OPEN ACCESS

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

To cite this article: V. Shkirskiy et al 2020 J. Electrochem. Soc. 167 041507

View the article online for updates and enhancements.
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. Prized ion exchange on droplet and SECCM with SECCM point measurements indicated that there was a significant spread of the meniscus 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 electrodissolution on individual low-index grains decreased in the order (1210) > (0110) > (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.

Supplementary material for this article is available online

© 2020 The Author(s). Published on behalf of The Electrochemical Society by IOP Publishing Limited. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/1945-7111/ab739d]
and NaClO₄ solutions.¹⁻¹ Experiments in aerated sulfate medium suggested that crystal orientation played no role, but rather the impurity level was critical.¹⁻³ Systematic investigations on single crystals in NaOH³⁻⁵ and (NH₄)₂SO₄⁵ and with single point EDC measurements on polycrystalline Zn in borate buffer solution showed that zinc surfaces became more susceptible to corrosion in the order (0001) < (011 0) < (1120), 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 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 (QRCs) 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. QRCs 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.⁶⁻⁵

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.⁵⁻³⁷ 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 QRC. 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.⁶⁰ 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 positioning stage (P-753.3C with E-665 controller, Physik Instrumente (PI), Germany), while the sample was placed on an x-y-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” protocol (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 FPG card (PCIe-7852R) controlled by a LabVIEW 2016 (National Instruments, U.S.A.) interface running the Warwick Electrochemical Scanning Probe Microscopy (WE-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 kHz (i.e., 1 data point every 2.618 V 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.
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 (1210) 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 electrocatalysis and dissolution processes. 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 Espresso software toolbox was used to perform plane wave basis set Kohn–Sham Density Functional Theory (DFT) calculations with ultrasoft pseudopotentials. Pseudopotentials were all taken from the PSLibrary, version 1.0. 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 Monkhurst-Pack grid of $4 \times 4 \times 1$ k-points with no origin shift was found to be adequate to converge energies with respect to Brillouin zone sampling.

Slab models of (0001), (0110) and (1210) Zn planes with a finite thickness of 5 layers were employed to model Zn-H binding energies and Zn electrodissolution 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 scheme as implemented in the Environ model. In the case of electrodissolution 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. 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 \( a = b = 2.712 \, \text{Å} \), \( c = 4.796 \, \text{Å} \). 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 \( (E_{\text{bV}}) \) and in a solvent \( (E_{\text{bS}}) \).

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 Å. 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 \( (E_{\text{bV/H}}) \). The equation below was used to compute binding energies:

\[
E_{\text{Zn-H}} = E_{\text{bV+H}} - E_{\text{bV}} - E_{\text{H}},
\]

where \( E_{\text{H}} \) 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 \( (E_{\text{Zn-Zn}}) \):

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

where \( E_{\text{Zn^2+}} \) 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 \( 2 \times 10^{-6} \) 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 \( 8 \times 10^{-4} \) eV atom\(^{-1} \) relative to all-electron calculations.\(^71 \) A Broyden charge density mixing\(^72 \) scheme, with local Thomas-Fermi screening\(^73 \) 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 scheme\(^77 \) with tolerances of \( 2 \times 10^{-5} \) eV per atom in energy, 0.05 eV per Å in maximum force, 0.002 Å 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\(_2\)SO\(_4\) in the nanopipet tip) is shown in curve 1 in Fig. 2a. The anodic branch starts at the anodic limit of \(-0.95 \text{ V to ca. -1.2 V, where the cathodic branch starts and extends}
\]

\[
\text{to the cathodic limit of -1.6 V. These data were recorded with a SECCM tip of ca. 150 nm diameter, yet ex situ secondary electron}
\]

![Figure 2](image-url)
imaging of the surface after these measurements shows relatively large SECCM footprints (Figs. 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. 1 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 Ar. 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.38,39 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 O₂ which can cross the oil/aqueous droplet phase boundary (Fig. 2b-2). However, the washing of the Zn surface by the oil phase under Ar. Figs. 2b-2 and 2b-3 is probably due to the washing of the Zn surface by the oil phase under Ar.

The potentiotodynamic 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 O₂ 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(0110)| ≈ |I(1210)| 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 in neutral and basic electrolytes showed identical behavior to their trend in the acid environment where the corrosion susceptibility increases in order of (0001) < (0110) < (1010). 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): (0110): (1210) = 1: 1.05: 0.47.61,62,55,56 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 literature61,62 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.61,62,68 If the binding energy is too low (less than ca. −2.75 eV25,84 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:

\[ H^+ + e^- \rightarrow H^* \] 

[3]

\[ H^* + H^+ + e^- \rightarrow H_2 + * \] 

[4]

\[ 2H^* \rightarrow H_2 + 2* \] 

[5] 

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
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, 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, 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 $(0001) < (1210) < (0110)$ 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 electrodissolution 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 SO$_4^{2-}$ adsorption. Third, Zn–H binding energies are site-specific (Table 1s in SI) whereas only averaged values are considered in Fig. 4a. These
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. 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 Zn$_{25}^+$ solvated cation, i.e. Zn electrodissolution energies defined quantitatively in Eq. 2. This framework has been successfully employed in the case of Fe electrodeposition currents measured by SECCM on polycrystalline Fe in H$_2$SO$_4$, and will be used herein.

Figure 4b shows the correlation between experimentally determined grain-specific Zn electrodeposition current and Zn electrodissolution energies from DFT calculations. The measured currents scale with the calculated $E_{Zn-Zn}$, 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 HERO), 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 electrode dissolution.5,6,8

To summarize, our nanoscale data suggest that polycrystalline Zn should be less susceptible to the corrosion at the macroscale in an acidic (10 mM H$_2$SO$_4$) 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 electrode dissolution) currents recorded on individual grains of polycrystalline Zn decreased in order $\{\bar{1}2\bar{1}0\} \geq \{01\bar{1}0\} \geq \{0001\}$. 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.

Acknowledgments

VS acknowledges financial support from the European Union’s Horizon 2020 research and innovation programme under grant agreement 792948 (NELMA). LY acknowledges funding support from the Engineering and Physical Sciences Research Council (EPSRC, U.K.). ED acknowledges Lubrizol Ltd. and the Warwick Collaborative Postgraduate Research Scheme for funding. CLB acknowledges financial support from the Ramsay Memorial Fellowship Trust. PRU gratefully acknowledges support from a Royal Society Wolfson Research Merit Award.

ORCID

V. Shkirskiy @ https://orcid.org/0000-0003-4289-9678
C. L. Bentley @ https://orcid.org/0000-0001-7867-6068
P. R. Unwin @ https://orcid.org/0000-0003-3106-2178

References

1. Y. Takahashi, A. Kumatani, H. Shiku, and T. Matsue, “Scanning probe microscopy for nanoscale electrochemical imaging.” Anal. Chem., 89, 342 (2017).
2. F. Andreotta and L. Fedrizzi, “The use of the electrochemical micro-cell for the investigation of corrosion phenomena.” Electrochim. Acta., 203, 337 (2016).
3. C. L. Bentley, J. Edmondson, G. N. Meloni, D. Perry, V. Shkirskiy, and P. R. Unwin, “Nanoscale electrochemical mapping.” Anal. Chem., 91, 4 (2019).
4. C. J. Park, M. M. Lohrengel, T. Hamelmann, M. Pilaski, and H. S. Kwon, “Grain-dependent passivation of surfaces of polycrystalline zinc.” Electrochim. Acta., 47, 3395 (2002).
5. M. M. Lohrengel, A. Moehring, and M. Pilaski, “Electrochemical surface analysis with the scanning droplet cell.” J. Anal. Chem., 367, 334 (2000).
6. H. Y. Ha, C. J. Park, and H. S. Kwon, “Effects of non-metallic inclusions on the initiation of pitting corrosion in 11% Cr ferritic stainless steel examined by micro-droplet cell.” Corros. Sci., 49, 1266 (2007).

Figure 4 (a) Zn–H binding energies from DFT (Eq. 1) and corresponding HER currents from Fig. 3. (b) Electrodeposition energies of a Zn monolayer normalized per atom from DFT (Eq. 2) and Zn dissolution currents from Fig. 3 for (0001), (1210) and (0110) 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.
11. J. W. Schultze and A. Bressel, “Electrochemical characteristics of intermetallic phases in aluminum alloys.” J. Electrochem. Soc., 152, B140 (2005).

10. J. M. Gregoire, C. Xiang, X. Liu, M. Marcin, and J. Jin, “Scanning droplet cell for high throughput electrochemical and photoelectrochemical measurements.” Rev. Sci. Instrum., 84, 025102 (2013).

14. A. W. Hassel and M. Seo, “Electrochemical and photoelectrochemical studies of the protective properties of ultra-thin films on zinc galvanized steel.” Surf. Coatings Technol., 228, 286 (2013).

19. J. Tsuji, K. I. Tamiya, and A. Nishikata, “Formation and growth of micro-droplets during the initial stage of atmospheric corrosion.” Electrochim. Acta., 49, 2709 (2004).

25. L. C. Yule, V. Shkirskiy, J. Aarons, G. West, B. A. Shollock, C. L. Bentley, and B. A. Shollock, “Nanoscale electrochemical visualization of the protective properties of ultra-thin films on zinc galvanized steel.” Surf. Coatings Technol., 228, 286 (2013).

28. P. R. Unwin, A. G. Güell, and G. Zhang, “Effect of grain size on corrosion.” Corros. Sci., 60, 10 (2010).

32. M. Kang, D. Momotenko, A. Page, D. Perry, and P. R. Unwin, “Soft-xray consistent pseudopotentials in a generalized eigenvalue formalism.” Phys. Rev. B., 41, 7892 (1990).

35. L. C. Yule, V. Shkirskiy, J. Aarons, G. West, B. A. Shollock, C. L. Bentley, and B. A. Shollock, “Nanoscale electrochemical visualization of the protective properties of ultra-thin films on zinc galvanized steel.” Surf. Coatings Technol., 228, 286 (2013).

36. C. H. Chen, K. E. Meadows, A. Cuharuc, S. C. S. Lai, and P. R. Unwin, “High resolution mapping of oxygen reduction reaction kinetics at polycrystalline platinum electrodes.” Phys. Chem. Chem. Phys., 16, 18545 (2014).

38. L. C. Yule, V. Shkirskiy, J. Aarons, G. West, B. A. Shollock, C. L. Bentley, and P. R. Unwin, “Nanoscale electrochemical visualization of grain-dependent anodic iron dissolution from low carbon steel.” Electrochim. Acta., 332, 153627 (2019).
67. H. J. Monkhorst and J. D. Pack, “Special points for Brillouin-zone integrations.” Phys. Rev. B., 13, 5188 (1976).
68. G. J. Martyna and M. E. Tuckerman, “A reciprocal space based method for treating long range interactions in ab initio and force-field-based calculations in clusters.” J. Chem. Phys., 110, 2810 (1999).
69. O. Andreussi, I. Dabo, and N. Marzari, “Revised self-consistent continuum solvation in electronic-structure calculations.” J. Chem. Phys., 136, 064102 (2012).
70. P. Giannozzi et al., “Advanced capabilities for materials modelling with Quantum Espresso.” J. Phys. Condens. Matter, 29, 465901 (2017).
71. K. Lejaeghere et al., “Reproducibility in density functional theory calculations of solids.” Science (80-.), 351, 5ad3000 (2016).
72. D. Vanderbilt and S. G. Louie, “Total energies of diamond (111) surface reconstructions by a linear combination of atomic orbitals method.” Phys. Rev. B., 30, 6118 (1984).
73. F. Trani, D. Ninno, G. Cantele, G. Iadonisi, K. Hameeuew, E. Degoli, and S. Ossicini, “Screening in semiconductor nanocrystals: Ab initio results and Thomas-Fermi theory.” Phys. Rev. B., 73, 245430 (2006).
74. J. Aarons, M. Sarwar, D. Thompsett, and C.-K. Skylaris, “Perspective: methods for large-scale density functional calculations on metallic systems.” J. Chem. Phys., 145, 220901 (2016).
75. P. Kratzer and J. Neugebauer, “The basics of electronic structure theory for periodic systems.” Front. Chem., 7, 106 (2019).
76. X. Zhang, B. Grabowski, F. Körnann, C. Freysoldt, and J. Neugebauer, “Accurate electronic free energies of the 3d, 4d, and 5d transition metals at high temperatures.” Phys. Rev. B., 95, 165126 (2017).
77. S. R. Billetter, A. J. Turner, and W. Thiel, “Linear scaling geometry optimisation and transition state search in hybrid delocalised internal coordinates.” Phys. Chem. Chem. Phys., 2, 2177 (2000).
78. T. Trivić, L. Gajić-Krstajić, N. Krstajić, and M. Vojnović, “On the kinetics of the hydrogen evolution reaction on zinc in sulfate solutions.” J. Serbian Chem. Soc., 66, 811 (2001).
79. S. Stankovic, B. Grgur, N. Krstajić, and M. Vojnović, “The kinetics of the hydrogen evolution reaction on zinc in EDTA solutions in the pH 3-10 range.” J. Electroanal. Chem., 549, 37 (2003).
80. T. Shinagawa, A. T. Garcia-Esparza, and K. Takenabe, “Insight on Tafel slopes from a microkinetic analysis of aqueous electrocatalysis for energy conversion.” Sci. Rep., 5, 1 (2015).
81. A. L. Barker, J. V. Macpherson, C. J. Slevin, and P. R. Unwin, “Scanning electrochemical microscopy (SECM) as a probe of transfer processes in two-phase systems: theory and experimental applications of SECM-induced transfer with arbitrary partition coefficients, diffusion coefficients, and interfacial kinetics.” J. Phys. Chem. B., 102, 1586 (1998).
82. X. L. Zhang, Z. H. Jiang, Z. P. Yao, Y. Song, and Z. D. Wu, “Effects of scan rate on the potentiodynamic polarization curve obtained to determine the Tafel slopes and corrosion current density.” Corros. Sci., 51, 581 (2009).
83. S. Trasatti, “Work function, electronegativity, and electrochemical behaviour of metals. III. electrolytic hydrogen evolution in acid solutions.” J. Electroanal. Chem., 39, 163 (1972).
84. L. Yan, Y. Sun, Y. Yamamoto, S. Kasamatsu, I. Hamada, and O. Sugino, “Hydrogen adsorption on Pt(111) revisited from random phase approximation.” J. Phys. Chem. B., 149, 164702 (2018).
85. A. Kolics and A. Wieckowski, “Adsorption of bisulfate and sulfate anions on a Pt (111) electrode.” J. Phys. Chem. B., 105, 2558 (2001).
86. A. C. Lasaga and A. Lüttge, “A model for crystal dissolution.” Eur. J. Mineral., 15, 603 (2003).
87. D. A. Sverjensky, “Linear free energy relations for predicting dissolution rates of solids.” Nature., 358, 310 (1992).