor was inserted at the air outlet of the cell.

Reflection absorption spectra were obtained using p-polarized light and averaging 1024 scans at a resolution of 8 cm^{-1} . They were recorded in absorbance units ($-\log R/R_0$), where R is the reflectance of the exposed sample and R_0 the background reflectance. Two different background spectra were collected. The first was obtained after 1 h in dry air ($\text{RH} < 0.1\%$), which was used to follow the water absorbance band during exposure. When the dry background spectrum was recorded, the air was changed to humidified conditions and a second background spectrum was collected after 20 min of exposure to clean humidified air. This spectrum was used in order to reduce the influence of gas-phase water that otherwise overlaps with the carboxylate compounds having similar wavenumbers in their absorption spectra. After this procedure, one spectrum was recorded which was defined as the spectrum for zero time of exposure. The zero spectrum was subtracted from all subsequent spectra in order to eliminate contributions of physisorbed water on the metal surface as well as other water contributions.^{10,11} Finally, after 1 h in humid air, the addition of acetic acid was made.

The frequency shift from the QCM was measured every minute with a frequency counter (Maxtek PM 740) and transformed to a mass change through the Sauerbrey equation¹²

$$\Delta f = -2f_0^2(\Delta m)(\rho_q v_q)^{-0.5} \quad [5]$$

where Δf is the frequency shift, f_0 the frequency at the starting point, ρ_q the density of quartz (2.648 g cm^{-3}), v_q the shear wave velocity ($2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$), and Δm the mass change per unit area (g cm^{-2}). For a QCM oscillating at a fundamental frequency of 5 MHz , the sensitivity is about $18 \text{ ng cm}^{-2} \text{ Hz}^{-1}$, corre-

sponding to approximately 2/3 of a monolayer of water.

Electrochemical measurements.—Electrochemical curves were performed using an EG&G PARC model 273A potentiostat/galvanostat. Coulometric reductions were made following the procedure in ASTM B825-92.¹³ The electrolyte solution was 0.1 M KCl with a saturated calomel electrode (SCE) reference electrode and a platinum mesh counter electrode. The cathodic current density was 0.05 mA cm^{-2} . The solution was rigorously purged with nitrogen to provide air-free conditions 20 min before the measurements and a rapid stream of nitrogen was passed over the electrolyte surface during the reductions. The equivalent thickness of copper oxides was obtained from Faraday's law

$$e = 10000(t \times I \times M)/(A \times n \times d \times F) \quad [6]$$

Here e is the thickness (nm), t is the required time to reduce the oxide (s), I is the galvanostatic current (mA), A is the exposed copper area (cm^2), M is the molecular weight of the copper oxide (g mol^{-1}), F is the Faraday constant ($9.65 \times 10^4 \text{ C mol}^{-1}$), n is the number of Faradays required to reduce one unit of molecular weight of the copper oxide, and d is the specific weight of the reduced oxide (g cm^{-3}). For every coulometric reduction curve (potential vs time) a differential curve was calculated to explain and also obtain the reduction time through consecutive inflection points at both ends of the potential plateaus for each reduced species.

In order to compare the results of IRAS measurements and electrochemical techniques, the exposed samples were masked on the side that was in contact with the Teflon holder of the IRAS chamber using a corrosion protection tape.

AFM measurements.—Copper sheet samples for the AFM measurements were of dimension $20 \text{ mm} \times 20 \text{ mm} \times 0.5 \text{ mm}$ and polished down to $0.25 \text{ }\mu\text{m}$, cleaned in ethanol for 20 min, dried with a fuss-free tissue to remove polishing particles, and then transferred to the exposure chamber. The AFM measurements (Quesant Instrument Ltd.) were carried out in contact-mode operation on copper exposed to 0, 1, 10, 40, and 90 h in the same exposure conditions as for the other measurements.

Grazing incidence X-ray diffraction measurements.—Grazing incidence X-ray diffraction patterns were obtained by a Philips MRD instrument for selected samples using a parallel plate from 10 to 70° , step 0.1° .

Results and Discussion

IRAS.—Figure 2a and b displays the spectra of a copper-coated quartz crystal exposed at 95% RH and 120 ppb of acetic acid. The spectra reveal the intensity of different peaks after 0, 1, 20, 50, 72, 83, and 96 h of exposure. The cuprite (Cu_2O) peak ($\sim 648 \text{ cm}^{-1}$) shows a very fast growth rate during the first hours of the experiments. After 20 h of exposure a broad band at 3400 cm^{-1} appears that can be attributed to stretching vibration of water and possibly also to hydroxyl groups present in the corrosion products. Peaks within the region $1000\text{--}1600 \text{ cm}^{-1}$ can be observed, with more details seen in Fig. 2b showing the final spectrum taken at 96 h. The main peaks at $1420\text{--}1427$ and $1573\text{--}1589 \text{ cm}^{-1}$ correspond to the symmetric, $\nu_s(\text{COO}^-)$, and asymmetric, $\nu_a(\text{COO}^-)$, stretching vibration of the carboxylate ion.¹⁴ The peak at 1357 cm^{-1} corresponds to the symmetric bending vibration of the methyl group, $\delta_s(\text{CH}_3)$, and the peak located at 1064 cm^{-1} to the rocking vibration of the same group, $\rho_r(\text{CH}_3)$. The assignments of the peaks are according to the infrared spectra for sodium acetate, as salt or in solution.¹⁴ The observed separation of the carboxylate peaks $\nu_s(\text{COO}^-)$ and $\nu_a(\text{COO}^-)$ was between 155 and 162 cm^{-1} .

The fact that the intensities of the symmetric and asymmetric vibration of the carboxylate ion exhibit similar time dependence and similar amplitudes suggests a more random orientation of the carboxylate groups on the surface.⁴ After ending the exposure, the atmosphere was changed to dry conditions ($\% \text{RH} < 0.1$), and each

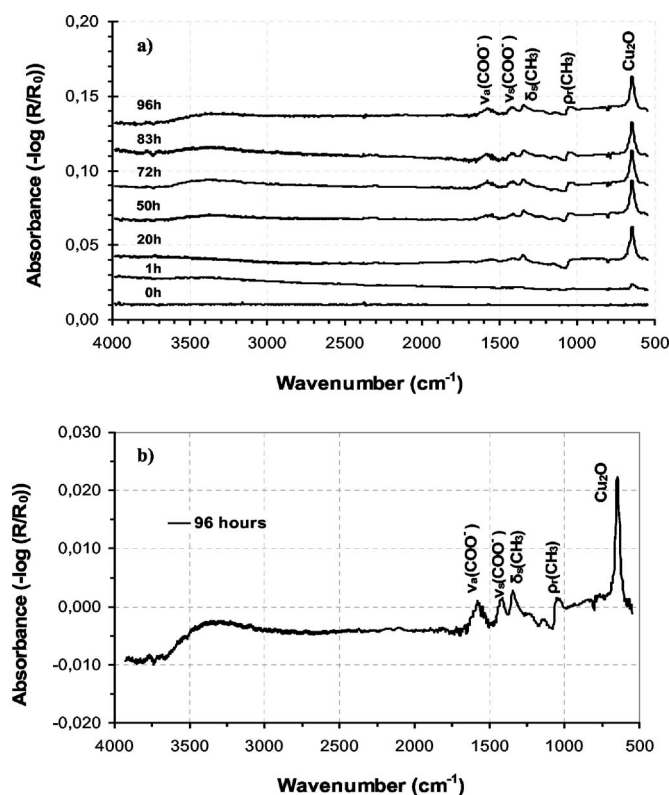


Figure 2. In situ IRAS spectra of copper-coated quartz crystal at 95% RH and 120 ppb acetic acid (a) after different exposure times and (b) after 96 h.

sample was kept dry for 2 h before a new spectrum was monitored. Peaks seen at dry conditions were still detected but the broad band due to the OH groups and water had decreased slightly. This suggests that the corrosion products formed may contain OH groups or H_2O . Possible phases could be hydrated copper acetate $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ or copper hydroxide acetate $[\text{Cu}_4(\text{OH}) \times (\text{CH}_3\text{COO})_7 \cdot 2\text{H}_2\text{O}]$, both of which have previously been observed under similar exposure conditions.⁹

IRAS spectra of copper foils that were exposed in the same way as the copper-coated quartz crystals showed the same peaks and essentially the same intensities as the corresponding IRAS spectra of copper-coated quartz crystals, as displayed in Fig. 3.

To elucidate the corrosion kinetics qualitatively, the relations between the intensity of cuprite and of the symmetric and asymmetric stretching vibration of the carboxylate ion vs exposure time are shown in Fig. 4. The results are the average of three independent

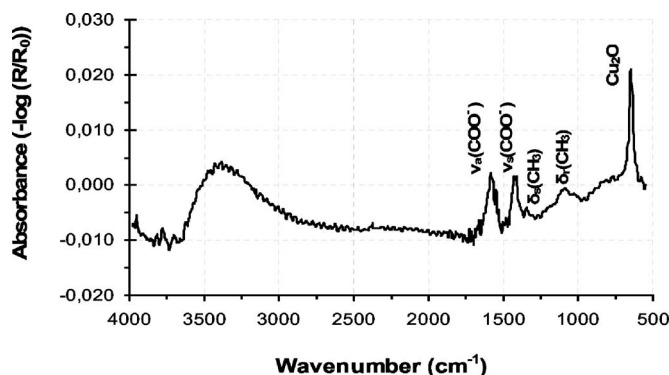


Figure 3. In situ IRAS spectra of copper foil at 95% RH and 120 ppb of acetic acid after 96 h.

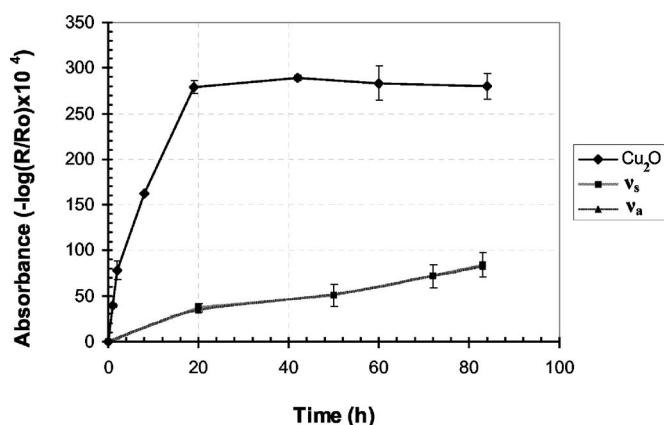


Figure 4. Intensity of symmetric $\nu_s(\text{COO}^-)$ and asymmetric $\nu_a(\text{COO}^-)$ stretching vibrations and of cuprite as a function of exposure time for copper exposed at 95% RH and 120 ppb of acetic acid.

experiments with different, freshly prepared, copper-coated quartz crystals exposed at 95% RH and 120 ppb of acetic acid. A fast growth rate is observed during the first 20 h, after which the intensity is more or less constant. The intensity of the $\nu_s(\text{COO}^-)$ and $\nu_a(\text{COO}^-)$ peaks, of nearly equal absorbance, grew continuously throughout the exposure time.

QCM.—The chemical species identified by IRAS were also quantified by combining the intensity of identified peaks with corresponding mass-gain data, as obtained through QCM measurements at the same exposure time. In previous studies a linear relationship between the absorbance due to the copper (I) oxide and the mass gain measured by QCM was demonstrated.¹⁰ Similarly, a linear relationship between changes of the water absorbance band ($\sim 3400 \text{ cm}^{-1}$) and simultaneous mass changes detected by QCM were deduced in experiments with gold-covered quartz crystals exposed to humidified air.^{10,15}

Figure 5 shows the total mass gain for a copper-coated quartz crystal exposed at 95% RH and 120 ppb of acetic acid after about 100 h of exposure. After completion of the exposure, the sample was left in dry conditions for 2 h, and a decrease of the total mass was observed when changing from humid to dry conditions. The mass loss observed in Fig. 5 was $0.63 \mu\text{g cm}^{-2}$ and is assumed to correspond to the loss of water integrated in the corrosion products or of physisorbed water. The remaining mass originates most likely from copper (I) oxide and water-free copper acetate, e.g., $\text{Cu}(\text{CH}_3\text{COO})_2$.

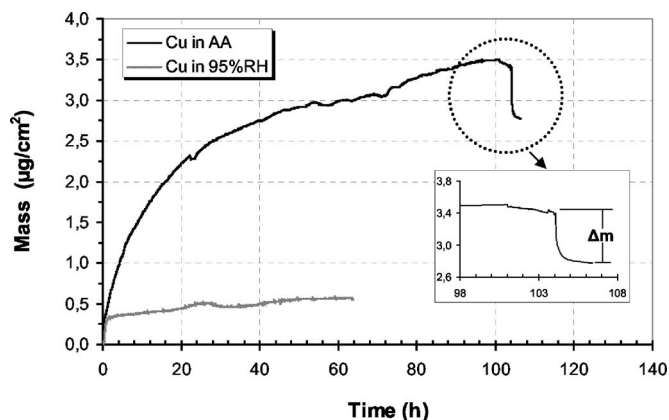


Figure 5. Total mass gain measured by QCM of copper at 95% RH with and without 120 ppb of acetic acid, deduced from QCM combined with IRAS.

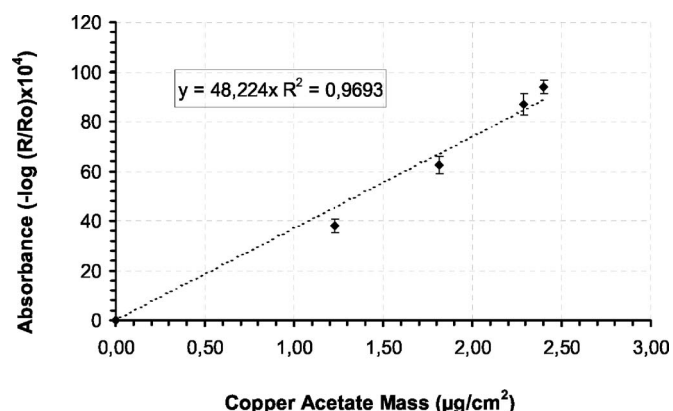


Figure 6. Relation between the intensity of the symmetric vibration of the carboxylate peak band at 1422 cm^{-1} , measured by IRAS, and the equivalent mass of copper acetate from QCM.

The equivalent mass of cuprous oxide and of water vs exposure time was calculated by combining the changes in absorbance of the water band ($\sim 3400\text{ cm}^{-1}$) and the cuprite peak ($\sim 648\text{ cm}^{-1}$) with corresponding changes from QCM. The cuprite quantity was calculated taking into account that QCM only measures the addition or removal of mass, so that the real mass gain due to Cu_2O was multiplied by 8.94 (the molar weight of Cu_2O divided by the molar weight of O) to obtain the actual mass increase of Cu_2O . The data were obtained from exposures of Cu to humidified air (95% RH) with no acetic acid added. The increase in mass due to the formation of copper acetate, finally, was estimated by calculating the difference between the total mass (QCM) and the mass of cuprite (IRAS/QCM) and of water (IRAS/QCM) at every exposure time in humidified air to which acetic acid was added. Similarly as for cuprite, the mass increase due to copper acetate formation was transformed into total mass of copper acetate by multiplying with 1.54 [i.e., the molar weight of $\text{Cu}(\text{CH}_3\text{COO})_2$, 181.5, divided by the molar weight of $2\text{CH}_3\text{COO}^-$, 118].

The relationship between the calculated mass of copper acetate and the corresponding amplitude of the absorbance due to the symmetric vibration of the carboxylate peak is presented in Fig. 6. As is observed, a linear fit is found up to a copper acetate mass of $2.5\text{ }\mu\text{g cm}^{-2}$ with very low scattering in data. It should be stressed that the quantified mass data obtained from IRAS are based on the assumption that the copper acetate consists of $\text{Cu}(\text{CH}_3\text{COO})_2$.

Figure 7 is a summary of the equivalent masses obtained from

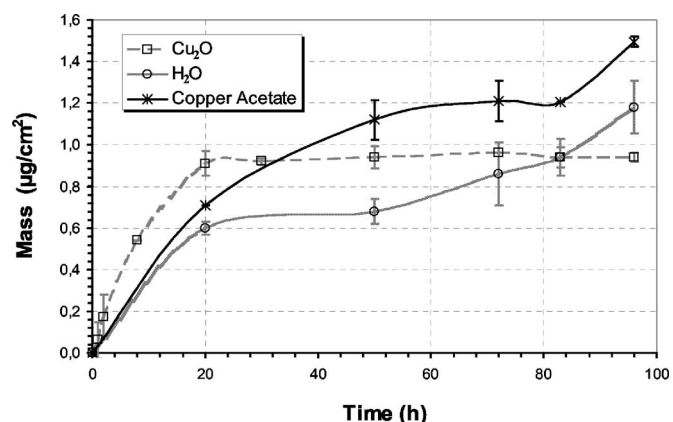


Figure 7. Summary of the equivalent mass of cuprite, water, and copper acetate deduced by combined QCM/IRAS. Copper exposed at 95% RH and 120 ppb of acetic acid.

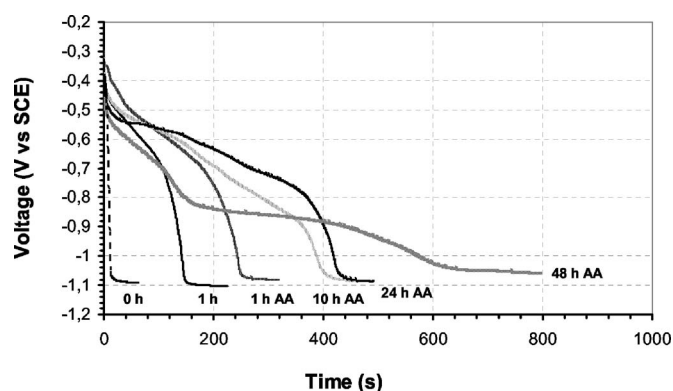


Figure 8. Coulometric reduction curves for copper samples exposed to 95% RH and 120 ppb acetic acid during 1 h (labeled 1 h AA), 10 h (10 h AA), 24 h (24 h AA), and 48 h (48 h AA). Curves before exposure (0 h) and after 1 h (1 h) in humidified air with no acetic acid are also displayed.

IRAS/QCM for cuprite, water, and copper acetate as a function of exposure time. As is evident from the figure, the kinetics show a very fast growth of cuprite in the beginning followed by a more stagnant growth, while the mass increase due to copper acetate and of water follows a more constant mass growth rate. An approximately constant mass increase ratio between copper acetate and water ($\Delta m\text{CH}_3\text{COO}/\Delta m\text{H}_2\text{O}$) close to 1.5 suggests that water may form part of the copper acetate phase. Another contribution to the increasing mass of water may be the increasing surface roughness with exposure time (see later AFM section), from which follows that more physisorbed water may be accommodated along the surface. To validate the quantified masses obtained for cuprous oxide, coulometric reduction of copper foils exposed to the same conditions as the copper-coated quartz crystals were performed, as presented next.

Coulometric reduction.—Figure 8 shows the coulometric reduction curves for copper samples exposed to 95% RH and 120 ppb of acetic acid for several exposure times. A reduction of an unexposed sample (0 h) was made in order to compare the results before and after the exposure. This unexposed sample shows a small plateau between -400 and -500 mV vs SCE . The plateau is assigned to the reduction of an amorphous copper (I) oxide¹⁶ present before the exposure. When the oxide layer is completely reduced, the potential falls down until the reduction plateau is attained corresponding to the hydrogen evolution close to -1100 mV vs SCE . All samples investigated exhibit a hydrogen evolution potential at approximately -1100 mV vs SCE . After 1 h in pure humid air the amorphous copper (I) oxide grows, as is also confirmed by the cuprite absorbance measured by IRAS (Fig. 4). With the addition of acetic acid, new plateaus appear around -500 to -550 mV vs SCE and -750 to -850 mV vs SCE , respectively. The presence of these plateaus has previously been associated with two different cuprous oxides.^{5,16-20} The more easily reduced phase (from -500 to -550 mV vs SCE) corresponds to a precursor Cu_xO that has the same crystallographic structure as Cu_2O but with a mixed valence $[\text{Cu}(0) + \text{Cu}(I)]$ containing interstitial metallic copper in the Cu (I) oxide phase. The less easily reduced phase is attributed to the reduction of crystalline and stoichiometric Cu_2O .^{18,21}

When the exposure time increases, the quantity of the cuprous oxide increases, as is observed by the larger reduction time. To obtain better confidence, the derivative of the curves was calculated, as is shown in Fig. 9, and the corresponding thickness derived (Table I). The thickness of the precursor copper (I) oxide seems to increase until 24 h (see Fig. 8) and then slightly decrease. Meanwhile, the crystalline copper (I) oxide increases with exposure time. The equivalent mass and thicknesses of cuprite shown in Table I include both the amorphous, crystalline, and total copper (I) oxide,

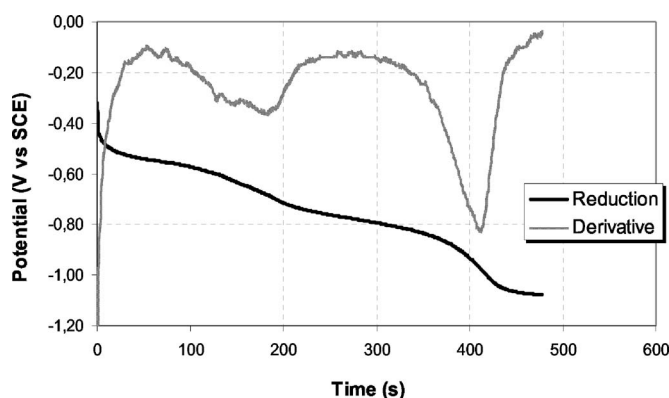


Figure 9. Coulometric reduction curve and its derivative for copper exposed to 95% RH and 120 ppb acetic acid during 10 h.

assuming the same density of 6.0 g cm^{-3} for all phases. Homogeneous layers and complete reduction of all species is also assumed.

As evidenced from Table I, the thickness of the total mass of the cuprite layer increases throughout the whole exposure time, showing a rapid growth rate during the first 10 h and then a more moderate growth rate until 96 h. With IRAS a tendency of a reduction of the cuprite peak could be discerned at longer exposure time (see Fig. 4), probably due to a loss of copper surface reflectivity with larger amounts of corrosion products present. Hence, within the limits of accuracy, the data imply that copper acetate does not form at the expense of cuprite but rather forms in a process parallel to the cuprite formation.

The copper acetate was barely detected with coulometric reduction, indicating that the sensitivity of the coulometric technique is not as high as that of IRAS. It may also be that the initial copper acetate compound has a higher solubility during earlier stages and therefore dissolves when submerged in the solution.

The thickness of the total copper (I) oxide layer,^{16,22} as obtained from coulometric reduction, was also compared with data from IRAS/QCM (Fig. 4 and 7). The results are displayed in Fig. 10, in which the IRAS absorbance of cuprite for various exposure times has been plotted both against thickness as obtained with coulometric reduction and as obtained with IRAS/QCM. The data exhibit a linear relation with excellent agreement between all three methods. The scattering of data is relatively low and the values are the results of triplicate experiments after 0, 1, 10, 24, 48, and 96 h.

AFM.—AFM measurements in contact mode were used to investigate the morphology of the corrosion products and how it changes with the exposure time. Figure 11 shows a series of images, including that of a freshly polished copper surface (a) and those of copper surfaces that have been exposed to 95% RH and 120 ppb of acetic acid during 10 (b), 30 (c), and 90 h (d). The polished surface before exposure displays scratches from the diamond polishing procedure, whereas the exposed samples exhibit cubic-shaped crystal-

Table I. Average mass and thickness of phases in corrosion products on copper exposed at 95% RH and 120 ppb acetic acid.

Time (h)	Average mass ($\mu\text{g/cm}^2$) and thickness (nm) Mass/thickness		
	Cu ₂ O precursor	Cu ₂ O crystalline	Cu ₂ O total
1	$1 \pm 0.2/1 \pm 0.4$	$3 \pm 0.1/5 \pm 0.2$	$3 \pm 0.3/5 \pm 0.4$
10	$5 \pm 0.3/8 \pm 0.6$	$2 \pm 0.7/3 \pm 1.2$	$7 \pm 0.7/11 \pm 1.2$
24	$5 \pm 0.4/9 \pm 0.7$	$2 \pm 0.1/4 \pm 0.2$	$8 \pm 0.3/13 \pm 0.5$
48	$3 \pm 0.2/6 \pm 0.4$	$5 \pm 0.3/8 \pm 0.5$	$8 \pm 0.6/13 \pm 0.9$
96	$3 \pm 0.6/5 \pm 1$	$6 \pm 0.4/10 \pm 0.7$	$9 \pm 1/15 \pm 2$

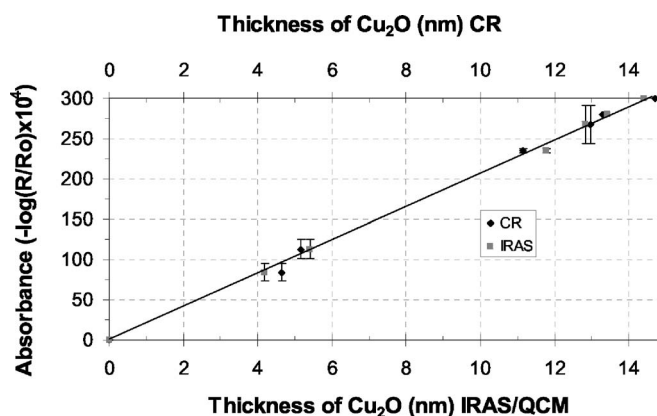


Figure 10. Relation between the absorbance of the cuprous oxide peak band at 648 cm^{-1} measured by IRAS, cuprite thickness obtained by IRAS/QCM, and cuprite thickness obtained by coulometric reduction.

lites, most likely from cuprite, that seem to cover the whole copper surface. The dimensions of the crystallites increase with exposure time, both along and perpendicular to the surface, ranging from typically 150 nm after 10 h, over 350 nm after 30 h, to 1000 nm after 90 h. As a consequence, the surface topography of the cuprite layers also increases with time, especially between 30 and 90 h, although the thickness of the cuprite layer exhibits no significant increase (Fig. 7) during the same time interval.

Figure 12a exhibits AFM topography images of a copper sample exposed for 90 h that shows the formation of locally growing features over a more uniform film of cuprite. These rounded features are largely attributed to copper acetate, in accordance with the IRAS spectrum from the same exposure time. The precipitation of the acetate seems to be localized, with an average diameter after 90 h of between 5 and 10 μm and an average height of several hundreds of nm. Smaller cuprite crystallites cover the whole surface, as discussed in Fig. 11, whereas only larger cubic-shaped crystallites are visible in Fig. 12a. An area in the central part of this figure has been expanded in Fig. 12b, exhibiting a rounded large crystallite, charac-

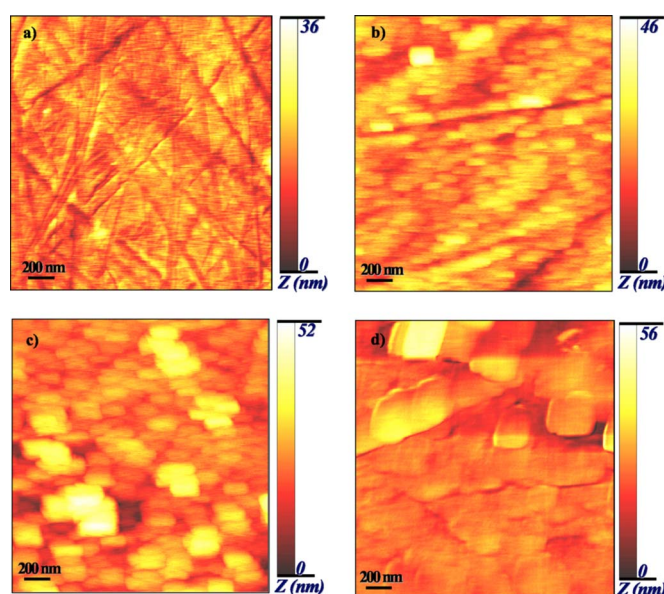


Figure 11. (Color online) AFM images of a copper surface (a) before exposure and after (b) 10 (c) 30, and (d) 90 h of exposure at 95% RH and 120 ppb of acetic acid. The scan size is $4 \mu\text{m} \times 4 \mu\text{m}$ and the z range for each image is indicated.

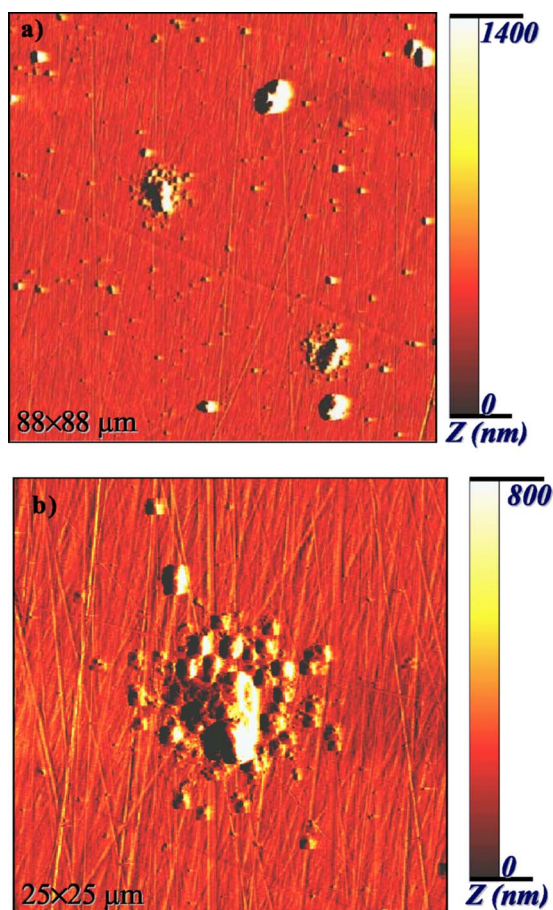


Figure 12. (Color online) AFM images of a copper surface exposed at 95% RH and 120 ppb of acetic acid after 90 h with scan size (a) $80\ \mu\text{m} \times 80\ \mu\text{m}$ and (b) $20\ \mu\text{m} \times 20\ \mu\text{m}$. The z range is $1.3\ \mu\text{m}$ from black to white.

teristic of copper acetate, surrounded by many cubic-shaped smaller crystallites from cuprite. This and other similar observations suggest that the formation of copper acetate is accompanied by an enhanced formation of cuprous oxide.

To conclude, the AFM images reveal the uniform growth of cubic-shaped cuprous oxide crystallites that increase in size from 100 nm to $1\ \mu\text{m}$ and also the local growth of rounded copper acetate crystallites sized 5–10 μm .

Grazing incidence X-ray diffraction.—The grazing incidence diffractograms for copper plates exposed during 4 days to 95% RH and 120 ppb of acetic acid show the only crystalline phases detected to be copper (I) oxide (Cu_2O) and some copper (II) hydroxide $\text{Cu}(\text{OH})_2$, but no crystalline phases due to copper acetate were observed. The results suggest that the copper acetate may be amorphous or present in amounts below the detection level.

General.—The complementary nature of IRAS and QCM and the fact that a good agreement can be found between the quantified data from both techniques enables us to deduce the absolute amounts of water, cuprite, and copper acetate in the corrosion products formed under in situ conditions. Further support for the quantification procedure is given by coulometric reduction, again showing good agreement with the quantified IRAS/QCM data. From Fig. 6 and 10 it can be concluded that the equivalent thickness of cuprite or the mass-per-surface-area unit of copper acetate for a given IRAS absorbance can be estimated with a relative accuracy of 10% or better.

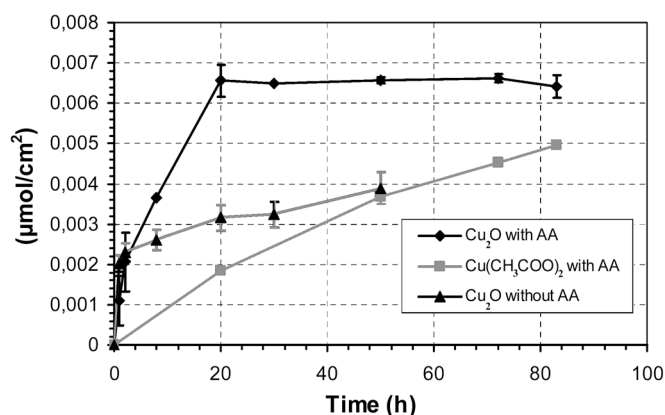
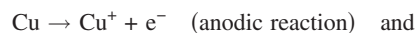


Figure 13. Molar quantity ($\mu\text{mol cm}^{-2}$) of cuprite formed with and without acetic acid and of copper acetate as a function of exposure time for copper exposed at 95% RH, 20°C , and 120 ppb acetic acid.

Based on the IRAS/QCM results, the molar quantities of cuprite and of copper acetate vs exposure time have been calculated and are presented in Fig. 13. When copper is exposed to humidified air (95% RH) without acetic acid, it forms immediately a film of cuprous oxide (Cu_2O), characterized by a fast initial growth rate and a slower growth rate with prolonged exposure. With a relative accuracy of 10% the quantified data can be fitted to follow a logarithmic growth rate, such as the Cabrera–Mott theory for low-temperature corrosion.²³ In this logarithmic growth rate the growth is based on cation migration under the influence of a potential that builds up across the growing oxide film. However, when copper is exposed to humidified air with 120 ppb of acetic acid, the growth rate is initially very fast but levels off with a thickness of about 13 nm after the first 20 h of exposure. The cuprite growth is initially faster with acetic acid than without and shows a growth rate that deviates from logarithmic. The cuprous oxide covers the whole copper surface, as seen in Fig. 11, and the cuprite crystallites grow in size up to 90 h (see previous AFM section), although the average cuprite thickness does not increase after the first 20 h.

According to the reaction mechanisms proposed by Notoya,⁸ the formation of a carboxylate complex ($\text{Cu}-\text{CH}_3\text{COO}$) should produce twice as many moles of copper acetate [$\text{Cu}(\text{CH}_3\text{COO})_2$] than of cuprous oxide (Cu_2O), (see Reaction 2). However, as is shown in Fig. 13, the growth of cuprite is faster than copper acetate and exhibits different kinetics, which shows that the actual reaction mechanism is different from Reaction 2.

Instead, the quantitative results presented in this paper are proposed to follow the general atmospheric corrosion mechanism outlined in the GILDES model.²⁴ It includes the formation of carboxylate containing surface species⁷ and the concept of proton- and ligand-induced dissolution.^{4,24} A prerequisite for the mechanism is the presence of the aqueous adlayer, which under current conditions amounts to approximately $1\ \mu\text{g cm}^{-2}$ (Fig. 7), corresponding to approximately 30 monolayers of physisorbed water. The aqueous adlayer produces surface hydroxyl bonds over the cuprite surface, and the dominant electrochemical reactions are as follows



The hydroxyl bonds have properties for ion exchange and can be replaced by ions present in the aqueous adlayer, such as protons (H^+) and acetate ions (CH_3COO^-), which have formed upon dissociation of acetic acid in the aqueous adlayer. The result is a ligand-induced dissolution triggered by the weakness of the surface metal atoms that participate in the ion exchange.^{24,25} Copper dissolves initially as cuprous ions²⁴ that may either react with liberated hy-

droxyl ions (OH^-) to form cuprous oxide or may oxidize to cupric ions, react with acetate ions, and form copper acetate. As the dissolution process continues, precipitates of copper acetate are formed and grow over localized points of the surface until they reach a mean diameter of between 5 and 10 μm after 90 h of exposure. The copper acetate may tentatively react with copper and reform the surface complex⁸ (as proposed in Eq. 3), which creates conditions for more copper to be dissolved and more cuprous oxide and copper acetate to precipitate in the aqueous adlayer. A similar ligand-induced dissolution mechanism has recently been proposed for zinc exposed to acetic acid and acetaldehyde, evidencing the presence of adsorbed acetate species and subsequent precipitation of zinc-acetate.²⁶ Studies are currently ongoing in the author's laboratory to elaborate the model further through similar studies of atmospheric corrosion of copper induced by formic acid and propionic acid.

Conclusions

The initial atmospheric corrosion copper in 120 ppb of acetic acid at 95% RH and 20°C has been followed by an integrated IRAS/QCM system. Cuprous oxide, copper acetate, and water were identified as surface species during ongoing corrosion, and their absolute amounts could be quantified as a function of exposure time up to 100 h. The quantification procedure is based on linear relationships observed between the absorbance of species detected by IRAS and corresponding mass changes monitored by QCM. At a given IRAS absorbance, the absolute amounts per surface area of cuprous oxide and of copper acetate can be estimated with a relative accuracy of 10% or better.

The integrated IRAS/QCM measurements, supported by coulometric reduction of surface species and AFM, show an initial fast and uniform formation of a cuprous oxide that reaches 13 ± 1 nm thickness (equivalent to 6.5 ± 0.5 nmol/cm²) after some 20 h. With prolonged exposure the average thickness remains the same within the experimental accuracy, whereas an increase in cuprous oxide crystallites is observed from 100 nm to 1 μm . Copper acetate, most presumably in hydrated form, exhibits a localized growth and forms rounded features with diameter from 5 to 10 μm and a height of 100 nm.

The results can be interpreted following the general atmospheric corrosion model GILDES. In this model proton- and ligand-induced dissolution of cuprous ions form a central part, followed either by formation and precipitation of cuprous oxide or by oxidation of cuprous to cupric ions and subsequent formation and precipitation of copper acetate.

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PAPER II



Initial Atmospheric Corrosion of Copper Induced by Carboxylic Acids

A Comparative In Situ Study

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A procedure based on infrared reflection absorption spectroscopy integrated with a quartz crystal microbalance has been developed and used for comparison of initial atmospheric corrosion of copper induced by formic, acetic, and propionic acid. The absolute mass of individual constituents of corrosion products formed, mainly cuprous oxide or cuprite, copper carboxylate, and water or hydroxyl groups, could be obtained under in situ conditions during exposure in 120 ppb of carboxylic acid concentration, 95% relative humidity, 20°C, and up to 96 h of exposure. The quantitative data exhibit consistency between all acids and with postanalysis performed by coulometric reduction. Two spatially separated main pathways have been identified: a proton-induced dissolution of cuprous ions followed by the formation of copper(I) oxide, and a carboxylate-induced dissolution followed by the formation of copper(II) carboxylate. The first pathway is initially very fast but levels off, grows more uniformly over the surface, and dominates in acetic acid. The second pathway exhibits a more constant growth rate and localized growth, and dominates in formic acid. Propionic acid exhibits low rates for both pathways. The difference between the carboxylic acids with respect to both total corrosion rate and carboxylate-induced dissolution can be attributed to their dissociation constants and deposition velocity. © 2007 The Electrochemical Society. [DOI: 10.1149/1.2773627] All rights reserved.

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Atmospheric corrosion of copper induced by organic acids is a phenomenon that has been observed for a long time, and it is well-established that these acids form one of the dominant classes of organic compounds in the atmosphere.¹ Especially indoors, metal-carboxylates and other organic compounds have been found as constituents in corrosion products on, e.g., sculptures and electronic devices. Typical indoor concentrations for acetic acid and formic acid are around 20 ppb (volume parts per billion).² Cano et al.³ found an early failure in a copper tubing used in air-conditioning units to be induced by organic acids in combination with sulfur- and chloride-containing corrosive species. The same research group performed investigations on copper samples exposed to synthetic air with acetic acid or formic acid at concentrations from 0 to 300 ppm (volume parts per million) at 100% relative humidity (RH). The corrosion products formed in acetic acid contained cuprite, copper acetate dehydrate, and copper hydroxy acetate dihydrate, whereas with formic acid the corrosion products contained cuprite, copper hydroxide monohydrate, and copper formate tetrahydrate.⁴⁻⁶ The corrosion rate reported was higher in acetic acid than in formic acid. The corrosion behavior of copper immersed in aerated propionic acid solutions was studied by Baah⁷ exploring the influence of concentration and exposure time on corrosion rate. Echavarría et al.⁸ performed exposures of copper in propionic acid vapors ranging from 10 to 300 ppm at 100% RH. The identified copper compounds in the corrosion products were cuprite, copper hydroxide, and propionate or copper hydroxy propionate. More recently, Cano et al.⁹ studied the copper corrosion in oxalic acid vapor exposures at similar conditions as above, and found that the patina formed contained cuprite and copper butyrate. When comparing the results under similar exposure conditions, relative humidity, and concentration of organic acid during exposure times up to 21 days, the corrosivity decreased in the following order: acetic acid > formic acid > butyric acid > propionic acid. The trend followed the dissociation rate of the acids. The exception was formic acid, which was explained by a stronger adherence of corrosion products formed in the presence of this acid.⁹

As is evident from this brief literature survey, most studies of atmospheric corrosion of copper induced by carboxylic acids have been performed at concentrations higher or much higher than 1 ppm,

far above realistic indoor or outdoor concentrations. In order to compare the corrosion effect of carboxylic acids on copper under more realistic concentrations, this paper aims at characterizing and quantifying the initial corrosion rates and corrosion products on copper exposed to acetic, formic, and propionic acid in the ppb level range. The study is based on a unique instrumental setup with infrared-reflection absorption spectroscopy integrated with a quartz crystal microbalance (QCM) for quantitative in situ surface analysis, as was previously described in detail for the initial atmospheric corrosion of copper induced by acetic acid.¹⁰

Experimental

Two kinds of copper specimens were used to follow the corrosion processes. Copper-coated quartz crystals (Maxtek) with a resonance frequency of 5 MHz were polished with 1 and 0.25 μm diamond paste and ethanol cleaning in between, then pickled during 30 s in 5% amidosulfonic acid (H_3NSO_3), and finally rinsed three times in ethanol (99.5% purity) and flushed in nitrogen. The samples had a diameter of 25.4 mm with an evaporated chromium film (approximately 50 nm thick) to improve the adhesion between the quartz and copper, and a copper film of 350 nm thickness. Besides the copper-coated quartz crystals, specimens of copper (99.5% purity) sized $20 \times 20 \times 0.5$ mm were abraded with silicon carbide papers down to 1200 mesh, rinsed in ethanol, polished with 1 and 0.25 μm diamond paste, and cleaned with ethanol.

The corrosive air was produced by mixing humid and dry air using an adsorption drier (Zander KEA 400), with the dry air passing along a permeation tube (Vici Metronics) containing acetic, formic, or propionic acid. The concentration of each acid was around 120 ppb, as verified by weight analysis of the permeation tube before and after the exposures. The exposures were carried out at $95 \pm 3\%$ RH with a laminar flow of velocity 3.5 cm/s along the sample surface and a temperature of $19.5 \pm 0.5^\circ$. These exposure conditions can be compared with normal indoor conditions, typically from 0 to 20 ppb of acid concentration, 30 to 80% RH, and 10 to 100 cm/s air flow rate.

The combined infrared reflection absorption spectroscopy (IRAS)-QCM setup consists of a cylindrical chamber made of stainless steel where the internal surfaces are covered with Teflon. The exposure chamber is integrated with an infrared spectrometer (Bio-Rad FTS 60A) for in situ surface chemistry monitoring and a QCM sensor (Maxtek PM 740) for in situ mass change measurements. All spectra were taken with a resolution of 8 cm^{-1} using *p*-polarized light and averaged over 1024 scans. They were recorded in absorbance units $[-\log(R/R_0)]$, where R is the reflectance of the exposed

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sample and R_0 the reflectance of the background. The QCM measurements were obtained with a frequency counter, taking one data point per minute and transforming frequency shift to mass change by using the Sauerbrey equation.¹¹

In addition to these in situ measurements, coulometric reduction of copper plates was carried out in order to quantify the amount of copper(I) oxide in the corrosion products and validate the results obtained by the combined IRAS-QCM analysis. The samples were masked on one side using a corrosion protection tape. The reduction curves were performed using an EG&G PARC model 273A potentiostat-galvanostat following the procedure in ASTM B825-92.¹² The electrolytic solution was 0.1 M KCl with a SCE reference electrode and a platinum mesh counter electrode. The cathodic current density was 0.05 mA cm⁻². The solution was rigorously purged with nitrogen to provide air-free conditions 20 min before each measurement, and a rapid stream of nitrogen was passed over the electrolyte surface during the reductions. The equivalent thickness of copper(I) oxides was obtained from Faraday's law.

The morphology after different exposures was followed with atomic force microscopy (AFM, Quesant Instrument, Ltd.). Prior to exposure the copper samples were polished down to 0.25 μm , cleaned in ethanol for 20 min, dried with a fuzz-free tissue to remove polishing particles, and then transferred to the exposure chamber. The AFM measurements were carried out in contact mode operation after exposure of copper before and after 96 h with the same exposure conditions as described above.

Selected samples were also analyzed by grazing incidence X-ray diffraction (GIXRD) obtained with a Philips MRD instrument at the Department of Materials Chemistry, Uppsala University, using a parallel plate from 10 to 70° in steps of 0.1°.

Results and Discussion

Interpretation of IRAS spectra.—Figure 1 displays the spectra of copper-coated quartz crystals exposed at 95% RH and 120 ppb of (a) acetic, (b) formic, and (c) propionic acid, respectively, after 96 h. The spectrum for the acetic acid case has been discussed previously.¹⁰ It contains a copper(I) oxide peak (648 cm⁻¹) as the most intensive peak, a broad band at 3400 cm⁻¹ attributed to stretching vibrations of water and possibly also due to hydroxyl groups as part of the corrosion products. Peaks due to the bending (δ_s – 1357 cm⁻¹) and rocking (ρ_r – 1064 cm⁻¹) vibrations of the CH₃ group are also seen.⁴ Two main peaks with approximately the same intensity and corresponding to the symmetric (ν_s – 1420 to 1427 cm⁻¹) and antisymmetric (ν_a – 1573 to 1589 cm⁻¹) stretching vibrations of the carboxylate ion¹³ are used in a later section to follow the kinetics of the copper carboxylate growth. Figure 1b displays the corresponding peaks for formic acid. Similar peaks as for acetic acid are found for the OH-water region (broad band at 3400 cm⁻¹) and for copper(I) oxide (655 cm⁻¹). The most intense peak of the spectrum corresponds to the antisymmetric stretching vibration (ν_a – 1597 to 1604 cm⁻¹), whereas the symmetric stretching vibration (ν_s – 1354 cm⁻¹) shows lower intensity.¹³ Both peaks increase in intensity with exposure time. The peak next to the symmetric stretching vibration of carboxylate¹⁴ is the in-plane CH bend (δ) at 1381 cm⁻¹. Peaks due to the CH stretching vibrations ($\sim 2808\text{cm}^{-1}$), CH out-of-plane bending vibration (π) at 1056 cm⁻¹, and some deformations around 1100 cm⁻¹ are also seen.¹³ The bending vibration of the carboxylate group¹³ (δ) is seen at around 763 cm⁻¹. A sharp peak around 3572 cm⁻¹ is due to the vibrations of hydroxyl groups in Cu(OH)₂, and corresponds to free OH not involved in any hydrogen bonds.¹⁵ This peak is only seen upon exposure in formic acid, not in the other acids studied.

The spectrum for propionic acid exhibits much smaller peaks than for formic acid or acetic acids at similar exposure conditions. In order to better highlight the peaks of propionic acid, the y-axis of Fig. 1c was expanded seven times relative to the y-axis of Fig. 1a and b. The peaks around 1600 and 1419 cm⁻¹ correspond to the antisymmetric and symmetric stretching vibration of the carboxylate

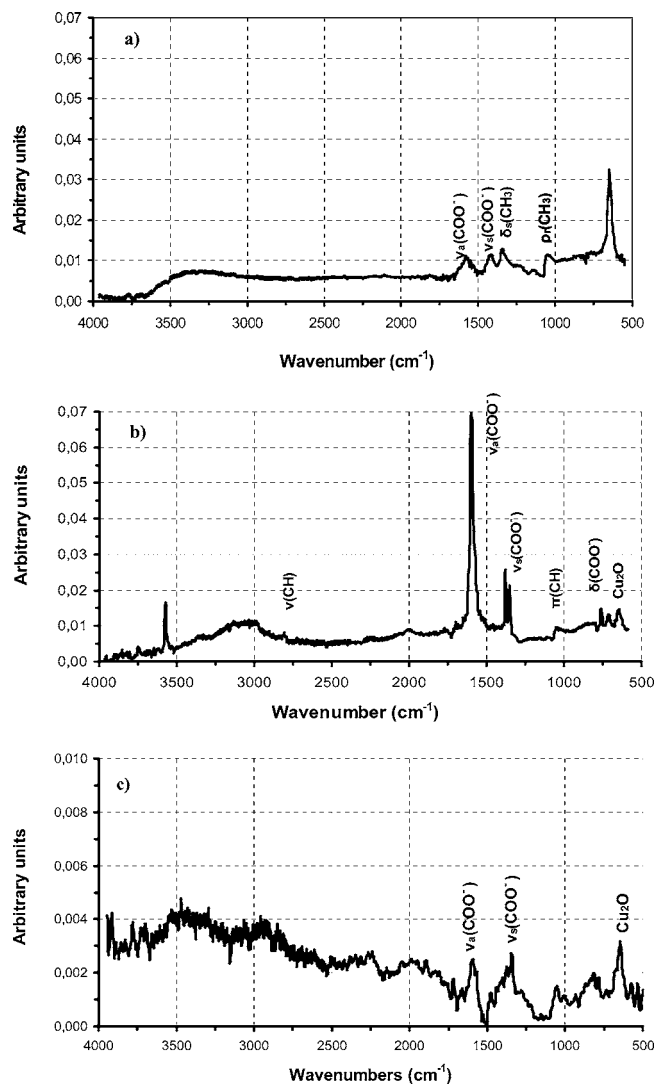


Figure 1. In situ IRAS spectra of copper-coated quartz crystals after 96 h exposure in 120 ppb of (a) acetic acid, (b) formic acid, and (c) propionic acid, at 95% RH and 20 °C.

group, indicating the formation of copper propionate.⁸ Other important peaks originate from cuprite (648 cm⁻¹) and from OH/H₂O (3400 cm⁻¹).

The absence of any peak around 1690–1770 cm⁻¹, where the C=O stretch of physisorbed and solvated carboxylic acid would be expected,¹⁶ suggests evidence of copper carboxylate formation, rather than adsorption of the carboxylic acid. The difference in wave number between the antisymmetric and symmetric stretching vibration of the carboxylate ions (Δ) for the three acids are between 155–162 cm⁻¹ for acetic, 247–254 cm⁻¹ for formic, and 181 cm⁻¹ for propionic acid. The Δ value for acetic acid is very close to the data reported for copper(II) acetate in aqueous solution¹⁷ and for copper exposed to 10 ppm of acetic acid,⁵ which might suggest ionic or bridging acetate coordination.^{17,18} The Δ -value for formic acid is in agreement with that reported by Bastidas et al.,⁶ and in a similar way the Δ -value for propionic acid is in agreement with that reported by Echavarría et al.⁸ for copper exposed to propionic acid. All Δ -values observed provide further evidence for the formation of copper carboxylates.

Kinetics of copper carboxylate growth based on IRAS.—In order to follow the kinetics of copper carboxylate formation, the absorbance of the antisymmetric vibration ν_a (Fig. 2a) and the ratio

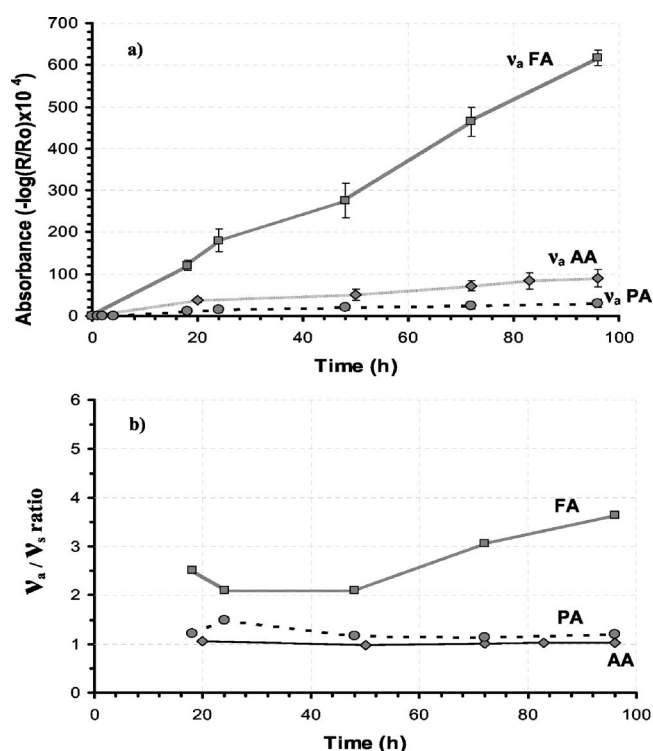


Figure 2. (a) Intensity of the antisymmetric stretching vibration ν_a (COO⁻) as a function of exposure time for copper exposed at 95% RH, 20°C in 120 ppb of acetic (AA), formic (FA), and propionic acid (PA). The lines between points are only drawn as a visual aid. (b) Intensity ratio of the antisymmetric-symmetric stretching vibration (ν_a/ν_s) as a function of time for copper exposed at 95% RH, 20°C in 120 ppb of acetic, formic, and propionic acid.

between the absorbance of the antisymmetric (ν_a) and the symmetric (ν_s) stretching vibrations (Fig. 2b) were plotted as a function of time for each acid. The data shown are the average of three independent exposures of copper-coated quartz crystals. A linear growth of carboxylate with time is observed for all acids. A faster kinetics is seen for formic acid than for the other acids, indicating a higher corrosion rate.

The use of *p*-polarized light implies that absorbates on the metal surface having a vibrating dipole component along the surface normal will absorb IR radiation. This so-called surface selection rule makes it possible to determine the orientation of the absorbates on the metal surface.¹⁹ Acetic and propionic acid exhibit approximately the same absorbance for the antisymmetric and symmetric vibrations (Fig. 2b), suggesting that the acetate and propionate ions exhibit a random orientation in the corrosion products.²⁰ Formic acid, however, exhibits approximately three times higher absorbance for the antisymmetric than the symmetric peak, which suggests that the formate ions preferentially are orientated with the C-O-O axis more perpendicular to the copper substrate.¹⁶

The growth rate for cuprite (Fig. 3) goes up very fast and then levels off. Acetic acid results in the highest growth rate up to about 20 h of exposure, followed by formic acid and then propionic acid. Comparing the growth rates of copper carboxylate with that of cuprite shows that acetic acid promotes the formation of cuprite over carboxylate, while formic acid does the opposite. Propionic acid is the least aggressive acid with the lowest formation rates for both cuprite and copper carboxylate.

Quantification of compounds in the corrosion products based on IRAS and QCM.—The quantification of the different species detected in the corrosion products formed are considered next. The results are based on copper-coated quartz crystals exposed to all three acids using the recently reported quantification procedure

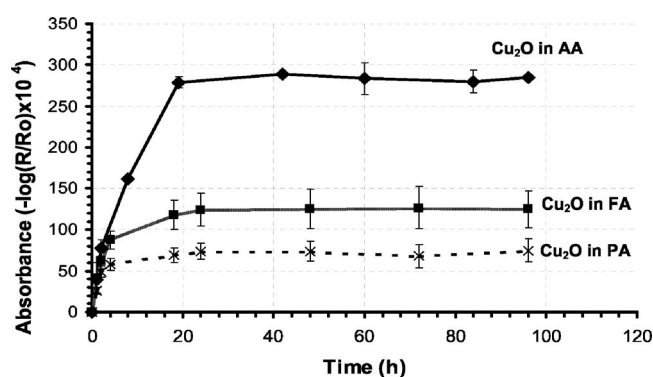


Figure 3. Intensity of copper(I) oxide band at 640 cm⁻¹ as a function of time for copper exposed at 95% RH, 20°C in 120 ppb of acetic, formic, and propionic acid. The lines between points are only drawn as a visual aid.

based on QCM integrated with IRAS.¹⁰ In short, the total mass increase caused by the exposure and obtained by QCM is successively reduced first by the mass due to water, then by the mass due to cuprite, whereby the remaining mass is assumed to originate from copper carboxylate formed. The relationship between the absorbance band of water, and possibly of hydroxyl groups, located at around 3400 cm⁻¹, has been correlated with the mass increase of water, as deduced with QCM by means of gold-coated quartz crystals exposed to various relative humidities.^{10,21,22} Similarly, a relationship was previously found between the absorbance band of cuprite at 648 cm⁻¹ and the mass increase caused by cuprite formation (QCM), when copper-coated crystals were exposed to clean humidified air at different relative humidities and exposure time.^{10,20} The mass increase due to carboxylate formation, finally, was obtained by subtracting the water and cuprite masses at each exposure time from the total mass (QCM). The exception to this procedure was formic acid, for which it was necessary also to subtract the mass corresponding to the formation of copper hydroxide, Cu(OH)₂. This could be accomplished by means of coulometric reduction (see later section) of exposed copper plates, whereby a plateau was detected⁶ at -770 mV vs SCE, which could be attributed to the formation of Cu(OH)₂ according to IRAS. The mass of Cu(OH)₂, as obtained with coulometric reduction, could be correlated with the absorbance of the peak at 3572 cm⁻¹ for the same compound (IRAS). From the relationship obtained, the absolute mass of Cu(OH)₂ could be deduced at any exposure time. Figure 4 displays the total mass change

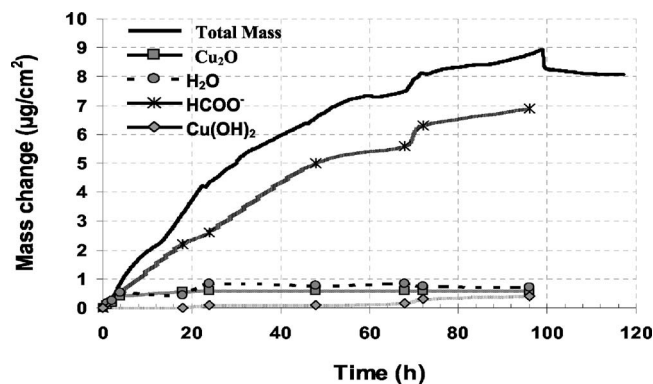


Figure 4. Total mass gain measured by in situ QCM as a function of time, and corresponding individual mass gains due to formation of Cu₂O, Cu(OH)₂, copper formate, and adsorption or absorption of H₂O or hydroxyl groups, deduced from in situ IRAS-QCM during exposures at 95% RH, 20°C, and 120 ppb of formic acid. The lines between points representing IRAS data are only drawn as a visual aid.

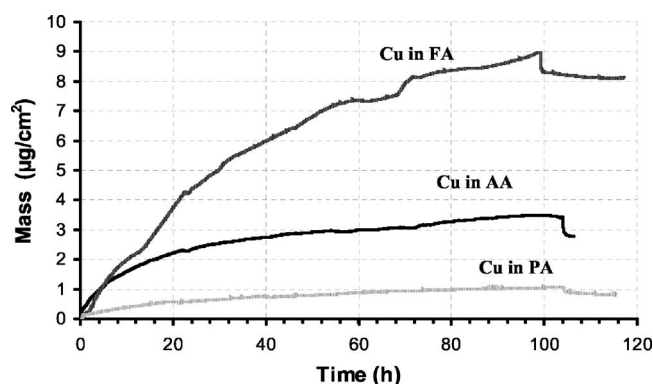


Figure 5. Total mass gain measured by in situ QCM as a function of exposure time for copper exposed to 120 ppb of acetic, formic, and propionic acid at 95% RH and 20°C.

vs time of copper exposed to 120 ppb of formic acid at 95% RH (QCM), and the corresponding individual mass changes due to formation of Cu_2O , $\text{Cu}(\text{OH})_2$, copper formate, and H_2O adsorbed on or absorbed into the corrosion products. After termination of each exposure in humidified air, the sample was left in dry air for at least 2 h. Hereby a mass decrease could be monitored by QCM, from which the absolute amount of more loosely bonded, presumably physisorbed, water after each exposure time could be deduced.

Figure 5 is a compilation of all total mass changes of copper (QCM) when exposed to acetic acid, formic acid, and propionic acid during 96 h of exposure. In qualitative agreement with IRAS data already presented, formic acid induces the largest mass increase rate, about three times higher than acetic acid and nine times higher than propionic acid. The total mass changes displayed in Fig. 5 have been resolved into individual mass changes, as discussed before, and are presented in Fig. 6a-c for acetic, formic, and propionic acid, respectively. In order to highlight the relatively small mass changes of propionic acid, the y-scale in Fig. 6c was expanded seven times as compared to Fig. 6a and b. The data are based on triplicates and show the largest variations for formic acid. In all cases the growth rate was highest initially, followed by a more constant growth rate in the case of copper carboxylate formation, or a leveling off in the case of cuprite formation or water adsorption or absorption. Copper hydroxide formation also exhibits a more constant growth rate, as seen in Fig. 6b for formic acid.

Estimation of deposition velocity.—The fact that the growth rates of carboxylates have been determined quantitatively can be used to estimate the so-called deposition velocity of the acids, which is defined as the ratio between the deposition rate of any compound and its concentration in the gas phase.²³ The deposition rate of the carboxylic acids has been obtained from the growth rate of each carboxylate species under steady-state conditions, usually between about 24 and 96 h of exposure (Fig. 6a-c). The highest deposition velocity obtained is, as expected, for formic acid with a value of 0.014 cm s^{-1} , followed by acetic acid (0.007 cm s^{-1}) and propionic acid (0.003 cm s^{-1}). Similar values of deposition velocity and the same trend have been reported previously for formic acid (0.006 cm s^{-1}) and acetic acid (0.005 cm s^{-1}), which is a confirmation of the reliability of the quantification procedure. To our knowledge no value for the deposition velocity of propionic has been reported.

Quality assurance check of the quantification procedure.—Because the amount of cuprous oxide has been measured with three independent techniques in this study, IRAS, QCM, and coulometric reduction, the data from the different techniques can be compared with each other to check the consistency of results obtained. We start by discussing the determination of cuprous oxide by means of coulometric reduction. Figure 7 displays the coulometric reduction

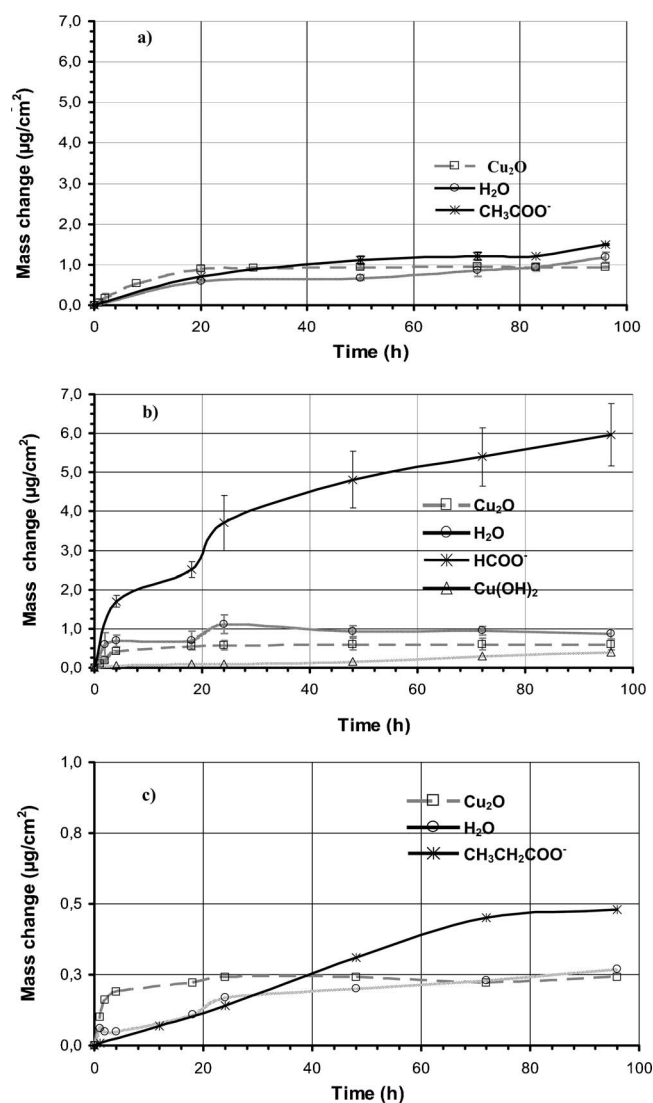


Figure 6. (a) Mass gain due to formation of Cu_2O , copper acetate, and adsorption or absorption of $\text{H}_2\text{O}/\text{OH}$ as a function of exposure time, deduced from in situ IRAS-QCM exposures at 95% RH, 20°C, and 120 ppb of acetic acid. The curves between points are only drawn as a visual aid. (b) Mass gain due to formation of Cu_2O , $\text{Cu}(\text{OH})_2$, and copper formate, and adsorption or absorption of $\text{H}_2\text{O}/\text{OH}$ as a function of exposure time, deduced from in situ IRAS-QCM exposures at 95% RH, 20°C, and 120 ppb of formic acid. (c) Mass gain due to formation of Cu_2O , copper propionate, and adsorption or absorption of $\text{H}_2\text{O}/\text{OH}$ as a function of exposure time, deduced from in situ IRAS-QCM exposures at 95% RH, 20°C, and 120 ppb of propionic acid.

curves for copper plates exposed during 96 h in 120 ppb of each carboxylic acid and 95% RH. For comparison, a corresponding curve for copper exposed to humidified air with no acid added is also shown. All curves exhibit two plateaus at around -500 mV vs SCE and at -850 mV vs SCE, respectively. The first plateau corresponds to a precursor, Cu_xO , of Cu_2O with the same crystallographic structure as Cu_2O but with a mixed valence [$\text{Cu}(0) + \text{Cu}(\text{I})$] containing interstitial metallic copper in the cuprous oxide matrix.^{24,25} The second plateau (at -850 mV vs SCE) corresponds to the less easily reduced phase of the two and has been attributed to crystalline Cu_2O .^{24,25} The absolute amounts of the total sum of cuprous oxide ($\text{Cu}_x\text{O} + \text{Cu}_2\text{O}$) are highest in the presence of acetic acid, in qualitative agreement with previously discussed IRAS-QCM

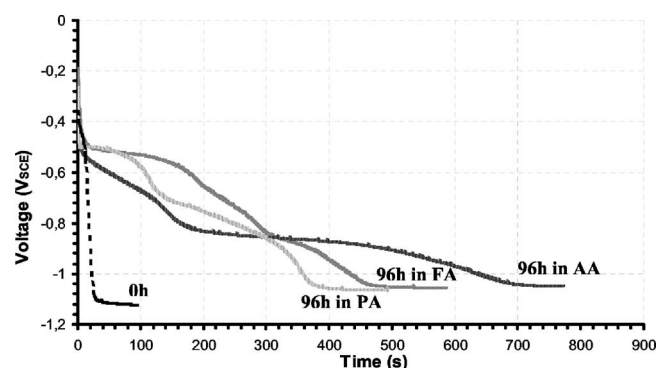


Figure 7. Coulometric reduction curves for copper samples exposed to 95% RH, 20°C, and 120 ppb of acetic (labeled “AA”), formic (labeled “FA”), and propionic acid (labeled “PA”) after 48 and 96 h of exposure. A reference curve before exposure (labeled “0 h”) obtained in humidified air with no organic acid added is also displayed.

data. A deeper look reveals that the precursor (Cu_xO) dominates over the crystalline oxide (Cu_2O) in formic acid, whereas the opposite holds true in acetic acid.

Figure 8 compiles all data generated for cuprite with the three analytical techniques. It shows the relationship between the absorbance of the cuprite band at 648 cm^{-1} (IRAS) and the corresponding cuprite thickness (QCM), and the relationship between the absorbance of the same cuprite band (IRAS) and the corresponding copper(I) oxide thickness obtained with coulometric reduction. In these calculations the cuprite density was set at 6.0 g cm^{-3} , and it was assumed that the cuprite layers were homogeneous and completely reduced during coulometric reduction. The data collected in Fig. 8 represent triplicates for each acid after 0, 1, 10, 24, 48, 72, and 96 h of exposure. A linear relationship was obtained with a regression coefficient of 0.92 and a standard deviation of ± 0.11 . The values suggest that the overall accuracy is around 12% when transforming IRAS absorbance data of cuprite to absolute amounts, independent of acid and copper substrate (solid copper plate or copper-coated quartz crystal).

Topography information based on AFM.—Figures 9a–d show AFM images obtained in contact mode for copper samples exposed 96 h in 120 ppb of acetic, formic, and propionic acid at 95% RH. In

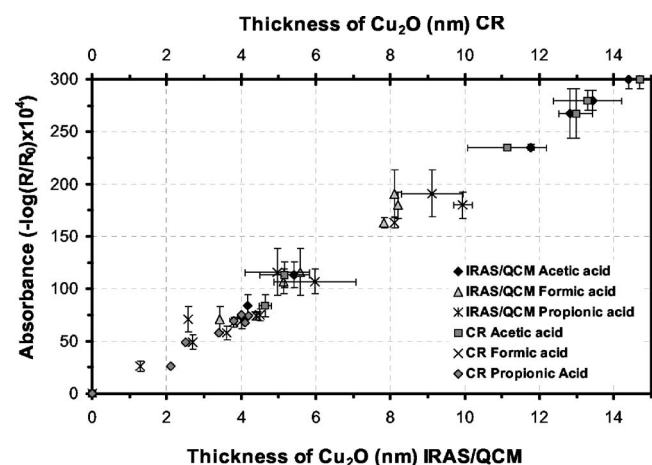


Figure 8. Relation between the absorbance of the copper(I) oxide at 640 cm^{-1} measured by IRAS, cuprite thickness obtained by IRAS-QCM, and cuprite thickness obtained by coulometric reduction of copper exposed at 95% RH, 20°C in 120 ppb of acetic, formic, and propionic acid for different exposure times.

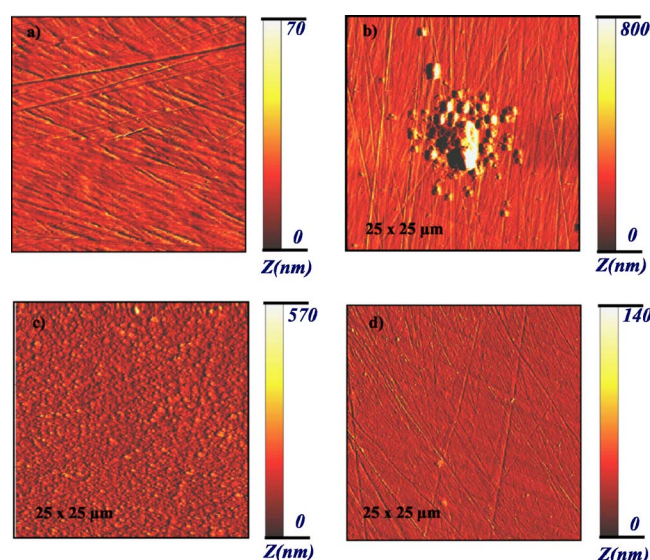
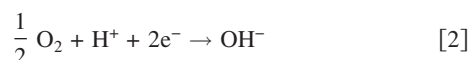


Figure 9. (Color online) AFM images of copper (a) before exposure and after 96 h exposure at 95% RH, 20°C in 120 ppb of (b) acetic, (c) formic, and (d) propionic acid. Scan size $25 \times 25\text{ }\mu\text{m}$.

order to compare with the initial state, a diamond polished copper surface prior to exposure is also shown. The polished copper surface contains scratches due to the diamond paste. After exposure to acetic acid cubic-shaped crystallites are seen, which most likely originate from cuprite.¹⁰ With increasing exposure time corrosion products appear on localized areas, most likely consisting of copper acetate (Fig. 9b). Copper exposed to formic acid forms less cuprite than acetic acid, as discussed in previous sections, and the corrosion products exhibit more elongated features. The height range in the AFM images is 70 nm for the unexposed sample, around 800 nm after exposure in acetic acid, 570 nm in formic acid, and 140 nm in propionic acid, evidencing the increase in topography range with growth of corrosion products.

General discussion.—The integrated and quantified IRAS and QCM data, together with the complementary AFM analysis, make it possible to propose a sequence of reactions involved in the initial atmospheric corrosion of copper induced by carboxylic acids in humidified air. The mass of physisorbed water (Fig. 4), assumed to originate mainly from the aqueous adlayer, is approximately the same for formic and acetic acid (around $1.0\text{ }\mu\text{g cm}^{-2}$). With a mass of an equivalent monolayer of water equal to around 30 ng cm^{-2} , the average thickness of the aqueous adlayer corresponds to about 30 monolayers of water. For propionic acid the aqueous adlayer is approximately half of that for the other acids. The water layer forms conditions for electrochemical reactions and deposition of the organic acids. The dominant electrochemical reactions are the oxidation of copper (anodic reaction) and reduction of oxygen (cathode reaction)



Following the general outline of Gildes,²³ the presence of the aqueous adlayer produces a hydroxylated surface which creates sites for ligand exchange with species deposited into the adlayer, primarily protons and carboxylate ions that form upon deposition of the carboxylic acid into the aqueous adlayer. This ligand exchange is believed to be an important prerequisite for the dissolution of cuprous ions from the oxide surface.²³

According to the quantified IRAS-QCM data, formic acid results in the highest corrosion rate, followed by acetic and propionic acid.

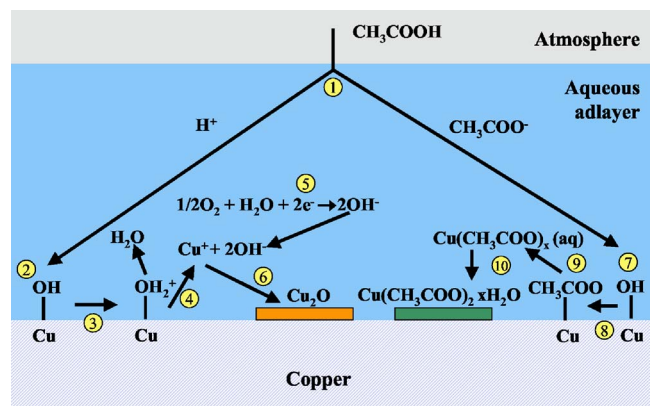


Figure 10. (Color online) Schematic description of possible pathways for proton- and ligand-induced dissolution and precipitation for initial acetic acid-induced atmospheric corrosion of copper.

This observation can be explained by at least two different properties of the acids. The acid dissociation constant²⁶ in aqueous solution at 25°C for formic, acetic and propionic acid is 1.77×10^{-4} , 1.76×10^{-5} , and 1.34×10^{-5} . From this follows that the degree of dissociation of the acids decreases in the order formic acid > acetic acid > propionic acid. The result is a higher concentration of both protons and carboxylate ions for ligand exchange at the hydroxylated surface in the case of formic acid. The second property is the deposition velocity, which could be given quantitative numbers in this study, and was shown to decrease in the same order: formic acid (0.014 cm s^{-1}) > acetic acid (0.007 cm s^{-1}) > propionic acid (0.003 cm s^{-1}). This difference is what would be expected qualitatively from the amount of nonpolar groups of each acid, and their inherent property to decrease their water solubility and kinetically constrain the deposition rate and deposition velocity of the acids into the aqueous adlayer.

The AFM images and IRAS-QCM data confirm the formation of cuprite and copper carboxylate at different sites of the surface. This provides evidence for at least two different spatially separated pathways for corrosion product formation (Fig. 10). The first consists of proton-induced dissolution of cuprous ions, subsequent reaction of the cuprous ions with hydroxyl ions produced in the cathodic reaction, and formation and precipitation of cuprite. This pathway is more frequent in acetic acid, compared to the other acids, and also seems to promote the formation of more crystalline cuprite, as revealed by coulometric reduction. The other pathway consists of ligand (carboxylate)-induced dissolution of cuprous ions, formation of dissolved cuprous or cupric carboxylate species, that eventually precipitate as copper(II) carboxylate. This pathway dominates in formic acid, whereas propionic acid results in the lowest rates of both pathways.

The formation of copper(II) hydroxide, $\text{Cu}(\text{OH})_2$, in the presence of formic acid cannot be explained solely on the basis of properties of the acids discussed so far. A possible explanation may be local pH variations along the surface caused by the lateral distribution of anodic and cathodic areas. It may well be that formic acid with more pronounced anodic areas, characterized by lower pH because of the hydrolysis of water induced by dissolved cuprous ions, creates local conditions at cathodic areas of the copper surface with high enough pH to produce the copper(II) hydroxide.

No technique discussed so far reveals the exact formula of the copper carboxylates formed. For this reason, copper plates were analyzed by means of GIXRD after exposure to formic and acetic acid for 4 days (96 h). No evidence of any copper carboxylate could be seen. However, when extending the exposure to 8 days, clear evidence was seen for Cu_2O , CuO , and copper hydroxyl formate $[\text{Cu}(\text{OH})(\text{HCOO})]$ in the case of formic acid, and Cu_2O , CuO , and hydrated copper hydroxyl acetate $[\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO}) \cdot \text{H}_2\text{O}]$ in

the case of acetic acid. This information can be compared with the ratio between the mass of carboxylate and the mass of water or hydroxyl groups as depicted in Fig. 6a and b. The ratio ($\Delta m \text{CH}_3\text{COO} / \Delta m \text{H}_2\text{O}-\text{OH}$) for acetic acid is near 1.5 ± 0.2 (Fig. 6a), and the ratio ($\Delta m \text{HCOO} / \Delta m \text{H}_2\text{O}-\text{OH}$) for formic acid is near 6.5 ± 2.5 . Meanwhile, the copper carboxylate-phases identified by GIXRD give a $[\Delta m \text{CH}_3\text{COO} / \Delta m (\text{OH})_3]$ close to 1.2 and ($\Delta m \text{HCOO} / \Delta m \text{OH}$) close to 2.7 for acetic and formic acid, respectively. Considering that this comparison is based on several assumptions, the data can be said to agree relatively well.

Conclusion

A procedure based on IRAS-QCM for quantitative in situ analysis has been used to compare the initial atmospheric corrosion of copper induced by 120 ppb of acetic, formic, and propionic acid at 95% RH and 20°C during up to 96 h of exposure.

1. Formic acid resulted in a total corrosion-induced mass gain of $6.0 \text{ } \mu\text{g cm}^{-2}$ after 4 days of exposure, followed by $1.5 \text{ } \mu\text{g cm}^{-2}$ for acetic acid and $0.5 \text{ } \mu\text{g cm}^{-2}$ for propionic acid.

2. The absolute mass of individual constituents of corrosion products formed, mainly cuprous oxide or cuprite, copper carboxylate, and water or hydroxyl groups, could be obtained in situ as a function of exposure time.

3. The absolute mass per surface area of cuprous oxide could be estimated from the IRAS absorbance band of cuprite with a relative accuracy of 12% or better. The quantitative data for cuprous oxide showed consistency between all acids studied and with postanalysis performed by coulometric reduction.

4. The absolute mass gain per surface area of copper carboxylate formed could be used to estimate the deposition velocity for all acids as follows: formic acid (0.014 cm s^{-1}) > acetic acid (0.007 cm s^{-1}) > propionic acid (0.003 cm s^{-1}).

5. The results were interpreted using the Gildes model for initial atmospheric corrosion, whereby two spatially separated main pathways could be identified: proton-induced dissolution of cuprous ions followed by the formation of copper(I) oxide, and carboxylate-induced dissolution followed by the formation of copper(II) carboxylate. The first pathway is initially very fast but levels off, grows more uniformly over the surface, and dominates in acetic acid. The second pathway exhibits a more constant growth rate and localized growth, and dominates in formic acid. Propionic acid exhibits low rates for both pathways.

6. The difference between the carboxylic acids with respect to both corrosion rate and carboxylate-induced dissolution follows the same order as their corresponding dissociation constants and deposition velocity.

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PAPER III

Intended for publication in Corrosion

Molecular *in situ* studies of atmospheric corrosion*

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Key words: atmospheric corrosion, Cu, Zn, carboxylic acids, *in situ*, surface analysis, SCF-HF-DFT calculation

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Abstract

Atmospheric corrosion involves chemical, electrochemical, and physical processes in three phases (solid, liquid, and gas) and two interfaces (solid/liquid and liquid/gas). Because of inherent experimental and conceptual difficulties, scientific efforts to characterize this highly complex interfacial regime came relatively late into the field. With the access and development of surface and interface sensitive analytical techniques, it has lately become possible to perform molecular *in situ* analyses of the interfaces involved in atmospheric corrosion.

This Whitney award paper presents some highlights from our fundamental research in atmospheric corrosion, including results from the most recent efforts in our research group to provide a molecular picture of the interfacial regime that governs atmospheric corrosion. Using copper or zinc as substrate, formic acid, acetic acid, acetaldehyde or propionic acid as corrosion stimulator in the humidity-containing atmosphere, results will be presented with particular emphasis on probing the metal oxide/water interface (by infrared reflection absorption spectroscopy combined with the quartz crystal microbalance and sum frequency generation) and the water/gas interface (by sum frequency generation), respectively. Theoretical calculations are also presented, which aid in interpreting the *in situ* spectroscopy data.

The multi-analytical effort provides evidence of the importance of the solid/liquid interface over the liquid/gas interface. In all, the results can be interpreted to follow the conceptual framework of GILDES, a general model for atmospheric corrosion. Taking copper as example, identified surface species and reaction pathways include proton- and carboxylate-induced dissolution of the cuprous ion, followed either by formation and precipitation of cuprous oxide or by oxidation of cuprous to cupric ions and subsequent formation and precipitation of copper carboxylate.

Introduction

This paper is a summary of the 2007 W.R. Whitney Award lecture presented during the NACE CORROSION/2007 conference in Nashville. The award was received by the first author “*For his outstanding contributions to the study of atmospheric corrosion, and for his major role in corrosion science education*”. Hence, the lecture and paper is on fundamental insight gained in this highly complex and important form of corrosion. Atmospheric corrosion was for most of the 20th century a subject of engineering study, largely with empirical approaches. In the last decade or so it became possible to perform more well-controlled laboratory and field studies, both indoors and outdoors, as well as computer model investigations of the most important atmospheric corrosion processes.

The intent of this paper is to present results from ongoing activities aiming at a more molecular understanding of atmospheric corrosion. These activities are based on earlier developments in the research group of *in situ* analysis of the metal/atmosphere interfacial regime based on four independent techniques, namely infrared reflection absorption spectroscopy (IRAS, monitors the surface chemistry during atmospheric corrosion)¹, quartz crystal microbalance (QCM, integrated with IRAS, monitors changes in mass)², atomic force microscopy (AFM, displays surface topography changes)³ and sum frequency generation (SFG, reveals molecular information from the solid/liquid or the liquid/gas interface)⁴. A theoretical counterpart to the experimental studies is GILDES⁵, a multi-phase computational model for atmospheric corrosion, which considers the most important chemical and physical processes in six different regimes of the metal/atmosphere interface.

The model systems studied in this work contain either copper or zinc as metal substrates and formic acid (HCOOH), acetic acid (CH₃COOH), propionic acid

(C₂H₅COOH) or acetaldehyde (CH₃CHO) as gaseous corrosion stimulator. The interest in carboxylic acids and aldehydes goes back to earlier findings from indoor exposed metals, where the pronounced role of organic indoor pollutants was explored⁶.

Experimental

Combined IRAS/QCM measurements.— Details of the IRAS/QCM set up has been described previously.^{1,2} The exposure of copper and zinc samples was performed in a Teflon covered stainless steel chamber in which an infrared spectrometer (Digilab FTS 40 Pro) for IRAS measurements was integrated with a quartz crystal microbalance (QCM). Reflection absorption spectra were obtained with p-polarized light and averaging 1024 scans at a resolution of 4 or 8 cm⁻¹. The spectra were recorded in absorbance units (-log R/R₀), where R is the reflectance of the exposed sample and R₀ the background reflectance. Further details regarding the background spectra are presented in ref. 2. The frequency shift from the QCM was measured every minute with a frequency counter (Maxtek PM 740) and transformed to a mass change through the Sauerbrey equation⁷.

The IRAS and QCM measurements were integrated by allowing the infrared beam to impinge onto the quartz crystal of the QCM at grazing incidence (88° versus the normal). On each quartz crystal a chromium film (50 nm thick) and a copper film on top (350 nm thick) was deposited. Separate IRAS-measurements were also performed on diamond polished (0.25 μm) zinc and copper samples. Further details regarding surface preparation and surface cleaning are given in ref. 8.

SFG measurements.— A Nd:YAG picosecond laser (EKSPLA) with an output wavelength of 1064 nm, 24 ps long pulses and a repetition rate of 20 Hz was used to

pump an optical generator/optical parametric amplifier (OPG/OPA, Laservision). The energy of the generated infrared beam is around 300 μJ and the bandwidth is 7-9 cm^{-1} . The beam configuration has a co-propagating geometry, with the visible and infrared beams at incident angles of 55° and 63° respectively. The generated sum-frequency beam was focused through a monochromator, collected by a photomultiplier tube, and averaged by an integrated boxcar. The SFG-spectra were mainly obtained through PPP-polarization (the solid/liquid interface) and SSP-polarization (the liquid/gas interface) and normalized by measuring infrared and visible beam energies. Further details are given in refs. 4 and 9.

Exposures.— The corrosive air was produced by mixing humid and dry air, with the dry air passing along a permeation tube (Vici Metronics) containing formic, acetic and propionic acid or acetaldehyde. The exposures were conducted in the range from $85 \pm 3\%$ to $95 \pm 3\%$ RH, a concentration of between 80 and 120 ppb (volume parts per billion) of each gas, a laminar flow of velocity 3.5 cm/s along the sample surface and a temperature of $19.5 \pm 0.5^\circ$.

Theoretical calculations.— Theoretical calculations were performed on $\text{Cu}_2\text{O}(100)$ and $\text{ZnO}(100)$ interacting with a formic acid molecule and with one or several water molecules added consecutively. All quantum mechanics calculations were performed with the Gaussian03 package¹⁰. In all cases, a full structure optimization was carried out at the Density Functional Theory (DFT) level of calculation, with the hybrid exchange¹¹ the correlation functional B3LYP¹² and the Land2dz pseudopotential basis set¹³. The solvent was assumed to follow the PCM description¹⁴ to which one or several molecules were added. The calculations were performed at the National Supercomputer Center at Linköping University, Sweden¹⁵,

and the SGI-Altix450 server at the Bioinformatics and Molecular Simulation Center at Talca University, Chile¹⁶.

Results and Discussion

The outline of this section is as follows. In the first part the relative importance of the interfaces involved (solid/liquid and liquid/gas) are explored by a combination of IRAS and SFG. Evidence will be presented that shows the importance of the solid/liquid interface over the liquid/gas interface. The section to come will then focus on the solid/liquid interface through a combination of IRAS and QCM, with particular emphasis on the identification and quantification of species involved in initial atmospheric corrosion. The last two sections concern the very first stages of atmospheric corrosion, both from an experimental (SFG) and from a theoretical (SCF-HF-DFT calculation) perspective.

Comparison of the role of the solid-liquid and liquid-gas interfaces.— In order to explore the relative importance of the interfaces in atmospheric corrosion the transformation of acetaldehyde to acetic acid/acetate has been studied from an atmospheric corrosion perspective, either through analysis of the solid/liquid interface (IRAS, using zinc as substrate exposed to the aqueous adlayer) or the liquid/gas interface (SFG, using a water solution rather than the aqueous adlayer as substrate exposed to the gas)¹⁷. The initial atmospheric corrosion of zinc induced by either acetaldehyde or acetic acid has been investigated and compared with respect to the nature of the corrosion products formed. The effect of relative humidity has also been explored. Figure 1 displays *in situ* spectra of zinc exposed to either 100 ppb acetic

acid (upper) or 80 ppb acetaldehyde (lower) at the same relative humidity (90%) and exposure time (300 minutes).

With the exception of the sloping background, the spectra appear fairly similar, and several peaks suggest the formation of zinc acetate. The dominant peaks in both cases are the symmetric and antisymmetric carboxylate stretching vibrations¹⁸ at 1419 and 1569 cm^{-1} . The absence of physisorbed compounds is manifested by the absence of a peak at $\sim 1690\text{-}1790\text{ cm}^{-1}$, characteristic of the C=O stretch¹⁹. A comparison of the peak intensities between the symmetric and antisymmetric carboxylate stretching vibrations for exposure to acetic acid and acetaldehyde reveals that the relative values in both cases are in agreement with bulk zinc acetate¹⁹. Thus, the acetate films formed is assumed to be randomly oriented, at least for shorter exposure periods in both acetic acid- and acetaldehyde-induced corrosion. According to the surface selection rule²⁰, an alignment with the carboxylate C_2 axis either perpendicular or parallel to the surface normal would have yielded IRAS spectra where either the symmetric or antisymmetric carboxylate stretch were absent. In all, both acetaldehyde and acetic acid result in the formation of similar reaction products, mainly consisting of randomly oriented zinc acetate.

This result is in marked contrast to analogous studies of the water/air interface studied by SFG, where no signs of any acetate formation can be seen. Figure 2 exhibits *in situ* SFG spectra of water solutions containing 7 mole % of either acetaldehyde or acetic acid. The acetaldehyde spectrum with the symmetric methyl stretch at 2944 cm^{-1} is due to a hydration process when acetaldehyde is in contact with water during which a gem-diol ($\text{CH}_3\text{CH}(\text{OH})_2$) is formed¹⁷. Together with other peaks in the spectrum, representative of acetaldehyde, the spectrum provides no evidence of any formation of acetate or acetic acid at the water solution surface. The acetic acid spectrum, on the

other hand, is dominated by the symmetric methyl stretch at 2945 cm^{-1} representative of acetic acid¹⁷.

The overall conclusion is that acetaldehyde at the water/air interface remains in a hydrated form without transforming into acetic acid or acetate. At the zinc/water interface, on the other hand, both acetaldehyde and acetic acid result in zinc acetate formation. In more general terms, this conclusion highlights the importance of the solid/liquid interface over the liquid/gas interface. In what follows we consider the solid/liquid interface in more detail using copper and carboxylic acids as ingredients of our model system.

Quantified in situ studies of copper exposed to carboxylic acids.— A unique quantification procedure for *in situ* analysis has been developed based on integration of IRAS and QCM. This procedure enables the nature and quantity of different species to be identified during initial atmospheric corrosion of copper exposed to humidified air with addition of carboxylic acid²¹. The results to follow are based on copper-coated quartz crystals exposed to the three smallest carboxylic acids. The total mass increase caused by the exposure is the sum of mass changes due to three species identified during initial atmospheric corrosion: water, cuprite, and carboxylate. The relationship between the absorbance band of water, and possibly of hydroxyl groups, located at around 3400 cm^{-1} , could be correlated to the mass increase of water, as previously deduced with QCM by means of gold-coated quartz crystals exposed to various relative humidities^{2,8,22}. Similarly, a relationship was found between the absorbance band of cuprite at 648 cm^{-1} and the mass increase caused by cuprite formation (QCM), when copper-coated crystals were exposed to clean humidified air at different relative humidities^{2,21}. The carboxylate mass, finally, was obtained by

subtracting the water and cuprite mass changes at each exposure time from the total mass measured by QCM. The exception from this procedure was formic acid, in which case it was necessary also to subtract the mass corresponding to the formation of copper hydroxide, $\text{Cu}(\text{OH})_2$. This could be accomplished by means of coulometric reduction of exposed copper plates, whereby a plateau was detected at -770 mV vs. SCE¹⁹, which could be attributed to the formation of $\text{Cu}(\text{OH})_2$, according to IRAS.

The results for copper in formic, acetic and propionic acid environments can be interpreted to follow the GILDES model²⁴, in which two different pathways of reactions may occur during initial atmospheric corrosion: proton- and ligand (carboxylate)-induced dissolution processes, respectively. A schematic picture of the pathways and reactions involved are principally depicted in figure 3, taking copper and acetic acid as example. After dissociation of the organic acid (step 1 in fig. 3), both protons and carboxylate ions may interact with the hydroxylated surface formed upon exposure with the aqueous adlayer. Two reaction pathways can be discerned. The first involves proton-induced dissolution of cuprous ions (steps 2-4), subsequent reaction of cuprous ions with hydroxyl ions produced in the cathodic reaction (step 5), followed by the formation and precipitation of cuprite (step 6). The second pathway involves ligand-induced dissolution of the cuprous ions and release of an aqueous copper carboxylate species from the surface (steps 7-9), and subsequent precipitation of copper (II) carboxylate (step 10) into which water and hydroxyl groups may have been incorporated. Depending on acid, one route seems to dominate over the other. Acetic acid triggers copper (I) oxide formation, as evidenced from IRAS/QCM. Formic acid, on the other hand, stimulates carboxylate-induced dissolution, whereas propionic acid is the lowest stimulant for both pathways. These differences can partly be explained by their acid strength and content of non-polar groups. The acid

dissociation constant decreases in the order²⁵: formic acid (1.77×10^{-4}) > acetic acid (1.76×10^{-5}) > propionic acid (1.34×10^{-5}). The deposition velocity of each acid, calculated from the quantified IRAS/QCM data, turns out to follow the same order: formic acid (0.014 cm s^{-1}) > acetic acid (0.007 cm s^{-1}) > propionic acid (0.003 cm s^{-1}), in good agreement with data reported in the literature²⁶. Hence, higher acid strength and also higher deposition velocity seem to favour the overall corrosion rate, and also the second pathway governed mainly by carboxylate-induced dissolution of copper. Having identified carboxylate species as crucial for the initial atmospheric corrosion induced by carboxylic acids, we turn next to the possible *in situ* identification of the metal-carboxylate interfacial species by SFG (corresponding to step 8 in figure), and the multi-layer growth of metal-carboxylate films (step 10) as observed by IRAS. This is summarized in the next section, with zinc as substrate and formic acids as corrosion stimulator.

In situ surface analysis of the solid-liquid interface.— Figure 4 displays the spectra from SFG and IRAS for zinc exposed under the same conditions in both cases: 120 ppb of formic acid and 85% RH. The spectral region of interest highlights the vibrations of the carboxylate group (COO^-). The vibrational modes of this group in the formate ion adsorbed on zinc oxide is the symmetric stretch at 1350 cm^{-1} and the ant symmetric stretch at 1630 cm^{-1} ²⁷. The IRAS spectrum was collected in humid air, while the SFG spectrum was measured in dry atmosphere, whereby the wave number increased about 10 cm^{-1} ²⁸.

The obvious difference between the SFG and IRAS spectra is the symmetric stretch at 1350 cm^{-1} . In the IRAS spectrum it is clearly visible while with SFG no symmetric stretch peak is discerned. The absence of the symmetric stretch in the SFG spectrum

can be explained by a different orientation of the formate ion on the surface, probed with SFG, compared to the same ion in multi-layer films, which IRAS mainly measures. The fact that the symmetric stretch is absent in the SFG spectrum can possibly be explained by the surface selection rule²⁰, which states that a vibrational mode with the dipole moment parallel to the surface is inactive. Accordingly, the formate ion is suggested to tilt towards the surface, which makes the carboxylate antisymmetric stretch more active and the symmetric less active. Several bonding configurations have been proposed for formic acid adsorbed on different crystal orientations of ZnO, including monodentate^{27, 29} and bidentate bridging²⁹⁻³⁰. No experimental evidence from the current study favors any of these configurations.

From the intensity ratio between the symmetric and antisymmetric stretches in the IRAS spectrum, and with the antisymmetric stretch being more intense, it can be concluded that the preferred orientation of zinc formate in the multi-layer films formed also is tilted more towards the surface, but not as pronounced as for the interfacial zinc formate seen in the SFG spectrum.

To conclude, formate species could be identified under *in situ* conditions either as constituent of the multi-layer film or as interfacial species, whereby different orientations of zinc formate were discerned by IRAS and SFG respectively. The nature of the interfacial zinc formate species is discussed in more detail in the next section through a theoretical calculation.

SCF-HF-DFT calculations on the solid-liquid interface.— With reference to figure 3 and the SFG results in the preceding section, the aim of these theoretical calculations is to elucidate possible interactions between the formate ion and the zinc oxide surface during early stages of atmospheric corrosion. The zinc oxide surface was

modeled using a cluster concept with periodically repeated groups of atoms in virtual space having chemical properties similar to the real ZnO(100) unit cell. In addition, the outermost oxide atoms were terminated by hydrogen atoms because of the assumed surface hydroxylation that occurs upon adsorption of the aqueous adlayer onto the zinc oxide surface. In the calculations to follow, the zinc oxide structure was frozen, whereas the oxygen-hydrogen bonds could vary in orientation. Figure 5 (left) shows the molecular configuration of a hydroxylated ZnO(100) surface used as starting point for the calculations.

Figure 5 (right) displays the resulting geometry based on calculations with the hydroxylated ZnO(100) surface interacting with one formate ion and one water molecule. The most immediate conclusion is that the formate ion binds directly to the ZnO(100) substrate through two zinc-oxygen bonds, without any participation of hydrogen bonding originating from surface hydroxyl groups or the water molecule. This result is clearly different from analogous calculations with Cu₂O(100) as substrate interacting with one formate ion and one water molecule. In this case the calculations suggest that the interaction between formate and cuprite is very weak and that bonding only can take place if hydrogen bonding is involved via surface hydroxyl groups or water³¹.

Following the scenario of figure 3, and assuming analogous pathways for zinc and copper, the much stronger interaction between the formate ion and ZnO(100) than between the formate ion and Cu₂O(100) may have consequences for the initial atmospheric corrosion kinetics. Hence, we propose that the strong interaction between the formate ion on zinc results in a faster formic acid-induced dissolution on zinc than on copper and therefore faster initial corrosion kinetics on zinc. Figure 6 is in

accordance with this proposal and shows that the formate-induced corrosion kinetics on zinc is much faster than on copper.

Concluding remarks

This paper highlights possible experimental and theoretical ways of obtaining more molecular insight into the interfacial regime that governs atmospheric corrosion of metals. The initial atmospheric corrosion of copper or zinc has been explored *in situ* with carboxylate acids and humidity as corrosion stimulators. The combination of SFG and IRAS provides unique evidence of the relative importance of the solid/liquid interface over the liquid/gas interface. A deeper insight into the solid/liquid interface has been obtained when integrating IRAS and QCM, whereby the nature and quantity of species could be identified that participate in the carboxylic acid-induced atmospheric corrosion of copper. SFG combined with IRAS has furthermore revealed the different nature of zinc-formate species formed during initial stages of zinc induced by formic acid, and complementary SCF-HF-DFT calculations suggest that the formate ion interacts stronger with a zinc substrate than with a copper substrate. The latter finding may be one reason for the much faster corrosion kinetics found on zinc than on copper.

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The receipt of the 2007 W.R. Whitney Award is a great recognition of the efforts of our research group at the Division of Corrosion Science of the Royal Institute of Technology, Stockholm, to better understand atmospheric corrosion phenomena through a surface science approach. In addition to the co-authors of this paper, Christofer Leygraf gratefully acknowledges the following present or previous co-workers: Inger Odnevall Wallinder, Dan Persson, Johan Tidblad, Mikael Forslund, Ted Aastrup, Jonas Weissenrieder, Saeid Zakipour, Daniel Wallinder, Wenle He, and Sofia Bertling. He is also greatly indebted to Prof. Gabor Somorjai, University of California, Berkeley, USA, and to Prof. Steven Baldelli, University of Houston, USA, for sharing their knowledge in surface science and sum frequency generation, to Prof. em. Einar Mattsson and Dr. Vladimir Kucera, former Swedish Corrosion Institute, Stockholm, for introducing him into the field of atmospheric corrosion, and to Prof. T. Graedel, Yale University, New Haven, USA, for jointly writing the book "Atmospheric Corrosion".

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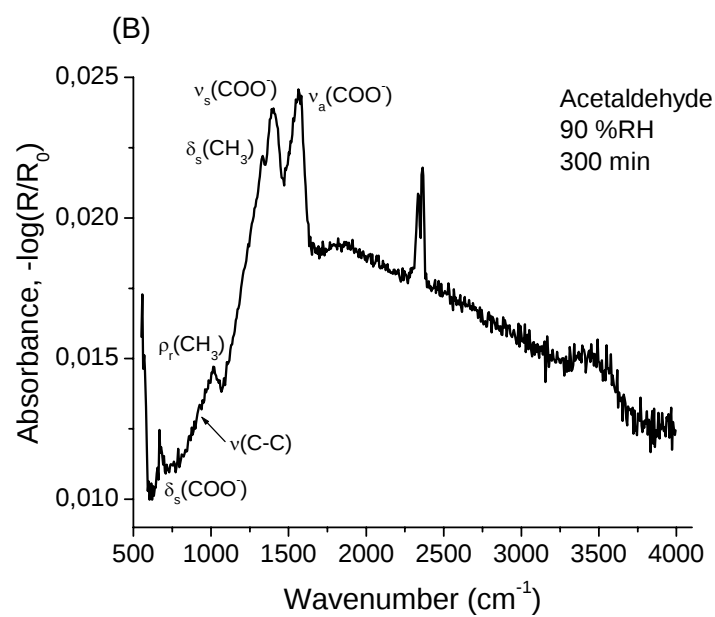
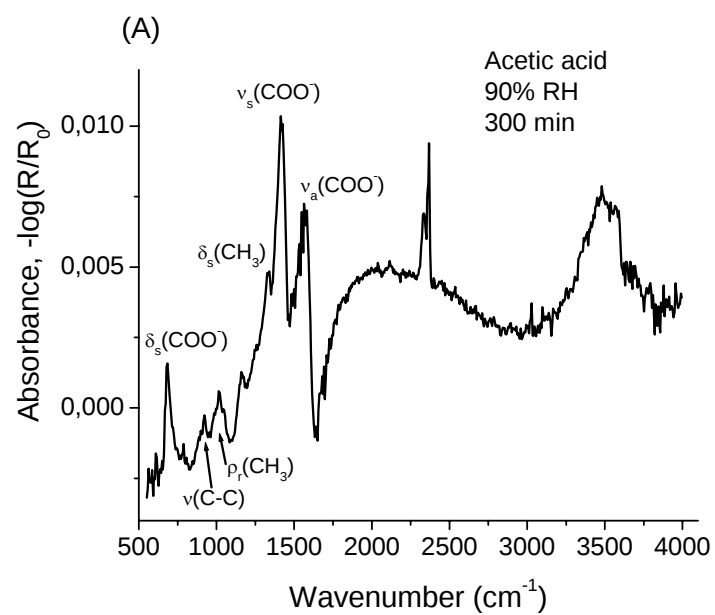


Figure 1. *In-situ* IRAS spectra of zinc exposed for 300 minutes to humidified air (90%) with 100 ppb of acetic acid (a), and to 80 ppb of acetaldehyde (b).

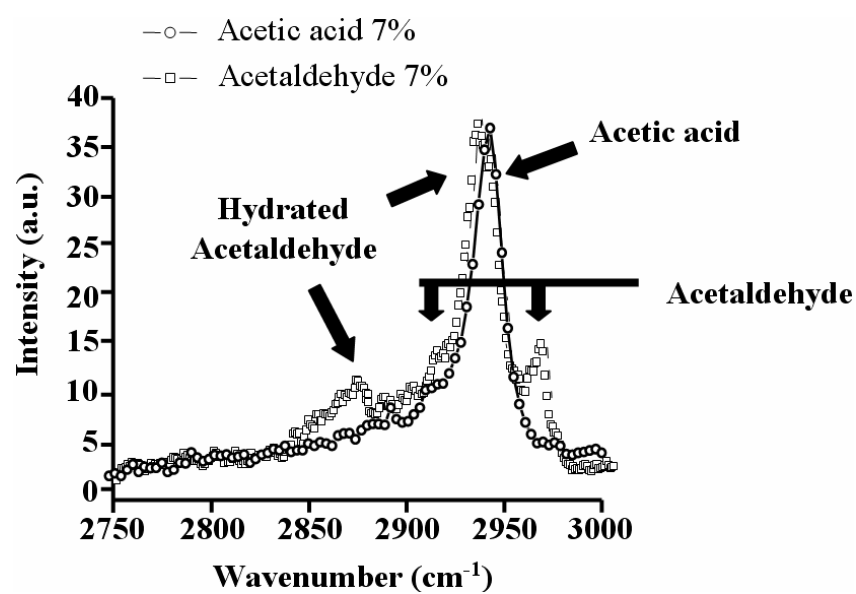


Figure 2. *In situ* SFG spectra of 7 mole % acetaldehyde and 7 mole % acetic acid solution.

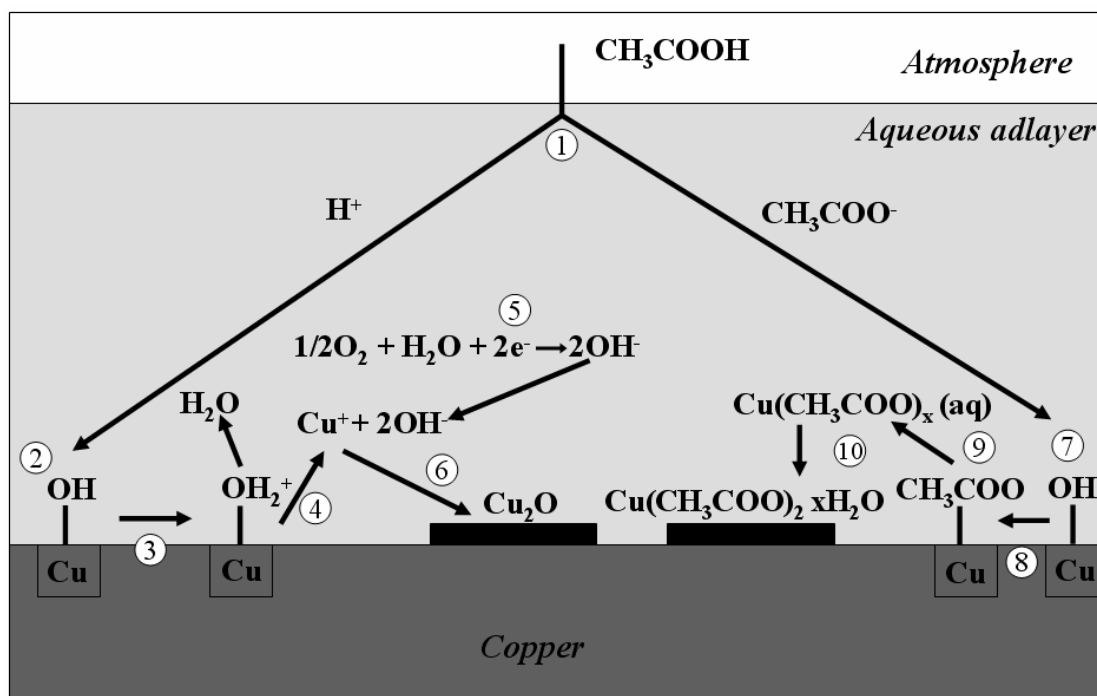


Figure 3. Schematic description of reaction pathways for the formation of copper (I) oxide (step 1 to 6) and copper (II) carboxylate (step 7 to 10) during initial atmospheric corrosion of copper by humidified air and acetic acid.

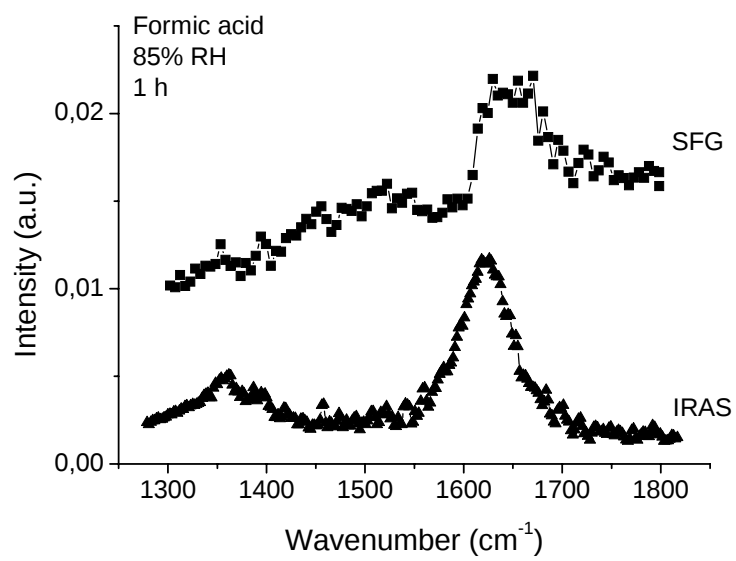


Figure 4. Zinc exposed to formic acid and 85% RH for 1 h. Upper: SFG spectrum. Lower: corresponding IRAS spectrum.

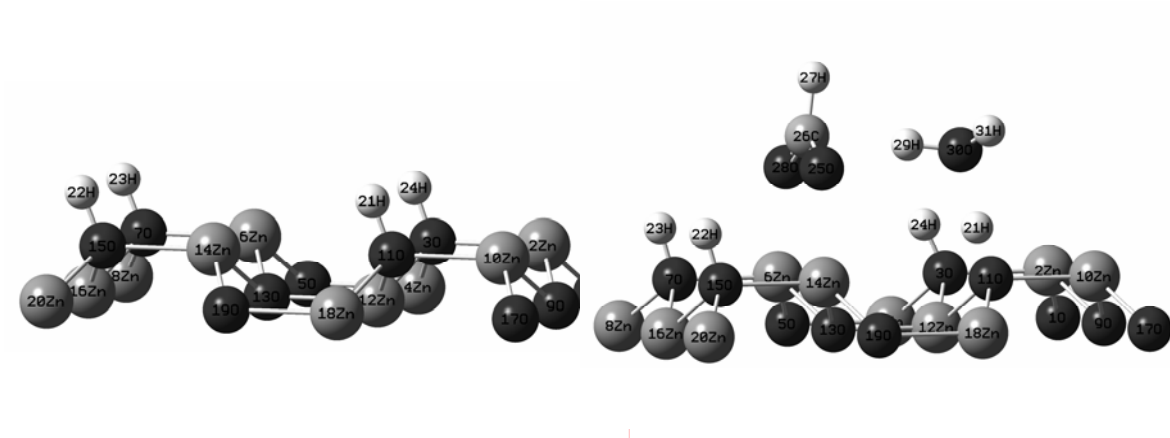


Figure 5. Left: The hydroxylated ZnO(100) surface with repetitive units used as a starting point for the theoretical calculations. Zn: grey large; O: dark large; H: light small. Right: the resulting configuration of the formate ion, showing a bonding between oxygen atoms of the formate species and zinc atoms of the substrate. Hydrogen bonding with water or surface hydroxyl groups does not participate in the bonding between zinc oxide and the formate ion.

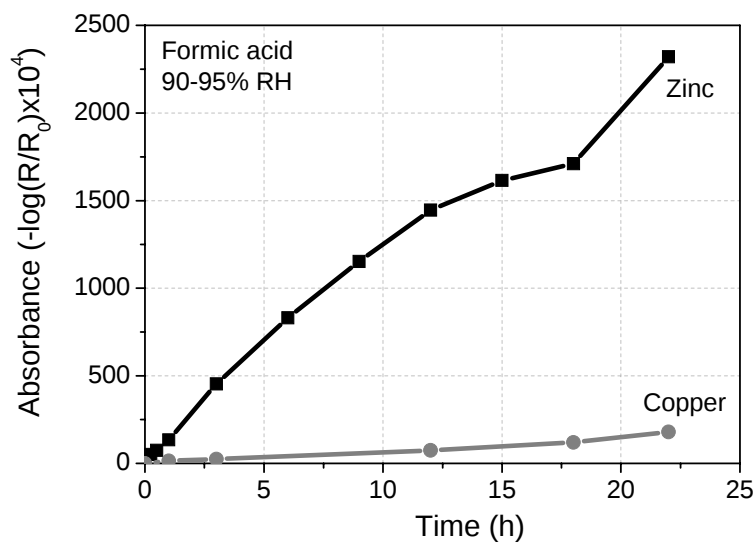


Figure 6. Comparison of formate growth on zinc and copper. The data have been obtained by plotting the IRAS absorbance of the antisymmetric formate peak as a function of time of zinc and copper during exposure in humidified air (90-95% relative humidity) to which the same concentration (120 ppb) of formic acid was added.

PAPER IV

CATHODIC REDUCTION MODEL OF COPPER OXIDES FILMS FORMED IN PRESENCE OF ACETIC ACID

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ABSTRACT

A cathodic reduction model of oxide films formed on copper in presence of acetic acid has been proposed. The simulation is based on copper oxides obtained during 21 days in climatic chamber experiments with 0, 500 and 800 ppb of acetic acid at 95% RH. It was found that as the concentration of the acid increases, the formation of the copper oxide (I) increases. The cathodic reduction was carried out in 0.1M KCl until hydrogen evolution indicating the end of the reduction. The curves were modeled taking into account the electrochemical reduction of copper (II) oxide (CuO), amorphous cuprite (Cu_2O)_{am}, intermediate cuprite (Cu_2O)_{in}, crystalline cuprite (Cu_2O)_{cr}, and hydrogen. These oxides have been previously detected in similar conditions and are considered to follow the Langmuir isotherm. No evidence of copper carboxylate was found by the electrochemical method. The result shows a relative accuracy of 0.98 or better in R2 coefficient.

Keywords: Cathodic reduction, atmospheric corrosion, copper, acetic acid.

INTRODUCTION

When exposed to the atmosphere, copper forms a thin layer of corrosion products called patina. This patina can be constituent of several corrosion products depending of the environment. Thus, indoor measurements have proved the formation of copper-carboxylates, such as copper acetate and copper

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formate determined by surface analysis studies [1]. Likewise, atmospheric corrosion of copper influenced by organic acids has been observed, and it is well-established that these acids form one of the dominant classes of organic compounds in the atmosphere. Previous studies have been done on copper samples exposed to synthetic air with acetic acid at high relative humidities, showing mostly amorphous cuprite, crystalline cuprite and copper acetate dehydrate [2,3]. In similar conditions, exposures on copper with formic, propionic and butyric acid exhibits the presence of the two types of cuprites together with the copper carboxylates [4-7].

On the other hand, different types of copper oxides formed at the copper surface have been recognized depending of the conditions [8-12]. As reported by Miley [13], the oxide layers are composed of cuprous oxide (Cu_2O) and cupric oxide (CuO). Other authors have reported three kind of copper (I) oxide, namely “precursor”, intermediate and “bulk” cuprite [14]. Accordingly, the selective determination of the two oxides having different properties is important for corrosion characterization, so, the most popular techniques used to characterize the oxides are electrochemical methods and more recently, spectroscopy methods [14]. However, there are two different views regarding correct interpretation of measurement data [15]. The aim of the present work is to propose a mechanism by which copper oxides formed in presence of acetic acid are reduced in potassium chloride.

EXPERIMENTAL

Sample preparation—Copper samples of 2x2 cm of 99.5% of purity were used in the experiments. They were cut and polished with silicon carbide paper down to 1000 mesh, cleaned with ethanol (99.5% purity) and finally dried with cold air before exposure.

Climatic chamber exposures—Measurements in synthetic atmosphere was performed during 21 days, in an exposure chamber at constant temperature of 25°C. A relative humidity of 95% was obtained by mixing water saturated air flow with dry air flow. The samples were located vertically inside a glass vessel. The experiments were done with 0, 500 and 800 ppb of acetic acid by using a permeation tube filled with pure acetic acid.

Cathodic reduction— Potentiodynamic reduction measurements were performed on the copper plates to characterize corrosion products produced by synthetic air. All the experiments were done by triplicate. The reductions were made by using an electrochemical cell with a platinum plate used as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The working electrode was the copper samples with a small hole by which were hanging in a platinum wire. The support solution was 0.1M of KCl according with the procedure described in ASTM standard [16]. The Solution was purged with pure nitrogen 20 min before and during the measurements. A potentiostat/galvanostat Bas Zahnner was used with scanning rate of $1\text{mV}\cdot\text{sec}^{-1}$, from the corrosion potential until -1.4V to secure the complete reduction of the species.

RESULTS AND DISCUSSION

Exposures of copper without any pollutant—Fig. 1 shows the reduction curves of copper samples exposed in synthetic air at 95%RH without any acetic acid concentration, during 10, 30, 60, 120 and 150 minutes. As a reference, an unexposed sample, previously polished and cleaned was reduced. The reduction charge value for each reduction peak found with the potentiodynamic curves, were calculated as the integration of the area between the experimental curve and the background line, both taken between two selected potential values. Fig. 2 displays the reduction charge amount

against exposure time. The charge was calculated from Fig. 1 for each experiment. There is not evidence of a reduction peak in the reference sample, going directly to the hydrogen evolution close to -0.95 V (SCE). After 10 min of exposure, a peak around -0.56V vs. SCE was found, corresponding to the amorphous cuprite, referred here as $(\text{Cu}_2\text{O})_{\text{am}}$ present at the surface before any exposure time [14]. This oxide is present in all exposures times and the amount remains approximately constant (see Fig. 2).

After 30 min of exposure, a second copper (I) oxide is found close to -0.8V, that could be associated with the intermediate cuprite, referred here as $(\text{Cu}_2\text{O})_{\text{in}}$ having a reduction potential more negative than the amorphous one. It has been suggested that the intermediate oxide is obtained through transformation of $(\text{Cu}_2\text{O})_{\text{am}}$ and has a limited life [14]. In our case, the intermediate oxide grows after 30 min of exposures and then decrease until disappear it for longer exposures (Fig. 2). Finally, a third copper (I) oxide, referred here as crystalline oxide $(\text{Cu}_2\text{O})_{\text{cr}}$ was found after 60 min of exposure, and grows until the end of the experiment. There is no presence of cupric oxide (CuO) in these measurements.

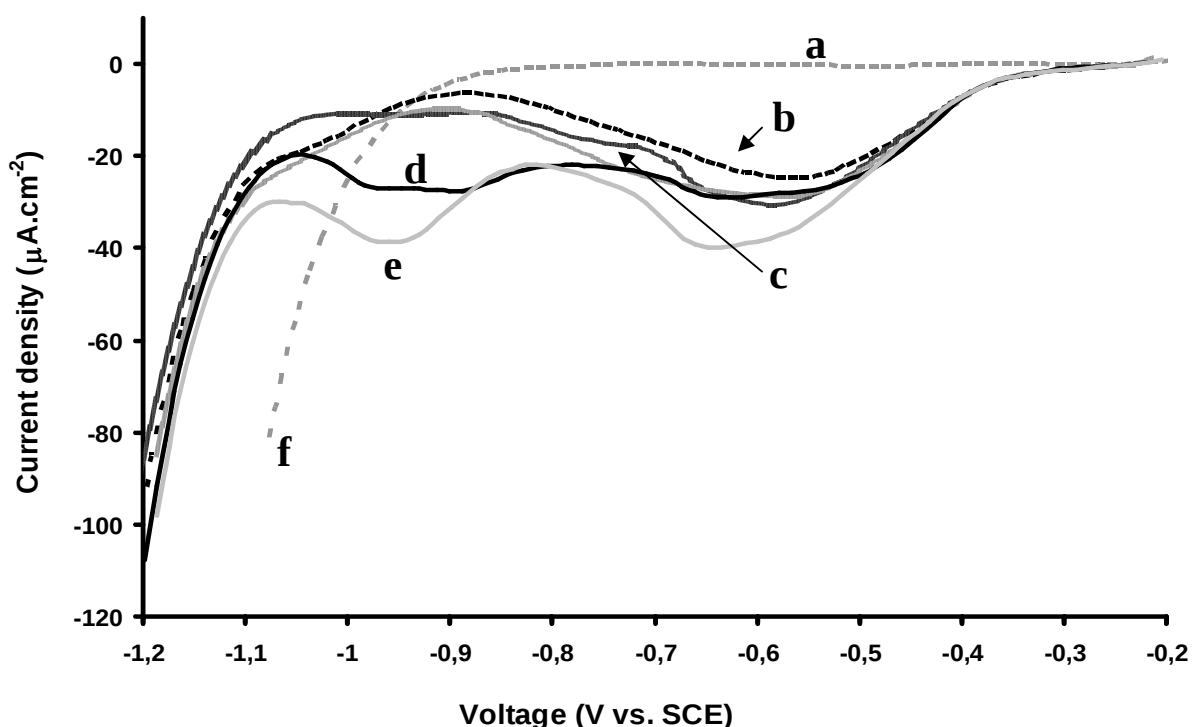


FIGURE 1 – Potentiodynamic reduction curves of copper in deaerated 0.1M KCl solution ($v = 1\text{mV}\cdot\text{sec}^{-1}$) of unexposed sample (a), exposed sample in pure air during 10 min (b), 30 min (c), 60 min (d), 120 min (e) and 150 min (f).

Electrochemical reduction of copper after exposures in air with 500 and 800 ppb of acetic acid— Fig. 3-4 displays potentiodynamic reduction curves of copper exposed to 500 and 800 ppb of acetic acid at 95% RH. With experiments at 500 ppb, it is possible to see an increment in the current density with time, indicating growth of corrosion rate. Similar peaks compare with exposures in pure air are found. The peaks are located close to -0.65, -0.81 and -1V vs. SCE during the whole experiment. Thus, we can conclude that these exposures produces three kind of copper (I) oxides at the copper surface. Fig. 4 presents potentiodynamic curves of copper exposed to 800ppb of acetic acid in the same humidity conditions. When comparing the two concentrations of acetic acids, it is possible to see that after 21 days of exposures, the dominant reduction peak is the “bulk” or crystalline cuprite. Fig. 5a-b displays the reduction charge amount corresponding to the two

concentrations tested. The comparison shows that the amount of the oxides increases as increase the exposure time. The amorphous cuprite amount after 21 days is almost 5 times larger that the crystalline one in 500ppb and 2 times in 800ppb of acetic acid.

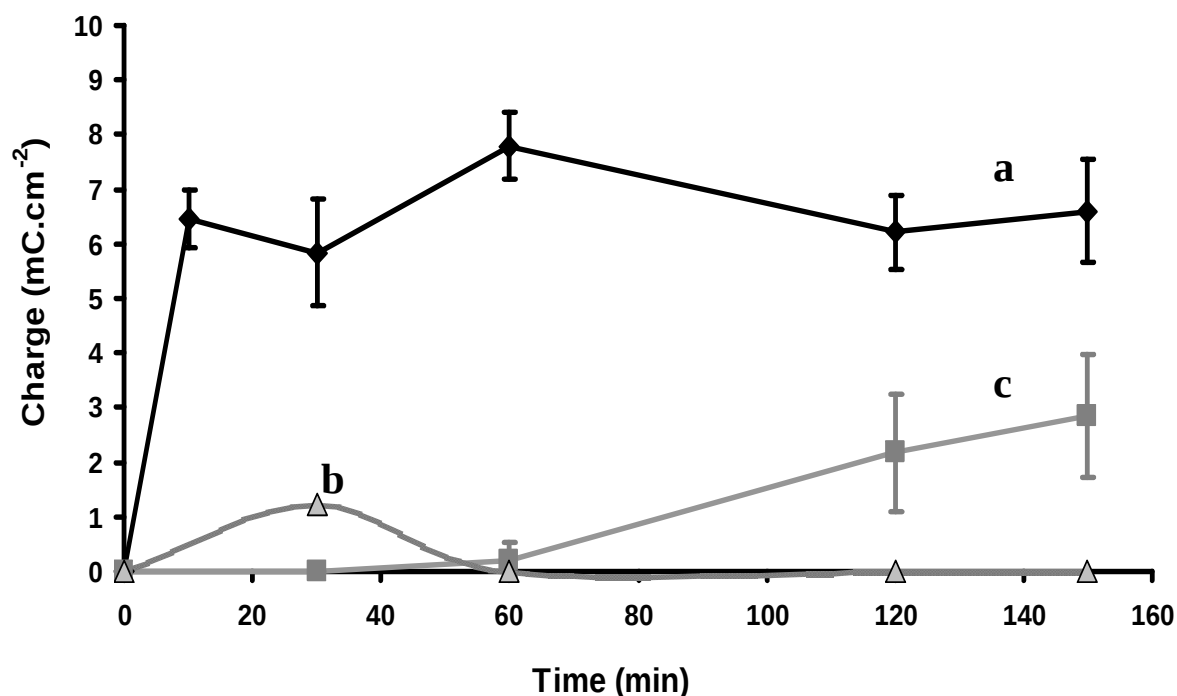


FIGURE 2 – Variation of oxides reduction charge amount with time of (a) amorphous cuprite $(\text{Cu}_2\text{O})_{\text{am}}$, (b) intermediate cuprite $(\text{Cu}_2\text{O})_{\text{in}}$ and (c) crystalline cuprite $(\text{Cu}_2\text{O})_{\text{cr}}$.

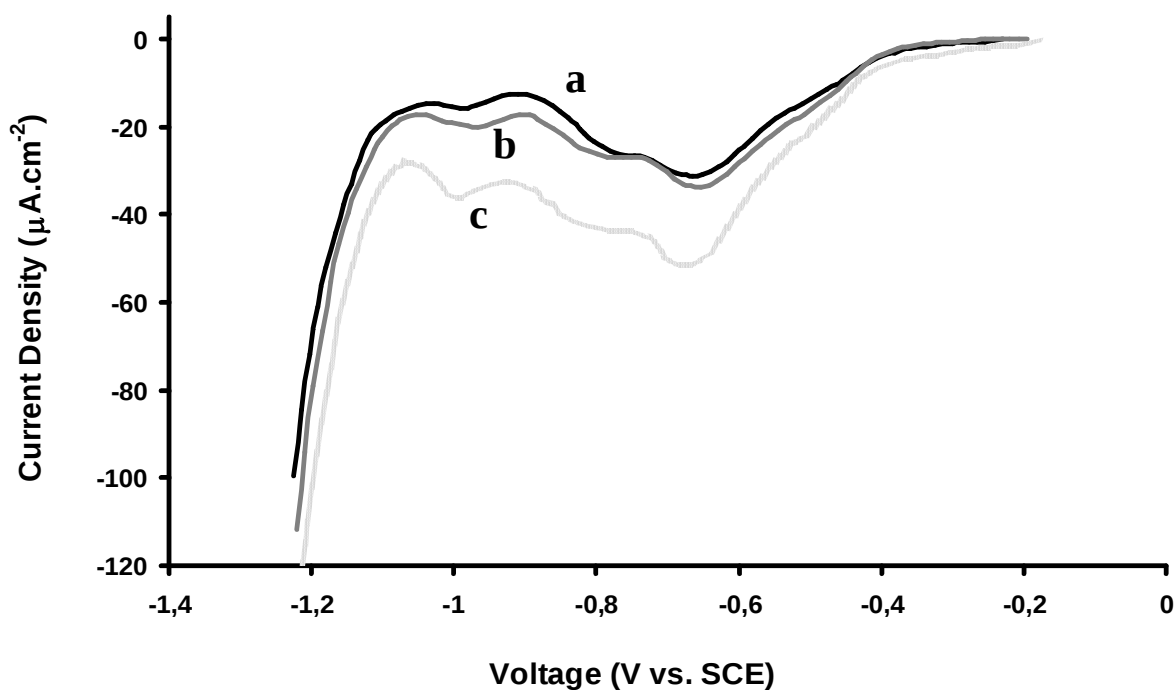


FIGURE 3 – Potentiodynamic reduction curves of copper in deaerated 0.1M KCl solution ($\nu = 1\text{mV}.\text{sec}^{-1}$) after exposures in 500 ppb acetic acid at 95%RH during 7 days (a), 14 days (b) and 21 days (c).

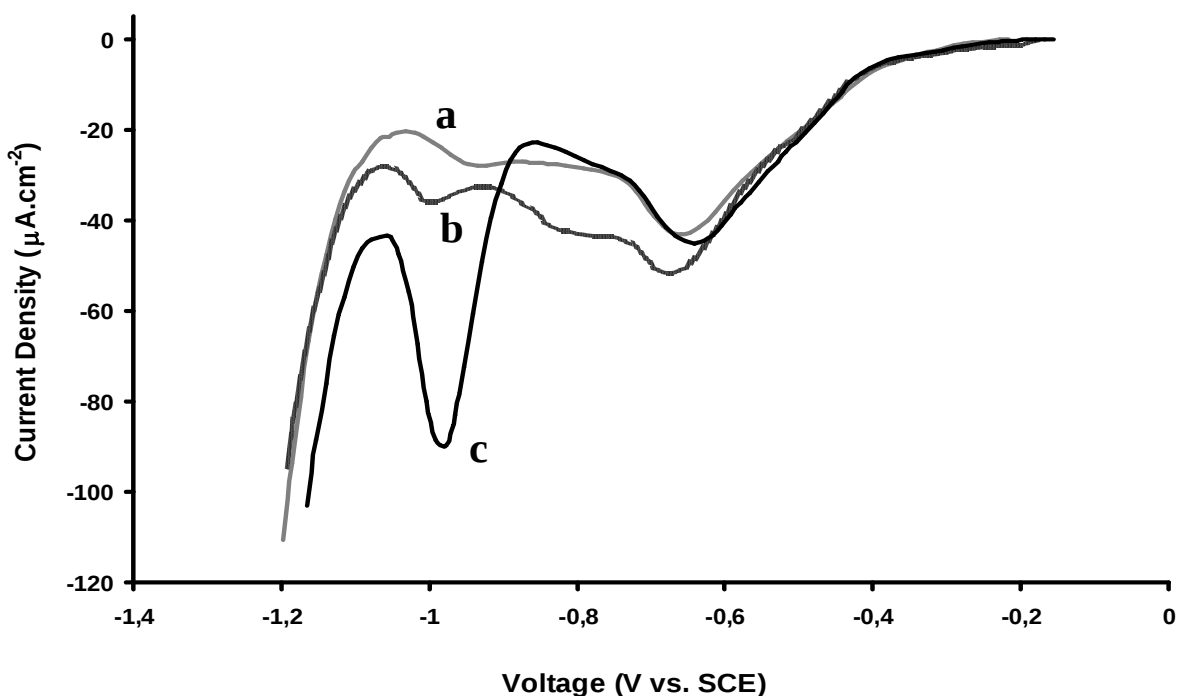


FIGURE 4 – Potentiodynamic reduction curves of copper in deaerated 0.1M KCl solution ($\nu = 1\text{mV}\cdot\text{sec}^{-1}$) after exposures in 800 ppb acetic acid at 95%RH during 7 days (a), 14 days (b) and 21 days (c).

A new peak around -0.42V vs. SCE is seen for exposures of copper in 800ppb of acetic acid. This peak could be related to the presence of copper (II) oxide, named tenorite, with a reduction potential range referred as -0.25 to -0.38V vs. SCE according with literature [14]. The tenorite amount has a maximum at 14 days and then decreases slightly at 21 days of exposure. Another important aspect is that the minimum seen for amorphous cuprite coincides with the maximum of the intermediate copper (I) oxide. This can support the idea of transformation of the first oxide with some kind of “rearrangement” of the non-stoichiometric form described by Deutscher [8]. The amount of amorphous cuprite calculated for 500ppb of acetic acid continues increasing with time; meanwhile with 800ppb reach a maximum after 7 days and the amount levels off. Neither, exposures to 500ppb or 800ppb acetic acid level exposures produces copper carboxylates compounds because of the lack of reduction peaks more negative than -1V . Copper acetate compounds are very soluble in water, which can be explain by the unseen acetate peaks, at least for the concentration level tested. For larger concentration of the acid, it is possible to form several kind of carboxylates compounds; i.e copper hydroxiacetate, that can be insoluble and then possible to detect during the potentiodynamic reduction.

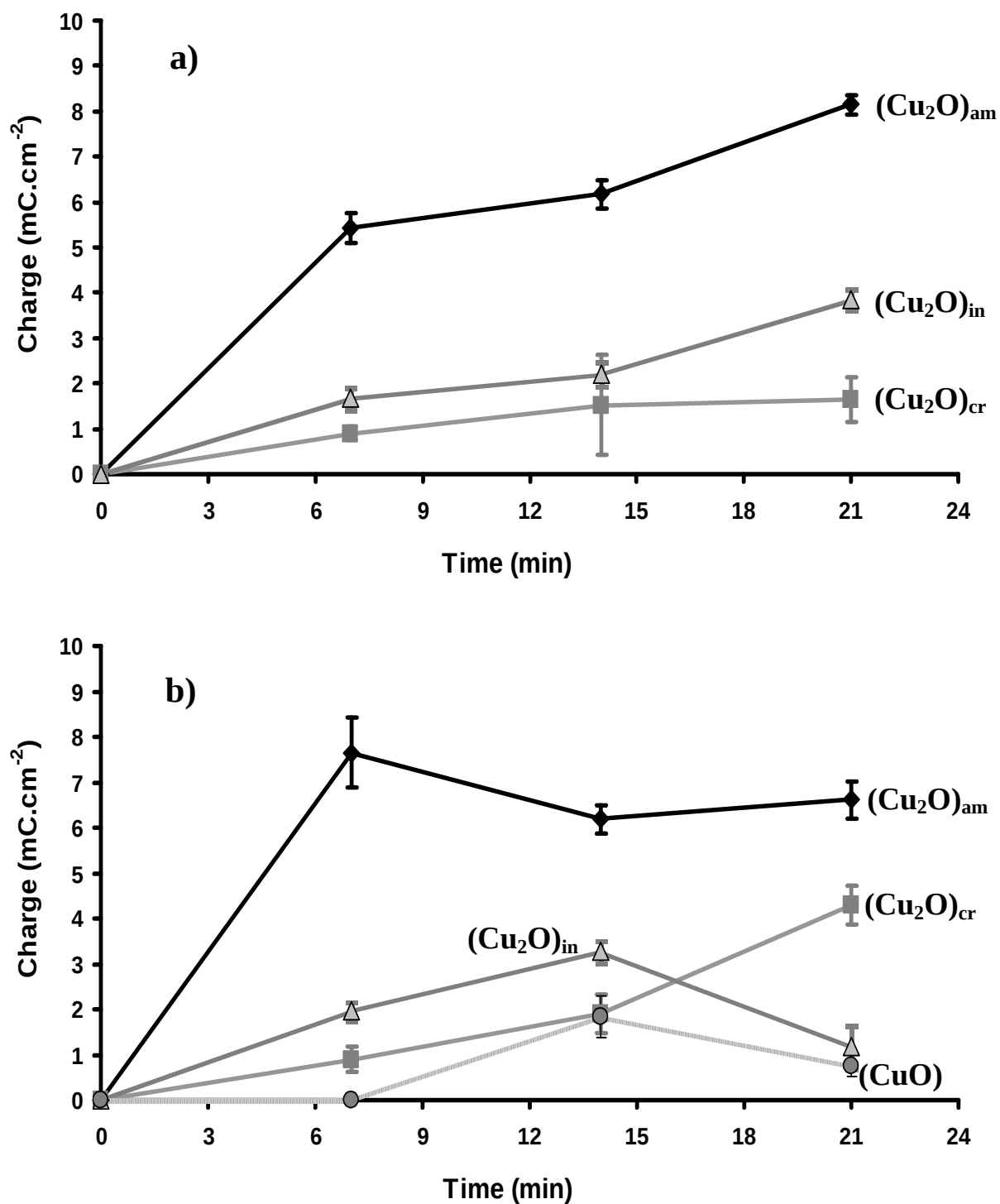


FIGURE 5a-b – Variation of oxides reduction charge amount with time of copper samples exposed to (a) 500ppb acetic acid and (b) 800ppb of acetic acid.

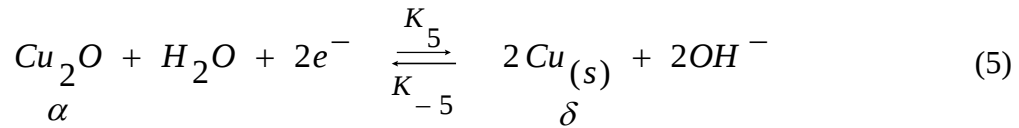
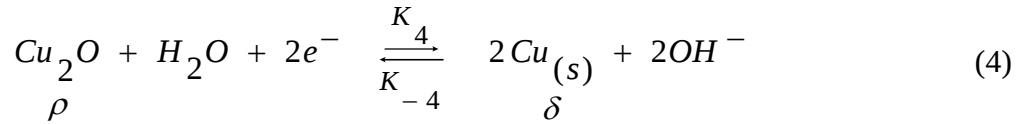
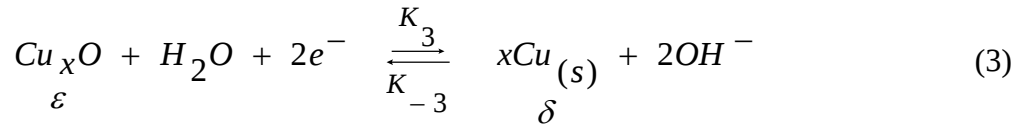
Cathodic reduction model of copper oxides—The cathodic reduction of copper oxides have two reduction sequences, but, in concordance with the pH-E diagram for copper [17] and previous work with potentiodynamic curves performed in similar conditions [6-7,14,18-20], we proposed that the

reduction of the copper oxides begins with a reduction of the copper (II) oxide in two steps as follows:



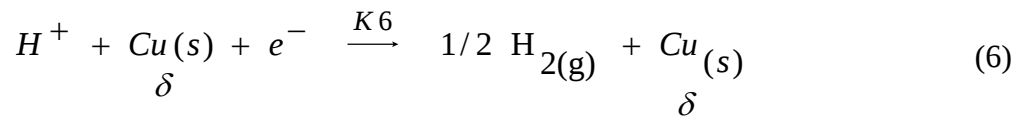
where θ , γ and α are the surface coverage of the species Cu(II), Cu^{*}(I) and Cu(I) respectively.

The reduction of the cupric oxide goes with the K_1 reaction to produce adsorbate specie named Cu^{*}(I). The Cu^{*}(I) specie is an intermediate, that lately reduces to copper (I) oxide. Then we have the reduction of the three copper (I) oxides present at the surface, according to:



where ε , ρ and α are the surface coverage of the amorphous cuprite (Cu₂O)_{am}, intermediate cuprite (Cu₂O)_{in} and crystalline cuprite (Cu₂O)_{cr} and δ is the coverage of the remaining copper surface.

Finally, we have the hydrogen evolution over the copper surface following the equation:



where K is the potential dependent parameter being $K_i = K_{0i} \cdot \exp(-b_i E)$; $K_{-i} = K_{0i} \cdot \exp(b_i E)$ and $b_i = F/RT$.

No overlapping of this coverages is considered, thus $\delta = 1 - \theta - \gamma - \alpha - \varepsilon - \rho$. We assume that all of the adsorption-desorption follows the Langmuir-type isotherm. Base on this hypothesis, the charge balance gives the total reduction current flowing through the electrode interface:

$$I_{\text{Total-red}} = I_{\text{Cu(II)}} + I_{\text{Cu}_x\text{O}} + I_{(\text{Cu}_2\text{O})_i} + I_{\text{Cu}_2\text{O}} + I_{\text{H}_2} \quad (7)$$

$$I_{\text{Total-red}} = F * [(-K_1\theta) + (-2K_3\varepsilon + (2/x)K_{-3}\delta) + (-2K_4\rho + K_{-4}\delta) + (-2K_5\alpha + K_{-5}\delta) - (K_6\delta)] \quad (8)$$

K_2 does not intervene in the charge balance because the related reaction neither produces nor consumes electrons. The surface coverages are potential- and time dependent parameters. Since I is expressed in A.cm^{-2} , K implies implicitly the concentration expressed in mole.cm^{-2} . The mass balance of the species allows one to express the time dependence of the coverages through differential equations:

$$\beta_1 \frac{d\theta}{dt} = \beta v \frac{d\theta}{dE} = -K_1\theta \quad (9)$$

$$\beta_2 \frac{d\gamma}{dt} = \beta v \frac{d\gamma}{dE} = K_1\theta + K_{-2}\alpha - K_2\gamma \quad (10)$$

$$\beta_3 \frac{d\varepsilon}{dt} = \beta v \frac{d\varepsilon}{dE} = -K_3\varepsilon + K_{-3}\delta \quad (11)$$

$$\beta_4 \frac{d\rho}{dt} = \beta v \frac{d\rho}{dE} = -K_4\rho + K_{-4}\delta \quad (12)$$

$$\beta_5 \frac{d\alpha}{dt} = \beta v \frac{d\alpha}{dE} = -K_5\alpha + K_{-5}\delta \quad (13)$$

β is the constant linking the fraction of the coverage and the surface concentration of adsorbed species expressed in mole.cm^{-2} . β_i values are considered to be equal to 10^{-8} (mole.cm^{-2}) which corresponds to about one monolayer. The scanning rate v is set to 0.001V.sec^{-1} according with the experimental setup.

The constant K values are computer simulated to give satisfactory fitting results. To perform this, one attempts to reproduce the experimental results by modifying the least number of $K_{0,i}$ values. The kinetic constant values used for the simulation calculation of the sample exposed during 14 days to 800 ppb of acetic acid are summarized in Table I. A calculated potentiodynamic reduction curve corresponding to this experiment is presented in Fig. 7 compared with the real reduction curve. We found a correlation coefficient of 0.98.

Table I. Kinetic parameter used to simulated the experimental curve of copper exposed during 14 days in 800 ppb of acetic acid

k_{01}	b_1	k_{-01}	b_{-1}	k_{03}	b_3	k_{-03}	b_{-3}	k_{04}	b_4	k_{-04}	b_{-4}
4.4E-14	19.9	9.1E-06	1.2	2E-14	17.6	3.2E-14	2.67	1.2E-14	15	8E-13	1.5

k_{05}	b_5	k_{-05}	b_{-5}	k_{06}	b_6
3.6E-14	10.9	0	1.64	4E-15	10.4

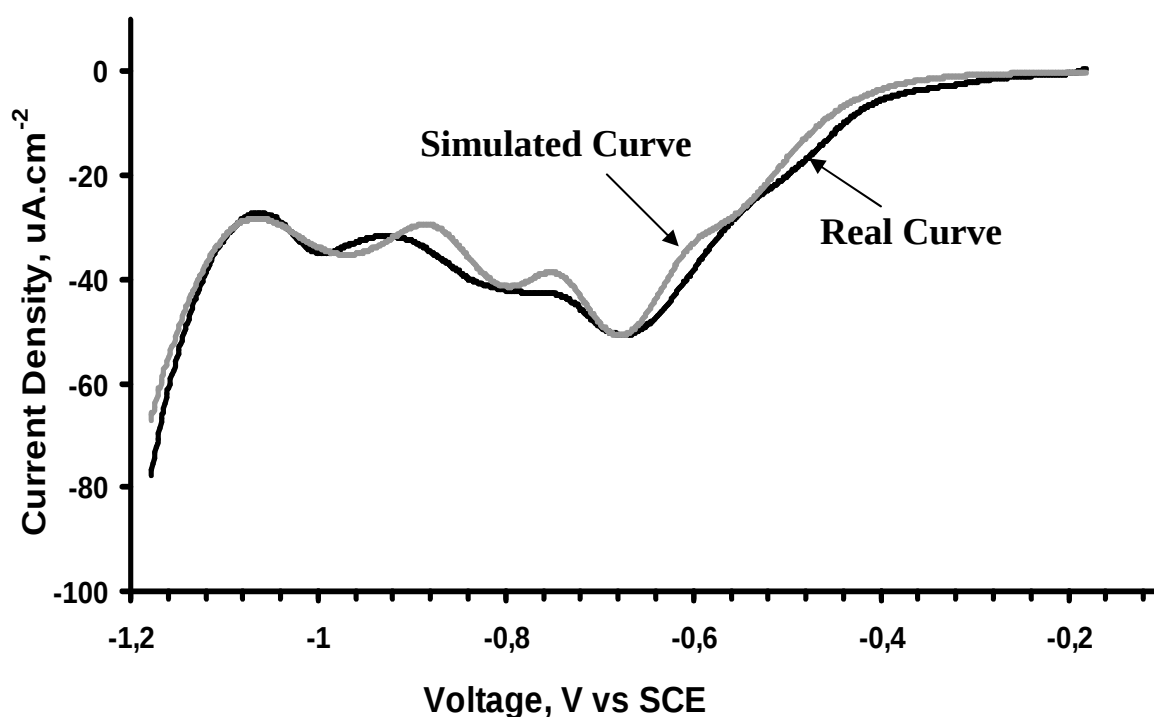


FIGURE 6 – Potentiodynamic reduction curve of copper in deaerated 0.1M KCl solution ($v = 1\text{mV}\cdot\text{sec}^{-1}$) after 14 days of exposure in 800 ppb of acetic acid solutions compared with calculated potentiodynamic reduction curve.

CONCLUSIONS

An electrochemical reduction model was proposed to fit potentiodynamic curves of copper exposed to acetic acid atmosphere. The model was applied to reduction of these compounds in 0.1M KCl, which involves copper (II) oxide [CuO], and three kind of copper (I) oxides [(Cu₂O)_p, (Cu₂O)_i and Cu₂O]. The good agreement of the model with the experimental data allows us to support the idea of the reduction sequence involving the copper oxides, from copper (II) type oxides and then the reduction of three copper (I) oxides.

Copper exposed at 95%RH and 0-800ppbv of acetic acid shows copper (I) oxides species. There is no evidence of copper acetate compounds according to the cathodic reduction technique, because of the possible high solubility of this type of compounds. With increasing acetic acid concentration in the air (0-800) ppb, the corrosion rate increases, measured as reduction charge density.

ACKNOWLEDGEMENTS

The authors express their gratitude to COLCIENCIAS (Colombian Institute for Development of Science and Technology) for the financial support.

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PAPER V

Electrochemical Reduction Modeling of Copper Oxides Obtained During *In Situ* and *Ex Situ* Conditions in Presence of Acetic Acid

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ABSTRACT

Potentiodynamic reduction technique was used to study the mechanism of copper oxides formed in presence of acetic acid. All reductions were performed in neutral conditions (KCl 0.1M) until hydrogen evolution. Copper oxides were produced under an environment containing 0, 500 and 800 ppb of acetic acid at high relative humidities. Experimental results were compared with electrochemically produced oxide films, which were obtained imposing anodic potentials to copper specimens in several concentrations of pure acetic acid, of 1, 0.1, 0.01 and 0.001M. It was found that as the concentration of the acid decreases, the formation of the copper oxide (I) increases. Same peaks were found in the simulated environment. The curves were modeled taking into account the electrochemical reduction of copper (II) oxide (CuO), amorphous cuprite (Cu₂O)_{am}, intermediate cuprite (Cu₂O)_{in}, crystalline cuprite (Cu₂O)_{cr}, and hydrogen. These oxides have been previously detected in similar conditions. No evidence of copper carboxylate was found by the electrochemical method.

Keywords: Potentiodynamic reduction, atmospheric corrosion, copper, acetic acid.

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1. INTRODUCTION

Copper patinas are characterized by been chemical and structurally complex. Copper patinas have been studied for periods of times, as long as 200 years[1]. During natural weathering, copper goes through a number of stages. Salmon-pink is the colour for clean copper with essentially no surface oxide as for example after acid cleaning. After exposure to the atmosphere, copper rapidly turns to the more familiar “copper” colour due to a thin surface oxide [1]. On further exposure, the colour darkens to brown and then to black as the oxide grows in thickness. These changes in colour are all due to cuprite formation with chemical formula Cu_2O wherein copper is in the +1 oxidant ion state. Further reaction with trace atmospheric impurities implies that copper goes through +2 oxidation state. So, it is found that this patina can be made of several corrosion products depending of the environment. It is common to find copper exposed to indoor environments, where has been proved the formation of copper-carboxylates, such as copper acetate and copper formate determined by surface analysis studies [2].

It has been found that copper samples exposed to synthetic air polluted with acetic acid at high relative humidities, shows mostly amorphous cuprite, crystalline cuprite and copper acetate dehydrate [3, 4]. Similarly, copper exposed to formic, propionic and butyric acid exhibits the presence of the two types of cuprites together with the copper carboxylates [5-8].

Different types of oxides formed on copper surfaces have been recognized depending of the conditions [9-13]. Miley [14], early concluded that the oxide layers are composed of cuprous oxide (Cu_2O) and cupric oxide (CuO). Other authors have reported three kind of copper (I) oxide, namely “precursor”, intermediate and “bulk” cuprite [15]. Accordingly,

the selective determination of the two oxides having different properties is important for corrosion characterization [16]. The most popular techniques used to characterize the oxides are electrochemical methods [13-15, 17-25], X-ray photoelectron spectroscopy (XPS) [26, 27] and more recently, spectroscopy methods [15, 19]. However, there are two different views regarding correct interpretation of measurement data [17-18, 28-29]. The oxide reduction order is interpreted from copper (II) oxide to copper (I) oxide, or it could be interpreted the other way around. The aim of the present work is to propose a reduction mechanism of copper oxides formed in presence of acetic acid and anodically produced in pure acetic acid.

2. EXPERIMENTAL

2.1. Sample preparation and atmospheric exposures—Copper sized 2x2 cm of 99.5% of purity were used in the experiments. They were cut and polished with silicon carbide paper down to 1000 mesh, cleaned with ethanol (99.5% purity) and finally dried with cold air before any exposure.

Measurements in synthetic atmosphere were performed during 21 days, inside an exposure chamber at 25°C. A relative humidity of 95% was obtained by mixing water saturated air flow with dry air flow. Samples were located vertically inside a glass vessel. The experiments were done with 0, 500 and 800 ppb of acetic acid by using an emission tube previously filled up with pure acetic acid. Emission rate was confirmed with gravimetric measurements of the tube.

2.2. Electrochemical polarization—Copper samples were polarized up to +1V_{SCE} in concentrations of 1, 0.1, 0.01 and 0.001M of acetic acid. Polarization was performed in

order to electrochemically produce corrosion products on the copper surface comparable to the atmospheric produced ones. After each polarization, the samples were washed with deionized water and located in the electrochemical cell to proceed with the reduction. All the experiments were done by triplicate.

2.3. Potentiodynamic reduction— Potentiodynamic measurements were performed on the copper plates to characterize corrosion products produced in synthetic air and by anodic polarizations. Electrochemical reductions were made by using an electrochemical cell with a platinum plate used as counter electrode and a saturated calomel electrode (SCE) ($E = 0.241 \text{ V/SHE}$) as reference. Working electrode was the copper samples with a small hole by which they were hanged using a platinum wire. Support solution was 0.1M of KCl purged with pure nitrogen 20 min before and during the measurements. A potentiostat/galvanostat Bas Zahnner was used with a scanning rate of $1 \text{ mV} \cdot \text{sec}^{-1}$, from the corrosion potential down to -1.4 V to secure the complete reduction of the species.

3. RESULTS AND DISCUSSION

3.1. Exposures without any pollutant—Fig. 1 shows the reduction curves of copper samples exposed in synthetic air at 95%RH without any pollutant, during 10, 60, and 150 minutes. After 10 min of exposure, a peak around -0.56 V vs. SCE was found, corresponding to the amorphous cuprite, referred here as $(\text{Cu}_2\text{O})_{\text{am}}$ present at the surface before any exposure time [15]. A second copper (I) oxide can be observed, referred here as crystalline oxide $(\text{Cu}_2\text{O})_{\text{cr}}$ with potential of reduction more negative than the amorphous one. This oxide was found after 60 min of exposure, and grows until the end of the experiment.

3.2. *Electrochemical reduction of copper after exposures in acetic acid*—Fig. 2-3 displays potentiodynamic curves of copper exposed to 500 and 800 ppb of acetic acid at 95% RH. Exposures at 500 ppb exhibit an increment in the current density with time, indicating growth of the corrosion rate. Reduction peaks are located close to -0.65, -0.81 and -1V vs. SCE during the whole experiment. The peak found close to -0.8V could be associated with the intermediate cuprite, referred here as $(\text{Cu}_2\text{O})_{\text{in}}$ having a reduction potential more negative than the amorphous one. It has been suggested that the intermediate oxide is obtained through transformation of $(\text{Cu}_2\text{O})_{\text{am}}$ and has a limited existence [15]. In our case, the intermediate oxide grows during the whole experiment with 500ppb of acetic acid, but with exposures at 800ppb the intermediate cuprite reaches a maximum after 14 days and then decreases. It is possible to conclude that these exposures produce three kinds of copper (I) oxides at the copper surface. When comparing the two concentrations of acetic acids we found that after 21 days of exposure, the dominant reduction peak is the “bulk” or crystalline cuprite. Reduction charge value for each reduction peak was found from the potentiodynamic curves; it was calculated as the integration of the area between the experimental curve and the background line, both taken between two selected potential values.

Fig. 4 displays the reduction charge amount against exposure time calculated for copper exposed to 800ppb of acetic acid. Each measurement was done by triplicate. As we can see, the oxides amount increases as increasing the exposure time. Amorphous cuprite amount after 21 days is almost five times larger in 500ppb and two times in 800ppb of acetic acid compared with unexposed measurements. A new peak around -0.42V vs. SCE is seen for exposures of copper in 800ppb of acetic acid. This peak could be related to the presence of copper (II) oxide, named tenorite, with a reduction potential range referred as -

0.25 to -0.38 V vs. SCE according with literature [15]. Tenorite amount has a maximum at 14 days and then decreases slightly at 21 days of exposure. Another important aspect is that the minimum observed for amorphous cuprite coincides with the maximum of the intermediate copper (I) oxide. This can support the idea of transformation of the first oxide or some kind of “rearrangement” of the non-stoichiometric form described by Deutscher [9]. Although the total amount of amorphous cuprite calculated for the two concentrations remains constant after 21 days, with 500ppb of acetic acid continues increasing with time, meanwhile with 800ppb reach a maximum after 7 days and then the amount levels off. Neither, exposure to 500ppb or 800ppb levels appears to produce copper carboxylates compounds as no reduction peaks were observed below -1V. However, copper acetate compounds are very soluble in water, which can explain the unseen acetate peaks, at least for the pollutant levels tested. For larger concentration of acid, we can form several kind of carboxylates compounds; *i.e* copper hydroxiacetate, that can be insoluble and then possible to see during the potentiodynamic reduction [4].

3.3. Reduction of copper samples after polarization in acetic acid solutions—Fig. 5 displays the reduction curves of electrochemically produced oxides in different concentrations of acetic acid. The anodic polarizations were performed from the open circuit potential until +1V vs. SCE at scanning rate of $1\text{mV}\cdot\text{sec}^{-1}$. The first reduction curve shows a broad peak around -0.5V vs. SCE which is the amorphous oxide. Diminishing of the acid concentration results in more oxide, reaching a maximum at 0.1M, and then slightly decreasing until 1M. There was not detected the presence of intermediate oxide. Moreover, crystalline cuprite appears after polarization in 0.01M with a large reduction current density which increases when copper is polarized in 0.001M electrolyte. As can be seen in the figure, oxide reduction potential is shifted to lower potentials with increase in

acetic acid concentration. This can be interpreted as follows, when the acid concentration decreases during oxide formation, pH increases allowing the formation of a more thermodynamically stable oxide according with the Pourbaix diagram of copper in water [30]. Likewise, the oxide seems to be more stable taking into account the small displacement of the reduction peak to more negative potential for the crystalline cuprite.

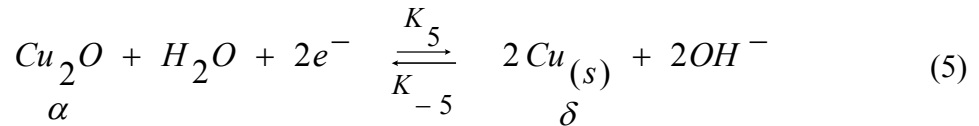
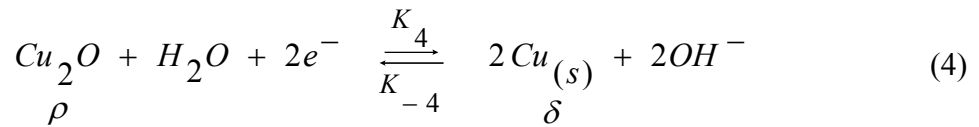
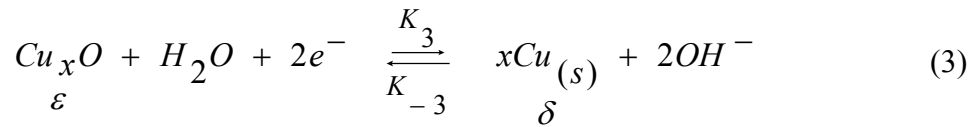
When comparing the electrochemically produced oxides with the atmospheric produced ones; it is found that exposure to concentration of 800ppb of acetic acid could produce similar oxide amount than polarization at 0.01M of acetic acid. This prove that the electrochemical method is a reliably technique to produce this type of compounds. Like in the case of atmospheric exposures, no evidence of copper acetate was found according to the potentiodynamic reduction curves.

3.4. Cathodic reduction model of copper oxides—Cathodic reduction of copper oxides is supposed to occur according with some authors with the reduction of the copper (I) oxide first and then the reduction of the cupric oxide. But, in concordance with the pH-E diagram for copper [30] and previous work with potentiodynamic curves performed under similar conditions [15], it is proposed that the reduction of the copper oxides begins with a reduction of the copper (II) oxide in two steps as follows:



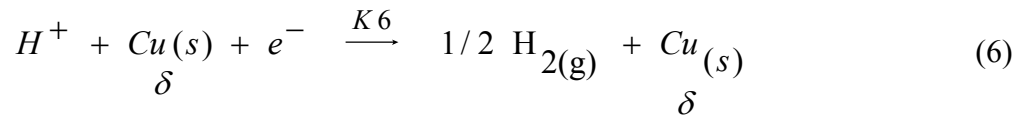
where θ , γ and α are the surface coverage fractions of the species Cu(II), Cu^{*}(I) and Cu(I) respectively.

Reduction of the cupric oxide goes through the K_1 reaction to produce an adsorbate specie Cu^{*}(I). The Cu^{*}(I) specie is an intermediate, that lately reduces to copper (I) oxide. Then we have the reduction of the three copper (I) oxides present at the surface, according to:



where ε , ρ and α are the surface coverages of the amorphous cuprite (Cu₂O)_{am}, intermediate cuprite (Cu₂O)_{in}, crystalline cuprite (Cu₂O)_{cr} and δ is the coverage of the remaining copper surface.

Finally, we have the hydrogen evolution over the copper surface following the equation:



where K is the potential dependent parameter being $K_i = K_{0i} \cdot \exp(-b_i E)$; $K_{-i} = K_{-0i} \cdot \exp(b_i E)$ and $b_i = F/RT$.

Presence of copper (I) oxide amorphous and crystalline has been found not only in the same acetic acid environment, but in presence of formic and propanoic acid. The confirmation of the oxides seen in this type of environments by means of grazing incidence x-ray diffraction and infrared reflection absorption spectroscopy can be found elsewhere [4, 31]. No overlapping of this coverages is considered, thus $\delta = 1 - \theta - \gamma - \alpha - \varepsilon - \rho$. We assume that all of the adsorption-desorption follows the Langmuir-type isotherm. Base on this hypothesis, the charge balance gives the total reduction current flowing through the electrode interface:

$$I_{\text{Total-red}} = I_{\text{Cu(II)}} + I_{\text{Cu}_x\text{O}} + I_{(\text{Cu}_2\text{O})_i} + I_{\text{Cu}_2\text{O}} + I_{\text{H}_2} \quad (7)$$

$$I_{\text{Total-red}} = F * [(-K_1\theta) + (-2K_3\varepsilon + (2/x)K_{-3}\delta) + (-2K_4\rho + K_{-4}\delta) + (-2K_5\alpha + K_{-5}\delta) - (K_6\delta)] \quad (8)$$

K_2 does not intervene in the charge balance because the related reaction neither produces nor consumes electrons. Surface coverage fractions are potential- and time dependent parameters. Since I is expressed in A.cm^{-2} , K has implicitly the concentration expressed in mole.cm^{-2} . The mass balance of the species allows one to express the time dependence of the coverages through differential equations:

$$\beta_1 \frac{d\theta}{dt} = \beta v \frac{d\theta}{dE} = -K_1\theta \quad (9)$$

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$$\beta_3 \frac{d\varepsilon}{dt} = \beta v \frac{d\varepsilon}{dE} = -K_3 \varepsilon + K_{-3} \delta \quad (11)$$

$$\beta_4 \frac{d\rho}{dt} = \beta v \frac{d\rho}{dE} = -K_4 \rho + K_{-4} \delta \quad (12)$$

$$\beta_5 \frac{d\alpha}{dt} = \beta v \frac{d\alpha}{dE} = -K_5 \alpha + K_{-5} \delta \quad (13)$$

β is the constant linking the fraction of the coverage and the surface concentration of adsorbed species expressed in mole.cm^{-2} . β_i values are considered to be equal to 10^{-8} (mole.cm^{-2}) which corresponds to about one monolayer. The scanning rate v is set to 0.001 V.sec^{-1} according with the experimental setup.

Coverage fraction values and the constant K are computer simulated to give satisfactory fitting results. To perform this, one attempts to reproduce the experimental results by keeping the b_i value independent of pH and by modifying the least number of $K_{0,i}$ values. Kinetic constant values used for the simulation calculation are summarized in Table I. A comparison of the measured potentiodynamic reduction curve after exposures during 14 days in 800ppb of acetic acid and the calculated potentiodynamic reduction curve is presented in Fig. 6. We can see that both curves are very similar, and we found a correlation coefficient of 0.987. For almost all experiments the correlation was 0.985 or better except for exposure after 21 days in 800ppb where the correlation was 0.92. The low correlation found in 800ppb environment could be explained by the fact that the copper surface has more than one monolayer of corrosion products, in all cases causing that the amount of crystalline cuprite exceeds the simulated amount done with the assumption of one monolayer. The proposed reduction mechanism provides a tentative explanation of the

potentiodynamic reduction curves, however there is not evidence of the species $\text{Cu}^*(\text{I})$. In this paper we proposed a model that could explain the curves by making several assumptions, but an accurate model is necessary for the entire comprehension of the reduction curves and further pH-local measurements and spectroscopic methods are needed to verify the reaction mechanism.

Evolution of surface coverage with potential corresponding to exposures after 21 days in acetic acid environment is presented in Fig. 7. All the oxides present at the copper surface begins with high coverage close to the open circuit potential and then decreases with more negative potential values. Initial coverage of the crystalline oxide is greater than the amorphous and intermediate ones which is clearly seen from reduction curves in Fig. 2 and 3. Intermediate and amorphous cuprite present coverage of almost zero after -0.8V, meanwhile the crystalline cuprite decreases its coverage after -1V, as stated before. On the contrary, coverage associated with the hydrogen reduction begins with a small value to high potential values, and increases when decreasing the potential until complete a full coverage of the surface. At the end of the reduction; close to -1.2V, the surface coverage belongs just to the hydrogen evolution as we expected. When comparing both pollutant level tested, it is possible to see greater amounts of copper (I) oxides in 800ppb exposures. The entire copper oxides amount is verified with its coverage, taking into account the initial value. These means that the proposed model is able to describe the potentiodynamic changes when the electrochemically or atmospheric produced copper oxides are reduced.

The results of the simulation of copper oxides reduction after been polarized in pure acetic acid are presented in Table II. The fitting has been done with the same proposed reduction mechanism that the one used to explain the potentiodynamic curves in acetic acid

atmospheric exposures. Similarly, the fitting was above 0.98 for 1 and 0.1M of acetic acid, meanwhile the simulation of copper in 0.01 and 0.001 is not very accurate because of the large amount of crystalline cuprite that creates difficulties to simulate the data as with the 800ppb of acetic acid atmospheric exposures.

Concluding Remarks—Copper oxides were produced in atmospheric conditions with presence of acetic acid. Electrochemical characterization of the oxides was possible using a reduction modeling taking into account the presence of copper (II) oxide and the previously found copper (I) oxides in three forms. Using the modeling and the reduction charge calculated as the area between two selected potentials, allow us to estimate the amount of copper oxides that are comparable with the reported by the literature. Moreover, the presence of the copper compounds was confirmed by obtaining the same products using polarization of fresh copper surfaces in several concentrations of pure acetic acid. Current work deals with ex situ electrochemical characterization of copper compounds produced in pure formic and propionic acid.

4. CONCLUSIONS

An electrochemical reduction model was proposed to fit potentiodynamic curves of copper exposed to acetic acid atmosphere or electrochemically produced oxides samples. The model was applied to reduction of these compounds in 0.1M KCl, which involves copper (II) oxide [CuO], and three kind of copper (I) oxides [(Cu₂O)_{am}, (Cu₂O)_{in} and (Cu₂O)_{cr}]. The good correlation of the model with the experimental data allow us to agree with the reduction sequence involving the copper oxides, from copper (II) type oxides and then the copper (I) oxides.

Copper exposed at 95%RH and 0 to 800ppbv of acetic acid shows copper (I) oxides species. There is no evidence of copper acetate compounds according with cathodic reduction technique, because of the possible high solubility of this type of compounds. As increasing acetic acid concentration in the air (0-800) ppb, the corrosion rate increases, measured as reduction charge density.

The production of copper oxides by anodic polarization in pure acetic acid solutions is useful to form a layer containing crystalline and amorphous copper (I) oxides. The reduction potentials of the copper oxides are affected by the acetic acid concentration.

5. ACKNOWLEDGEMENTS

The authors express their gratitude to COLCIENCIAS (Colombian Institute for Development of Science and Technology) for the financial support.

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Figure Captions

Figure 1. Potentiodynamic curves of copper in deaerated 0.1M KCl solution ($v = 1\text{mV.sec}^{-1}$) of pure air exposed samples during 10 min (a), 60 min (b) and 150 min (c).

Figure 2. Potentiodynamic curves of copper in deaerated 0.1M KCl solution ($v = 1\text{mV.sec}^{-1}$) after exposures in 500 ppb acetic acid at 95%RH during 7 days (a), 14 days (b) and 21 days (c).

Figure 3. Potentiodynamic curves of copper in deaerated 0.1M KCl solution ($v = 1\text{mV.sec}^{-1}$) after exposures in 800 ppb acetic acid at 95%RH during 7 days (a), 14 days (b) and 21 days (c).

Figure 4. Variation of oxides reduction charge with time for copper samples exposed to 800ppb of acetic acid.

Figure 5. Potentiodynamic curves of copper in deaerated 0.1M KCl solution ($v = 1\text{mV.sec}^{-1}$) after polarization in 1M (a), 0.1M (b), 0.01M (c) and 0.001M (d) of acetic acid solutions.

Figure 6. Potentiodynamic curve of copper in deaerated 0.1M KCl solution ($v = 1\text{mV.sec}^{-1}$) after exposure in 800ppb of acetic acid during 14 days compared with the simulated potentiodynamic curve.

Figure 7. Evolution of the calculated surface coverage with the potential for copper reduction in deaerated 0.1M KCl solution ($v = 1\text{mV}\cdot\text{sec}^{-1}$) after exposure during 21 days in 500 (a) and 800ppb (b) of acetic acid.

**Table I. Kinetic parameters used to simulate the experimental curves in acetic acid
environment**

Time (days)	Concentration (ppbv)	k₀₁	k₀₃	k₀₄	k₋₀₄	k₀₅	k₋₀₅	b₋₅	k₀₆
7	500	6.9E-14	2.0E-14	1.5E-14	8.0E-13	3.6E-14	2.0E-11	1.6	4.0E-15
14	500	7.3E-14	2.0E-14	1.4E-14	8.0E-13	3.6E-14	1.0E-11	1.6	4.0E-15
21	500	4.4E-14	2.0E-14	1.0E-14	8.0E-13	3.1E-14	1.0E-11	1.6	6.0E-15
7	800	5.7E-14	2.0E-14	2.0E-14	1.0E-12	5.6E-14	3.0E-11	1.6	4.0E-15
14	800	4.4E-14	2.0E-14	1.2E-14	8.0E-13	3.6E-14	1.0E-11	1.6	4.0E-15
21	800	7.0E-14	3.0E-14	3.2E-14	8.0E-13	2.7E-14	6.0E-11	2.2	5.0E-15

For all experiments, the following parameters were kept constant: $b_1=19.9$; $k_{-01}=9.1\text{e-}6$;
 $b_{-1}=1.2$; $k_{-03}=3.2\text{e-}14$; $b_3=17.6$; $b_{-3}=2.7$; $b_4=15$; $b_{-4}=1.5$; $b_5=10.9$ and $b_6=10.4$.

Table II. Kinetic parameters used to simulate the experimental curves obtained by ex situ conditions

Concentration (M)	k₀₁	k₀₃	b₃	k₀₄	k₋₀₄	k₀₅	k₋₀₅	k₀₆
1	2.4E-13	7.1E-14	17.6	1.5E-14	3.5E-14	1.3E-13	2.0E-11	2.0E-15
0.1	1.4E-12	2.0E-13	17.2	5.2E-14	8.0E-13	1.1E-13	1.0E-11	3.0E-15
0.01	1.5E-13	4.0E-14	17.6	4.4E-14	8.0E-13	3.6E-14	1.0E-11	3.0E-15
0.001	1.4E-13	2.0E-14	17.4	2.0E-14	5.0E-13	4.6E-14	2.0E-11	4.0E-15

For all experiments, the following parameters were kept constant: $b_1=19.9$; $k_{-01}=9.1\text{e-}6$;
 $b_{-1}=1.2$; $k_{-03}=3.2\text{e-}14$; $b_{-3}=2.7$; $b_4=15$; $b_{-4}=1.5$; $b_5=10.9$; $b_{-5}=1.6$ and $b_6=10.4$.

Figure 1

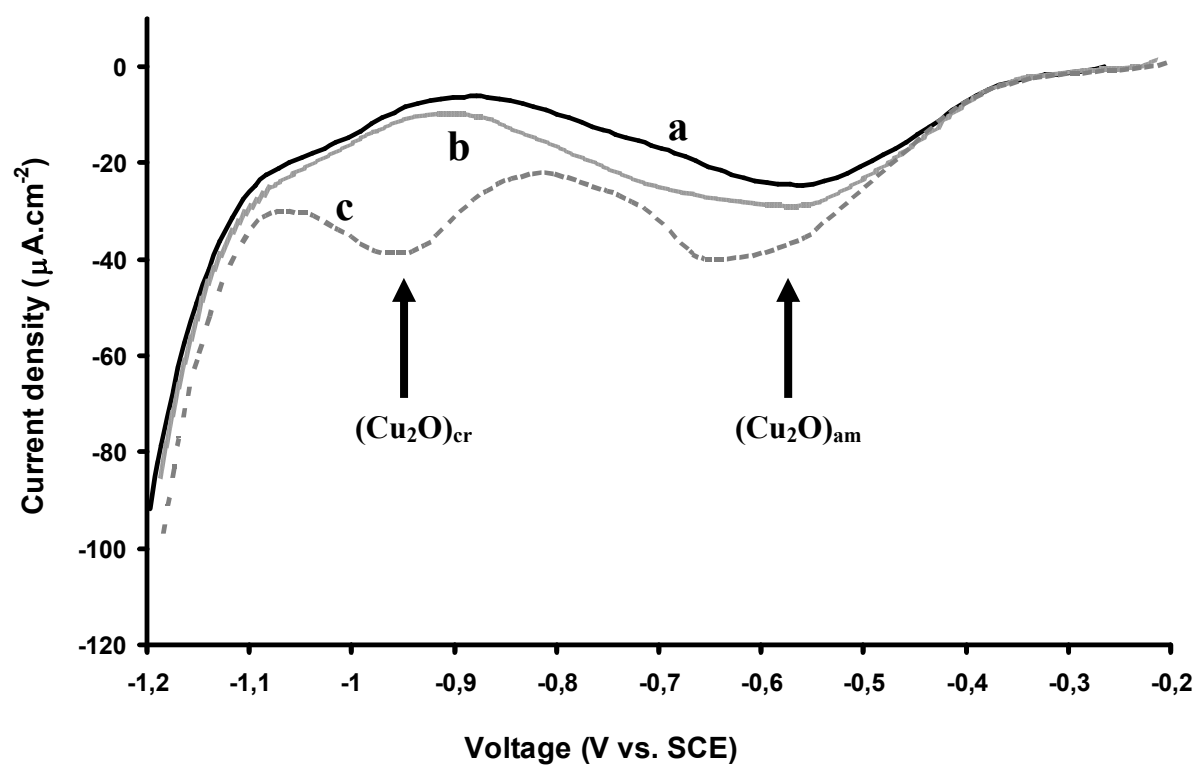


Figure 1.

Figure 2

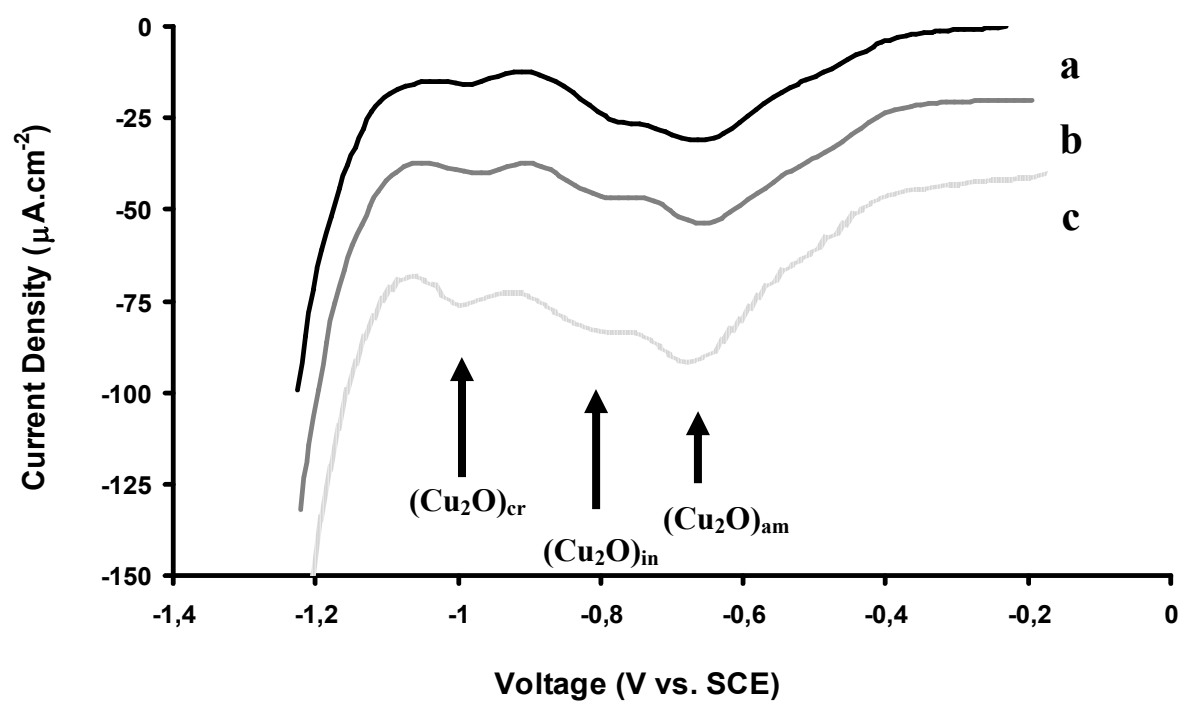


Figure 2.

Figure 3

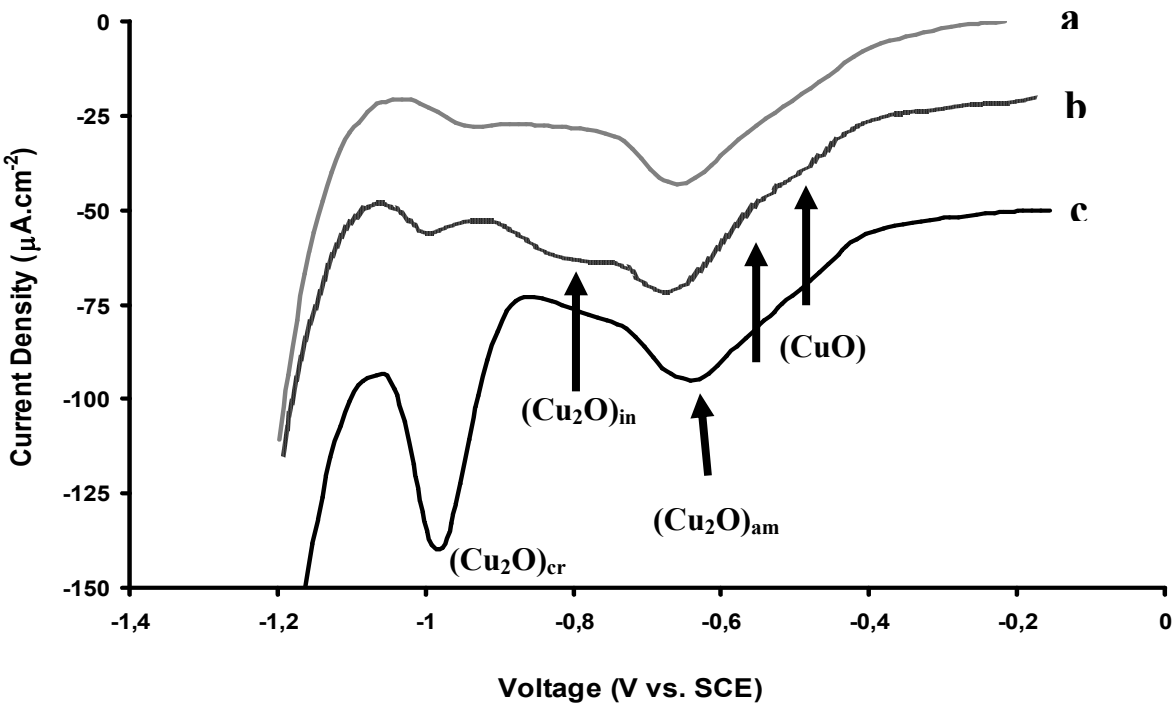


Figure 3.

Figure 4

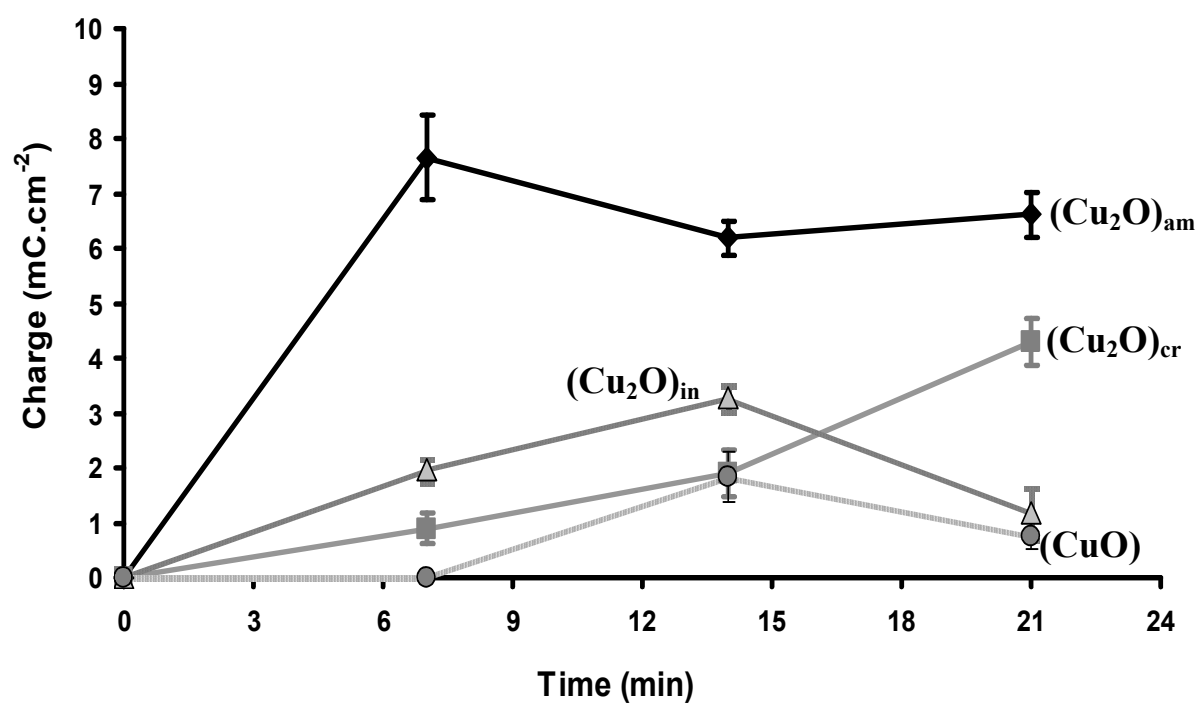


Figure 4.

Figure 5

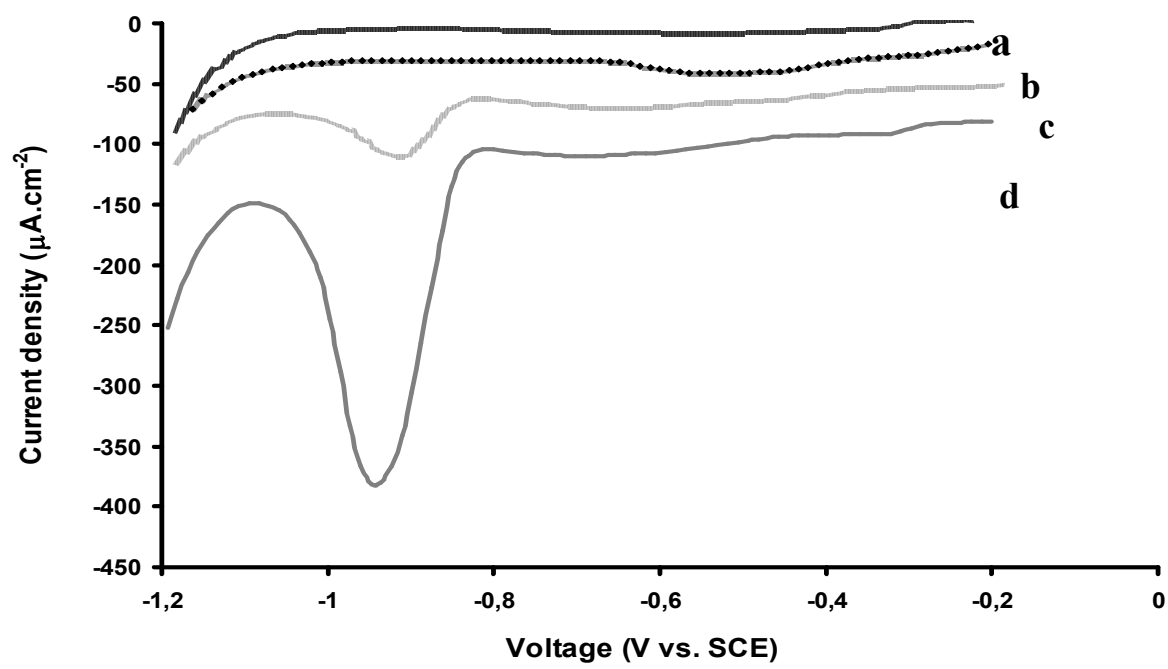


Figure 5.

Figure 6

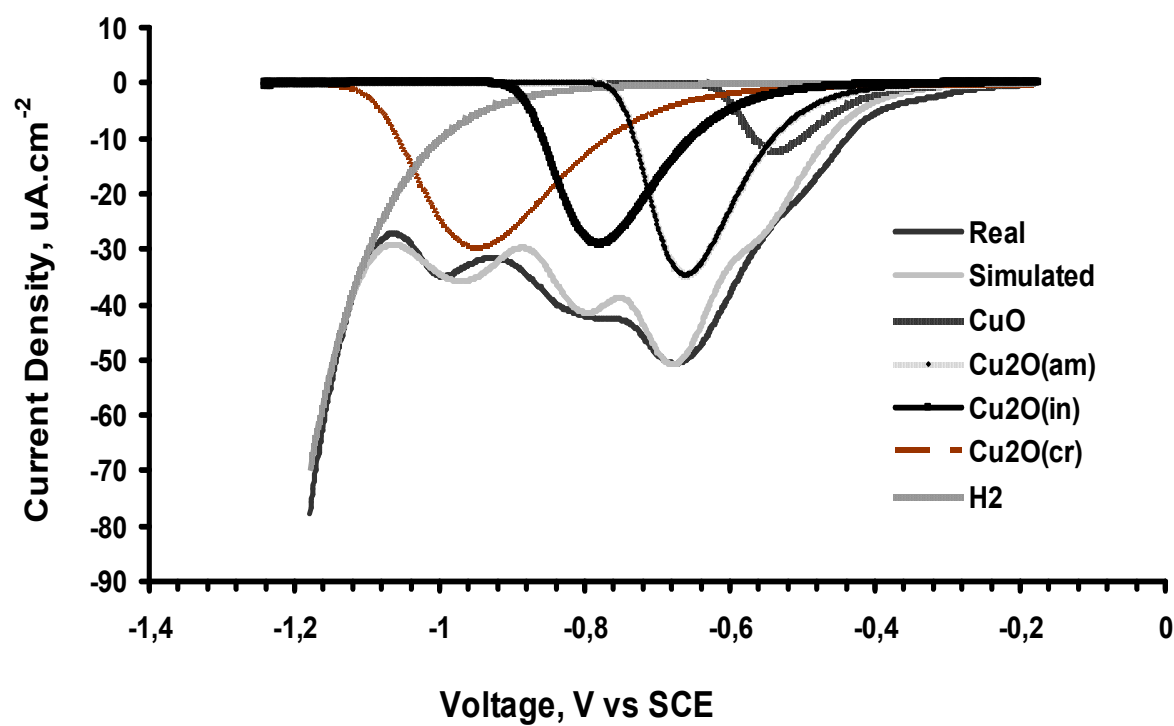


Figure 6.

Figure 7

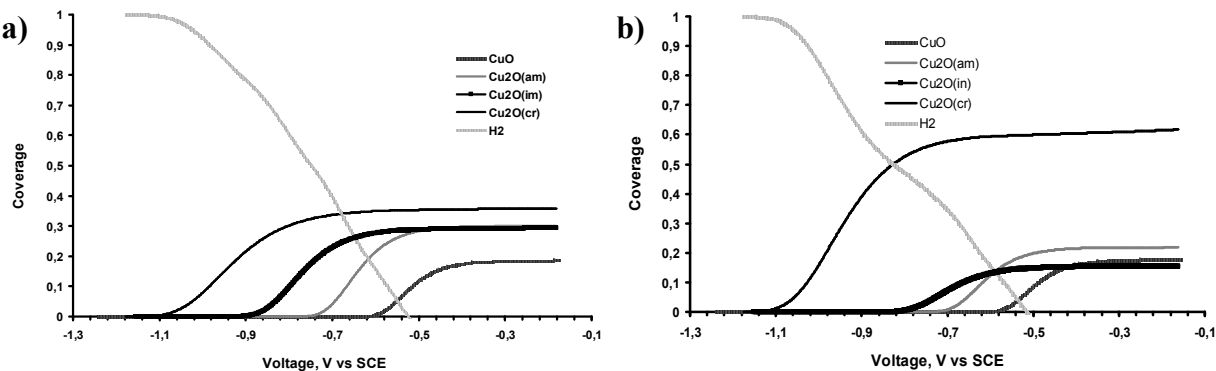


Figure 7.