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Denissen, Paul J.; Homborg, A.M.; Garcia, Santiago J.

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Interpreting Electrochemical Noise and Monitoring Local Corrosion by Means of Highly Resolved Spatiotemporal Real-Time Optics

Paul J. Denissen,^{1,z} Axel M. Homborg,² and Santiago J. Garcia^{1,z}

¹Novel Aerospace Materials Group, Faculty of Aerospace Engineering, Delft University of Technology, 2629 HS Delft, The Netherlands

²Netherlands Defence Academy, 1781 AC Den Helder, The Netherlands

Real-time optical analysis is used to improve the interpretation of electrochemical noise signals (EN). The concept is presented for the case of AA2024-T3 under immersion in various NaCl concentrations. An in-house developed optical-electrochemical technique allowed for high spatiotemporal resolution and was used to visualize and quantify surface changes in parallel with monitoring EN signals. EN analysis was performed in the time-frequency domain using continuous wavelet transform (CWT). Correlations between the two procedures enabled the identification of corrosion processes in time, such as de-alloying, etching, pitting and subsurface corrosion. Besides this, optical measurements at higher magnification were used to analyse a smaller section of the exposed metal with a spatial resolution below 1 μm . This enabled the quantification on the size, number and nearest neighbor distance of local corrosion events, such as pits and corrosion rings. The set-up and optical protocol allowed for the first time (i) to establish a direct relationship between EN signals and the occurrence of specific localized corrosion phenomena and (ii) an in-situ highly-resolved monitoring of local corrosion processes. As a final result of the optical analysis we introduce a straightforward illustration that allows the direct identification of EN features to macroscopic local corrosion phenomena.

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In wet corrosion studies, prior knowledge of the evaluated systems normally plays a crucial role when aiming at a correct interpretation of the measured electrical signals during immersion. Back in the 90s Hugh Isaacs already emphasized the difficulty of correlating current and potential fluctuations, defined as electrochemical noise (EN), to local corrosion processes.¹ Despite the attempts, this remains a largely unsolved issue, typically only addressed in the past by optical inspection after the corrosion activity has occurred.

Individual electrochemical phenomena that are localized in time generate singularities, or transients, in the EN signal. These transients are characterized by a distinct energy distribution over a (set of) timescale(s) which are different than the rest of the EN signal, providing them a specific shape and duration. Nevertheless, these EN transients are often superimposed in time, making it difficult to correctly interpret the signals in the time domain. Deconvolution of the transients can be achieved by analysing the EN data in the time-frequency domain, allowing a more robust description of their appearance. For instance, Aballe et al. used discrete wavelet transforms in the late 90s² to analyse EN, while Homborg et al. introduced the Hilbert-Huang transform to relate specific domains in the time-frequency spectra to different types of corrosion processes based on their transient characteristics.³⁻⁶ One of the most recent works proposes the use of continuous wavelet transform (CWT) to analyse EN in relation to corrosion processes.⁷ The CWT procedure operates in the time-frequency domain by the scaling and translation of a wavelet at a number of timescales. The energy distribution of the EN signal over the different timescales can in turn be attributed to the occurrence of processes primarily under either activation, diffusion or mixed control.^{2,8-11} Nevertheless, complementary measurements after the corrosion test such as optical microscopy,¹² SEM/EDS,¹³ and Raman,¹⁴ are still required. While this approach can be used to obtain information on the final type of degradation, it does not provide any real-time information on the corrosion process in relation to the electrochemistry. Time-resolved information can only be achieved by combining electrochemistry with a supplementary techniques such as in-situ XRD¹⁵ or optical

microscopy in real-time.¹⁶⁻¹⁸ In the particular case of EN, gathering information on the corrosion processes that can be directly related to the EN signals would boost the potential use and robustness of this technique.

In previous works we introduced how the in-situ combination of real-time optics and electrochemistry can be used as an inexpensive and straightforward method to correlate electrochemical impedance spectroscopy to macroscopic corrosion-related phenomena of metals and coatings in corrosive media.^{17,18} In this work we go one step further with an improved setup that shows how real-time optics with high spatiotemporal resolution and image analysis can be combined with EN to follow local corrosion processes. To demonstrate the concept we analyzed the corrosion processes of AA2024-T3 immersed in salt solutions at different concentrations. Optical measurements were performed using a low magnification setup with a pixel density of 0.33 pixels per micron and a high magnification setup with 2.7 pixels per micron using two different cameras. The lower magnification enables the identification of all surface-related processes occurring at a macroscopic scale ($<5 \mu\text{m}$ resolution), while the high magnification allows a more detailed sub-micron view of a smaller surface area. The use of a newly developed image analysis procedure allows the isolation of the pixels changing in time (i.e. affected by the corrosion process) from the unchanged pixels (i.e. not affected). This process enabled the visualization of the corrosion processes normally non-detectable with microscopy images at the same resolution. The higher magnification approach also allowed the clear identification in time and quantification of corrosion-related features, such as the amount, size and nearest neighbor distance of pits and oxide rings, which have previously only been observed by post-immersion inspection by SEM. The electrochemical potential noise (EPN) monitored in parallel with the optical analysis serves as a basis for the time-frequency electrochemical analysis using CWT as previously shown for steel.¹⁹ The in-situ combination of optical and electrochemical analysis allowed for the first time to directly assign electrochemical signals to specific corrosion processes (e.g. de-alloying, trenching, pitting and oxide formation). As a result, a plot correlating the optical and electrochemical analysis to corrosion processes is introduced.

^zE-mail: P.J.Denissen@tudelft.nl; S.J.GarciaEspallargas@tudelft.nl

Figure 1. a) Schematic illustration of the cell used for the optical and electrochemical measurements. The scheme shows the two-electrode setup and the varying positions of the two microscope cameras (for high or low magnification studies) with respect to the two AA2024-T3 working electrodes (WE1 and WE2). b) Image of the optical-electrochemical cell used in this study in the Faraday cage.

Experimental

Optical-electrochemical setup.—Figure 1 shows the improved optical-electrochemical setup used in this work derived from our previous studies.^{17,18}

The current and potential signals for EN were recorded with an Ivium Compactstat using IviumSoft V2.86. The electrochemical current noise (ECN) was measured between the two parallel working electrodes (see sample preparation) with the Compactstat acting as zero resistance ammeter (ZRA). The electrochemical potential noise (EPN) was measured between the two working electrodes and a Metrohm double-junction (Ag/AgCl/sat. KCl) reference electrode (RE). The required sampling frequency to record faster occurring fluctuations was set to 20 Hz, combined with a low-pass filter of 10 Hz (Nyquist frequency at this sampling rate). The maximum range of the ZRA was automatically determined depending on the local dynamic range of the ECN signal, with a lower limit of 100 nA and an upper limit of 1 μ A. The maximum range of the potentiometer was set at a lower limit of 100 mV and an upper limit of 400 mV. The EN data, processed using Matlab from MathWorks, showed that the potential signals from EN provided all relevant information for this study and therefore the current signals, despite initially analyzed, were not further used.

Compared to the setup used in our previous works,¹⁸ a new geometry of the optical-electrochemical cell was used for the alignment of the high-resolution microscope. Two different magnification cameras from Dino-Lite with a 5.0 megapixel CMOS sensor (2592×1944 pixels) were used. For the low magnification ($60\times$) an AM7915MZTL camera combined with an adjustable 8-LED ring for bright-field lighting was used. This enabled a pixel density of 0.33 pixels per micron at a working distance of 37 mm. For high magnification measurements ($420\times$) an AM7515MT4A camera in coaxial lighting mode was used. This enabled a pixel density of 2.7 pixels per micron at a working distance of 8 mm. The cameras were controlled with DinoCapture 2.0 and programmed to record an image every 10 seconds simultaneously with the electrochemical measurements. Quantitative optical information was obtained through an automated image analysis procedure in ImageJ which can be found in the supplementary information (SI 1).

The optical-electrochemical setup was placed inside a Faraday cage to avoid external electrochemical and optical interferences.

Electrochemical analysis.—The electrochemical analysis as described in this work uses the CWT approach in the time-frequency domain. An analytic Morlet wavelet was applied to calculate the CWT spectrum. The CWT was calculated using 10 voices per octave, which implies that 10 logarithmically spaced frequencies were calculated for each factor of two frequency range. Following established protocols,²⁰ a symmetric extension of the EN signal at the beginning and at the end by reflection ('symmetric padding') was applied to mitigate bound-

Figure 2. Background removal procedure subtracting the initial intensity of each pixel in x and y of the first image from the intensity of all subsequent images.

ary effects in the CWT spectrum. The choice whether or not to apply padding, and if so, which method to apply has a significant effect on the artefacts that may arise at the edges of the spectrum.

The CWT spectrum shows the distribution of the energy in the EN signal over time and range. In order to facilitate the interpretation of features visible in the CWT spectrum, in the present work those scales are transferred into instantaneous frequencies. Although transients containing relatively high instantaneous frequencies (i.e. above 10^{-1} Hz) are present in the EN signals, the CWT spectra of the entire signals are dominated by relatively low instantaneous frequencies, in many cases around 10^{-2} Hz and lower. In this frequency domain, local maxima in the CWT spectrum are correlated with optical observations. Those represent large timescale processes that last from several hundreds up to one thousand seconds.

Optical analysis.—In order to obtain higher resolved quantitative information on the corrosion processes our recently introduced optical analysis protocol of corroding surfaces¹⁷ was improved as presented here. The cameras used in this work are equipped with controllable exposure time and automated magnification determination. This significantly simplifies the optical analysis and eliminates the need of calibration and compensation in contrast/brightness of the images. The analysis is further improved by performing a recursive repositioning procedure on the images to remove misalignments occurring during the measurement due to movements of the camera or electrochemical cell. This alignment procedure enables the possibility to remove the optical features visible at the beginning of the immersion for each individual pixel, which was not possible with our previous protocol.¹⁷ The algorithm is based on the work of P. Thévenaz et al., whereby each image is used as template with respect to the next one in time, so that the repositioning proceeds by propagation.²¹ The first image is used as anchor to reference all other images. The allowed transformations are based on the rigid-body approach, whereby the mapping of coordinates takes the form shown in Equation 1:

$$x, y = \{\{\cos \theta, -\sin \theta\}, \{\sin \theta, \cos \theta\}\} \cdot u + \Delta u \quad [1]$$

This procedure allows both translational and rotational transformations of the images. The background removal is done by subtracting the initial intensity (i_0) of each pixel in x and y of the first image, from the intensity of all subsequent images (i_n) as shown in Equation 2 and illustrated in Figure 2.

$$i_{\text{Difference}}(x, y) = |i_n(x, y) - i_0(x, y)| \quad [2]$$

With this procedure, a pixel that becomes either lighter or darker compared to its initial intensity is taken observed as a “changed pixel”, whereby the difference in intensity with the initial pixel ($t = 0$) is translated to an increase in intensity. All processed images are converted to 8-bit (256 bin grey-scale, bin 0 for black and bin 255 for

a) Global corrosion study

b) Local corrosion study

Figure 3. Sample containing two AA2024-T3 working electrodes (WE1 and WE2) embedded in an epoxy casting resin indicating the optical field of view for a) the global corrosion study with low magnification camera and b) the local corrosion study with high magnification camera.

white). This allows obtaining a half-normal intensity distribution in the greyscale histogram attributed to the pixels corresponding to the optically changed area. In order to calculate the changed surface area, the high intensity signals corresponding to the corrosion-related optically detectable features (e.g. pitting corrosion, intergranular corrosion and deposits on the surface) are isolated from the low intensity background (unchanged surface) using a static thresholding with a lower bin limit of 30. This step is necessary to remove random statistical fluctuations (shot noise) recorded by the photodetector when the charge carriers (photons) traverse a gap. The total changed surface area (S_{changed}) is calculated using Equation 3:

$$S_{\text{changed}} (\%) = \frac{N_p}{w_p \cdot h_p} \cdot 100\% \quad [3]$$

Where N_p is the number of changed pixels, w_p the width resolution and h_p the height resolution in pixels.

Sample preparation.—A single 3 mm thick commercial bare AA2024-T3 sheet provided by Kaizer Aluminium served as working electrode. $2 \times 2 \text{ mm}^2$ pillars were milled out from this sheet and connected to a copper wire using copper adhesive tape. One sample was prepared by embedding two pillars using epoxy casting resin as shown schematically in Figure 3.

The surface of the sample was freshly prepared 30 min prior to immersion by grinding up to grit 4000 with SiC paper and polishing to a final roughness of $1 \mu\text{m}$. This was followed by ultrasonic cleaning in ethanol and drying with compressed air. The global and the local measurements were performed using the same sample, but after re-polishing between the tests. The global corrosion study used a low magnification camera (see optical-electrochemical setup), recording all optical changes at both working electrodes simultaneously (Figure 3a). The local corrosion study used a high magnification camera, allowing only a part of WE1 to be optically monitored (Figure 3b).

A similar sample was prepared using two high purity (5N) aluminum rods with a diameter of 3.2 mm for the verification of the experimental data. The reference results, showing an optically and electrochemically stable system, can be found in the supplementary information (SI 2). All measurements were performed in Millipore Elix 3 UV filtered water containing 0.5M, 0.05M or 0.005M NaCl at an ambient temperature of $20 \pm 2^\circ\text{C}$ and were repeated at least two times for each salt concentration. Before the start of each measurement, the opto-electrochemical cell was filled with 50 ml electrolyte solution.

Results and Discussion

The results are divided in three sections in order to present the data obtained with the optical-electrochemical setup. In the first section the electrochemical noise (EN) data are analyzed in relation to the global (low magnification) optical data analysis. In the second section a more detailed local optical analysis is performed on a new measurement using the high magnification camera to identify the phenomena not captured in the low magnification optical analysis. In the third section we introduce a final plot summarizing the correlation between the EN signals to the different macroscopic corrosion phenomena identified with the optical analysis.

Global corrosion study (low optical magnification and EN).—

Figure 4 shows the combined EN and optical results from the global corrosion study on AA2024-T3 immersed in 0.05M NaCl. Figures 4a–4f shows the raw EPN signal and corresponding CWT spectrum at different immersion time windows: $t = 0\text{--}1800\text{s}$ (a, d), $t = 200\text{--}1800\text{s}$ (b, e), and $t = 1800\text{--}10000\text{s}$ (c, f). The immersion time (t) is indicated on the x-axis, the instantaneous frequencies (f) of the EPN signal on the y-axis, and the local amplitudes of the wavelets by the color bar for the CTW spectrum. The first 200s or 1800s are removed from Figures 4e and 4f, respectively, to magnify the visualization of the instantaneous frequencies appearing at lower amplitudes. It is also important to note that in Figure 4d the edge-effect is present at the beginning of the measurement (described in the method section and clearly observable in the reference measurement on high purity aluminum in SI 2). This edge-effect is not related to any occurring corrosion processes, but is a result of the boundary conditions which play a significant role at the beginning and the end of the measurement when the signals have a low amplitude. Enlargements of the raw EPN data and CWT spectrum can be found in SI 3.1 and 3.2. Figure 4g shows the real-time raw images, recorded during the EPN measurement, whereby differences in intensity of the pixels are caused by surface features (e.g. sample roughness, lightning condition and corrosion processes). Figure 4h shows the processed optical images after the analysis of removing the background as explained in the methods section. Figures 4i–4j shows the optically changed surface area as calculated from the analyzed images at short and long immersion times of $t = 0\text{--}1800\text{s}$ (i) and $t = 0\text{--}10000\text{s}$ (j) and can be used to investigate the kinetics of the optically detectable time-dependent processes.

Four different time-dependent stages of activity can be observed according to the raw EPN signal and CWT spectrum as marked with the numbers 1–4 in Figures 4a–4c and discussed here below:

Figure 4. Combined optical-electrochemical results for AA2024-T3 immersed in 0.05M NaCl. 4a-c show the raw EPN signal and 4d-f the corresponding CWT spectrum for the entire exposed surface at different immersion time periods of $t = 0-1800$ s, $t = 200-1800$ s, and $t = 1800-10000$ s, respectively. 4g-h show the real-time optical raw images (g), processed images (h) showing unchanged (black) and changed pixels (white) in time and the extracted quantitative information of the optically detectable surface changes for short (i) and long immersion times (j). Scalebar represents 0.5 mm.

1. From $t = 0$ s to $t = 200$ s the EPN signal (Figure 4a) increases with 300mV and the CWT spectrum (Figure 4d) shows no significant amplitudes of instantaneous frequencies above 10^{-2} Hz, indicated by the absence of colors other than the dark-blue low amplitude background. In addition, there is a large low-frequency contribution, below 10^{-2} Hz, indicated in red. The raw optical images (Figure 4g) show several features at $t = 10$ s due to surface scratches, compositional differences, and glare caused by the ring-light (e.g. bottom of WE1 and bottom left of WE2). Nevertheless, no new optical features were detected in the first 200s with this magnification and prior to image treatment. Figure 4h on the other hand, shows something different after implementing our image processing protocol, removing all initial features at $t = 0$. Now surface changes do occur during the first 200s immersion, despite the relatively low magnification. These surface-changes can be explained by the occurrence of individual corrosion events that take place at a dimension below the resolution of the microscope which become detectable after accumulation of these single events using the global image analysis. Figure 4i shows the calculated surface area variation with time. From $t = 0$ s to $t = 200$ s the surface rapidly changes with a rate of $0.0175\%s^{-1}$ and $0.02\%s^{-1}$ for WE1 and WE2, respectively leading to a total surface change of 3–4% at 200s immersion.

The optical results indicate that during the first 200s immersion a relatively high surface activity has taken place at specific locations leading to detectable surface changes (pixels becoming darker or lighter). This period corresponds with the significant increase of the EPN signal (Figure 4a) combined with the largest energy contribution in the CWT spectrum (Figure 4d). These optically observable features, electrochemically expressed as high energetic processes (CWT) with a strong increase of the EPN signal,²² can be related to local anodic and cathodic processes Intermetallic (IM) particles leading to, amongst others, de-alloying of copper-rich S-phase and θ -phases resulting in early-stage pitting and the formation of oxide caps at the IM sites.¹³ The low frequency signal in the CWT spectrum is thereby attributed to dealloying, which is a relatively slow surface diffusion controlled process at the IM particles.

2. From $t = 200$ s to $t = 400$ s the EPN signal (Figure 4b) reaches a steady-state stage and shows many high frequency fluctuations with a relatively small amplitude, resulting in a CWT spectrum (Figure 4e) dominated by short time-scale processes with an instantaneous frequency ranging from approximately 4×10^{-2} Hz to 1 Hz. Figure 4i shows that the surface changed increases but at lower kinetics between $t = 200$ s and $t = 250$ s. This is then followed by a drop of the surface changed of approximately 0.5% at $t = 400$ s. To understand this decrease in surface changes with respect to the first image it is important to clarify that the changed surface is calculated from the analyzed images after removing all the optical effects observed at $t = 0$ s. In other words, a pixel has optically changed when it becomes either lighter or darker in time with respect to its original state ($t = 0$ s). This can therefore be explained by pixels that became darker during the first 250s and turned lighter again between $t = 250$ s and $t = 400$ s (or vice versa), until the pixel matches its original state. We attribute this process to the transition from one corrosion process to another at the very same location (pixel). Interestingly, this optically detectable transition takes place when the EPN signal stabilized and the CWT spectrum shows a shift from low frequency to high frequency transients. By combining the EPN signal with the quantified surface changes it is argued that new corrosion processes take place after $t = 200$ s whereby the formed oxide caps on the IM phases start to dissolve, resulting in a decrease of changed surface area, combined with the initiation of new (meta)stable pits and trenching. This is in good agreement with SEM/EDS studies on AA2024-T3 after a similar immersion times.¹³
3. From $t = 400$ s to $t = 1800$ s the EPN signal (Figure 4b) shows fluctuations with a larger amplitude than in stage 2. Simultaneously, the CWT spectrum (Figure 4e) shows concurrent pro-

cesses on a larger timescale in the frequency range from approximately 4×10^{-3} Hz to 4×10^{-2} Hz, with the largest local maxima between 7×10^{-3} Hz and 3×10^{-2} Hz. Figure 4i shows that the surface changes increases again but at a much slower rate compared to stage 1 ($0.003\%s^{-1}$ for both working electrodes). This indicates that at around $t = 400$ s a different corrosion process dominates (instead of dealloying and pit initiation in stage 1–2). From the analyzed images (Figure 4h) it can be seen that the (white) spots seem to grow in size after $t = 400$ s at the same time as new smaller spots appear. These observations suggest that a slower corrosion process, such as oxygen diffusion-controlled corrosion processes, take place at the IM particles after pit-initiation (i.e. pit growth²³). As time progresses the number of large transients in the EPN signal and fast occurring fluctuations in the CWT spectrum reduces, indicating that fewer initiation events are taking place. This process is combined with a shift to lower frequency and amplitude. We attribute these to composition and size differences between individual IM particles which are attacked at different moments in time. The reduction in high frequency transients over time is attributed here to a decrease in the number of new pits.

4. After $t = 1800$ s the EPN signal (Figure 4c) further stabilizes while the CWT spectrum (Figure 4f) shows a further decrease of instantaneous frequencies, indicating a change from localized smaller time scale processes to larger time scale processes. This is further accompanied by several local maxima, as indicated in Figure 4f, with instantaneous frequencies between 10^{-3} Hz and 10^{-1} Hz ($t = 1800$ –3600s, $t = 3800$ –4200s, $t = 5300$ –6200s, and $t = 7900$ –9100s). Figure 4g shows that, even without image analysis, the raw images clearly show surface changes after $t = 3000$ s. The treated images (Figure 4h) show that such surface changes take place already in the period 1800–3000s and appear as white spots growing in size, clustering or appearing as new. This process proceeds over time until at $t = 5000$ s several large spots with a diameter beyond $50 \mu\text{m}$ become visible. Considering that IM phases on AA2024 are generally reported to be smaller than $50 \mu\text{m}$ in diameter and only cover approximately 3% to 4% of the surface^{24,25} and that these values are largely surpassed after 1800s according to the image analysis, we attribute the largest amount of changes after $t = 1800$ s to heavy subsurface corrosion (e.g. intergranular corrosion) leading to thick oxides deposition on the surface. When measuring the surface changes over the whole exposed area (Figure 4j) it appears that these changes grow gradually over time, at a relatively lower kinetics than in stage 3 and with WE1 (indicated in red) being slightly less active after $t = 3000$ s than WE2 (indicated in green). Nevertheless, when a small area is analyzed (squares in Figure 4h and blue and magenta lines in 4j) clear jumps start to appear for the changes surface. Oxide deposits appear on the WE1 selected area after roughly $t = 3000$ s, after which it stabilizes to grow further after $t = 6000$ s, whereas the oxides at the selected location of WE2 appear after $t = 4000$ s and keeps on growing. This local analysis on selected areas of the surface was performed on several other locations with high surface changes (SI 3.3). As a result we found that the changes starts to appear at specific moments in time (i.e. around $t = 2000$, $t = 3000$, $t = 4000$, $t = 6000$, and $t = 8700$ s). Although the appearance of these oxides coincide with the four local maxima in the CWT spectrum (indicated in Figure 4c), oxides do not start appearing and stop growing at the exact same periods. This mismatch in time indicates that the formation of surface oxides is the result of earlier occurring electrochemical corrosion processes underneath the surface and, in some cases, lags behind the corresponding electrochemical charge transfer.

In order to confirm the observations sketched above as well as the robustness of the protocol we repeated the tests and analysis at different salt concentrations. Figure 5 shows the combined EN and optical results for the global corrosion study on AA2024-T3 using 0.005M NaCl. A close analysis to this Figure 5 allows identifying exactly the same stages (numbered also 1–4) as discussed above for

Figure 5. Combined optical-electrochemical results for AA2024-T3 immersed in 0.005M NaCl. 4a-c show the raw EPN signal and 4d-f the corresponding CWT spectrum for the entire exposed surface at different immersion time periods of $t = 0$ -1800s, $t = 200$ -1800s, and $t = 1800$ -10000s, respectively. 4g-h show the real-time optical raw images (g), processed images (h) showing unchanged (black) and changed pixels (white) in time and the extracted quantitative information of the optically detectable surface changes for short (i) and long immersion times (j). Scalebar represents 0.5 mm.

Figure 4 but delayed in time, at different amplitudes and with lower surface kinetics, as expected for lower salt concentrations.

Although this low-magnification optical analysis gave a significant fundamental insight on the interpretation of EN and the corrosion processes, a high-magnification study was followed to bet-

ter identify local corrosion processes as will be discussed here onwards.

Local corrosion study (high optical magnification).—The high-magnification optical tests were also performed in parallel with EN.

Figure 6. High magnification optical results for AA2024-T3 immersed in 0.05M NaCl between $t = 60$ s and $t = 1800$ s. The original images are shown in (a) including red, green and blue markings (circles and stars) related to particle appearance over time at $t = 60$ s, $t = 1000$ s, and $t = 1800$ s, respectively. (b) shows the time-evolution of the detected particles using identical color code as in (a). (c) and (d) show the particle density and average particle size evolution with time respectively. Scale bar represents 50 microns.

As seen in the SI (section 4.1 and 4.2), the EN features and analysis is comparable to the one discussed above. Nevertheless, as a result of the higher magnification (and impossibility to make smaller samples) the optical analysis is only performed on a small area as shown in the experimental section. For this reason, not all the observed electrochemical signals can be correlated to the optical changes as shown in the previous section and the analysis will primarily be based on optics.

Figure 6 shows the optical results between $t = 60$ and $t = 1800$ s for AA2024-T3 immersed in 0.05M NaCl. While Figure 6a shows the raw images with defects (corrosion features) evolving in time (colored circles and stars), Figure 6b shows a time-overlapped analyzed image. This figure allows identifying the location and appearance of individual particles (IMs, corrosion spots), their time of growth and the distance to their nearest neighbors. These calculations were possible due to the higher pixel density of the high magnification camera and were performed using the automated particle analysis from ImageJ, combined with Delaunay triangulations on nearest neighbor distances.²⁶ This approach also enabled the calculation of the

particle density (Figure 6c) and average particle size (Figure 6d) in each image.

From the original images shown in Figure 6a it becomes clear that there are already surface features visible after $t = 60$ s of immersion. Due to different lighting conditions compared to the low-magnification study (Figure 4), the intensity of the reflected light in this case reduces with the surface roughness (i.e. darker when rougher). Several dark spots with a diameter smaller than $10 \mu\text{m}$ (marked with stars in red in Figure 6a) are visible right after immersion. These were not visible right after polishing (optical image before corrosion test can be found in SI 4.3). This indicates that these locations are revealed within the first 60 s immersion (no optical data could be obtained between 0 and 60 s). In addition to these black spots, there are also lighter particles with a diameter larger than $10 \mu\text{m}$ visible after $t = 60$ s (circled in red in Figure 6a). Contrary to the black spots, these were already observed prior to the immersion experiment (SI 4.3). Their appearance can be explained by local compositional differences, resulting in a different surface roughness after polishing.²⁷ After $t = 120$ s, the black spots continued to increase in size while the lighter particles started to etch away (became darker). The image particle-analysis allowed quantifying such changes in time (Figures 6c and 6d). This revealed that the number of particles increases toward 100 particles/ mm^2 , and $5 \mu\text{m}$ average particle diameter in the first 120 s exposure. This average size is similar to the mean IM particle diameter being reported to be between 2 and $5 \mu\text{m}$ based on compositional analysis on AA2024-T3.²⁸ We therefore suggest that the black spots here detected are related to pitting at IM particles during the first 120 s. It should be highlighted that this observation was not possible with EN, low-magnification analysis, and SEM/EDS studies after similar immersion-times.¹³ At 1000 s pits have grown further in size (marked in red in Figure 6a) and new pits appeared (circled in green in Figure 6a), reaching a total of 490 particles/ mm^2 (Figure 6c) with an average particle diameter of $8 \mu\text{m}$ (Figure 6d). From the graphical representation (Figure 6b) it can be seen that the particles have a circular shape and that they are distributed within an average nearest neighboring distance of $55 \mu\text{m}$. The total number of pits after $t = 1000$ s is close to the expected IM particle density, which was reported to be between 270 and 530 particles/ mm^2 .^{24,27,29} These findings suggest that most IM particles are being attacked within the first 1000 s. This corresponds to the highest activity (largest amplitudes) in the instantaneous frequency range between 4×10^{-2} Hz and 1 Hz in this time-period visible in the CWT spectrum (SI 4.1). After $t = 1000$ s, the number of pits remains remarkably stable until $t = 1800$ s, while the diameter of the particles increases further to stabilize at $11 \mu\text{m}$. From the graphical representation in Figure 6b it can be confirmed that the pits at $t = 1000$ s (in green) to $t = 1800$ s (in blue) have grown in size and only a small number of new particles has emerged. This consequently results in comparable average nearest neighbor distance of $52 \mu\text{m}$. The CWT spectrum in SI 4.1 also shows a decreased activity in the instantaneous frequency range between 4×10^{-2} Hz and 1 Hz, whereas the instantaneous frequencies below 10^{-2} Hz remain active in this region. This corresponds well with the optical analysis relating this to relatively stable, long timescale, pit growth.

Figure 7 shows the optical results on the local corrosion study between $t = 60$ and $t = 1000$ s for AA2024-T3 immersed in 0.05M NaCl.

Figure 7a shows that after 1800 s the number and size of particles increases again (indicated in green in Figure 7a) so that, at around $t = 3000$ s, there are 977 particles/ mm^2 with an average particle diameter of $12 \mu\text{m}$ (Figures 7c–7d). From the graphical representation (Figure 7b) it becomes obvious that the newly appeared particles remain relatively small, while the particles that are already present have significantly grown in size. This is in line with the deductions from the CWT spectrum in this period (SI 4.1), highlighting the same localized corrosion processes. After $t = 3000$ s the particle density grows until 900–1100 particles/ mm^2 , while the average particle diameter remains increasing, toward $25 \mu\text{m}$ at $t = 10000$ s. At this stage, both the density and average diameter of the particles are significantly larger compared to the reported IM particle size and density, indicating that trenching

Figure 7. High magnification optical results for AA2024-T3 immersed in 0.05M NaCl between $t = 60$ s and $t = 10000$ s. The original images are shown in (a) including red, green, and blue circles related to particle appearance over time at $t = 1800$ s, $t = 3000$ s, and $t = 10000$ s, respectively. (b) shows the time-evolution of the detected particles using identical color code as in (a). (c) and (d) show the particle density and average particle size evolution with time respectively. Scale bar represents 50 microns.

and sub-surface corrosion processes have resulted in the deposition of oxides on the surface. From the graphical representation (Figure 7b) it becomes clear that at $t = 10000$ s (indicated in blue) particles are clustered together while new locations have emerged in between the clusters. This results in a sudden drop of the nearest neighbor distance to $36 \mu\text{m}$. This indicates that, besides the formation of oxides around the pits, more complicated co-operative corrosion processes take place (e.g. coupling of neighboring IM particles by “cross-talk” between activation and passivation processes leading to corrosion rings³⁰). Although corrosion processes were clearly visible from CWT- as well as global optical analysis, the quantification of surface features from pitting up to the formation of corrosion rings over time have previously only been observed by optical and SEM analysis after the sample had been removed from the electrolyte.

Correlation between EN signals and macroscopic corrosion features from optical analysis.—Figure 8 shows a summary of the observed features for AA2024-T3 (both as EPN signal and CWT spectrum) coupled to macroscopic corrosion processes observed with and

Figure 8. Correlation of characteristics in the EPN signal and CWT spectrum with macroscopic local corrosion phenomena for the case of AA2024-T3 as a result of real-time optical analysis.

quantified by real-time optical inspection. This figure serves to illustrate the interpretation of corrosion information by integration of the electrochemical and optical technique. In the first stage de-alloying takes place, which can be observed electrochemically by a large drift in the EPN signal and by a significantly high low-frequency contribution below 10^{-2} Hz in the CWT spectrum. In the optical analysis this de-alloying manifests itself by a sudden increase of surface changes. This is followed by the formation of pits, observable in the EPN signal and CWT spectrum by high frequency fluctuations, combined with trenching and pith growth on a larger timescale in the frequency range around 10^{-2} Hz in the CWT spectrum. Optically, the transition from de-alloying to trenching and pit formation is observed by a shift to slower surface changes over time (stage 2). Subsequently, co-operative and sub-surface corrosion processes start to appear and are visible in the EPN signal by a relatively stable signal with a few large fluctuations, and in the CWT spectrum by local maxima at large timescales. In the optical analysis these phenomena become apparent by the total amount of surface changes exceeding the percentage of covered area by IM phases, combined with a stabilisation of the surface coverage at later stages. Experiments at different salt concentrations show comparable electrochemical and optical characteristics, however the respective phenomena occur earlier in time for higher salt concentrations, and additionally with a different intensity.

Conclusions

Real-time optical analysis of the corrosion process is presented in this work as a powerful approach to improve the readability of electrochemical fluctuations in EN and their correlation to macroscopic corrosion phenomena and time evolution. An in-house optical-electrochemical setup was developed to simultaneously capture both optical changes and electrochemical fluctuations that appear on the metal substrate under immersion. In this work, the corrosion processes and stages of AA2024-T3 have been investigated at different salt concentrations whereby detailed optical analysis served as a basis for the interpretation of the raw EPN signal and the EPN signal analyzed in the time-frequency domain using CWT. Low magnification optical measurements (60x) allowed capturing all the surface changes appearing on the exposed metal surface with a $3 \mu\text{m}$ resolution. Image analysis was developed for the removal of surface features that were not related to corrosion (e.g. scratches, compositional differences and glare) and enabled the detection of local surface changes

that could not be observed in the raw images. The highly resolved data, obtained from the different types of analyses, allowed the collective determination of time- and space- dependent corrosion processes such as de-alloying, trenching, pit growth, co-operative and subsurface corrosion. A second measurement was performed at higher magnification ($420\times$), capturing only a small section of the exposed metal, but at a much higher optical resolution ($<1\ \mu\text{m}$). This, together with the use of our optical analysis protocol, enabled a time-resolved quantification of corrosion-related surface features (e.g. size, amount and nearest neighbor distance of newly appearing pits) whereby the local changes in time corresponded well with the global CWT- and optical analysis. Finally, an integrated optical and EN illustration was created to simplify the interpretation of the raw EPN signal, as well as the CWT spectrum, while allowing the detection of different corrosion processes over time. The results illustrate the robustness of using real-time optical microscopy to visualize and quantify the corrosion processes while they take place, thereby improving the interpretation of electrochemical signals, such as EN, in a straightforward way.

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ORCID

Paul J. Denissen <https://orcid.org/0000-0003-1201-2765>
 Axel M. Homborg <https://orcid.org/0000-0001-8740-2317>
 Santiago J. Garcia <https://orcid.org/0000-0002-2211-9972>

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