A novel respirometric approach to monitor atmospheric corrosion kinetics is presented. Simultaneous real-time monitoring of the H₂ evolution reaction (HER) and the O₂ reduction reaction (ORR) is possible with a combination of optical O₂ sensor measurements with gravimetric volume sensitive techniques or pressure sensor based techniques in closed chambers. The respirometric method is a universal, non-destructive tool applicable to any metal or alloy. It shows a high sensitivity for low corrosion rates and has a high time-resolution. Different examples of relevant engineering metals and alloys will be provided. Mass loss validation measurements carried out at the end of exposure show a good correlation with the total recorded cathodic charge. For metals with different oxidation states the average valency in the corrosion products can be calculated from the cathodic charge together with mass loss. The versatility of the novel monitoring technique is further demonstrated by studying the influence of wet-dry cycling, temperature steps or changes in the gas composition in situ. The rate of HER, ORR and total corrosion rate during these changing exposure conditions can be tracked directly on the same sample. Overall the new method contributes to bridging the gap between lab tests, accelerated testing and field exposure.

This paper is the first of a series that describes new in situ methods for real-time monitoring of corrosion rates. The respirometric methods presented are non-electrochemical and are applicable to any metallic sample. In the first part, different techniques to monitor atmospheric corrosion rates under thin electrolyte films will be presented. Part II will focus on respirometric approaches to monitor corrosion rates under immersion conditions. Finally, the respirometric method will be combined with electrochemical measurements.

Atmospheric corrosion under thin electrolyte films is one of the most important but also most complex corrosion scenarios. The factors to be considered are e.g. contamination by hygroscopic particles, gas composition of the atmosphere, electrolyte film thickness, surface conditions, temperature and the influence of wet-dry cycles. As a result, lab tests or accelerated corrosion tests often fail to predict the corrosion behavior found in the real world. The determination of reliable corrosion rates under different exposure conditions in laboratory experiments is a key prerequisite for gaining insight into the corrosion mechanisms and for the development of better accelerated tests. However, the existing methods to measure corrosion rates during atmospheric exposure come with several limitations.

For example, the well-established mass loss method is based on weighing the sample before the exposure and after the removal of the corrosion products at the end of the exposure period. The amount of metallic mass loss corresponds to an average corrosion rate over the total exposure time. To be able to identify if the corrosion rate changes during exposure, multiple samples with different exposure times need to be exposed. These multiple samples could show a scatter in their corrosion behavior because of varying microstructure, sample preparation and because they did not necessarily experience exactly the same exposure conditions. Therefore, usually multiple replicates are needed which increases the amount of samples even further. Moreover, the process of corrosion product removal is destructive. Consequently, the effect of different exposure conditions cannot be followed directly on the same sample with the mass loss technique.

Optical profilometry to determine the volume loss after removal of the corrosion products can give a hint on the localization of the corrosion damage but suffers from the same limitations as mass loss related to the destructive corrosion product removal process. The use of X-ray computed tomography to visualize the corrosion progress can overcome this shortcoming. Mass gain measurements can be used to estimate the amount of corrosion that has occurred on the sample. This measurement is only indicative since the mass gain depends on the composition of the corrosion products and is also influenced by the absorbed water. To be able to measure the dry mass gain the corrosion process has to be interrupted by the drying step. Alternatively, the wet mass gain including the weight of the water layer could be monitored. The quartz crystal microbalance offers a very high mass resolution but is only applicable in comparably mild corrosive environments.

Electrochemical methods are difficult to carry out under thin electrolyte layers present in atmospheric corrosion because of complicated placement of the electrodes, inhomogeneous current distribution and possible electrical contact loss. Besides, the interpretation of the electrochemical data can be non-trivial. Nevertheless, there is a number of studies that employ electrochemical measurements in atmospheric corrosion.

Electrical resistance sensors have been developed to monitor the rate of reduction of the cross section of a metal track by corrosion. The ability to monitor real-time corrosion rates in the field and during accelerated testing makes this approach very promising. Possible drawbacks of the resistance method lie in the conductive electrolyte film or inhomogeneous corrosion of the sensitive track that could influence the measured resistance. The corrosion behavior of the narrow metal track could differ from a bulk sample and could also depend on the microstructure resulting from the deposition method of the track. The sensors are commercially available only for a limited range of substrates.

A straightforward approach to measure atmospheric corrosion kinetics is presented in this paper. To monitor the rate of the cathodic reactions. According to mixed-potential theory, the rate of the oxidation reactions and hence the corrosion rate is directly related with the rate of the cathodic reduction reactions. The main cathodic reactions in aqueous corrosion are the O₂ reduction reaction (ORR, Eq. 1) and the H₂ evolution reaction (HER, Eq. 2).
The idea of the presented respirometric methods is to monitor both reactions by the change in the number of gas molecules due to HER and ORR. Particularly, while for the ORR O₂ gas is consumed, the HER is accompanied by the generation of gaseous H₂ molecules. An analogous approach is widely used in the studies of metabolic processes like respiration of animals, plants, cells, or microorganisms. The term respirometry describes techniques to assess the rate of a metabolic process in terms of the uptake rate of an electron acceptor (e.g. O₂, nitrate) or in terms of the production rate of its reduced form (e.g. methane in the case of anaerobic respiration). In a corrosion process, the electron acceptor is usually either O₂ or H₂O and it is more convenient to monitor the reduced form of water, namely H₂.

Although it is obvious that monitoring the cathodic reaction rate provides a direct, non-destructive measurement of the corrosion rate, there are only a few examples where this approach was used in corrosion science. In the field of atmospheric corrosion, Stratmann et al. used a differential pressure sensor to monitor the pressure decrease due to oxygen consumption of a corroding iron sample. Matthiesen measured the consumption of O₂ due to the degradation of cultural heritage materials with an optical O₂ sensor in closed vials, flexible gas-tight bags and in situ on larger artefacts. Hydrogen evolution measurements are more common in corrosion studies, especially for immersion conditions. However, these methods are restricted to samples that corrode mainly by ORR or mainly by HER. In reality, many systems corrode with a combination of both cathodic reactions simultaneously. For example, there is strong evidence that besides HER as a main cathodic reaction, ORR also plays a role in the atmospheric corrosion of the Mg alloy AZ91. There are other examples where H₂ evolution can occur, although ORR is expected to be the main cathodic reaction. This includes the evolution of H₂ from pits on corroding aluminium or (stainless) steels. HER resulting from the galvanic coupling of defective Zn coatings on steel can lead to H₂ embrittlement and stress corrosion cracking. A method to quantify the exact contribution of HER and ORR under different exposure conditions is lacking in the literature.

Therefore, the aim of this work is to develop sensitive real-time methods to directly monitor both HER and ORR simultaneously. The here presented corrosion rate monitoring methods are universal and can be applied to any metal or alloy substrate which can be bare, precorroded, coated or even to galvanic couples. The respirometric method allows the determination of real-time corrosion rates under realistic exposure conditions and is capable to follow changing exposure conditions in situ. This is realised by a combination of optical O₂ sensor measurements with gravimetric volume sensitive techniques or pressure sensor based techniques in closed chambers. To demonstrate the possibilities of the new techniques, measurements of different relevant engineering metals and alloys are presented. Validation of the respirometric methods was carried out with mass loss. First results of a flow cell setup that enables real-time monitoring during wet-dry cycling will be also presented.

### Respirometric Approach

The idea of the presented respirometric method is to monitor both HER and ORR by the change in the number of gas molecules. An attempt to classify the approaches that can be used to monitor atmospheric corrosion kinetics is presented in Fig. 1. The basic measurement principles that can be employed are, on the one hand, to measure the volume change of the gas phase under constant pressure conditions and, on the other hand, to measure the pressure change in a closed chamber with a fixed volume. In the volumetric approach the gas volume will increase due to the evolved H₂ gas or decrease due to the consumption of O₂ during ORR. Similarly, in the manometric approach HER leads to a pressure increase while ORR leads to a decrease in pressure.

The pressure changes in the manometric approach can be monitored for example with an absolute pressure sensor or with specific gas sensors. For instance, optical O₂ sensors are only sensitive to the partial pressure of O₂. The measurement principle is based on the quenching of the luminescence of an oxygen sensitive indicator dye. The PyroScience REDFLASH indicator used in this study is excited with sinusoidally modulated red light and emits light in the near infrared. The oxygen concentration can be determined from the phase shift of the emitted light. The advantage of the optical system compared to electrochemical sensors is the possibility to conduct non-invasive measurements through transparent vessels. This reduces the risk of leakage. Furthermore, O₂ is not consumed by the measurement process.

Many volumetric respirometers have been developed to detect changes in the gas volume. A sensitive technique used in this study is the gravimetric method, originally presented by Curioni. This approach is based on measuring the change in buoyancy associated with the volume of gas collected in a submerged container that is connected to a balance. With this setup it is possible to monitor for example H₂ evolution of corroding Mg or Al under immersion conditions. Recently, it was shown that gravimetric measurements are also suitable to monitor HER rates during atmospheric exposure of Mg alloys. The same principle can be used to monitor atmospheric corrosion of metals with ORR as a main cathodic reaction. In this case the consumption of O₂ leads to a decrease in the air volume surrounding the sample in the submerged container. This leads to a decrease in the buoyant force exerted by the gas volume that can be recorded by the balance as an increase in the apparent weight of the submerged container. The ORR rate can be calculated from the slope of the weight curve.

To be able to monitor both HER and ORR simultaneously, the volumetric approach or the manometric approach can be combined with an O₂ sensor. Consequently, the number of O₂ molecules consumed can be subtracted from the change in the total number of gas molecules to get the number of H₂ molecules evolved.

As with any respirometer, background respiration, i.e. the consumption of O₂ or the evolution of gas that is not related to the studied corrosion process, has to be avoided or determined by experiments without samples. Since the respirometric principle is based on the consumption of O₂, prolonged exposure will eventually lead to the depletion of O₂. If the O₂ concentration drops significantly, changes in the ORR rate could occur. Another important gas that could get depleted in a stationary exposure is CO₂ that can be incorporated into the corrosion products as carbonates. To prevent depletion or pressure build-up, the concepts of flow-through respirometry or intermittent-flow respirometry can be adapted.

Continuous flow-through measurements can be conducted by analyzing the concentration changes in a gas stream with a known flow rate after it has passed a chamber with the corroding sample. Because the changes in concentration in a continuous flow are small, sensitive and expensive gas analyzers are needed for such a setup. Besides, the flow rate has to be controlled and measured accurately, which further complicates this approach.

The idea of intermittent-flow respirometry is based on the manometric approach to measure HER and ORR in a fixed volume chamber. The chamber is closed during the measurement phase to allow monitoring of the corrosion rate. Periodically, the chamber is opened for flushing and closed again to measure, ideally in an automated way. In this manner, the exposure conditions can be kept constant. The flush phase can be also used to change the conditions inside the chamber, e.g. change the humidity or the composition of the gas phase.
Experimental

Materials and sample preparation.—Die cast high purity Mg alloy AZ91 plates with a thickness of 2 mm were supplied by DGS Druckgussysteme AG, Germany. High purity AZ31 sheet material was obtained from MgF Magnesium Flachprodukte GmbH, Germany. Zn foil (0.125 mm thickness, purity 99.99%, typical analysis ppm: Fe < 19, Cd < 19, Cu < 50) and Fe foil (0.125 mm thickness, purity 99.5%, typical analysis ppm: C 1200, Mn 5000, S 500, P 500) was obtained from Advent Research Materials Ltd, England. Al alloy sheet according to the VW specification TL094 (equivalent to EN AW-6016) with 1 mm thickness supplied by Aleris International, Inc. was used in the as-received state (T4). The pure Cu samples (Cu-ETP, CW004A) had a thickness of 4 mm and 99.9% purity.

Specimens with approximate dimensions of 30 × 20 mm were cut and a hole was drilled to attach a nylon string. The sample surface was prepared by grinding to 1200 grit with SiC paper and cleaning with ethanol. Prior to exposure, the samples were contaminated with different amounts of NaCl using different methods. For AZ91 and Zn samples, NaCl was applied using an ultrasonic aerosol generator that atomizes a nearly saturated NaCl solution to a fine mist. Fe, Cu and AZ31 samples were contaminated by repeated, homogeneous spraying of a saturated NaCl solution and immediate drying with hot air. For Al TL094 and the intermittent-flow experiments, where multiple samples were exposed together in the chamber, NaCl was applied with laboratory paper towel soaked with saturated NaCl on pre-heated substrates and immediately dried with hot air.

Gravimetric setup for volumetric atmospheric corrosion rate monitoring.—The gravimetric setup for monitoring atmospheric corrosion rates is shown in Fig. 2 and has been described before. In brief, the sample was submerged inside a container surrounded by humid air. The change in the buoyant force exerted by a change in the volume of the gas in the container is recorded by a balance. As a modification to the previous setup to decrease the exchange of gases between the gas volume and the surrounding solution, a nitrile butadiene rubber flexible barrier was introduced. This barrier allows the volume of the gas to expand or compress but limits the exchange of O2 or H2 with the surrounding solution (deionized water). A small amount of a saturated K2SO4 salt solution inside the gas volume was added to regulate the relative humidity (RH) to about 97%. To measure the O2 partial pressure in the gas volume surrounding the sample, an optical O2 sensor spot (Pyroscience, Germany) was glued at the inside wall of the collection container. An optical O2 meter (Piccolo2OEM, Pyroscience, Germany) was used to make non-invasive measurements with an optical fibre that is positioned directly above the O2 sensor spot without touching the collection container. Wet-dry cycles were realized with the Mg alloy AZ31. Samples mounted in epoxy and contaminated with 200 μg cm−2 NaCl were placed horizontally in an open setup without the flexible rubber barrier. In this case, the RH was adjusted by changing the solution in contact with the gas phase surrounding the sample. The container with the sample was alternately submerged in either deionized water (wet phase, 100% RH) or saturated Mg(NO3)2 solution (dry phase, ≈54% RH). Imaging of the surface during exposure was carried out with a USB microscope PCE-MM 400 in order to construct a time-lapse video of the corrosion progress. The effect of temperature steps on an AZ31 sample was investigated by switching from room temperature exposure to thermostated baths with 4 °C or 40 °C. The solution was saturated K2SO4 and the equilibrium RH over this solution varies only slightly in this temperature range.

Static setup for manometric atmospheric corrosion rate monitoring.—The static setup to monitor HER and ORR during atmospheric corrosion with the manometric approach is shown in Fig. 3a. The corroding sample was exposed in a closed chamber with a fixed volume. A DURAN® GL 45 laboratory glass bottle (100 ml) was...
used as a chamber. The chamber volume was determined by weighing the amount of water needed to fill the chamber. According to ideal gas law the change in pressure for a given change in the number of gas molecules is higher in a smaller volume chamber. In this work, inert glass balls were used to reduce the volume available for the gas molecules in the chamber. This was done to increase the sensitivity to detect small ORR or HER rates in a shorter time.

The chamber was closed by a DURAN® GL 45 bromobutyl rubber stopper that is highly impermeable to gases. A Bosch Sensortec BME280 combined sensor (SparkFun Electronics breakout board) measured total pressure, temperature and relative humidity inside the chamber. The sensor was connected to an Arduino Uno microcontroller via a gastight feedthrough that was realized by piercing connector pins through the bromobutyl rubber stopper. The readings of the BME 280 sensor were transmitted via an I2C Interface to the Arduino microcontroller which was connected to a computer. A modified Arduino script to control the system was written based on the example code provided by Sparkfun. The BME 280 sensor was used in forced mode, where it was put to sleep in between the measurements to minimize self-heating of the sensor. The script returns the sensor readings in a comma separated format. A terminal application (CoolTerm) was used to capture the received data in a text file. To monitor the partial pressure of oxygen inside the chamber, an optical O2 sensor spot was glued to the inside of the transparent chamber wall. An optical fiber and a Piccolo2OEM optical O2 meter were used to make non-invasive O2 measurements. The RH in the chamber is controlled by adding a small amount of a saturated K2SO4 salt solution that has an equilibrium RH of around 97%. The gas-tightness of the setup is a source of error of the measurements but was found to be satisfactory.

**Flowcell setup for manometric atmospheric corrosion rate monitoring.**—The flowcell atmospheric corrosion setup to realize intermittent-flow measurements based on the static manometric approach is depicted in Fig. 3b. An inlet and outlet that can be opened or closed by solenoid valves were integrated in the rubber stopper. The 12 V powered solenoid valves were switched on or off by a relay module that was controlled by the Arduino microcontroller. An Arduino script was written to periodically open the chamber for flushing and close the chamber for measuring the pressure changes. Different flushing media were used to test the influence of wet-dry cycling or the influence of O2 partial pressure on the corrosion rate. A pump (EHEIM air200) was used to flush the chamber with humidified air or lab air. Dry artificial air, pure N2 or pure O2 was supplied by a gas cylinder. In order to start each measurement phase at ambient atmospheric pressure, the outlet solenoid valve was closed with a delay of 2 s after the inlet solenoid valve was closed. To increase the signal to noise ratio, multiple NaCl contaminated samples were exposed together in the chamber. The leak rate of the setup is a source of error of the measurements but was found to be satisfactory.

**Evaluation of HER and ORR rates.**—The ideal gas law can be used to calculate the amount of substance associated with the volume changes or the pressure changes due to HER and ORR. In a first step, the change in the total number of gas molecules can be calculated from the change in gas volume $\Delta V(t)$ (gravimetric setup) or from the change in total pressure $\Delta p(t)$ (manometric setup):

$$\Delta n_{\text{tot}}(t) = \frac{\Delta p(t) \cdot \Delta V(t)}{R \cdot T(t)}$$  \[3\]

where $R$ is the ideal gas constant and $T(t)$ is the temperature of the gas. Changes in the number of O2 molecules can be obtained by the changes in the O2 partial pressure $\Delta p_{O_2}$ from the optical O2 sensor,
Accordingly (Eq. 4),
\[
\Delta n_{O_2}^{\text{optical}} = \Delta n_{O_2} \cdot \frac{V(t)}{RT(t)}
\]  

In the manometric setup, the gas volume \( V \) of the chamber is constant and the experiment is independent of the atmospheric pressure. In the volumetric setup the volume is a function of time and can be calculated from the measured weight signal as described previously.23 Note that \( \Delta p(t) \) in the volumetric setup is not constant but changes with the atmospheric pressure. For accurate measurements, changes in the atmospheric pressure during the experiment must be considered.

The temperature of the experiment should be maintained constant or measured at the position of the gas volume. Accurate temperature recording is a prerequisite for both the calculation of the amount of gas molecules, as well as for the internal automatic temperature compensation of the optical \( O_2 \) sensor. In this work the chamber was submersed in a water bath that was not temperature controlled. Temperature was measured by the external Pt100 sensor of the optical \( O_2 \) sensor that is located inside the water bath at the outer wall of the chamber. For the manometric measurements a second temperature measurement is carried out by the BME280 Sensor inside the chamber. For these experiments the mean value of both temperature measurements is used for the calculations.

While for the volumetric setup the temporal evolution of RH inside the gas volume is not accessible, it can be measured in situ by the RH sensor with the manometric setup. This allows calculation of the water vapor pressure \( p_{H_2O}(t) \) from the saturation vapor pressure \( p_{H_2O}^{sat} \) (Eq. 5), and compensation for the changes in the number of \( H_2O \) molecules in the gas phase \( \Delta n_{H_2O} \):
\[
p_{H_2O}(t) = RH(t) \cdot p_{H_2O}^{sat}
\]

For systems that corrode by only either HER or ORR, the number of \( H_2 \) generated or \( O_2 \) molecules consumed can be directly determined from the change in total number of gas molecules by subtracting \( \Delta n_{H_2O} \):
\[
\Delta n_{H_2/O_2} = \Delta n_{tot} - \Delta n_{H_2O}
\]

For systems with mixed HER and ORR contributions, the number of \( H_2 \) molecules evolved can be determined by subtracting also the changes due to \( O_2 \) consumption, as determined by the optical \( O_2 \) sensor (Eq. 7). The \( H_2/O_2 \) amount of substance is converted to a cathodic charge using Faraday’s law and the derivative of the charge vs time curve results in the current.
\[
\Delta n_{H_2} = \Delta n_{tot} - \Delta n_{O_2}^{\text{optical}} - \Delta n_{H_2O}
\]

It should be noted that \( CO_2 \) in the gas volume can get depleted by the incorporation in the corrosion products in the form of carbonates. This consumption of \( CO_2 \) would lead to an underestimation of the amount of \( H_2 \) detected. However, for the static exposure setups the error is limited to the amount of around 400 ppm of ambient \( CO_2 \) and can be neglected. For the flow cell atmospheric setup the level of \( CO_2 \) is restored with every flush phase. In this case the underestimation can sum to a noticable error, depending on the frequency of flushing and the uptake of \( CO_2 \) by the sample.

**Mass loss measurements.**—After exposure, to remove the corrosion products, the samples were immersed in a pickling solution (Zn: 250 g l\(^{-1}\) glycine solution, Fe: 500 ml l\(^{-1}\) HCl with 3.5 g l\(^{-1}\) of hexamethylenetetramine, Cu: 50 g l\(^{-1}\) amidosulfonic acid, AZ91: 200 g l\(^{-1}\) CrO\(_3\)) according to ISO 8407.33 The amount of metal loss was determined by weighing the samples before exposure and after removal of the corrosion products. The value was converted to an anodic charge using Faraday’s law. In the case of metals with different possible valency, the average oxidation state of the metal in the corrosion products \( Z \) was calculated from the total cathodic charge and the mass loss amount of substance \( n_{ML} \):
\[
z = \frac{Q_{cath}}{n_{ML} F}
\]

**Results and Discussion**

**Gravimetric volumetric experiments.**—Figure 4 shows the results of a pure Zn sample contaminated with NaCl that was exposed to a humid environment (97% RH) with the gravimetric atmospheric setup without the optical \( O_2 \) sensor. ORR is expected to be the major cathodic reaction on Zn in the pHR range of 4–11.24,35 The weight signal recorded by the balance increased during exposure. This can be explained by the consumption of \( O_2 \) gas that leads to a decrease in the gas volume and thus to a decrease in the buoyant force. The weight signal is disturbed by the temperature and pressure variations during the measurement. After compensating for these influences, reliable charge curves were obtained, assuming that ORR is the dominant cathodic reaction for Zn. The total amount of cathodic charge is in good agreement with mass loss (\( Q_{cath}/Q_{ML} = 89.9\% \)). This demonstrates that the atmospheric gravimetric setup is suitable to monitor in real-time the corrosion rate during atmospheric exposure of metals that corrode mainly via \( O_2 \) consumption.

An example of simultaneous HER and ORR monitoring with the gravimetric atmospheric setup combined with optical \( O_2 \) measurements is shown in Fig. 5. AZ91 contaminated with NaCl was exposed at RH \( \approx 97\% \). The total gas volume \( V(t) \) can be calculated from the weight changes recorded by the balance. Since HER is the dominant reaction, the weight signal decreases with time, due to the evolved \( H_2 \) gas. The amount of \( O_2 \) consumed is calculated from the \( p_{O_2}(t) \) signal and the \( V(t) \) signal. Note that by definition the partial pressure of \( O_2 \) will decrease with an increase in the available gas volume even if no \( O_2 \) is consumed. The AZ91 sample, however, really does consume \( O_2 \) which is reflected in the positive \( O_2 \) charge curve. The true \( H_2 \) charge curve was obtained by correcting the total amount of gas changes for the amount of consumed \( O_2 \). Real-time current densities of HER, ORR and total corrosion rate can be obtained from the slope of the charge curves. The ratio of the total...
Cathodic charge to mass loss is 87.8% and ORR contributes with 16.9% to the total cathodic charge. To understand and quantify the effect of temperature changes or wet-dry cycles on the corrosion rate are important aspects in the development of accelerated corrosion tests. The gravimetric method is able to monitor the HER rate under changing exposure conditions as demonstrated in the following on the Mg alloy AZ31. These experiments were performed without the concurrent O2 sensor measurement. Temperature changes were realized by submerging the collection container with the sample in saturated K2SO4 solutions with different temperature (Fig. 6). As expected, the HER rate increases with increasing temperature. As the HER is an activation controlled reaction, the rate follows the steps in the temperature. Overlaid, there is also a general trend towards decreasing corrosion rate with time. This trend can be attributed to the continuous blocking of active sites with insulating corrosion products.

Changes in RH can be achieved by switching the solution in contact with the gas phase in the collection container. In the experiment shown in Fig. 7, the humidity was cycled between wet (DI H2O; 100% RH) and dry (sat. Mg(NO3)2; 54% RH) every 48 h. Real-time HER rates were calculated from the slope of the weight curve recorded by the balance. As can be seen, the humidity and the electrolyte thickness did not change instantly after switching the solution. Especially drying was slow and it took over 15 h until the electrolyte droplets disappeared. For the experiment shown in Fig. 7 and Video 1, the HER rate was comparably low in the first wet phase and further decreased in the first part of the drying phase. For a RH of 54%, corrosion did not stop, but continued at a measurable rate. In the second part of the dry phase the HER rate increased and it can be observed that a high number of new active corrosion fronts emerged which is accompanied by an increase in the HER rate. The breakthrough of the Mg surface film can be explained by the increase in chloride concentration during drying. In the subsequent wet phase, H2 evolution proceeded at the active sites generated in the dry phase, at a rate that is higher compared to the first wet phase. Although the same behavior could be found in the next cycle, it can not be generalized that drying always leads to an increase in the corrosion rate of the subsequent wet phase. In other experiments (see e.g. Video 2 in supporting information), the opposite behavior was found. In this case, the corrosion rate was high in the first wet period and the drying step increased the protectiveness, probably by consolidating the corrosion product film. The homogeneity of the salt distribution and the availability of uncorroded, silvery parts on the surface seem to be responsible for the different corrosion behavior, but further work is necessary. As for the method itself, it can be stated that gravimetric measurements can provide reliable real-time information on the corrosion kinetics also during changing exposure conditions.

Considerations regarding the gravimetric volumetric approach.—As shown, the gravimetric volumetric respirometric method provides sensitive real-time measurements with a good correlation of the cathodic charge with mass loss. The small discrepancy between the gravimetric, respirometric method and mass loss can be explained with the following points:

a) Excessive cleaning during the removal of corrosion products leads to base metal removal and overestimated mass loss.
b) Errors can result from the measurement of parameters needed to calculate the cathodic charge. This includes the accuracy of the balance, the partial pressure of O₂ by the optical sensor (accuracy: ±2 hPa), the measurement of temperature (accuracy: ±0.5 °C) and atmospheric pressure (accuracy: ±2 hPa). Further errors can result from the determination of the volume of the collection assembly and the determination of the density of the solution.

c) Loss of H₂ gas by diffusion into the surrounding solution or entry of O₂ gas from the surrounding solution would lower the cathodic charge registered by the gravimetric method. Without the flexible rubber barrier the dissolution of H₂ in the surrounding solution was shown before. With the introduction of a flexible rubber barrier, this effect should be strongly reduced. The loss of H₂ by uptake in the sample itself is considered to be negligible.

To increase the sensitivity of the gravimetric method, the air volume under the collection container should be small in order to decrease the effect of external influences like atmospheric pressure and temperature variations. Another possibility is to use a solution with a higher density to increase the changes in buoyant force exerted by a given change in the gas volume.

There are several points that complicate the gravimetric approach. One major concern regards the volume of the gas phase that is not constant and influences the calculated amount of O₂ in the gas phase. Even if no O₂ is consumed in an experiment, the O₂ partial pressure will fall if there is a volume increase due to H₂ evolution. Therefore, the determination of the amount of O₂ is not an independent measurement but is affected by errors in the volume determination with the balance. Moreover, the dilution due to H₂ evolution could have an influence on the ORR rate. Another aspect is the gas exchange at the interface of gas phase with the liquid phase where the assembly is submerged in. In order to prevent the exchange of O₂ or H₂ at this interface, the system should be closed by a flexible barrier. That way the balance can still detect changes in buoyancy that is caused by HER or ORR but there is not such a pronounced loss of H₂ or a possible source of O₂. However, with the flexible barrier the total amount of H₂ gas evolution or O₂ consumption is limited by the ability of the barrier to follow the changes in the volume. Closing the system with the flexible barrier complicates any attempts to periodically restore the experiments initial concentration of O₂ or CO₂ or changing the exposure condition by flushing with different gases or different humidity. Consequently, this approach is more suitable for static exposure where the depletion of O₂ or CO₂ is tolerated.

**Static manometric experiments.** — The first example experiment of the static manometric setup is the exposure of a pure Cu sample contaminated with NaCl in a 97% RH environment (Fig. 8). It is well accepted that ORR is the dominant reduction reaction in Cu corrosion, although there is debate if traces of H₂ are evolved under anoxic conditions. For the sake of this study, the influence of HER can be neglected and Cu is an ideal example of a sample that corrodes only via ORR. In this case the signal of the O₂ optical sensor should match the signal of the pressure sensor, since both should register the decrease in O₂ partial pressure. In Fig. 8 it can be seen that the charge curves of both sensors overlap very well after the correction of the influence of temperature and water vapor pressure. This leads to the conclusion that reliable measurements are possible both with the optical O₂ sensor and with the pressure sensor if the actual temperature and vapor pressure are considered. A direct validation of the Cu experiment with mass loss is not possible, because the exact oxidation state of Cu in the formed corrosion products is unknown. Cu corrosion products are typically composed of an inner Cu⁺-containing layer and an outer Cu₂⁺-containing layer. Therefore, the oxidation state is expected to be somewhere in between one and two. Assuming that the recorded cathodic charge is a good measure of the amount of corrosion that has occurred, the average oxidation state of the corrosion products can be calculated with Faraday’s law. Hence, the valuable information of the global oxidation state of the corrosion products is directly accessible through the combination of the respirometric method with mass loss. For this experiment, the calculated value is 1.9 which suggests that 10% cuprous and 90% cupric corrosion products were formed.

![Figure 8](image1.png)

**Figure 8.** Static exposure of a pure Cu sample contaminated with NaCl in the manometric setup at elevated RH. O₂ equivalent charge curves can be calculated from the decrease in total pressure or O₂ partial pressure. Temperature and water vapor pressure have to be taken into account for reliable results.

![Figure 9](image2.png)

**Figure 9.** ORR charge curves of five different Zn samples contaminated with NaCl obtained with the pressure sensor or the optical O₂ sensor. See Video 4 in supporting information for a time-lapse video of the corrosion progress.
Video 3 in the supporting information confirms that black CuO is visually found as the main corrosion product. A better system to validate the method with mass loss is Zn, where the expected oxidation state of the corrosion products is two. Figure 9 shows the cathodic O₂ equivalent charge measurements of five Zn samples contaminated with NaCl exposed in the static manometric setup at elevated RH. A very good match of the signal of the pressure sensor and the optical O₂ sensor was found. From this it can be concluded that ORR is the dominant cathodic reaction for Zn atmospheric corrosion under these conditions. The absence of substantial amounts of H₂ can be explained by the sluggish HER kinetics on Zn. Higher NaCl loading increases the corrosion rate which can be explained by a higher availability of electrolyte and an increased active surface area. The variability of results for samples with the same nominal conditions is attributed to differences in the homogeneity of the salt application that leads to a different corrosivity. The comparison of the total cathodic charge of pressure sensor and optical O₂ sensor with the mass loss carried out at the end of exposure is presented in Fig. 10. An excellent correlation with mass loss and the two sensors validates the technique and proves that reliable real-time corrosion rate monitoring is possible with either of the sensors. This is the basis to be able to monitor also mixed systems with both ORR and HER simultaneously.

One example of such a mixed system is demonstrated in Fig. 11, where an AZ91 Mg alloy sample contaminated with NaCl was exposed in the static manometric setup at 97% RH. The upper part shows the raw data obtained from the combined pressure, temperature and RH sensor and of the optical O₂ sensor. The pressure signals were corrected for the temperature influence, water vapor pressure and for the consumption of O₂.

Video 3 in the supporting information confirms that black CuO is visually found as the main corrosion product.

A better system to validate the method with mass loss is Zn, where the expected oxidation state of the corrosion products is two. Figure 9 shows the cathodic O₂ equivalent charge measurements of five Zn samples contaminated with NaCl exposed in the static manometric setup at elevated RH. A very good match of the signal of the pressure sensor and the optical O₂ sensor was found. From this it can be concluded that ORR is the dominant cathodic reaction for Zn atmospheric corrosion under these conditions. The absence of substantial amounts of H₂ can be explained by the sluggish HER kinetics on Zn. Higher NaCl loading increases the corrosion rate which can be explained by a higher availability of electrolyte and an increased active surface area. The variability of results for samples with the same nominal conditions is attributed to differences in the homogeneity of the salt application that leads to a different corrosivity. The comparison of the total cathodic charge of pressure sensor and optical O₂ sensor with the mass loss carried out at the end of exposure is presented in Fig. 10. An excellent correlation with mass loss and the two sensors validates the technique and proves that reliable real-time corrosion rate monitoring is possible with either of the sensors. This is the basis to be able to monitor also mixed systems with both ORR and HER simultaneously.

One example of such a mixed system is demonstrated in Fig. 11, where an AZ91 Mg alloy sample contaminated with NaCl was exposed in the static manometric setup at 97% RH. The upper part shows the raw data obtained from the combined pressure, temperature and RH sensor and of the optical O₂ sensor. The pressure signals were corrected for the temperature influence, water vapor pressure and for the consumption of O₂.

In the lower part of Fig. 11 the HER charge curves with different degree of correction are plotted. The smoothest H₂ charge curve was obtained after correcting for both temperature and water vapor pressure influences. This curve can be further corrected for the number of O₂ molecules that were consumed. As a result, the contribution of ORR in Mg alloy atmospheric corrosion can be shown unambiguously.

Table I. Comparison of total recorded cathodic charge with mass loss for three exposures of AZ91 samples contaminated with 200 μg cm⁻² NaCl.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Exposure time (h)</th>
<th>Q_{o₂} (C)</th>
<th>Q_{O₂} (C)</th>
<th>Q_{total} (C)</th>
<th>Q_{act} (C)</th>
<th>Q_{total} %</th>
<th>Fraction of ORR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ91_1</td>
<td>48</td>
<td>47.7</td>
<td>4.4</td>
<td>52.1</td>
<td>54.8</td>
<td>95.1</td>
<td>8.4</td>
</tr>
<tr>
<td>AZ91_2</td>
<td>48</td>
<td>54.6</td>
<td>7.0</td>
<td>61.6</td>
<td>63.2</td>
<td>97.5</td>
<td>11.4</td>
</tr>
<tr>
<td>AZ91_3</td>
<td>61</td>
<td>69.6</td>
<td>4.2</td>
<td>73.8</td>
<td>74.9</td>
<td>98.5</td>
<td>5.7</td>
</tr>
</tbody>
</table>
synchronous real-time monitoring of HER and ORR rates is possible with the combination of pressure sensor and optical O2 sensor. The comparison of the total cathodic charge with mass loss and the fraction of ORR for three replicate samples of AZ91 is summarized in Table I. Again, an excellent correlation was found with \( Q_{\text{total}}/Q_{\text{ML}} \) values above 95%. ORR has a share of around 6%–11% in the total cathodic charge for these experimental conditions.

Another interesting material to study with the new monitoring method is Al alloys. As the corrosion rate of Al is generally low, multiple NaCl contaminated samples of a 6000 series Al alloy were exposed together in the static manometric setup (Fig. 12). This lead to a possible crevice situation with the samples touching each other. The initial two days of exposure are characterized by low rates of ORR and negligible HER rates. This phase could be described as an incubation phase where the samples are more or less passive. After two days, an increase in the ORR activity was observed. This can be explained with the breakdown of passivity and the beginning of localized active dissolution. With a further delay of almost one day, the onset of H2 evolution was observed. This point might be attributed to the onset of stable pitting corrosion. Indeed, pits could be found on all surfaces of the samples, not only on those that were touching each other. H2 evolves from the pits due to the aggressive chemistry that is formed inside. Acidification and high chloride concentration maintain depassivation and lead to direct contact of unprotected Al with water.40 This results in vigorous H2 evolution similar to anomalous H2 evolution generated locally at dissolving Mg sites.40,41 Further monitoring revealed an increasing HER rate and a decrease in ORR rate, while the total corrosion rate increased until H2 evolution reached a plateau. After that, the influence of ORR decreases and corrosion proceeds at a stable rate sustained mainly by HER. To explain the exact origin and influence of ORR and HER in Al alloy localized corrosion is out of the scope of this article. However, the results demonstrate the high potential of the real-time information provided by the respirometric method in elucidating the mechanism.

Figure 13 shows the results of three static exposures of pure Fe samples contaminated with 200 µg cm\(^{-2}\) NaCl. Again a very good correlation of the pressure sensor charge with the optical O2 sensor charge was found. This implies that HER does not contribute significantly to Fe atmospheric corrosion under these conditions. What is interesting in the case of iron is to look at the average oxidation state of Fe in the corrosion products that were formed during the exposure. This information is accessible by the combination of the respirometric method with mass loss. Earlier, it was found that the corrosion rate of iron can reach very high values during drying.40 To prevent any further Fe oxidation in the drying process, the removal of the corrosion products by the mass loss solution was carried out directly after exposure without drying. This way the cathodic charge recorded by the respirometric method should correspond to the anodic mass loss charge. The average oxidation state of Fe in the corrosion products was calculated from the average value of pressure sensor total charge and O2 sensor total charge together with the mass loss amount of substance. The results listed in Table II reveal that around 50% of the iron species are in the Fe\(^{2+}\)-state and the rest is Fe\(^{3+}\). The visual appearance of the corrosion products (see Video 5 in supporting information) suggests the presence of red-brown FeOOH and black FeO\(_2\) which exhibit z values of 3.00 and 2.66, respectively. Therefore a substantial amount of other Fe\(^{2+}\) species must be present, such as Fe(OH)\(_2\) or chloride-containing green rust.

**Intermittent-flow manometric experiments.—**Validation of the intermittent-flow setup with mass loss was carried out on the AZ91 system (Fig. 14). Multiple NaCl contaminated samples were exposed together in the chamber. The chamber was periodically opened every 60 min and flushed with wet air for 20 s. The RH eventually reached 90% after 48 h exposure. The uptake of water vapor by the salt on the samples to form a corrosive electrolyte can be seen by the decrease in RH during the measurement phases. The temperature increase at the beginning of each measurement period can be attributed to the heating of the solenoid valves that were used to open the chamber. This type of experiment leads to a sawtooth-like curve for the HER and ORR charge curves. The HER and ORR rates can be obtained from the slopes of these segments. Increasing rates for HER were found with increasing exposure time. This can be attributed to the increase in the availability of water on the samples. Cumulative charge curves were obtained by integrating the rates with a trapezoidal rule numerical algorithm. The total cumulative charge at the end of the experiment is compared with mass loss in Fig. 14b. From preliminary results with a CO2 sensor it was found that under these experimental conditions it can be assumed that CO2 is completely consumed at the end of each 1 h measurement phase.

Therefore, the contribution of this CO2 consumption to the HER charge was also taken into account, assuming 400 ppm CO2 consumption in each measurement cycle. A very good agreement between the total cathodic charge and the charge determined by mass loss was found. This gives confidence that also the real-time rates of the intermittent-flow approach are valid. The remaining small discrepancy can be explained by leakage, other errors in the determination of the cathodic charge, or corrosion during the application of the salt.

To demonstrate the versatility of the intermittent-flow respirometric method, an experiment with wet-dry cycles and changes in gas composition and temperature was conducted on AZ91 (Fig. 15). The effects of these changing exposure conditions on HER, ORR and total corrosion rates can be monitored simultaneously in real-time.

**Table II. Calculation of the average oxidation state of Fe in the corrosion products from the cathodic charge and mass loss.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Exposure time (h)</th>
<th>(Q_{\text{press. sens.}}) (C)</th>
<th>(Q_{\text{O2 sens.}}) (C)</th>
<th>(m_{\text{ML}}) (mg)</th>
<th>Average valency of Fe in the corrosion products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe_1</td>
<td>62</td>
<td>78.6</td>
<td>74.7</td>
<td>17.54</td>
<td>2.53</td>
</tr>
<tr>
<td>Fe_2</td>
<td>62</td>
<td>109.1</td>
<td>108.8</td>
<td>25.92</td>
<td>2.43</td>
</tr>
<tr>
<td>Fe_3</td>
<td>63</td>
<td>122.2</td>
<td>122.9</td>
<td>27.65</td>
<td>2.56</td>
</tr>
</tbody>
</table>
For example, it can be observed that during drying the HER rate decreases while the ORR rate increases. In some cases these opposed effects leave the total corrosion rate unchanged. This shows the importance of monitoring both HER and ORR simultaneously for a valid determination of the true corrosion rate. In the dry phases the fraction of ORR far exceeds the values found under static exposure at high RH and can reach up to 60% of the total corrosion rate. The ORR rate strongly depends on the diffusion of O₂ to the cathodically active sites. Therefore, mass transport is faster with the small electrolyte thickness found in the dry phase. A different effect is observed for the HER, where the rate tends to increase with the availability of water on the surface. This can be explained with a higher active surface area and better micro-galvanic coupling between the local cathodes and anodes.

An increase in temperature to 40 °C leads to an increase in the total corrosion rate that is mainly caused by a strong increase in the HER kinetics. An elevated O₂ partial pressure tends to increase the ORR rate, while the HER seems to be not much affected by the level of O₂ in the gas phase. It is not intended to draw definitive conclusions with these preliminary results, as it is difficult to vary one parameter without affecting other possible influences, e.g. humidity. Nevertheless, the ability to follow the changes in real-time on the same sample is a huge advantage of the new method.

Considerations regarding the manometric respirometric approach.—The manometric respirometric approach provides several advantages compared to the volumetric approach. With the closed system, there is no need to correct for variations in the atmospheric

**Figure 14.** Exposure of multiple AZ91 samples in the intermittent-flow respirometric setup with periodic wet air flushes every 1 h: (a) sawtooth-like HER and ORR charge curves and cumulative charge curves calculated from pressure, temperature and RH signals; (b) comparison of total cathodic consumed charge with mass loss charge after 48 h exposure.

**Figure 15.** Real-time response of HER, ORR and total corrosion rate of multiple AZ91 samples with changes in RH, O₂ partial pressure and temperature measured with the intermittent-flow respirometric setup. See Video 6 in supporting information for a time-lapse video with images of the corrosion progress.
pressure. There is no influence of the density of solution and the RH can be monitored in real-time. In a gas-tight, closed chamber only very limited exchange of O₂ or H₂ gas with the outside or chamber walls is expected. Furthermore, frequent intermittent flushing can prevent the build-up of strong partial pressure differences, making leakage or gas absorption into the sample or the chamber wall negligible.

All these aspects can explain the excellent correlation of the respirometric experiments with mass loss. The remaining discrepancy can result from the accuracy of the optical O₂ sensor to measure the partial pressure of O₂ (accuracy: ±2 hPa) and temperature (accuracy: ±0.5 °C), and the accuracy of the combined sensor for total pressure (accuracy: ±1 hPa), temperature (accuracy: ±1 °C) and RH (accuracy: ±3%). Another aspect that can introduce an error in the calculation of cathodic charge is the determination of the gas volume of the chamber or leakage.

The manometric respirometric approach is considered to be highly suitable to study atmospheric corrosion in real-time, non-destructively and with a high sensitivity for low corrosion rates. A strict detection limit for the respirometric method cannot be given. However, the sensitivity can be further increased by reducing the volume of the chamber, by increasing the active area of the corroding sample and by increasing the time of measurement. In a gas-tight system, it should be possible to measure even the smallest corrosion rates with respirometry, simply by waiting long enough to measure a significant change in pressure. As a result, the respirometric method is a highly promising tool to study mechanisms of atmospheric corrosion at realistic exposure conditions.

Conclusions

Different respirometric methods to monitor atmospheric corrosion kinetics were presented. The respirometric approach can be applied to any metal or alloy and is non-destructive. The following can be concluded:

- Simultaneous real-time monitoring of HER, ORR and total corrosion rates is possible by either volumetric or manometric measurements in combination with an optical O₂ sensor.
- The respirometric methods were validated by an excellent correlation between the total cathodic charge and mass loss.
- In-situ real-time monitoring during wet-dry cycles and changes in temperature or gas composition was demonstrated with the respirometric approach.
- It could be proven in several experiments that AZ91 corrodes partly via ORR. The contribution to the cathodic processes can reach over 60% depending on the RH.
- The onset of localized corrosion of an Al alloy could be followed with the respirometric method to reveal a shift in the contribution of ORR and HER with time.
- The average oxidation state of a metal in the corrosion products can be assessed with the total cathodic charge of the respirometric method combined with mass loss measurements. For pure Fe, a value of approximately 2.5 was found for the oxidized Fe species generated during exposure at high RH.
- The respirometric method can provide highly relevant real-time information that can promote mechanistic understanding of atmospheric corrosion and accelerated testing.

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References