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Nanoscale Scanning Electrochemical Cell Microscopy and Correlative Surface Structural Analysis to Map Anodic and Cathodic Reactions on Polycrystalline Zn in Acid Media

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Scanning electrochemical cell microscopy (SECCM) is used to map anodic and cathodic processes on polycrystalline zinc in 10 mM H₂SO₄, at the nanoscale. Electrochemical maps are correlated directly with structural data from electron backscatter diffraction applied to the same regions of the surface, and density functional theory (DFT) calculations are used to rationalize the data. Preliminary data on droplet stability with SECCM point measurements indicated that there was a significant spreading of the meniscus cell with an air atmosphere, attributed to changes in pH during the oxygen reduction reaction, compromising the lateral resolution of the SECCM measurement. Experiments with an argon atmosphere, as well as the application of a hydrophobic n-dodecane oil layer on the Zn interface, prevented spreading. Electrochemical maps of polycrystalline Zn surface under an Ar atmosphere indicated that the hydrogen evolution reaction (HER) and Zn electrodisolution on individual low-index grains decreased in the order $(\bar{1}2\bar{1}0) \geq (01\bar{1}0) > (0001)$. DFT calculations revealed a correlation between experimental values of current associated with HER and Zn dissolution reactions and the predicted hydrogen adsorption and Zn dissolution energies on individual facets, respectively. This work further advances SECCM as a technique for probing electrified interfaces and demonstrates its applicability to reactive metals.

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The corrosion of metal substrates is usually governed by the formation of local galvanic cells resulting from heterogeneities in the surface crystallographic structure and chemical composition. Electrochemical Droplet Cell (EDC) techniques have become indispensable tools for identifying the electrochemical activity of isolated entities in the metal matrix and pinpointing the sites most susceptible to the initiation of corrosion.^{1–3} Applications of these methods include point measurements of activities on individual grains^{4,5} or inclusions^{2,6,7} at the surface of metals, using probes at the scale of 10 s to 100 s of μm across.^{8,9} There has been some effort to make such techniques high throughput, but with mm-scale probes.¹⁰ In an effort to improve spatial resolution, micron-scale capillary probes^{11–14} have been reported, but are rarely used. Against this background, the introduction of scanning electrochemical cell microscopy (SECCM)^{3,15–17} presents new opportunities for the fast, high spatial-resolution characterization of chemical and electrochemical phenomena at surfaces. With SECCM, a spatial resolution at the 10 s of nm level, with dynamic electrochemical measurements in thousands of areas of a sample, are possible in a matter of minutes.^{3,18}

In SECCM, electrochemical measurements are confined to a small area of a sample surface with the use of a droplet formed at the end of an electrolyte-filled nanopipet (single¹⁶ or dual¹⁹ channel, equipped with one or two quasi reference counter electrodes (QRCEs), respectively).^{3,20} The SECCM configuration enables electrochemical measurements to be carried out directly at a series of targeted locations, usually numbering several thousand in an array. These large electrochemical datasets can be reviewed as maps and movies of electrochemical activity and further correlated with structural information from the surface characterization of identical locations.³ To aid such correlative multi-microscopy studies, a further bonus of SECCM is that topographical information is also recorded synchronously with the electrochemical activity.^{17,18,21} A wide range of processes and electrode materials have been studied with SECCM, including polycrystalline metals,^{22–25} transition metal

dichalcogenides,^{26,27} sp² carbon materials,²⁸ and battery cathode particles,^{29–31} as described in several reviews.^{3,18,32} Studies of the hydrogen evolution reaction (HER) on nanostructured MoS₂³³ demonstrated 50 nm spatial resolution of SECCM, in which the electrochemistry of particular surface features on the nm scale was characterized. Recent work on polycrystalline low carbon steel^{34,35} has shown that this approach can be successfully adapted in order to investigate electrochemical phenomena associated with corrosion processes.

The nanopipet probe used for SECCM does not make physical contact with the substrate and produces a 3-phase gas/electrolyte/substrate boundary (meniscus contact). This configuration enhances mass transport of gaseous reagents to reactive sites and facilitates the automated approach of the pipet to a substrate surface, making fast scanning across large areas possible.^{2,18,36} On the other hand, droplet stability on corroding (active) metals is an important consideration, as dynamic changes in the size of the meniscus would complicate the electrochemical signal and decrease SECCM spatial resolution.³⁷ Scanning Kelvin Probe inspection of Fe^{38,39} and Zn^{40–42} during atmospheric corrosion have suggested that the oxygen reduction reaction (ORR) drives electrolyte spreading. In this work we examine the meniscus droplet stability in SECCM measurements, comparing O₂ and Ar atmospheres, as well as under application of a n-dodecane oil, using Zn degradation in 10 mM H₂SO₄ as an exemplary system. We chose n-dodecane because it possesses hydrophobic and non-volatile properties and is chemically inert.⁴³ Often used as a model system to mimic engine oil,⁴⁴ reactivities of n-dodecane/liquid/metal interfaces can be of interest to corrosion applications in oil industries.⁴⁵

Zn is of considerable practical importance in the automotive industry, serving as a sacrificial cathode for steel substrates.⁴⁶ The crystallographic texture of Zn protective coatings can have a significant impact on the corrosion performance,^{47–49} but there is no consensus on the details of the effect. Coatings with a strong (0001) texture were reported to have better corrosion performance over coatings with (11 $\bar{2}$ 0) preferential orientation in deaerated NaCl solutions,⁵⁰ while the opposite situation was observed in spray tests

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and NaClO₄ solutions.⁵¹ Experiments in aerated sulfate medium suggested that crystal orientation played no role, but rather the impurity level was critical.⁵² Systematic investigations on single crystals in NaOH^{53–55} and (NH₄)₂SO₄,⁵⁵ and with single point EDC measurements on polycrystalline Zn in borate buffer solution⁴ showed that zinc surfaces became more susceptible to corrosion in the order (0001) < (01 $\bar{1}$ 0) < (11 $\bar{2}$ 0), correlated with the decreasing atomic packing density of the surface.

Given the above background, the primary goal of this work was to investigate droplet cell stability and susceptibility of the substrate to wetting, and how to overcome such issues in SECCM studies of corroding metal interfaces, using Zn corrosion in 10 mM H₂SO₄ as an exemplar system. Rationalization of nanoscale SECCM electrochemical data was performed using atomic-scale DFT simulations.

Experimental

Chemical reagents and electrode materials.—The 50 × 50 × 5 mm Zn foil (Goodfellow, U.K., 99.9%) was sectioned using an abrasive cutter to give a sample of ca. 5 × 5 mm size, which was mounted in a carbon-based conductive mount using a Buehler SimpliMet 3000 Mounting Press (Buehler, U.S.A.). The sample was polished on a polishing cloth (Buehler CarbiMet) using successively 320, 400, 600, 1200 grit SiC cooled with tap water. The final polishing step employed a polishing cloth (Buehler MicroCloth) with a 0.05 μm alumina suspension (MasterPrep Alumina, Buehler). The sample was then washed in acetone and deionized water, before being gently blown dry. The surface was additionally finished with an Ion Milling System (IM4000 plus, Hitachi Ltd., acceleration voltage of 4 kV, discharge voltage of 1 kV, Ar gas flow of 0.08 cm³ min^{−1}) for 5 min. For SECCM measurements, electrical connection to the sample was made with a copper wire connected to the outside of the conductive mount with carbon tape.

The Ag/AgCl quasi reference counter electrodes (QRCEs) were prepared by anodizing 0.125 mm diameter annealed silver wire (Goodfellow, U.K., 99.99%) at +1 V vs Pt counter electrode in a saturated KCl solution for 5–10 min. QRCEs of this type possess long-term stability and do not contaminate the surface investigated in a variety of electrolyte solutions on the timescale of SECCM measurements.⁵⁶

Sulfuric acid (Sigma-Aldrich, 96%), potassium chloride (Sigma-Aldrich, 99%), acetone (Sigma-Aldrich, 99%) and n-dodecane (Sigma-Aldrich, 99%) were used as supplied by the manufacturer. All solutions were prepared in deionized water (18.2 MΩ cm at 25 °C, Integra HP, Purite, U.K.).

SECCM measurements.—SECCM measurements utilized a home-built instrument described in detail elsewhere.^{33,57} Briefly, single-barreled nanopipet SECCM probes were pulled with a Sutter P2000 pipet puller from borosilicate glass of 1.2 OD × 0.69 ID × 100 L mm (30-0044 GC120F-10 Harvard Apparatus), to produce a tapered end with an internal circular diameter ca. 150 nm. Each nanopipet used was filled with 10 mM H₂SO₄, together with a Ag/AgCl wire placed in the back to serve as a QRCE. All potentials are quoted with respect to Ag/AgCl in 10 mM H₂SO₄ having +280 mV potential difference vs Ag/AgCl/(3 M KCl). The uncompensated resistance of the filled tip was determined to be 60 M by current-voltage measurements.⁵⁸ No correction was made for ohmic drop in the current measurements, but this could be done with the knowledge of the nanopipet resistance. The top of the nanopipet was sealed with superglue to minimize electrolyte evaporation from the back.

The SECCM probe was mounted on a z-piezoelectric positioner (P-753.3CD with E-665 controller, Physik Instrumente (PI), Germany), while the sample was placed on an xy-piezoelectric stage (P-621.2CD with E-625 controller (PI)) (Fig. 1a). The z-stage was also equipped with a stepper motor (8303 Picomotor Actuator, Newport, U.S.A.) for coarse movement. During each approach of the nanopipet, the Zn substrate (working electrode, WE) current (*I*) was used as a signal to detect when the meniscus cell had made contact

with the Zn substrate. The magnitude of the threshold current used for the studies herein was ca. 4 pA (at a substrate potential of −1.6 V vs QRCE). The nanopipet itself never made contact with the substrate. Voltammetric measurements were performed in the confined area defined by the meniscus cell created between the probe tip and substrate surface.

Electrochemical measurements at the substrate were made using a sweep voltammetric “hopping” protocol³³ (Fig. 1b). The nanopipet probe was approached to the substrate surface at a series of predefined locations in a grid (raster scan pattern) and, upon each landing, an independent potentiodynamic measurement was made, building-up a voltammetric profile of the substrate. A high voltammetric scan rate of 10 V s^{−1} was chosen in order to minimize the extent to which anodic dissolution and cathodic driven droplet spreading would occur. Mass transport in the nanopipet orifice is enhanced due to the contribution of the radial component in the tapered capillary.^{20,59} Therefore, steady-state conditions are established rapidly, allowing corrosion relevant measurements on the much shorter time scale in comparison to classical bulk corrosion experiments.^{25,34} Moreover, the rapid diffusional exchange between the tip orifice and tip bulk guarantees the refreshment of solution composition in the droplet upon each meniscus landing during SECCM mapping.^{20,59}

Before each measurement the substrate surface was cleaned from natively formed Zn oxides/hydroxides by sweeping the potential from −1.6 V to −0.9 V, immediately after meniscus contact with the Zn substrate, to guarantee a reproducible surface state (Fig. 1b). The final position of the z-piezoelectric positioner at approach (i.e., z-extension) was also used to produce a topographical map of the substrate synchronously. The hopping distance between landings (i.e., x-y spatial resolution) was in the range 1–2 μm, set precisely for each image scan. The SECCM set up was situated in an aluminum Faraday cage equipped with heat sinks and vacuum panels to minimize noise and thermal drift. The Faraday cage was positioned on an optical table (RS2000, Newport, U.S.A.) with automatic levelling isolators (Newport, S-2000A-423.5). The QRCE potential was controlled, with respect to ground and the current flowing at the substrate (working electrode), held at a common ground, was measured using a home-built electrometer. Data acquisition and instrumentation control were carried out using an FPGA card (PCIe-7852R) controlled by a LabVIEW 2016 (National Instruments, U.S.A.) interface running the Warwick Electrochemical Scanning Probe Microscopy (WEC-SPM, www.warwick.ac.uk/electrochemistry) software. The current was measured every 4 μs, which was averaged 128 times, with one point for transfer, to give a data acquisition rate of 516 μs (i.e., 1 data point every 2.6 mV at a voltammetric scan rate of 10 V s^{−1}). A home-built 8th order low-pass brick-wall filter unit with a time constant of 100 μs was utilized during data (current) acquisition.

After experiments, the raw data were processed using the Matlab R2018a software package. Data plotting was carried out using the Matlab R2018a and OriginPro 2019 64 bit software packages. All topographical and electrochemical activity maps (and movies) were plotted in Matlab, with no data interpolation.

Electrochemical measurements were performed under ambient air, with and without an application of ca. 1–3 mm thick layer of n-dodecane oil on Zn surface, and under a humid Ar atmosphere without oil. Environment control was achieved by placing the substrate and nanopipet in a sealed plastic box of 100 ml capacity, with sealed input and output gas channels.⁶⁰ A constant flow of Ar was bubbled through deionized water then through the box and deionized water on the other side of the box to guarantee no contamination from the air. The flow of Ar gas was launched 30 min before experiments and maintained during SECCM mapping.

Ex situ surface characterization.—After experiments in n-dodecane, the Zn surface was extracted and extensively washed with acetone and deionized water, and then dried under airflow to remove any oily residues from the surface verified with Energy-dispersive X-ray spectroscopy (EDS). In all other cases, the Zn surface was analyzed directly after SECCM experiments.

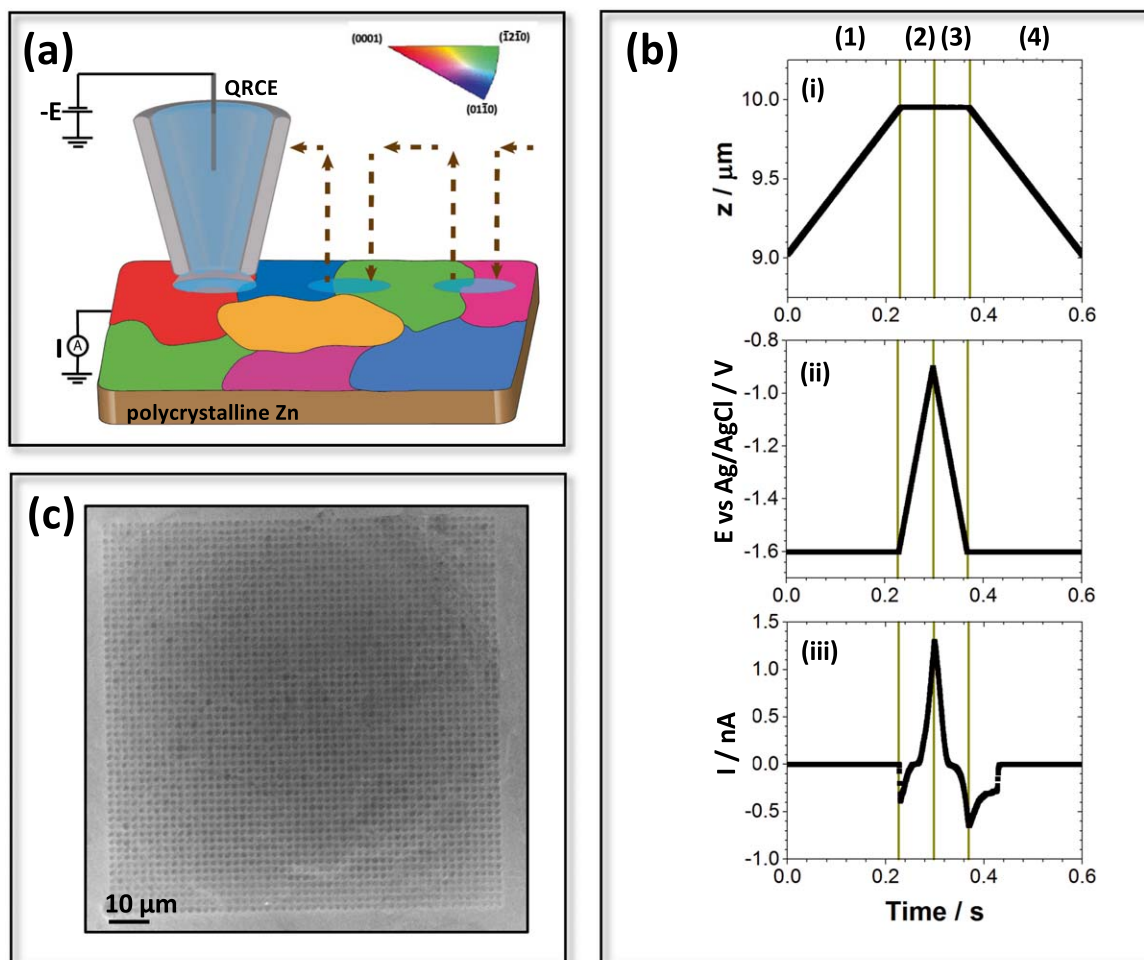


Figure 1. (a) Schematic of nanoscale synchronous electrochemical/topographical mapping using voltammetric hopping mode SECCM with a single channel nanopipet probe of ca. 150 nm of internal diameter. In this configuration, a potential was applied directly at the QRCE to control the working electrode (WE) potential (E), and the substrate WE current (I) was measured. I was also used as the signal to detect meniscus-surface contact during the approach. Arrows indicate movement of the nanopipet probe near the substrate surface during scanning. (b) Plots of (i) piezoelectric positioner z -extension, (ii) E and (iii) I as a function of time, during a single-hop of the SECCM nanopipet. The potential was kept at -1.6 V vs QRCE during the nanopipet approach and retraction, in periods (1) and (4), respectively. Once meniscus is contact, the substrate potential was swept from -1.6 V to -0.9 V to clean the Zn interface from any natively formed corrosion products (period (2)), and the voltammetric measurement was taken during period (3), when the potential sweep was reversed (voltammetric scan rate = 10 V s^{-1}). (c) Secondary electron contrast image of residues on Zn surface after SECCM mapping. Circular spots represent each area of meniscus contact.

Surface microscopy characterization was performed with a Zeiss SIGMA FE-SEM (Zeiss, Germany), using a Nordlys EBSD detector (Oxford Instruments, U.K.) and X-Max 50 mm² EDS detector (Oxford Instruments, U.K.). Secondary electron contrast SEM images were collected at 5 kV using InLens mode, and EBSD images were collected at 20 kV, with the sample tilted at 70° to the detector. Following EBSD characterization, grains that were either on or close to the low index orientations, (0001), (0110) and ($\bar{1}1\bar{2}0$) were selected for more detailed analysis. The criterion for plane selection set in this study was 10° deviation from the desired orientation. The precise locations of SECCM scanning areas were identified from secondary electron images (Fig. 1c).

Theory and simulations.—Although not without limitations, ground state energies are often used to explain kinetic data in electrochemistry, including “volcano” relationships in electrocatalysis⁶¹ and dissolution processes.⁶² Simplified systems were chosen herein (i.e. a plane of Zn atoms on a lattice, uniform dissolution/hydrogen adsorption) to provide a semi-empirical framework of rationalizing SECCM data on single Zn grains.

The Quantum Espresso⁶³ software toolbox was used to perform plane wave basis set Kohn–Sham Density Functional Theory (DFT)⁶⁴

calculations with ultrasoft pseudopotentials.⁶⁵ Pseudopotentials were all taken from the PSLibrary, version 1.0.⁶⁶ A plane-wave kinetic energy cut-off of 400 eV was found to converge binding energies to at least 2 significant figures (in eV units). A Monkhorst-Pack grid of $4 \times 4 \times 1$ k-points with no origin shift⁶⁷ was found to be adequate to converge energies with respect to Brillouin zone sampling.

Slab models of (0001), (0110) and ($\bar{1}1\bar{2}0$) Zn planes with a finite thickness of 5 layers were employed to model Zn-H binding energies and Zn electrodisolution energies. A vacuum gap of 7 Å on both sides of the slab in the z -direction was used to simulate open boundary conditions. Additionally, any remaining spurious interactions through the z -boundary were corrected using the Martyna-Tuckerman dipole correction scheme⁶⁸ as implemented in the Environ model.^{69,70} In the case of electrodisolution energies of Zn, the solvation model was used to account for solvent interaction energy terms between the surface and the solvent and between the dissolved zinc ions and the solvent. Parameters suggested previously were used to parameterize the continuum solvent model for water.^{69,70} With this approach, surface energies were converged down to 0.001 eV error.

Firstly, a variable-cell geometry optimization of the bulk metal cell was performed to find a converged lattice parameter. In the case

of hcp crystal structure of Zn, these were $a = b = 2.712 \text{ \AA}$, $c = 4.796 \text{ \AA}$. Slabs formed from the bulk metal were used in fixed-cell geometry optimization, constraining the position of the two layers furthest from the simulated surface to calculate the bare surface energy in a vacuum (E_{bV}) and in a solvent (E_{bS}).

To perform adsorption studies, hydrogen atoms were added manually onto the bare metal surface configuration in positions close to the high symmetry adsorption sites (see Fig. 1s in SI for details available online at stacks.iop.org/JES/167/041507/mmedia), with a vertical separation of ca. $2 \text{ \AA}$. These configurations were allowed to relax while keeping only the deepest two metal layers constrained, yielding the minimized energies of surface metal atoms and hydrogen in each adsorption configuration (E_{bV+H}). The equation below was used to compute binding energies:

$$E_{Zn-H} = E_{bV+H} - E_{bV} - E_H, \quad [1]$$

where E_H refers to the energy of a hydrogen atom in the center of a vacuum box with the same parameters used for the slab calculations. Initially, calculations were performed with 25, 50 and 100% surface coverage on (0001) plane. Since the difference in Zn–H energies was no more than 0.2 eV, 50% coverage was arbitrarily chosen for all further calculations and presented below.

To perform Zn dissolution studies, a single layer of Zn atoms was manually removed from the surface. The equation below was used to compute binding energies of Zn layer (E_{Zn-Zn}):

$$E_{Zn-Zn} = (E_{bS_n(layers)} - E_{bS_n-1(layers)} - n \times E_{Zn^{2+}})/n, \quad [2]$$

where $E_{Zn^{2+}}$ refers to the energy of a Zn^{2+} cation in the center of a solvent box, with the same parameters used for the slab calculations. Normalization by the number of atoms in a layer (n) was used to account for packing densities of individual grains.

An electronic energy convergence tolerance of $2 \times 10^{-6} \text{ eV}$ was used throughout these calculations. This is an extensive property. Therefore, the convergence of the total energy improves, relatively, with more atoms. In the worst case of single-atom calculations, this is still good, as the pseudopotential library we chose is only expected to give accuracy up to $8 \times 10^{-4} \text{ eV atom}^{-1}$ relative to all-electron calculations.⁷¹ A Broyden charge density mixing⁷² scheme, with local Thomas-Fermi screening⁷³ and Gaussian electronic smearing, with a smearing width of 0.1 eV were used to account for the metallic nature of the system. Using Gaussian smearing with a smearing width of 0.1 eV is a common technique in DFT calculations of metals,⁷⁴ to allow smooth convergence due to the smoothing of discontinuities between k-points and between occupied and unoccupied states. It has been shown to give accurate properties for metals.^{75,76} We used the BFGS geometry optimization scheme⁷⁷ with tolerances of $2 \times 10^{-5} \text{ eV per atom in energy}$, 0.05 eV per $\text{\AA}$ in maximum force, 0.002 $\text{\AA}$ in maximum atomic displacement and in the case of the variable-cell, bulk geometry optimization, 0.1 GPa maximum stress. We chose the BFGS energy tolerance in the same way as for the electronic minimization.

Results and Discussion

Influence of the atmospheric environment on polarization curves and meniscus stability.—An average of 10 potentiodynamic polarization curves, recorded in separate areas on the polycrystalline Zn surface in air (10 mM H_2SO_4 in the nanopipet tip) is shown in curve 1 in Fig. 2a. The anodic branch starts at the anodic limit of -0.95 V to ca. -1.2 V , where the cathodic branch starts and extends to the cathodic limit of -1.6 V . These data were recorded with a SECCM tip of ca. 150 nm diameter, yet ex situ secondary electron

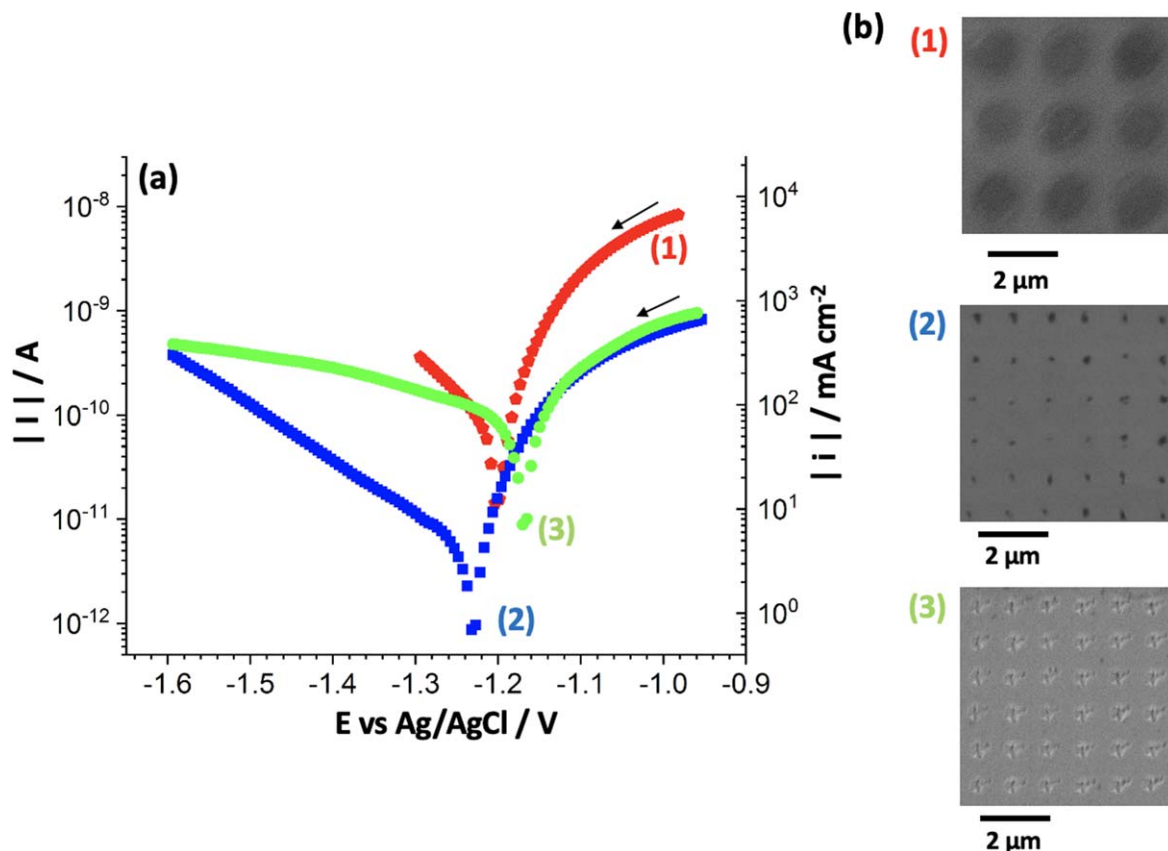


Figure 2. (a) Average of 10 SECCM polarization curves on a polycrystalline Zn surface in 10 mM H_2SO_4 and (b) secondary electron contrast images of individual landings on the surface for the cases of polycrystalline Zn electrode, each recorded (1) with an air atmosphere, (2) under Ar and (3) under air with a thin layer of n-dodecane oil on Zn interface. Arrows indicate the direction of the voltammetric scans. Left y-axis indicates current densities for the curves (2) and (3), where the meniscus was stable, and does not apply for the curve (1). A surface area of a circle of 100 nm radius was used for normalization.

imaging of the surface after these measurements shows relatively large SECCM footprints (Fig. 2b-1), indicating significant spreading of the droplet cell to ca. 2 μm in diameter. In stark contrast, when this experiment was repeated under an Ar atmosphere, the footprints from the meniscus landings had a diameter of 150–200 nm (Fig. 2b-2), similar to the tip size, indicating that wetting of the Zn surface by the meniscus was greatly suppressed. Minor deviation of footprint size is stochastic, showing no correlation with crystallographic texture (consult Fig. 1s in Supplementary Information—SI for more examples) that suggests similar wetting on different grains. Due to the much smaller size of the droplet, absolute values of anodic currents (curve 2 in Fig. 2a) were an order of magnitude smaller in comparison to the experiments made under air. The anodic branch is due to the anodic dissolution of Zn. We note that the droplet size was estimated only from ex situ SEM observations. Development of methodologies for in situ monitoring the meniscus size would be useful in the future for situations where the droplet contact might be dynamic.

The Tafel slopes in the cathodic branch are very different for these two different atmospheric environments. Due to the low solubility of oxygen in aqueous solution, the oxygen reduction reaction (ORR) current in SECCM is strongly dependent on oxygen transfer across the gas/meniscus interface.³⁶ There is not only a smaller cathodic current in an argon atmosphere but also a Tafel slope of ca. 0.16 V dec^{-1} as expected for the hydrogen evolution (HER), with a Volmer step as the rate-controlling in the Volmer-Heyrovsky reaction route.^{78–80} With oxygen present (air environment), the reaction is a mix of HER and ORR over this potential range.

Suppression of droplet spreading could also be achieved in aerated conditions, but with the application of n-dodecane (hydrophobic, non-volatile and inert oil) on the Zn surface, through which the SECCM tip, containing the aqueous solution was translated. In this configuration, the hopping mode protocol was identical to the measurements made in air, without the oil layer. The meniscus footprint size in Fig. 2b-3 is similar to that in the experiment under Ar (Fig. 2b-2). This is also confirmed by the values of the anodic currents in Fig. 2a-3, which are closely similar to the measurements under Ar.

The different contrasts between the images of the footprints in Figs. 2b-2 and 2b-3 is probably due to the washing of the Zn interface after n-dodecane application. On the other hand, the cathodic currents are larger than under argon, because the oil phase contains O_2 which can cross the oil/aqueous droplet phase boundary for reduction at the zinc electrode surface, in an “induced transfer mode,” similar to that used in scanning electrochemical microscopy at immiscible liquid/liquid interfaces.⁸¹

It is important to point out that the voltammetric scan rates applied for these measurements are far in excess of those used in conventional macroscale electrochemical corrosion measurements. This is possible because mass transport is very fast in this configuration due to fast quasi-radial diffusion (ca. 1 ms time constant for a tip of 75 nm radius with aqueous electrolytes).¹⁶ Thus, relatively fast voltammetric scan rates of 10 V s^{-1} can be employed to provide corrosion-relevant data (e.g. Tafel slopes) as reported previously^{33,34} and herein. On the other hand, it should be noted that the corrosion potentials are not meaningful herein due to distortion of potentiodynamic curves from non-faradaic currents (double layer charging and the contribution of stray capacitance) at low currents around open circuit potentials at the high 10 V s^{-1} sweep rate.^{34,82} The powerful aspect of SECCM herein is the voltammetric analysis of moderate to high overpotential data for Zn electrodisolution and the cathodic HER processes.

The difference in potentials at zero current ($E_{I=0}$) in Fig. 2a for the curves (1)–(3) can be explained using mixed potential theory assuming equal contribution of capacitive responses to polarization curves. The $E_{I=0}$ value of -1.16 V for curve (3) is more noble in comparison to -1.22 V of curve (2) due to enhanced cathodic

currents for curve (3) with similar contributions of anodic currents for both curves (2) and (3). Curve (1) illustrates the case where both cathodic and anodic activities are enhanced, resulting in $E_{I=0}$ value lying between the $E_{I=0}$ values of curves (2) and (3).

Grain specific electrochemical activity of polycrystalline Zn: HER and metal dissolution.—Potentiodynamic point measurements were extended to maps of electrochemical activities, recorded as described in the Experimental section. The measurements were performed under an Ar atmosphere, in order to exclusively probe HER in the cathodic branch of the potentiodynamic region. Moreover, the absence of O_2 increases the meniscus cell stability removing possible effects of different grain wetting on electrochemical maps as discussed above. An EBSD map of the region of interest on the polycrystalline Zn surface is shown in Fig. 3a, showing a wide range of grains of different crystallographic orientation. In conjunction with these crystallographic data, there is a pronounced electrochemical contrast between different grains in a movie of current maps given in SI. The contrast in current maps is consistent in all grains during Zn dissolution. It flips after the onset of cathodic reaction and stays consistent until the end of the voltage sweeping of -1.6 V. Due to this consistency, current maps at two characteristic potentials of -1.4 V and -1.1 V, illustrating HER and Zn dissolution, respectively, are shown in Figs. 3b and 3c. The synchronous topography recorded by SECCM is given in Fig. 3s in SI.

The electrochemical activities on the low index grains in Figs. 3b and 3c indicates the following order of activity, defined in terms of current magnitude $|I(0001)| < |I(0\bar{1}10)| \leq |I(\bar{1}2\bar{1}0)|$ for both HER and Zn dissolution. Histograms of current values collected from hundreds of individual measurements on these low index grains show the statistical significance of the reported data. Given the stochastic distribution of the meniscus cell size (Fig. 2b-2 and SI), and that this is grain-independent, gives confidence in the assignment of currents to electrochemical activities of the different grains, and not to their wetting properties.

Previous investigations on the corrosion of Zn single crystals^{53–55} in neutral and basic electrolytes showed identical behavior to our trend in the acid environment where the corrosion susceptibility increases in order of $(0001) < (0\bar{1}10) < (\bar{1}2\bar{1}0)$. To the best of our knowledge, HER on individual Zn grains has never been reported before. Authors generally link better corrosion resistance to the increase of the atomic packing densities of $(0001): (0\bar{1}10): (\bar{1}2\bar{1}0) = 1: 0.54: 0.47$.^{4,53–55} Below we rationalize SECCM data based on the estimation of ground-state energies and their qualitative correlation with the experimental values of current. Although with some limitations, DFT calculations of this type have been applied in the literature^{61,62} and can provide a semi-empirical framework for rationalizing electrochemical data at the nanoscale.

Rationalization of single grain reactivities using atomic-scale simulations.—*HER on Zn.*—The relative rate of HER at a particular electrode surface is often interpreted by hydrogen adsorption free energies on catalytic interfaces illustrated by the “Volcano” relationship.^{61,83} If the binding energy is too low (less than ca. -2.75 eV^{25,84} reported for a Pt(111) surface) the adsorption or Volmer step (Eq. 3) limits the overall reaction and likewise the desorption or Heyrovsky/Tafel (Eqs. 4–5) if the binding energy is too high:



where * donates an adsorption site on the metal surface.

In this context, we estimated Zn–H binding energies from DFT calculations on different Zn adsorption sites depicted in Fig. 2s

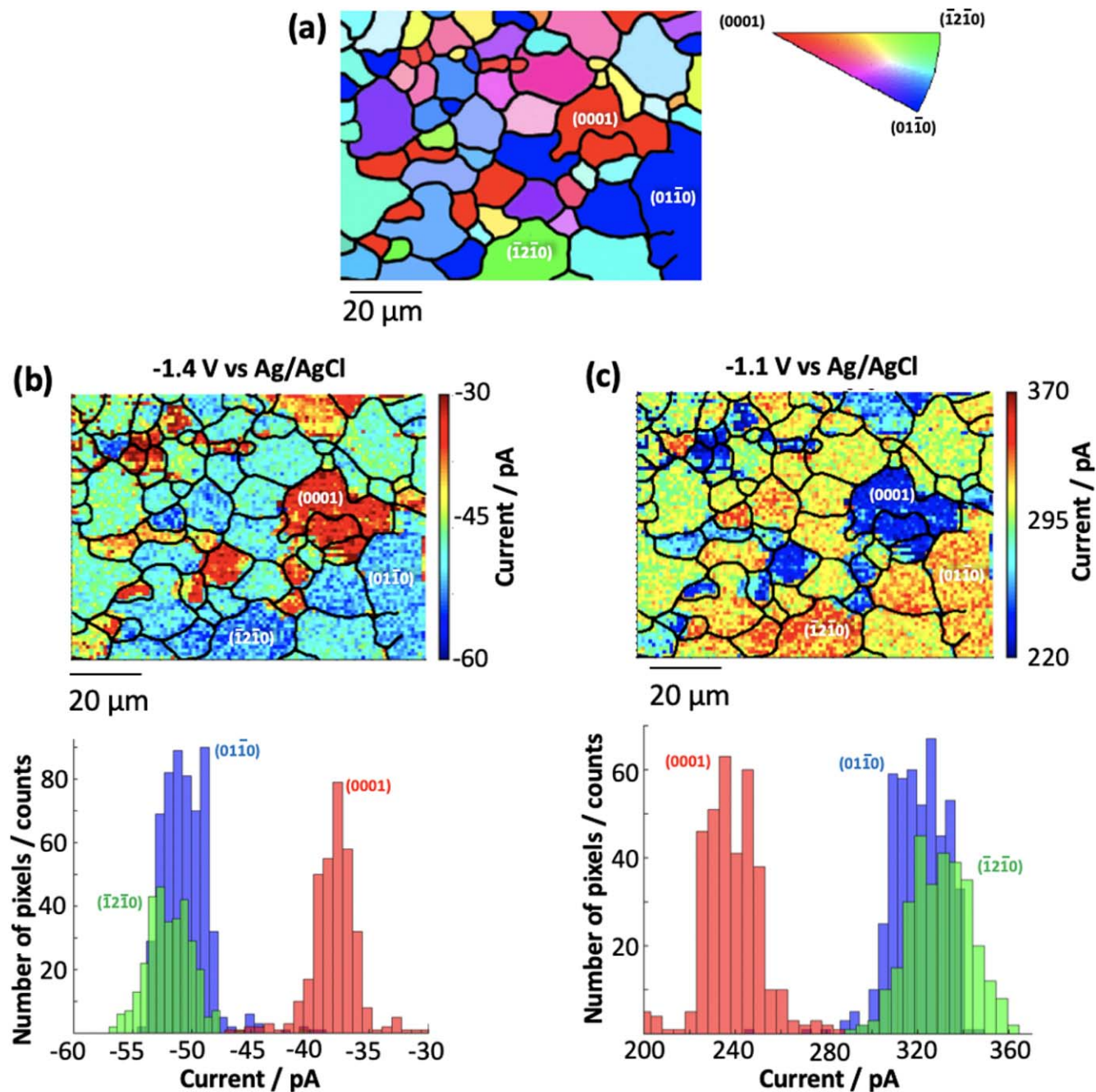


Figure 3. (a) Grain orientations of a region of interest of the polycrystalline Zn surface plotted in the standard stereographic triangle normal to the surface. SECCM current maps (top) and histograms of current distribution on individual (0001), (1̄2̄10) and (01̄10) facets (bottom) at (b) cathodic (−1.4 V vs Ag/AgCl) and (c) anodic (−1.1 V vs Ag/AgCl) overpotentials of a polycrystalline Zn surface under Ar. 10 pA corresponds to a current density of 8 mA cm^{−2}. Current maps contain 100 by 75 pixels (SECCM nanopipet hops) with a hopping distance (separation between pixels) of 1 μm. The selected grains deviated less than 10° from the desired orientations.

assuming 50% surface coverage. The absolute values of energies in Fig. 4a (refer to Table IS in SI for precise values) are close to the experimentally measured value ca. −1.5 eV previously reported on polycrystalline Zn metal,⁸³ reassuring the adequacy of our DFT calculations. All Zn–H bonding energies are below −2.75 eV implying a Volmer mechanism of HER that is in agreement with a Tafel slope of ca. 0.16 V dec^{−1} from SECCM data (see above). Noting that the Tafel slope of HER can be potential-dependent,⁸⁰ it is difficult to interpolate the cathodic current to 0 V vs reversible hydrogen electrode to define the exchange current values of HER. Instead, we took the HER currents at −1.4 V to construct the plots in Fig. 4a. The adsorption free energies increase in order (0001) <

(01̄10) < (1̄2̄10) that agrees with the trend of experimentally measured values of current.

Despite this agreement, the comparison should be treated with some caution due to the number of assumptions made. First, the DFT model considers a pristine crystal lattice of Zn whereas the real surface is likely to contain crystallographic defects due to Zn electrodisolution and chemical removal of natively formed Zn oxides upon meniscus landing. Second, the effect of solvent and anions have not been considered in the DFT simulations. The latter can have an effect of HER for example, by SO₄^{2−} adsorption.⁸⁵ Third, Zn–H binding energies are site-specific (Table 1s in SI) whereas only averaged values are considered in Fig. 4a. These

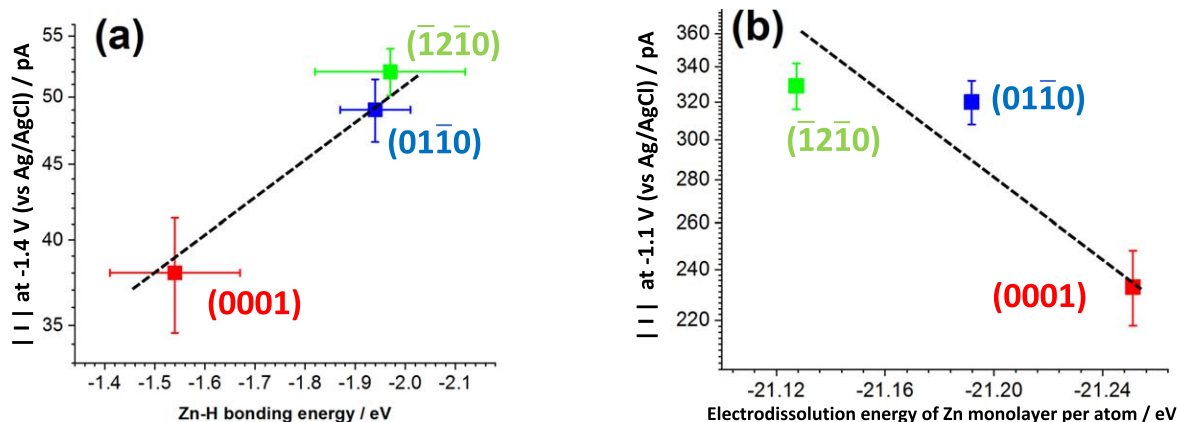


Figure 4 (a) Zn–H binding energies from DFT (Eq. 1) and corresponding HER currents from Fig. 3. (b) Electrodisolution energies of a Zn monolayer normalized per atom from DFT (Eq. 2) and Zn dissolution currents from Fig. 3 for (0001), ($\bar{1}2\bar{1}0$) and (01 $\bar{1}0$) Zn planes. 10 pA corresponds to a current density of 8 mA cm⁻². Error bars in the Y axis represent the standard deviation of currents recorded on identical facets in Fig. 4 and in the X axis, the error bars are the deviation of Zn–H energies between different adsorption sites (refer to Table IS in SI for precise values). Dotted lines are shown for the visual reference only.

oversimplifications make quantitative correlation difficult, and the dotted line in Fig. 4a is exclusively for visual reference. Indeed, Zn–H binding energies on different sites of crystallographic planes calculated by DFT range from -1.4 eV to -2.1 eV, whereas experimental values of currents (rate) showed a much more subtle grain dependence.

Zn dissolution.—Dissolution of a crystalline solid is complex, involving a number of interacting processes in parallel at different characteristic sites.^{86,87} In a simplified analogy to the “Volcano” relationship for HER, the Zn dissolution rate should be determined by Zn–Zn surface bonding energies ($E_{\text{Zn–Zn}}$) of specific planes in respect to an isolated Zn²⁺ solvated cation, i.e. Zn electrodisolution energies defined quantitatively in Eq. 2. This framework has been successfully employed in the case of Fe electrodisolution currents measured by SECCM on polycrystalline Fe in H₂SO₄³⁵ and will be used herein.

Figure 4b shows the correlation between experimentally determined grain-specific Zn electrodisolution current and Zn electrodisolution energies from DFT calculations. The measured currents scale with the calculated $E_{\text{Zn–Zn}}$, meaning that higher currents are recorded over the planes where Zn atoms are thermodynamically easier to remove. The minimum difference in dissolution energies of different grains ca. 0.05 eV is much larger than the 0.0001 eV convergence error, making the comparison possible. It must be emphasized that the DFT calculations are performed for a simplified system (the influence of anions and other species in the solution is not taken into account, and only the non-defective pristine crystal lattice is considered, as mentioned in the section above on HER), and should not be compared quantitatively with experiment. Nonetheless, the above mentioned analysis suggest a qualitative correlation of anodic dissolution currents and Zn–Zn surface bonding energies, consistent with a general framework for predicting the susceptibility of a metal surface to electrodisolution.^{35,62}

To summarize, our nanoscale data suggest that polycrystalline Zn should be less susceptible to the corrosion at the macroscale in an acidic (10 mM H₂SO₄) environment in the case of preferential (0001) crystallographic texturing of metal surfaces. In the future, the pseudo-single crystal SECCM approach combined with identical location surface characterization can be used as a quick and versatile tool to assist in the rational design of metal and alloy surfaces with improved performance with respect to corrosion.

Conclusions

This study has elucidated the kinetics of anodic and cathodic processes that are involved in the corrosion of zinc, as a function of the different surface crystallographic orientations. Focusing on low index

grains, under all considered conditions, both cathodic (HER) and anodic (Zn electrodisolution) currents recorded on individual grains of polycrystalline Zn decreased in order ($\bar{1}2\bar{1}0$) $\geq$ (01 $\bar{1}0$) $>$ (0001)). Electrochemical data on individual grains were found to correlate with atomic-scale DFT simulations of hydrogen adsorption and Zn dissolution energies, rationalizing the experimental observations, while noting the simplifications involved in the calculations. Direct comparison of experimental and predicted data emphasized the significant advances from the proposed SECCM methodology.

The dimensions and stability of the meniscus define the lateral resolution and reliability of SECCM data. Ongoing oxygen reduction reaction favored the meniscus spreading on corroding interfaces that can be suppressed by removing oxygen from the system and application of hydrophobic chemically inert oil, as shown herein with experiments under Ar and in n-dodecane oil deposited on the Zn interface.

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