A High-Throughput Artificial Pit Technique to Measure Kinetic Parameters for Pitting Stability

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The localized nature of pitting often makes it difficult to detect this form of corrosion damage, which can then accumulate, leading to catastrophic failure of high-value metallic assets such as aircraft components from fatigue crack initiation4,5 or perforation of containers for long-term nuclear waste storage.6,7 Structural integrity analyses can be greatly aided by predictive models that employ the knowledge of critical electrochemical parameters which describe pitting kinetics to calculate bounding sizes for maximum corrosion damage estimation.8,9,13 Such models often require values for a number of parameters, including the repassivation potential and the pit stability product.

The concept and measurement of the repassivation potential – the potential below which no further pit growth will occur – has been discussed in the context of a critical potential by several authors.14–18 Given the fact that an aggressive internal chemistry is required within the pit for continued growth,19,20–22 the repassivation potential can also be considered the lowest potential at which such chemistry can be maintained.23–24 Particularly in terms of a conservative lower bound for engineering practice, long-term testing23,31,35 using the repassivation potential has borne out the expectation that when samples are held at potentials below this value, neither do old pits continue to grow nor do new pits initiate.

Separately, the idea of describing a critical pit solution chemistry in terms of the dissolution flux required to maintain the minimum concentration of metal cations at the corroding surface has also been a focus of much research.14–18 For a theoretical one-dimensional pit, Galvele18 demonstrated that a critical product of the current density and pit depth – \( i \times x \) – must be maintained within the pit to prevent repassivation. This parameter, later termed the pit stability product,39 quantitatively represents the steady-state condition arising from the competition between the metal dissolution and diffusion fluxes30,34 which results in the maintenance of a sufficiently aggressive concentration of metal cations at the actively dissolving surface for continued pitting.

One of the challenges in localized corrosion has been developing methods to unambiguously determine these two parameters. Examination of the use of the repassivation potential as a conservative bounding design parameter has shown that it approaches a constant value after the passage of sufficiently large anodic charge densities, corresponding to the creation of deep pit depths.31,32 However, multiple pit nucleation will occur when bulk (large-area) samples are used, leading to difficulties in accurately determining the controlling \( i \times x \) in the maximum pit depth and in relating the measured total charge density to pit depth31 rendering it impossible to relate the measured repassivation potential to the pit stability product. In addition, dissolution products from a large area sample can be substantial enough to change the bulk solution chemistry, particularly for the large charge densities required, which could alter the experimental conditions intended for study. In order to obviate such difficulties, various methods to obtain single pits to permit more controlled studies of pitting kinetics have been reported, such as localizing a small working electrode area to separate from the rest of the surface which is covered with a protective lacquer or silicone adhesive30,42 as well as the ‘lead-in-pencil’ artificial pit electrode,7,38,43 i.e., a metal wire encased in an inert substrate. The latter approach resulted in an experimental configuration that could be used to simulate one-dimensional diffusion, permitting direct comparison of results to the theoretical formulation presented by Galvele.18

There are clear advantages to using the one-dimensional lead-in-pencil electrode as the experimental tool to study pitting kinetics. The measured kinetic parameters can be directly related to a single activated area, enabling a straightforward measurement of the pit depth. Once sufficiently deep pits are grown, this pit depth can then serve as the diffusion length for mass transport analyses and studies.32,37,40,43

Both the critical pit stability product \( \langle i \times x \rangle \) and the repassivation potential \( E_{rp} \) are kinetic parameters that describe the minimum aggressive chemistry that must be maintained locally inside the pit for stable pitting. The experimental technique described in this paper measures the pit stability product under a salt film, \( \langle i \times x \rangle_{saltfilm} \), as well as the \( E_{rp} \) from the same experiment using a lead-in-pencil artificial pit method in an experimental procedure adapted from studies31,42,44 that have measured these parameters separately. The amount of corrosion product formed in these experiments is negligible due to the small dimensions of the wire and therefore the same sample and bulk solution can be used for successive measurements at deeper pit depths. These adaptations increase both the efficiency and the volume of data collection as well as allowing for mapping of both \( E_{rp} \) and \( \langle i \times x \rangle_{saltfilm} \) in terms of a single experimentally controllable variable – the pit depth – thus contributing data towards a quantitative framework45 to connect the various parameters describing critical conditions for pitting stability.

**Experimental**

Sample preparation.— 316 L (California Fine Wire Company, Grover Beach, CA) and 17-4 PH (Fort Wayne Metals, Fort Wayne, IN) stainless steel wires, of diameters 50.8 μm and 88.9 μm respectively, were cast in epoxy. The composition of the wires is given in Table I. Once the epoxy had cured, the surface with the exposed wire was polished with 320 grit silicon carbide paper. This artificial pit

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The cyclic electrochemical technique discussed in this paper is schematically outlined in Figure 3. A Bio-Logic SP-150 potentiostat with the associated EC-Lab (Bio-Logic SAS, Claira, France) software was used for all the experiments. High-frequency (100 kHz) impedance measurements were used to determine the solution resistance of the cell for ohmic compensation. The impedance measurement was performed at the beginning of the experiment and once after 4 or 5 cycles of pit growth. Pitting was initiated in most cases by applying an anodic potential of +750 mV SCE for a short duration. For some samples, the application of brief (∼15 s) pulses of potential between +1.3 and +1.5 V SCE was required to initiate pitting. The sample was often most difficult to pit for the first cycle of the experiment. Once pit initiation had commenced as observed by the current density beginning to settle following a peak (as shown in Figure 3a), the applied potential was decreased to +450 mV SCE and held for a certain duration of time to grow the pit to a given depth. Once this depth was attained, a cathodic polarization scan was performed at a constant, user-specified scan rate (5 mV/s) as shown in Figure 3b from +450 mV SCE to −600 mV SCE. After this sequence, the pit was re-initiated and the cycle in Figure 3a was repeated. The pH of the bulk solution was measured after the experiments and was seen to be virtually the same as before the experiment was carried out, therefore indicating that using the same solution for all of the cycles of the experiment was appropriate. The low volume of dissolution products associated with the artificial pit electrode also meant that the same bulk solution could be used for successive cycles with little concern for change in bulk solution chemistry. The scan rate, the potentials used during the potentiostatic hold, and the potentiostatic hold times were all user-specified. All experiments were carried out at an average ambient temperature of 22 °C. The results shown and discussed in this paper are for data obtained in 0.6 M NaCl.

**Electrochemical cell set-up.**—The artificial pit electrode was rinsed with ethanol and DI water to remove any detritus from surface preparation, and then placed in the test cell apparatus with the exposed metal facing up in NaCl solution (Figure 2). The reference electrode used was a saturated calomel electrode and a platinum mesh served as the counter electrode.

**Electrochemical technique.**—The cyclic electrochemical technique discussed in this paper is schematically represented in Figure 1. The prepared surface was visually checked using an optical microscope to ensure that the exposed circular metal surface area of 2.03 × 10⁻⁵ cm² (316 L) or 6.21 × 10⁻⁵ cm² (17-4 PH) was flush with the epoxy.

**Table I. Composition of the stainless steel wires used (all values in weight percent).**

| Alloy   | C   | Mn  | P   | S   | Si  | Cr  | Ni  | Mo  | N   | Cu  | Fe  |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 316 L  | 0.019 | 1.356 | 0.030 | 0.0287 | 0.406 | 17.07 | 10.66 | 2.16 | 0.0499 | 0.232 | 67.98 |
| 17-4PH | 0.03 | 0.78 | 0.022 | 0.0020 | 0.49  | 15.26 | 4.58  | 0.42 | -   | 3.25 | 75.16 |

![Figure 1. Artificial pit electrode configuration.](image)

![Figure 2. Schematic of test cell.](image)

Data analysis – extraction of kinetic parameters.—As indicated in Figure 3, the method allowed for measurement of the repassivation potential $E_{rp}$ as well as the limiting current density ($i_l$), the latter of which can be used to obtain the pit stability product under a salt film ($i_l \cdot x_{saltfilm}$). Both kinetic parameters of interest were therefore obtained from the same experiment. A computer script was created using Matlab (The MathWorks, Inc., Natick, MA) to import time, potential, and current data for data visualization and analysis. Using Faraday’s law, the pit depth was calculated by numerically integrating the area under the current density versus time curve assuming stoichiometric dissolution of Fe, Ni, and Cr.

The value of the repassivation potential $E_{rp}$ was determined by the computer script as the potential during the linear polarization scan at which the values of Z% of the next $N$ current density data points in the scan were lower than 30 μA/cm². In the present study, $Z$ and $N$ were set to 70% and 30 points, respectively. The difference between the measured $E_{OCP}$ and $E_{rp}$ under these specified conditions and algorithm parameters was typically less than 2 mV and not greater than 20 mV. Further, the transition potential $E_T$ – the potential at which the corroding surface is no longer under a salt film (as defined by Laycock and Newman) was also obtained by the script from these data (Figure 3b).

The limiting current density was measured during the potentiostatic hold at +450 mV SCE. Because the change in the value of the current observed immediately upon stepping down the potential from +750 mV SCE was observed to be minimal, the reaction was considered to be under diffusion-limiting conditions (any further changes in current observed were due to pit growth during the potentiostatic hold). Current density data from only the latter 63% of the experiment was appropriate. The low volume of dissolution products associated with the artificial pit electrode also meant that the same bulk solution could be used for successive cycles with little concern for change in bulk solution chemistry. The scan rate, the potentials used during the potentiostatic hold, and the potentiostatic hold times were all user-specified. All experiments were carried out at an average ambient temperature of 22 °C. The results shown and discussed in this paper are for data obtained in 0.6 M NaCl.
Figure 3. Schematic summary of cyclic artificial pit experimental method. (a) Two cycles (corresponding to successive pit depths) of the technique are shown for 316 L, each consisting of i) a potentiostatic hold at +750 mV\text{SCE} to initiate pitting, ii) a potentiostatic hold at +450 mV\text{SCE} to grow the pit, and iii) a linear polarization scan to measure the kinetic parameters. Note that the dashed lines indicate current density and the solid lines indicate potential. (b) Potential versus current density plot generated from a linear polarization scan as shown in 3 (a), indicating \(E_{\text{rp}}\) (recorded by the dashed lines corresponding to \(i = 30 \, \mu A/cm^2\)), \(E_T\), and \(i_L\). Note that the scale used for the current density axis is logarithmic.

inversely proportional to pit depth, as shown in Equation 1.

\[
i_L = \frac{zFD\Delta C}{d} \quad [1]
\]

The terms in Equation 1 are defined and their values taken from the literature\textsuperscript{13,43,46–48} are listed as follows:

- \(i_L\): diffusion-limited dissolution current density
- \(z\): number of electrons transferred = 2.2
- \(F\): Faraday’s constant = 9645 C/mol-equivalent
- \(D\): diffusion constant of species of interest = \(8.24 \times 10^{-6}\) cm\(^2\)/s
- \(\Delta C\): concentration gradient of species of interest along pit depth with \(C = C_{\text{sat}} = 4.2\) M at pit bottom

The value of \(E_{\text{rp}}\) determined using the cyclic technique described was compared to the value of \(E_{\text{rp}}\) determined using 1 × 1 cm samples of 316 L\textsuperscript{12}. These 1 × 1 cm specimens were tested using the same experimental method as the artificial pit samples. The only difference was in the execution of the experimental method – whereas a single artificial pit sample was used on which successive charge density measurements were made, the 1 × 1 cm specimens necessitated using a separate sample for each charge density measurement owing to the initiation of multiple pits. After the experiment, the maximum visible pit depth on each sample was measured using a Hirox KH-7700 3-D digital optical microscope (Hirox-USA, Inc., Hackensack, NJ). The charge density \(q\) passed in that pit of depth \(d\) was estimated as shown in Eq. 2.a

\[
q = \frac{d \cdot \rho z F \cdot \text{MW}}{MW} \quad [2]
\]

The system being under diffusion control due to the presence of a salt film, linear regression performed upon these data provided the pit stability product under a salt film – (\(i \cdot x\))\text{saltfilm} – from the slope of the linear fit. This statistical fitting also served to examine whether the data obtained were indeed under one-dimensional diffusion-limited conditions.

Results

Linear polarization scans.— A potential versus current density plot was obtained from the linear polarization scan for each pit depth using the computer script. One such plot is shown in Figure 3b, indicating \(E_{\text{rp}}\) and \(i_L\) as calculated by the script using the algorithm described in the Experimental section. The value of the limiting current density \(i_L\) was observed to decrease with each subsequent cycle as shown in Figure 4, as expected with increasing pit depths in accordance with Eq. 1.

\[E_{\text{rp}}\] determination using Artificial Pit versus Bulk Sample.— The value of \(E_{\text{rp}}\) determined using the cyclic technique described was compared to the value of \(E_{\text{rp}}\) determined using 1 × 1 cm samples of 316 L\textsuperscript{12}. These 1 × 1 cm specimens were tested using the same experimental method as the artificial pit samples. The only difference was in the execution of the experimental method – whereas a single artificial pit sample was used on which successive charge density measurements were made, the 1 × 1 cm specimens necessitated using a separate sample for each charge density measurement owing to the initiation of multiple pits. After the experiment, the maximum visible pit depth on each sample was measured using a Hirox KH-7700 3-D digital optical microscope (Hirox-USA, Inc., Hackensack, NJ). The charge density \(q\) passed in that pit of depth \(d\) was estimated as shown in Eq. 2.a
Values of $\rho$, the density of the alloy ($= 7.92$ g/cm$^3$), and MW, the average molecular weight of the alloy ($= 55.85$ g/mol), were obtained from the literature.$^{13,17,23,24,26,28}$

From Equation 2, it can be seen that only the pit depth needs to be measured to obtain the charge density passed for a single pit. This method permitted the calculation of even irregularly shaped pits, based upon measuring only their depth. The deepest pit would be the one with the largest diffusion barrier, and thus was able to retain the aggressive solution at the lowest current density.$^{18}$ The measured $E_{rp}$ was associated therefore with the deepest pit and plotted against the charge density from the deepest pit as calculated using Eq. 1. A comparison of the $E_{rp}$ versus charge density results for the 1 cm$^2$ sample with charge density based on the nominal area (1 cm$^2$), the 1 cm$^2$ sample with the corrected charge density calculated as indicated in Eq. 2, and an artificial pit sample using the cyclic technique is shown in Figure 5.

High throughput results in assessing statistical reliability of data.— The value of $E_{rp}$ becomes relatively independent of pit depth for deep pits, as shown in Figure 5. The observation of a constant $E_{rp}$ for deep pits was consistent with the results reported in several studies in the literature.$^{7,13,27-29,31,35,45,49}$ Using the methodology described in this study, a statistically useful number of measurements of $E_{rp}$ could be performed on a single sample because multiple cycles were performed at pit depths where the $E_{rp}$ approaches a plateau, thereby obtaining a large dataset from which a mean $E_{rp}$ with standard deviation was estimated. For example, the mean $E_{rp}$ for the artificial pit data shown in Figure 5 was estimated by averaging the repassivation potential values corresponding to charge densities greater than 1,400 C/cm$^2$.

Comparison of results from cyclic and conventional artificial pit techniques.— The mean $E_{rp}$ values obtained with 316L artificial pit electrodes using both the cyclic technique as well as non-cyclic independent tests are shown for trials of the artificial pit technique in Figure 6. The results obtained using the cyclic technique were seen to be in good agreement with those of the individual (non-cyclic) tests.

Extraction of pit stability product values.— The proposed technique obtains the pit stability product under a salt film from the same experiment used to determine $E_{rp}$. The limiting current density under a salt film would be a linear function of the reciprocal of the pit depth if the pit is under one-dimensional diffusion control, with the slope of the line yielding the value of $(i \cdot x)_{\text{saltfilm}}$. Figure 7 shows these data plotted for 316L and 17-4 PH. For the 316L data, it was found that the value of $(i \cdot x)_{\text{saltfilm}}$ obtained was 0.830 A/m$^2$, with the extent of scatter in the data higher for shallow pits than for deep pits. In the case of 17-4 PH, the value of the estimated pit stability product under a salt film estimated was 0.7625 A/m$^2$, which was lower than that estimated for 316L.

Discussion

This cyclic artificial pit method exhibits the same regimes of rate control of pitting corrosion as observed by Laycock and Newman.$^{44}$ The applicability of this method to large area samples and the advantages of this method in obtaining statistically meaningful parameter values and improvements in experimental efficiency are discussed. Finally, the limitations of the experimental method and the rationale for user-specified parameters are commented on to aid with future use of this method.

Kinetic regimes.— As shown in Figure 3, the artificial pit samples experienced different types of reaction rate control in different regions of potential. During pit initiation at $+750$ mV$_{SCE}$, the precipitation of a salt film is marked by a peak and subsequent decrease in current density. Changing the potential from $+750$ mV$_{SCE}$ to $+450$ mV$_{SCE}$ for pit propagation did not alter the current density, indicating diffusion-limited dissolution of the metal under a salt film. During the linear polarization scan, once the potential became low enough for the salt film to start dissolving, the current response assumed a linear dependence on the potential, indicating ohmic control. These observations were consistent with the results from reported studies.$^{42-44,50}$ As the potential approached the measured value of $E_{rp}$, the anodic reaction was seen to be under activation control before repassivation occurred.

Artificial pit $E_{rp}$ measurements compare well with bulk sample testing.— As shown in Figure 5, the values obtained for repassivation potential measured by the cyclic technique were in good agreement with the results obtained from large area samples provided the charge density is corrected for the active area in the latter. The main advantage of using the artificial pit method for this purpose was that the small corroding area allowed large charge densities to be passed (i.e., deep pits to be obtained) to measure the lower bounding value of $E_{rp}$ without substantially changing the bulk solution chemistry. As an example in comparison, in a bulk 0.6 M NaCl solution volume of 1 L, if a charge density of 1,000 C/cm$^2$ were passed across a 316L working sample of nominal area 1 cm$^2$, even a total active area of just 10% would result in...
a sizeable change in bulk solution chemistry. A general application of Faraday’s law for such a test case results in a ferrous ion concentration of approximately $5 \times 10^{-3}$ M and a chromium ion concentration of approximately $1 \times 10^{-3}$ M, the hydrolysis of which would lower the pH of the bulk solution to 4.1 from 5.6.

Technique improves experimental efficiency.— The experimental method shortened both the time required for sample preparation as well as time required for pit growth. In studies reported in the literature, a different sample was used in each experiment to grow a pit to different depths. Using the technique employed in this study, less additional time was required to attain a deep pit because growth is cumulative over cycles. For example, in one experiment in which a pit was grown to a total depth of $1070 \mu\text{m}$ and the $E_{np}$ measured across the span of 10 intermediate pit depths, the total time for pit growth and parameter measurement using the cyclic technique was approximately 25% of the time required for the same procedure using separate experiments. Sample preparation time was also reduced because this technique used the same sample for measurements at successively deeper pits. Furthermore, automation in data analysis was achieved by writing a computer script that performed parameter determination, enabling rapid and direct assessment of kinetics at multiple pit depths. Implementation of the technique can thus lead to efficient exploration of parameter space using different experimental variables.

Technique accesses wide range of pit depths for statistical analysis of kinetic parameters.— Statistical analysis of the large volume of data that the technique permitted in obtaining was observed to provide some key information. The pit stability product under a salt film from plots of diffusion-limited dissolution current density versus the reciprocal of the pit depth for (a) 316 L, (b) 17-4 PH.

Figure 7. Determination of the pit stability product under a salt film from plots of diffusion-limited dissolution current density versus the reciprocal of the pit depth for (a) 316 L, (b) 17-4 PH.

Figure 8 compares the experimental flux obtained from the technique to the theoretical flux as a function of the pit depth expected based on cation transport for 316 L and 17-4 PH. Values for physicochemical parameters of the metal cation were assumed to be those of Fe$^{2+}$ (for instance, the cation diffusion coefficient was approximated by $D_{\text{ferrous}} = 8.24 \times 10^{-6} \text{ cm}^2/\text{s}$) as considered by literature studies that had also investigated the problem of mass transport in corroding one-dimensional stainless steel pits. The value of 0.830 A/m obtained as the estimate of the pit stability product under a salt film for 316 L was consistent with the results reported by Woldemedhin et al. for austenitic stainless steels in chloride solutions. For 17-4 PH, the $(i - x)_{\text{saltfilm}}$ value of 0.7625 A/m was lower than that of 316 L. Figure 8b shows that the plot of flux versus reciprocal of the pit depth for 17-4 PH follows the theoretical calculation based on Fe$^{2+}$ diffusion closely. A lower $(i - x)_{\text{saltfilm}}$ value corresponds to a lower diffusion flux, a result that can be rationalized based on the fact that 17-4 PH has a lower Ni content than 316 L. Furthermore, based on the in-situ X-ray work of Isaacs et al., Ni is also depleted in the saturated solution, resulting in a further decrease in the concentration gradient. As a result, the cation transport behavior in the 17-4 PH system would be expected to be closer to the case approximated by ferrous ion diffusion. Conversely for 316 L, a higher Ni content in the alloy implies that the concentration gradient is not as depleted as the 17-4 PH case, resulting in a higher diffusion flux. These analyses illustrate the utility of the proposed technique in obtaining statistical data from pits of various depths, from which kinetic information can be extracted.

Limitations of proposed technique.— The technique outlined in this study has some limitations that merit discussion. It was sometimes difficult to initiate pitting for 316 L samples, given their relatively high pitting resistance and small diameter which results in a lower density of surface inhomogeneities that are precursors to pit nucleation. This difficulty in initiating pitting, particularly on sequence cycling, may present an experimental challenge, especially when the technique is applied towards studying the effects of pitting inhibitors or highly corrosion-resistant materials. Ohmic compensation of the linear polarization scan would permit Tafel analysis in the potential range in which dissolution is no longer limited by diffusion under a salt film (i.e., where the salt film is not present). It was found that doing so in this region led to overcompensation at the potentials corresponding to high current densities. However, in the cases of determining the two kinetic parameters of interest, ohmic compensation is unlikely to play a major role because in the potential range where $E_{np}$ is measured, current densities are very
low, whereas in the potential range where $(i \cdot x)_{\text{saltfilm}}$ is measured, the anodic kinetics are under diffusion control.

Comments on user-specified parameters.— The scan rate for this study was chosen to be 3 mV/s because it represented a balance between slower scan rates used to simulate long-term, steady-state conditions approaching repassivation and faster scan rates which are employed to avoid dilution of the salt film and aggressive chemistry within the pit environment, so that estimates of the limiting current density can be made. Once the corroding surface is no longer under a salt film, a quasi-steady state ceases to exist and steady state measurements can no longer be performed.

The durations of the potentiostatic hold for each cycle were chosen such that a sufficient number of cycles could be performed in order to obtain adequate data for shallow pits as well as for deep pits. The durations of the holds corresponding to the shallower pits were shorter than for the deeper pits because the rate of change of pit depth decreases with increasing pit depth due to the lower current density for deeper pits.

The potential for re-initiation of pitting was chosen to be +750 mV$_{SCe}$ because this value was found to consistently high enough to initiate pitting. The potential chosen for pit propagation, +450 mV$_{SCe}$, permitted pit growth under a salt film while still allowing for a subsequent rapid polarization scan without substantial additional pit growth. These potential values are similar to those chosen for pit initiation and propagation in other anodic kinetics studies in the literature.

The algorithm to find the $E_{\text{rp}}$ utilized user-specified criteria. This approach was used instead of denoting $E_{\text{rp}}$ as the potential at which the current density first lower than 30 $\mu$A/cm$^2$ so that the effects of noise in the response signal were avoided. Given the low currents in the potential range where the $E_{\text{rp}}$ was measured, distortions due to noise and instrument tolerances were sometimes encountered, which could result in a single or few current density data points below 30 $\mu$A/cm$^2$ in a region of data displaying otherwise higher current densities. In such cases, the potential versus current density curve generated from the linear polarization scan, such as the one shown in Figure 3b, serves as a good reference against which the $E_{\text{rp}}$ value determined by the algorithm can be checked to ensure that the $E_{\text{rp}}$ determined was the appropriate one. Data smoothing with a moving average filter may also help in this regard.

Conclusions

A cyclic artificial pit technique was developed which permits the extraction of critical anodic kinetic parameters important in understanding pitting, the pit stability product under a salt film $(i \cdot x)_{\text{saltfilm}}$ and the repassivation potential $E_{\text{rp}}$ from a single experiment. The technique involves pit growth to progressively larger depths following each cycle of initiation-growth-repassivation as well as measurement of the limiting current density and the repassivation potential, both as functions of pit depth. In performing these measurements across a range of pit depths on the same sample, considerable time is saved in sample preparation as well as in the execution of the experiment itself, particularly with respect to deep pit growth and multiple parameter measurements at these depths. The technique and consequent automated data analysis results in a high throughput, which provides $E_{\text{rp}}$ and $(i \cdot x)_{\text{saltfilm}}$ measurements from a large dataset and permits statistical analysis of different experimental and environmental factors on these kinetic parameters. The technique also proved to be a more reliable method to determine both kinetic parameters, by avoiding sample area-based inaccuracies in $E_{\text{rp}}$ measurement and by obtaining pit stability product data from a wide range of pit depths.

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