



Communication—A New Approach for SVET Analysis Combined with In Situ Scratching

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A novel experimental approach is proposed for creating surface microdefects in situ during SVET analysis. Hot-dip galvanized steel samples fixed in the SVET cell and exposed to 0.05 M NaCl were scratched using a Berkovich indenter. The progress of corrosion activity at defect locations was continuously inferred by SVET scan lines starting 10 s after scribing. The time-dependent inhibitive effect of molybdate was appraised upon repetitive surface damage. The results highlight the interest of combining localized electrochemical techniques with in situ scratching for an improved understanding of time-sensitive corrosion/inhibition processes related to active microscopic defects.

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Manuscript submitted August 3, 2020; revised manuscript received September 28, 2020. Published October 12, 2020.

Supplementary material for this article is available [online](#)

The generation of defects through protective coatings is inevitable during the service life of protective systems. Yet, there is limited knowledge about the early stages of corrosion initiation after coating failure.^{1–3}

Local electrochemical techniques such as Scanning Electrochemical Microscopy (SECM), Scanning Vibrating Electrode Technique (SVET), Local Electrochemical Impedance Spectroscopy (LEIS) and Scanning Kelvin Probe (SKP) technique have gained significant ground for real-time monitoring of microscopic scale processes related to corroding defects.^{4–6} By measuring the current density above active defects, SVET has been particularly used for examining the influence of inhibitors and the self-healing/sacrificial properties of different coatings.^{4,5,7–13}

Further complexity lies in the timing for analyzing defects, as local corrosion processes are extremely time-dependent.² According to Montemor,¹⁴ the healing efficiency and the time-response of in-coating inhibitors are difficult to predict, and only a few studies addressed these specific issues.^{15,16} Yet, SVET has been able to evaluate the kinetics of self-healing response,¹⁰ the cathodic activation of corroding magnesium,¹⁷ among other time-related aspects.^{9,18,19}

For most of the failure scenarios involving artificial defects, it is difficult to assess their early corrosion responses because there are "empty" time slots between their creation (typically done ex situ) and the start of the local electrochemical measurement. SVET studies have indicated high corrosion activities at scratches right from the first possibly executed scans.^{8,10,11}

Two examples of the combined use of local techniques with in situ scratch methods could be cited: Schmutz and Frankel²⁰ demonstrated the local dissolution of AA2024 intermetallics using AFM in NaCl solution and a silicon tip for scratching. Likewise, the earliest stages of local current from pitting of 304 s were detected by AFM after scribing with a STM tip.²¹ These investigations provided insight into kinetic aspects of electrochemical processes of defects, demonstrating alternative approaches for accelerated corrosion monitoring. Nonetheless, the local analysis combined with in situ scribing methods remains a topic seldom addressed.

Concerning SVET analysis, the main drawbacks of the existing defect-related investigations are: their low reproducibility (generally manual scribing);^{1,5,8–12,22–25} the ex situ creation of defects (outside of the testing environment);^{10,12,24–26} and no assessment of the dynamic behavior of systems upon repetitive damage. Not surprisingly, the geometry/area/number of defects to be healed and the inhibition upon the occurrence of multiple damaging events remain open issues.¹⁴ Therefore, unique combinations of experimental

methods must be increasingly utilized together to push further advancement of anti-corrosion systems.

On the trail of a Lamaka et al.'s work,²⁷ whose pursuit of combining in situ techniques resulted in the monitoring of current density and pH at the same time frame, this work proposes a new SVET approach for assessing the corrosion activity of defects with reduced time lags between scratching and scanning (~10 s). The method was validated on hot-dip galvanized steel (HDG) in 0.05 M NaCl solution (corrosion inhibitor was eventually present). A metallic coating system was chosen as an attempt to isolate the primary corrosion effect induced by scratching, thus avoiding other corrosion-related degradation effects observed in organic/ceramic coatings. The approach proposed in this proof-of-concept work could be reproduced in diverse scenarios, making use of different coating systems/chemical environments/scribing schemes/time lapses.

Experimental

A commercial Berkovich indenter (diamond tip mounted in a stainless steel body, Synton-MDP, Switzerland) was assembled to a metallic screw beam (7 mm diameter, 12 cm length) with epoxy resin (Fig. 1). The screw-indenter assembly was fixed in a manual micromanipulator attached to a tilting base (Kite, M-3 (World Precision Instruments, United States)) (Fig. 1a). The micromanipulator allows a displacement control of 0.1 mm in the Y/Z axes and 10 μm in the X-axis (Fig. 1b). The whole assembly was tilted at ~45° (concerning the horizontal plane) for in situ scratching in the SVET cell (Fig. S1a is available online at stacks.iop.org/JES/167/131511/mmedia).

The reproducibility of the scratching method was validated on a reference 316L SS surface (Fig. S2). Following to this calibration procedure, the approach was progressed on a system more prone to corrosion upon damaging: hot-dip galvanized steel (further details of the HDG sample preparation are found in Fig. S1b). Moreover, the industrial surface treatment (skin-passing) of the specimens (Zn layer thickness of 20 μm) provided a ground for testing of engineered surfaces encountered in practice.

Virtually identical in situ scratches were produced either in air or in solution on individual HDG surfaces (indenter displacement = 36 μm). While in the former, the measurements started ~20 min after defect introduction, scratching in solution allowed tests to start only ~10 s after scribing (Fig. S3). In both cases, the local activity distributions were captured by performing line scans across the defects (the scanned scratch locations are indicated in Figs. S4a, S4b). Each 1 min line scan was ~1250 μm length and comprised 51 points. Scans were continuously repeated (~2 s time lag) at same locations up to 60 min after introduction of defects, resulting in 40 or

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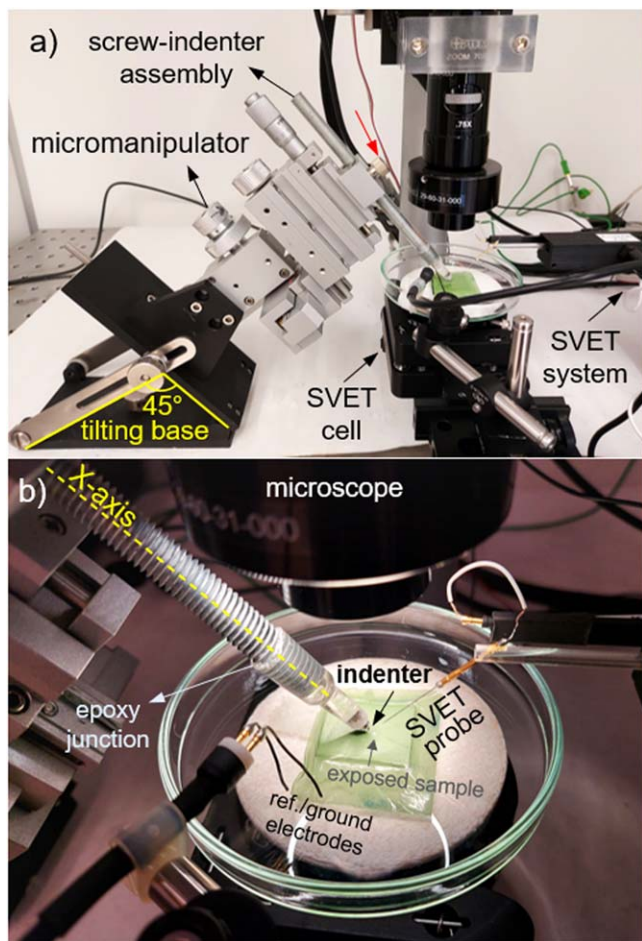


Figure 1. (a) screw-indenter assembly fixed in the micromanipulator (security screw indicated by a red arrow) attached to tilting base; (b) indenter apparatus placed for in situ scratching (along the X-axis) on samples fixed in the SVET cell.

60 line profiles of j_z for scratches produced in air or solution, respectively. The scan height was $150\ \mu\text{m}$ (full description of SVET parameters employed can be found elsewhere²⁵).

In a second experimental approach, the screw-indenter assembly performed repetitive in situ scribing on the same surface location. This setup was applied either in $0.05\ \text{M NaCl}$ or $0.05\ \text{M NaCl} + 5\ \text{mM Na}_2\text{MoO}_4$ media, using an indenter displacement of $36\ \mu\text{m}$. During 25 min, 30 s line scans (11 points, $\sim 600\ \mu\text{m}$ length) were continuously taken ($\sim 2\ \text{s}$ time-lag) across the defects. The scanned scratch locations are indicated in Figs. S4c, S4d)

Results and Discussion

Figure 2 compares two time-resolved line profiles of current density (j_z) obtained in $0.05\ \text{M NaCl}$ after scratching HDG surfaces in air (a) or solution (b). On the contrary to the defect produced before immersion, scratching in solution allowed the detection of electrochemical activity in the time frame comprised between $\sim 10\ \text{s}$ and $20\ \text{min}$ after the defect creation. The extra 20-line scans related to the early-stage activity of the scratch are highlighted in green. In-situ scratching in solution unraveled an early cathodic process (blue dots) that occurred in the vicinity of the defect region, on the top-surface of the Zn-layers. Furthermore, slightly different behaviors between both defects were observed during the time frame comprised between $20\text{--}60\ \text{min}$. Indeed, the maximum anodic j_z was higher for the scratch obtained in air ($\sim 200\ \mu\text{A cm}^{-2}$) than in solution ($\sim 150\ \mu\text{A cm}^{-2}$). The discrepancy in intensity between anodic/cathodic processes was because most of the intact Zn surface

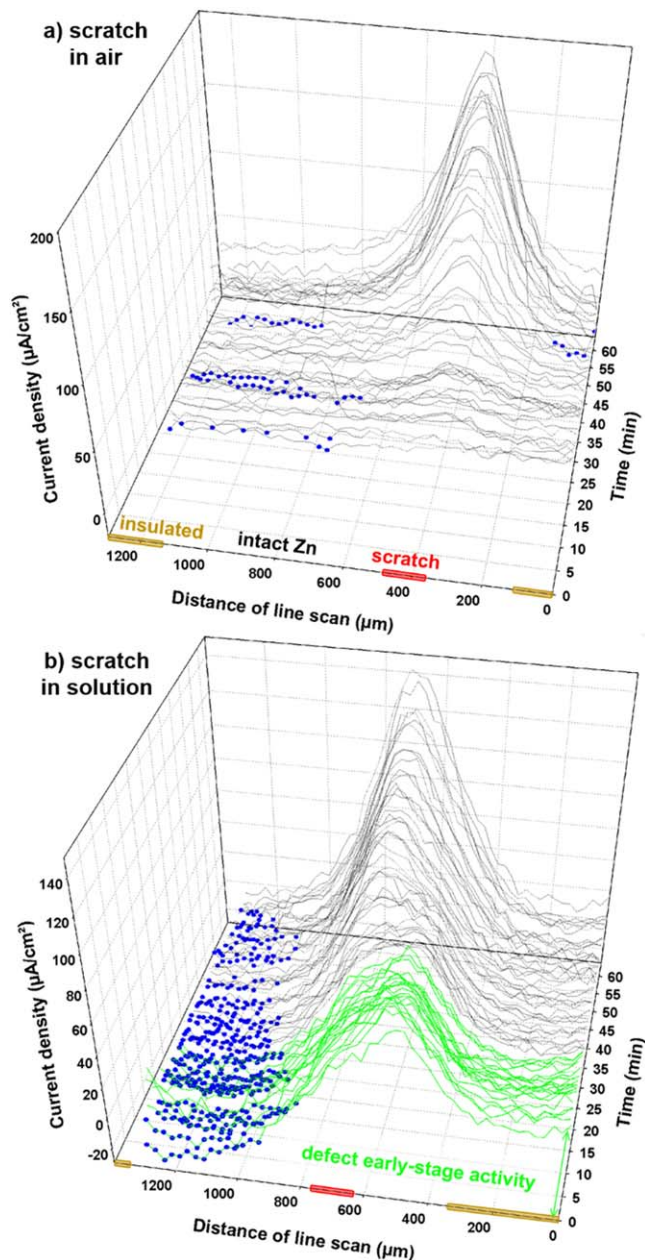


Figure 2. j_z line scans plotted against the time after the in situ introduction of defects on HDG. Current densities were collected up to 60 min of immersion in $0.05\ \text{M NaCl}$ along lines crossing scratches (locations indicated by red boxes) produced: (a) in air; (b) in solution. Points presenting cathodic activity are in blue. The 20 extra line scans gathered from $\sim 10\ \text{s}$ after scratching in solution are in green.

(active towards ORR^{28,29}) was far from the scratch and was not scanned (Topic S1). The resulting defects after the 60 min-tests presented nearly identical dimensions (Figs. S4a, S4b).

Although scratching was responsible for promoting passivity breakdown of the Zn-layers,¹ the rate of anodic activity increase differed (Fig. 2), with the defect produced in solution demanding more time for full activation. The different behavior achieved indicates the importance of local monitoring approaches in the initial stages of damaging. The local monitoring combined with in situ scratching would be particularly helpful for examining self-healing capability, in which a fast and controlled release of inhibitors during initial exposure is required.^{14,15}

Figure 3 exhibits time-resolved line profiles of j_z obtained between multiple in situ scribing performed on a same location of

a) 0.05 M NaCl

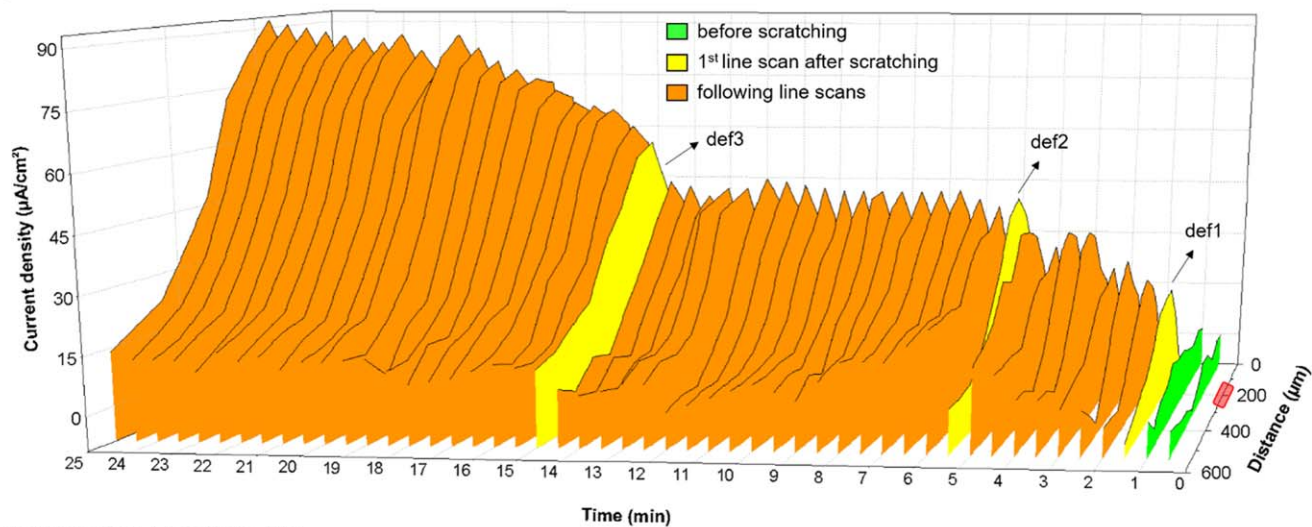
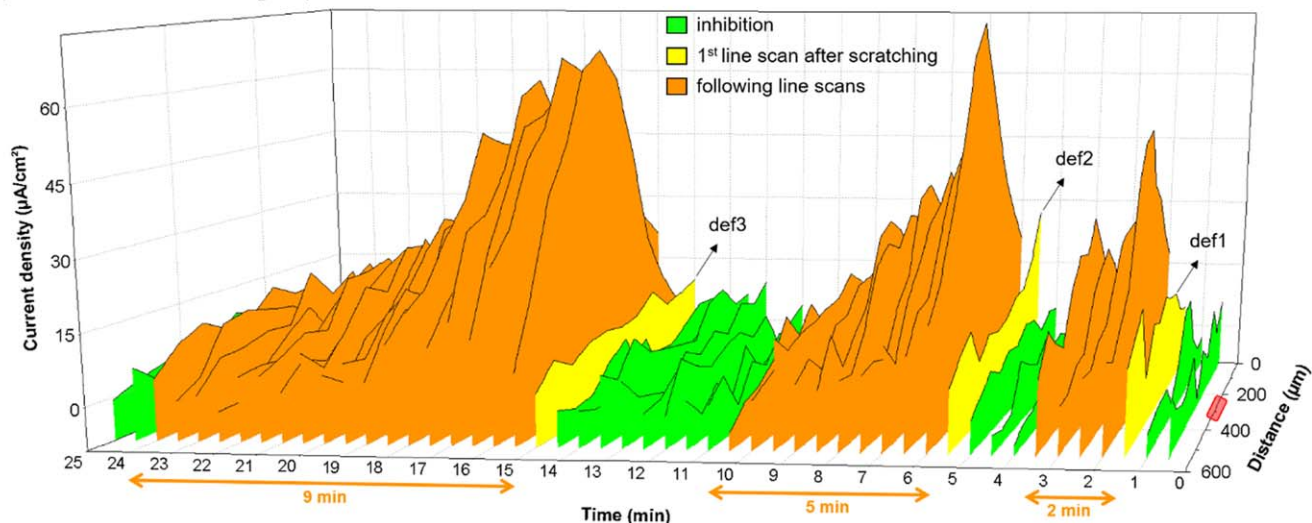
b) 0.05 M NaCl + 5 mM Na₂MoO₄

Figure 3. j_z line scans (30 s time lapses) plotted as a function of time during multiple in situ scratching of HDG surfaces. Current densities were collected over 25 min along lines crossing scratches (locations indicated by red boxes) in: (a) 0.05 M NaCl or (b) 0.05 M NaCl + 5 mM Na₂MoO₄. The first line scans obtained after each scratch (def1 = defect 1) are in yellow, and the following ones in orange. Lines in green represent: (a) scans achieved before scratching; (b) inhibition condition.

HDG surfaces exposed either to 0.05 M NaCl (a) or 0.05 M NaCl + 5 mM Na₂MoO₄ (b) electrolytes.

In the absence of inhibitor (Fig. 3a), multiple scratching resulted in increased anodic activity associated with the defect region. The first 30 s-line scans obtained after each hit (yellow curves) demonstrated a considerable increase of j_z as a function of time. The overall trend obtained indicated the progress of the corrosion process, with the maximum anodic j_z increasing from ~ 30 to $\sim 90 \mu\text{A cm}^{-2}$ upon repetitive damage.

The same multiple in situ scratching approach led to a different response in the presence of inhibitor (Fig. 3b). Corrosion was controlled before damaging, presenting $j_z = 0.78 \mu\text{A cm}^{-2}$ on average (this value was considered as a threshold for “inhibition”). In the first line scan acquired after the first scratch (def1), an increase in j_z ($9.87 \mu\text{A cm}^{-2}$ on average) was observed. In the following line scan (time = 2 min), j_z presented a considerable increase ($27.53 \mu\text{A cm}^{-2}$ on average). Then, the anodic activity steadily decreased during 2 min, but the surface remained active. At time = 4 min, inhibition of corrosion was attained (green curves). Next, a second defect was introduced (def2) and, once more, 30 s was necessary for the defect reaching full activity (time = 6 min). After

def2, the scratch remained active for a more extended period (~ 5 min) in comparison to def1 (~ 2 min). At time = 15 min, the surface was scribed once again at the same location (def3). Likewise, 30 s of initiation time was needed for full activation of the scratch. But this defect remained active for the most prolonged period recorded (~ 9 min). The resulting defects had similar dimensions (Figs. S4c, S4d).

According to reviews,^{2,14} proper model inputs need to capture the dependence of inhibitor release kinetics and predict/validate the ability to heal multiple damage events. The in situ scratching method allowed the assessment of time-related aspects of inhibition, i.e., the dynamic behavior of molybdate upon repetitive activation of the HDG surface (Topic S2). Therefore, this approach shows promise for tracking the release of inhibitors in self-healing systems subjected to a sudden increase in the exposed substrate area.

The line scan routines here employed were chosen to potentialize the main advantage of the in situ scratching; namely the possibility of assessing the early stages of corrosion of freshly created defects. However, such line approaches confined to a same (scratched) region should complement (and not substitute) j_z maps from the whole exposed surface.

Summary

The development of effective anti-corrosion technologies depends on the understanding of corrosion/inhibition processes related to microdefects. In this direction, the present study highlighted the necessity of novel experimental designs combining local electrochemistry tools with in situ protocols for creating defects.

It was demonstrated that the combination of SVET with in situ scratching is a powerful and easy-to-implement approach for early investigation of defect-driven localized corrosion. Considerably divergent responses were obtained for HDG specimens scratched in situ either in air or in solution. Furthermore, repetitive in situ scribing allowed the time-dependent action of a corrosion inhibitor to be appraised. Important time-related information of corrosion processes could be derived from the proposed method, such as kinetic aspects of depassivation and the dynamic behavior of inhibitors upon repetitive scribing.

The presented approach would be particularly useful for investigating self-repairing systems by determining the release rates of inhibitors and evaluating their long-term effectiveness.

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