System for *in situ* studies of atmospheric corrosion of metal films using soft x-ray spectroscopy and quartz crystal microbalance

J. Forsberg,^{a)} L.-C. Duda, A. Olsson, T. Schmitt, J. Andersson, and J. Nordgren
Department of Physics, Uppsala University, P.O. Box 530, S-751 21 Uppsala, Sweden

J. Hedberg and C. Leygraf
Division of Corrosion Science, KTH, SE-100 44 Stockholm, Sweden

T. Aastrup and D. Wallinder
Attana AB, Björnnäsvägen 21, SE-11347 Stockholm, Sweden

J.-H. Guo
Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720

(Received 13 February 2007; accepted 7 August 2007; published online 31 August 2007)

We present a versatile chamber (“atmospheric corrosion cell”) for soft x-ray absorption/emission spectroscopy of metal surfaces in a corrosive atmosphere allowing novel *in situ* electronic structure studies. Synchrotron x rays passing through a thin window separating the corrosion cell interior from a beamline vacuum chamber probe a metal film deposited on a quartz crystal microbalance (QCM) or on the inside of the window. We present some initial results on chloride induced corrosion of iron surfaces in humidified synthetic air. By simultaneous recording of QCM signal and soft x-ray emission from the corroding sample, correlation between mass changes and variations in spectral features is facilitated. © 2007 American Institute of Physics. [DOI: [10.1063/1.2777391](https://doi.org/10.1063/1.2777391)]

I. INTRODUCTION

Atmospheric corrosion, taking place between metal surfaces and the surrounding atmospheric environment,¹ is ubiquitous and generates enormous costs for society, affecting areas such as information technology, communication technology, national defense, and cultural heritage. It is most desirable to find ways to avoid and reduce atmospheric corrosion; therefore, it is necessary to gain an improved understanding of the underlying processes. Atmospheric corrosion involves chemical, electrochemical, and physical processes in three phases (solid, liquid, and gas) and two interfaces (solid/liquid and liquid/gas). The interfacial regime is recognized as a system with great experimental and theoretical challenges, partly because the surface sensitive techniques used to probe the regime must be compatible with atmospheric pressure conditions.

In order to improve our knowledge of the underlying chemical and physical processes, it is necessary to perform experiments under controlled conditions, i.e., *in situ* experiments, as a complement to field (outdoor) experiments. A number of *in situ* methods have been applied to atmospheric corrosion in the past, including monitoring the mass change of metal films using a quartz crystal microbalance (QCM), as well as Raman and infrared spectroscopies.³ Here, we present an approach to gain information at the molecular level by applying soft x-ray spectroscopy. Soft x-ray absorption and emission spectroscopies (SXAS and SXES) are powerful tools that provide detailed information, including elemental and symmetry selectivities, about the electronic

structure of the chemically active atomic orbitals in materials.

Our setup allows us to perform *real time* measurements so that the corrosion process can be studied at all its stages, particularly the early stages that are inaccessible otherwise. In other words, we want to mimic the actual environment in which corrosion happens, controlling the conditions such as ambient pressure, different levels of humidity, the presence of NaCl, and amounts of corrosion promoting pollutants, such as SO₂ and O₃. The processes taking place on the surface can thus be studied in two ways simultaneously: through SXES/SXAS providing chemical information and through QCM measurements providing information about the mass change and thus the corrosion rate.

The remainder of this article is structured as follows: In Sec. II, we describe the experimental equipment that we have developed for studying atmospheric corrosion *in situ* with soft x-ray spectroscopy. The core part of the system is an atmospheric corrosion (AC) cell that can be inserted into a standard vacuum chamber at a synchrotron radiation source and is described in Sec. II A. Sections II B–II D detail other parts of the experimental system. In Sec. III, we provide information about the important aspects of the sample preparation and experiment. Section IV provides a presentation of initial key results using the instrumental system, followed by the discussion and conclusions.

II. INSTRUMENT DETAILS

A. Atmospheric corrosion cell

The AC cell is essentially a sample holder with enhanced capability. The instrumental system described in this article

^{a)}Electronic mail: johan.forsberg@fysik.uu.se

FIG. 1. (Color online) Schematic cutaway drawing of the atmospheric corrosion cell to scale, with parts labeled. Cell holder and screws are omitted for clarity.

has been developed with the goal of covering a wide range of experimental requirements while being convenient for use. Two versions of atmospheric corrosion cells have been constructed and put into operation: one that has the core features for doing *in situ* soft x-ray spectroscopy and another one that also has the capability for *in situ* sample change and simultaneous QCM data recording. We will first describe the former and then briefly show how the latter features have been implemented.

The main part of the cell (Fig. 1) is machined from a single piece of polyetheretherketone (PEEK), an UHV compatible and chemically inert polymer material. PEEK is also easily machined and electrically insulating. The sample holder consists of a metal screw whose position can be adjusted to accommodate samples of varying thickness. The back side of the cell has a hole which can be used to feed electrical cables through to the sample holder, e.g., for QCM/temperature measurements or for electrochemical experiments. The hole can otherwise be sealed with epoxy resin or an O-ring equipped screw.

The front plate is detachable in order to mount samples and x-ray windows. This part is made out of steel or aluminium since it needs to be sufficiently thin to avoid obstruction of the x-ray path. The front plate is mounted on the cell with four screws. It can also hold solid reference samples for measurements.

The thin x-ray window is mounted on the front plate by means of epoxy glue or O-rings, depending on the required geometry. In the case where a large sample or a QCM crystal is situated behind the window, glue may be necessary since only very limited mechanical force can be exerted on the window substrate from the inside. The glue is used both for attaching the window to the front plate and as a vacuum sealant. A large O-ring is used as a vacuum seal between the front plate and the cell.

Alternatively, a pair of identical, thin O-rings are used,

one on each side of the window substrate. The front plate and cell needs to be slightly modified to accommodate this setup. The inner O-ring is used to vacuum seal the cell, and the outer one to evenly distribute the force on the delicate silicon substrate. Balancing the torque on the four screws on the front plate is important in order to achieve good sealing. Using O-rings instead of glue has the advantage of allowing easy changing of windows. Gluing typically makes it impossible to remove a window from the front plate without destroying it, and the gluing itself is a delicate process.

The holder for the cell is constructed as a straight tube, fitting through a standard CF40 manipulator and attached to the top flange. This enables the use of essentially any standard $xyz+\theta$ manipulator setup for mounting. It also makes the procedure of mounting and removing the cell simple since the manipulator can stay in place. The holder is designed so that the window is situated on the rotational axis of the manipulator.

The gas, at atmospheric pressure, passes through two thin steel tubes (inner/outer diameter of 0.5/0.8 mm, length of 600 mm) running from the top flange to the cell, one for ingoing flow and one for outgoing flow. The reason for choosing small inner diameter tubes is to keep the internal volume of the whole assembly down. Should the window break, all the air that is currently in the tubes will be let into the chamber. With these tube sizes it is possible to achieve a high enough flow of air (~ 10 ml/min) to maintain a relative humidity level of $>90\%$ without increasing the pressure more than a few percent over ambient atmospheric pressure.

The flange tubing feedthroughs are standard Swagelok® fittings with custom made Teflon gaskets for the very small tube diameter used. The feedthroughs can accommodate tube diameters of up to 3 mm outer diameter by using different gaskets. The tubes are connected to the cell by a clamped seal with compressed rubber or viton O-rings. There are also two electrical feedthroughs in the top flange. Vacuum compatible cables can be connected between these and the cell, allowing, e.g., sample current to be measured. Other possible uses include electrochemical experiments and temperature control.

For cases when in-vacuum sample exchange is required, a different version of the AC cell has been designed and built (Fig. 2). Many technical solutions are similar to the instrument described above, but the crucial difference is that the back part of the cell, including the sample, can be removed. This “plug” (a) is inserted in the main body of the cell sealed from vacuum in two stages by “x-rings” (d) using an appropriate force applied via a lever, operated from outside the vacuum, and wheels on a leaf spring (c). By the external lever the wheels are moved downward, releasing and clearing the way out for the plug, which can be subsequently picked up with a spring-loaded three-pin “fork” (j) on a standard transfer rod.

The inner compartment containing the sample is filled with the desired atmosphere by way of drilled narrow channels (h) that are connected to tubes (omitted in Fig. 2). The channels are situated in the front piece of the plug holder and must be pumped out prior to the removal of the plug. The outer compartment can be pumped separately through sepa-

FIG. 2. (Color online) Schematic internal cross section of the sample exchange system. (a) Detachable plug, (b) sample holder disk, (c) spring-loaded wheel, (d) x-ring seals, (e) O-ring used as a vacuum seal between the front piece and the main body, (f) x-ray window isolating the inner compartment (actual corrosion cell) from the chamber vacuum, (g) QCM crystal with the metal film sample, (h) air conduits, (i) pump hole to evacuate the outer compartment, and (j) spring-loaded three-pin “fork” for sample exchange. The image scale and proportions are only given approximately and some details have been omitted, such as electrical connectors to the QCM.

rate holes (i) and acts as a differential pumping stage.

Figure 3 shows three photographs of the in-vacuum sample exchange process. In Fig. 3(a), the transfer rod approaches the plug and the spring-loaded pins are aligned with the holes in the steel disk on the plug. Figure 3(b) demonstrates the turning and locking of the transfer rod onto the detachable plug (1) and the lowering of the sliding mechanism (2). The latter moves the spring-loaded wheel [Fig. 2(c)] down, releasing the plug. Figure 3(c) shows the plug being removed from the cell; the sample insertion process is done by reversing the order. Unfortunately, the in-vacuum exchange capability has the price of making the cell bulkier and more awkward to use. Therefore, we have used the other version of the AC cell described above whenever sample exchange and QCM monitoring are not needed.

B. Soft x-ray windows

A small thin membrane (typically $0.25\text{--}1\text{ mm}^2$ in area and $\approx 100\text{ nm}$ thick) of silicon nitride (Si_3N_4) or sp^3 -like

FIG. 3. (Color online) A series of photographs demonstrating the in-vacuum removal of the sample holder “plug” of the AC cell version that allows sample exchange.

carbon separates the vacuum of the analysis chamber from the AC cell environment. The silicon nitride membrane windows are commercially available from Silson Ltd. (www.silson.com). The carbon windows are made in-house by depositing diamondlike carbon on a silicon wafer which is subsequently etched from the back side to expose the carbon film. The size of the windows is determined by standard lithographic methods.⁶

The membrane allows both the incident and scattered soft x rays to pass through, making it possible to irradiate the sample film and record an emission spectrum. These membranes have been tested for pressure differences of up to 1.4–4 bars, depending on material, geometry, membrane size, and quality. The pressure difference should rarely exceed 1 atm during the actual experiment, but there is always a risk of breakage. There may also exist a risk of damage to the membranes if the radiation is very intense and focused. To further reduce the risk of exposing the beamline to atmospheric air pressure and contamination, interlocked safety valves have been installed to cut off the air flow to the cell in the event of a leak. These valves have electromagnetic actuators and are interlocked to a pressure gauge on the chamber, so that the valves will close should the pressure reach the predetermined set point, e.g., 1×10^{-7} mbar, within a few milliseconds.

The choice of membrane material mostly depends on the desired absorption edges to be studied. Good membrane transmission is necessary in order to acquire well-resolved spectra since strong absorption in the membrane material itself would impair the signal-to-noise ratio. Si_3N_4 membranes allow photons roughly between 300 and 400 eV (below the N K edge) as well as above 450 eV, while carbon membranes have a window around 100–275 eV (below the C K edge) as well as above 350 eV. Thus, the materials complement each other, covering much of the soft x-ray spectrum quite well.

C. Corrosive atmosphere production

We have built a portable computerized system for providing air at variable relative humidity (RH) and pollutant concentration. It is capable of delivering the required air flow of typically 10–20 ml/min, with RH at any desired level between 0% and 100%. The air is provided by a bottle containing a mixture of pure nitrogen and pure oxygen at natural atmospheric proportions at sea level ($\approx 79/21$). Humidification is achieved by bubbling a flow of air through pure water. The flow is sufficiently low for the air to take up moisture and reach saturation at 100% RH. This humid air is then mixed with a flow of dry air to achieve the desired RH by means of a three way solenoid valve. Humidity, flow, and temperature sensors are used to monitor the atmosphere in the tubing, and a LABVIEW® program has been written to control the whole system.

Atmospheric pollutants such as SO_2 may be introduced into the air by means of a permeation tube (PermaKemi, Sweden), a container with walls made of a special polymer that allows the pollution compound to diffuse out at a certain rate. This tube, which is calibrated to leak a small amount of the pollutant into its surroundings per unit of time

(14 ng/min) at ambient pressure and temperature, is inserted into the dry air flow. Although it is not possible to directly adjust the diffusion rate, it is somewhat dependent on temperature. The degree of pollution is controlled indirectly by regulating the air flow through the system per unit of time. The required concentrations are typically of the order of parts per billion (ppb), thus mimicking heavily polluted urban conditions.

The resulting artificially produced atmosphere is conducted through a silicon rubber tube to the cell, where it is attached to the safety valves connected to the internal tubing. Humidity sensors are mounted in line with the flow both directly before and after the cell for accurate measurements and control. Readings of humidity, pressure, and temperature are continually logged by a computer, together with QCM information when available.

D. Quartz crystal microbalance

The QCM technique is widely used for measuring very small mass changes in deposited thin films.⁷⁻⁹ The quartz crystal wafer¹⁰ is connected to an electronic oscillator circuit (Attana 80). In our case, the crystals are dimensioned to give a resonant frequency of around 10 MHz. The circuit outputs are connected to a frequency counter. Mass changes can be calculated from the change in frequency, with an accuracy of about 0.1 Hz, or 1 part in 10^8 . This corresponds to a mass change of less than 1 ng/cm².

Using the QCM technique presents some challenges for our kind of experiment since the quartz crystal is quite sensitive to mechanical stress. Therefore, it is very important that the crystal is mounted in such a way that minimizes the forces acting on it. It also responds significantly to small changes in temperature, a fact that has to be taken into account, e.g., when gas flows are changed. This problem can be solved by using temperature stabilization. The cut of the quartz crystal is also significant for the temperature response.

III. EXPERIMENTAL DETAILS

A. Soft x-ray spectroscopy

Soft x-ray spectroscopy is a chemically selective method for studying the electronic structure of materials. In addition to being able to distinguish between signatures from different elements, soft x-ray spectroscopy is sensitive to atomic species in different chemical environments. In particular, resonant soft x-ray emission spectroscopy is based on a two-photon process that links occupied and empty orbitals in a selective manner such that the resulting spectra contain much molecular and chemical information about the binding between different elements.

SXAS is a technique¹¹ to study unoccupied states above the Fermi level of a material. A core electron can be transferred into an empty state by x-ray excitation. Since the core electron levels are well separated for different atoms, the method is element selective. The transition rate of a core electron excitation depends on the density of empty states and is proportional to the absorption cross section. Thus, by measuring the absorption cross section one can obtain information about the state density at a certain energy relative to

the Fermi level. Since dipole selection rules apply, transitions are only allowed when the change of angular momentum of the electron, Δl , is ± 1 . This means that excitation at *p* edges (*s* edges) map out the *s* and *d* characters (*p* character) of the empty states.

Technically, in SXAS one often measures the number of core hole decay particles, which is proportional to the absorption cross section, that emerge from a thin layer penetrated by an x-ray beam. Usually, one detects either the current of low energy electrons (using a picoammeter) or the intensity of fluorescence photons (using, e.g., a channeltron or a photodiode) that leave the sample.

SXES is used to study occupied states below the Fermi level of a material. After core electron excitation the hole is rapidly refilled by an outer electron. There is a small but finite probability (it is small for soft x rays, but large for high energy x rays) that such a transition results in x-ray emission, so called fluorescence. If x-ray emission is excited at an absorption resonance, the process has the character of scattering. This is referred to as resonant inelastic x-ray scattering (RIXS).¹² RIXS is a highly selective spectroscopic technique since both excitation and emission are governed by dipole selection rules. The energy loss of the x rays in the scattering process reflects the excitation energy of the atomic system. In localized systems the final states have well-defined energies, leading to distinct spectral features whose energy splittings are determined by the crystal field. These are charge neutral excitations; i.e., the excited electrons remain bound to the atom. These energy levels are characteristic of the crystal environment and therefore carry important information.

In RIXS one excites the sample with x rays of a narrow energy bandwidth. The spectrum of the scattered x rays is detected by a wavelength dispersive grating spectrometer.² The spectral feature (peak) at the shortest wavelength (highest energy) corresponds to elastic scattering where no energy is taken up by the atomic system. Peaks at longer wavelengths (lower energies) are due to inelastic scattering where the atomic system has taken up the corresponding energy by, e.g., undergoing an electronic transition. Particularly strong inelastic scattering occurs at resonant energies, i.e., when the excitation energy is tuned to a prominent feature in the absorption spectrum. Moreover, since soft x-ray photons have a relatively large attenuation length, of the order of 100 nm, soft x-ray spectroscopy is also predominantly a bulk sensitive method.

B. Deposition of NaCl particles

NaCl may be deposited on the surface of the metal film to act as a corrosion accelerating agent. This can be done by dissolving the salt in ethanol and depositing a small drop of the solution on the surface. The alcohol evaporation leaves a residual layer of NaCl crystals of a few $\mu\text{g}/\text{cm}^2$. The presence of NaCl may accelerate the corrosion process by orders of magnitude. This procedure is described in greater detail in Ref. 3. We have also successfully tested the possibility to deposit NaCl by evaporation, which leaves a much more homogeneous film.

The Fe coated crystal is then inserted into the AC cell and exposed to an artificial atmosphere, as described above. A thin water layer forms on the metal surface as the salt deliquesces at sufficiently high relative humidity. On a clean, polished surface, the water layer has a thickness of up to approximately ten molecular monolayers, depending on the RH and temperature of the surrounding atmosphere.¹ If NaCl has been deposited, the NaCl crystals will deliquesce at relative humidity above 80%, and the total amount of water on the QCM is thereby increased. Each mass unit of NaCl will absorb approximately 1.5 mass units of water once it is completely liquefied.³

Upon drying, the NaCl solution deposited on the surface forms individual crystallites, which at the point of deliquescence again turn into small droplets containing chloride. These droplets act as initiation sites for local corrosion processes. A NaCl film deposited by evaporation will also give rise to crystallites, although only after the NaCl has been deliquesced and dried again. The resulting crystallites are typically smaller and more evenly spread across the surface with this method.

At the center of the droplet the metal passes into solution as positively charged metal ions (the anode reaction) and, simultaneously, releases electrons. The electrons will be captured by dissolved oxygen, mainly at the periphery of the droplet, thereby forming hydroxyl ions (the cathode reaction). The distribution of anodic and cathodic sites along the surface and the nature of the metal surface are important factors that determine the actual form of atmospheric corrosion. NaCl-induced atmospheric corrosion may result in, e.g., filiform corrosion on iron³ or more radially growing corrosion on copper.⁵

C. Sample preparation

Samples are positioned either on the sample holder inside the cell (see Fig. 1) or on the inside surface of the x-ray window. The sample holder is usable for any kind of sample, as long as it has a flat profile, since the window needs to be very close to the sample. This is partly because the absorption of the gas inside the cell will attenuate the beam and partly because geometrical shadowing may otherwise occur. Generally, for soft x-ray fluorescence spectroscopy, the angle between incoming beam and detector is about 90°.

A thin film sample on the inside surface of the window membrane may be deposited, e.g., by evaporation or sputtering. The fact that the film is irradiated from the back side entails a few limitations. For *in situ* studies, the film needs to be thin enough so that the sample material irradiated by the beam is part of the reaction to be studied but still thick enough to yield a good signal. For iron corrosion, films of around 50 nm in thickness are suitable.

Generally, the sample preparation process took place as follows: an iron or chromium film of 50–100 nm thickness was deposited onto a substrate (either a QCM or a Si₃N₄/carbon window) and covered with NaCl as described. The film was then corroded at RH above 90% for several days. *In situ* corroded samples were prepared in the same manner, although the corrosion step was performed in the AC cell, permitting simultaneous measurements.

FIG. 4. (Color online) Atmospheric corrosion of an Fe film with NaCl, monitored by QCM and humidity sensors. QCM frequency is displayed as difference from the start value. The missing part between ≈ 5 and 7 h in the QCM data is due to the loss of the QCM signal for a short period of time.

Figure 4 displays the QCM frequency and RH data collected during the corrosion process of an iron film that was prepared and corroded according to the above description. Soft x-ray measurements were conducted in the beginning and at the end of the process (Fig. 6). The frequency curve flattens out toward the end of the sequence, indicating that most of the iron film is corroded. The total change in frequency is 3000 Hz, which corresponds to a mass change of approximately $13 \mu\text{g}/\text{cm}^2$. This is consistent with an increase in mass corresponding to a complete corrosion of an approximately 100 nm thick Fe film into FeOOH. The fluctuations in humidity are induced by changing the parameters of the humidity system. As the corrosion proceeds, the QCM frequency changes by approximately 300 Hz between 0% and 100% humidity due to a water uptake of around $1.3 \mu\text{g}/\text{cm}^2$. This is equivalent to about 40 monolayers of water,⁴ which are absorbed during wetting of the corrosion products formed and of the NaCl present.

IV. EXPERIMENTAL RESULTS

We have performed initial studies on chromium and iron films subjected to air of controlled relative humidity. Soft x-ray absorption spectra and soft x-ray emission spectra from the samples were taken at different stages of the corrosion process and compared to the mass change detected by the QCM.

Initially, in order to investigate the instrument's *in situ* capability, oxygen *K*-edge measurements were made on a sample of chromium while subjected to dry and humid nitrogen. Chromium forms a passivating thin oxide layer that is inert to further corrosion. Changes in humidity only affect the water adlayer thickness; therefore, x-ray spectra will show the effect of these layers in the difference. Pure nitrogen was chosen as atmosphere in this case, instead of air, in order to eliminate the interfering signal from O₂ gas. The corresponding spectra are displayed in Fig. 5. XAS (partial photon yield) is shown in the small inset. An arrow indicates the excitation energy. Emission data with and without humid nitrogen are displayed in the upper diagram, and the difference between these two spectra is shown below, together

FIG. 5. (Color online) O K absorption (inset) and O K emission from a Cr surface in dry and humid N_2 present, respectively. The lower part of the figure shows the difference spectrum (of dry and humid conditions) compared to the spectrum of liquid water.

with a liquid water spectrum taken for reference.

We observe a small but significant difference between the spectra from the sample in these two environments. We attribute the change to the uptake of a very thin layer of water that forms on a surface when subjected to humid air. Although there is no simple normalization procedure to extract the difference between the two spectra, our result seems compatible with this interpretation. Gaseous water would produce a spectrum with much narrower peaks.¹³ The “background” oxygen signal is attributed to oxygen K emission from chromium oxide that forms on top of the deposited Cr layer.

In the next step we performed an AC cell experiment using an iron film. Figure 6 displays Fe L -edge absorption and emission data from the iron film made before the corrosion and after several hours of corrosion. A distinct energy shift of the Fe L -absorption spectra is observed and, in agreement with expectations, the onset of Fe L absorption is shifted to higher energies in oxidized iron due to chemical shift. The Fe L -emission spectra, taken at several different excitation energies, show an even stronger contrast between the two stages. It is clear that the surface of the iron film has gone through a chemical change.

V. DISCUSSION

Both the QCM-monitoring and the O K -emission results from the Cr surface (Fig. 5) corroborate the finding that a humid atmosphere indeed leads to reversible deposition of extra layers of water on surfaces compared to a dry atmosphere.

The measurements for Fe L edge (Fig. 6) show that x-ray spectroscopy is very sensitive to the oxidation by corrosion even when using thin metal films. We confirm that the corrosion rate is enormously enhanced as a consequence of the additional water layers. We have also performed *in situ* measurements on pressed powder reference samples of different pure iron oxides. This facilitates a detailed comparison to the chemistry that occurs in different stages of the corrosion process. Note that the present results were obtained with a layer

FIG. 6. (Color online) Iron L -edge absorption and emission spectra taken at different excitation energies. Locations indicated with arrows in the XAS spectra (inset) correspond to different XES excitation energies as labeled. The XAS energy scale has not been calibrated.

of NaCl on top of the metal surface. The effect of deliquescence of salt under high humidity conditions and the presence of chlorides probably make these results especially relevant for marine environments.

The fluorescence yield detection mode of acquiring L -edge absorption data can be problematic due to competing excitation channels (O K absorption and Fe L absorption) and the large difference in their transition rates. In other words, below the Fe L edge strong O K fluorescence is emitted due to core hole production at the O-sites, whereas at the Fe L resonance this channel is quenched and replaced by the less efficient Fe L -emission channel, and therefore the total fluorescence yield is reduced. This leads to a nonproportionality of the total fluorescence yield to the absorption cross section and erratic intensity (inversion effects). Instead, partial fluorescence yield was recorded by using the x-ray emission spectrometer in low resolution with the drawback of a much lower count rate. Sample current measurements in the cell are also nontrivial due to the presence of air and charging of the insulating x-ray window material. Sample current measurements on the reference compounds are usually simple as long as the electrical conductivity is sufficiently high.

Previous related *in situ* studies investigating corrosion/oxidation products have been reported using a range of different and mostly hard x-ray techniques, such as synchrotron radiation x-ray diffraction (SR-XRD)/XAS,¹⁴ extended x-ray absorption fine structure (EXAFS),^{15,16} and grazing incidence x-ray diffractometry (GIXD),¹⁷ but also soft x-ray microscopy.¹⁸ The hard x-ray regime lacks vacuum require-

ments which makes the instrument design less complicated. Soft x rays, on the other hand, allow more detailed electronic structure determination and chemical sensitivity. Our flow through design is also a novel feature compared to a similar soft x-ray absorption study.¹⁸

Other techniques have been used to study atmospheric corrosion processes with films of, e.g., Fe and Cu. Attempts to characterize the corrosion products formed on iron under similar exposure conditions with *in situ* infrared reflection absorption spectroscopy (IRAS) have given ambiguous results.³ The corrosion products formed could not be attributed to any of the reference samples studied (α - and γ -FeOOH). Parallel optical microscopy studies showed that the NaCl-induced corrosion of iron resulted in approximately 10 μm wide and elongated corrosion products (filaments), characteristic of filiform corrosion. The mechanism proposed emphasized the heterogeneous nature of the corrosion attack, with an anodic area enriched in chlorine located in the front of the growing filament and a large cathodic area in the tail of the filament primarily consisting of some form of FeOOH.

We have presented an instrumental system for performing combined *in situ* soft x-ray spectroscopy and QCM-monitoring of atmospheric corrosion processes. One advantage over other *in situ* techniques is the chemical selectivity of soft x-ray spectroscopy, particularly soft x-ray emission spectroscopy or RIXS. The combination yields unique information on the molecular level and allows us to chemically analyze corrosion processes of thin metal films under well controlled conditions in real time. We expect that this will lead to a better understanding, as well as new questions about the important topic of atmospheric corrosion.

A first test, as presented in this article, was to follow the chloride induced atmospheric corrosion of iron. Changes in iron *L*-edge absorption and emission spectra could be observed *in situ* upon atmospheric corrosion, and mass change monitored continuously by the quartz crystal microbalance upon exposure to humidified air at atmospheric pressure.

It is desirable to extend our *in situ* method to yield higher lateral resolution in the future because it is known that iron corrosion, e.g., progresses inhomogeneously over the

sample surface (filiform corrosion). *In situ* studies of other gaseous, liquid, and mixed systems using our apparatus are conceivable, such as inhomogeneous catalysis, electrochemical cells, or hydrogen storage.¹⁹ The presented instrument should be easily modifiable to fit the specific requirements in many such cases.

ACKNOWLEDGMENTS

This work was supported by the Swedish Research Council (VR) and the Göran Gustafsson Foundation (GGS). The experimental work was performed at BL511 at MAX-LAB in Lund (Sweden) and at BL7 at ALS in Berkeley, CA. The authors would like to thank the staff at these two facilities for their support during the experiments.

- ¹C. Leygraf and T. Graedel, *Atmospheric Corrosion* (Wiley, New York, 2000).
- ²J. Nordgren, G. Bray, S. Cramm, R. Nyholm, J.-E. Rubensson, and N. Wassdahl, *Rev. Sci. Instrum.* **60**, 1690 (1989).
- ³J. Weissenrieder and C. Leygraf, *J. Electrochem. Soc.* **151**, B165 (2004).
- ⁴M. Forslund and C. Leygraf, *J. Electrochem. Soc.* **144**, 105 (1997).
- ⁵Z. Y. Chen, D. Persson, A. Nazarov, S. Zakipour, D. Thierry, and C. Leygraf, *J. Electrochem. Soc.* **152**, B342 (2005).
- ⁶M. Madou, *Fundamentals of Microfabrication* (CRC, Boca Raton, FL, 1997).
- ⁷G. Sauerbrey, *Z. Phys.* **155**, 206 (1959).
- ⁸C.-S. Lu and O. Lewis, *J. Appl. Phys.* **43**, 4385 (1972).
- ⁹C.-O. Olsson and D. Landolt in *Analytical Methods in Corrosion Science and Engineering*, edited by P. Marcus and F. Mansfield, (Taylor & Francis, Boca Raton, FL, 2006).
- ¹⁰QCM equipment and crystals were obtained from Attana AB, Björnnäsvägen 21, SE-11347 Stockholm, Sweden.
- ¹¹J. Stöhr, *NEXAFS Spectroscopy* (Springer, Berlin, 1992).
- ¹²A. Kotani and S. Shin, *Rev. Mod. Phys.* **73**, 203 (2001).
- ¹³J.-E. Rubensson, L. Petersson, N. Wassdahl, M. Bäckström, and J. Nordgren, *J. Chem. Phys.* **82**, 4486 (1985).
- ¹⁴M. G. Dowsett and A. Adriaens, *Anal. Chem.* **78**, 3360 (2006).
- ¹⁵S. Mukerjee *et al.*, *J. Electrochem. Soc.* **142**, 2278 (1995).
- ¹⁶J. McBreen, W. E. O'Grady, K. I. Pandya, R. W. Hoffman, and D. E. Sayers, *Langmuir* **3**, 428 (1987).
- ¹⁷S. Sathiyarayanan, M. Sahre, and W. Kautek, *Corros. Sci.* **41**, 1899–1909 (1999).
- ¹⁸K. E. Kurtis, W. Meyer-Ilse, and P. J. M. Monteiro, *Corros. Sci.* **42**, 1327 (2000).
- ¹⁹L. C. Duda, P. Isberg, P. H. Andersson, P. Skytt, B. Hjorvarsson, J.-H. Guo, C. Sâthe, and J. Nordgren, *Phys. Rev. B* **55**, 12914 (1997).