

Optimizing Amorphous Molybdenum Sulfide Thin Film Electrocatalysts: Trade-Off between Specific Activity and Microscopic Porosity

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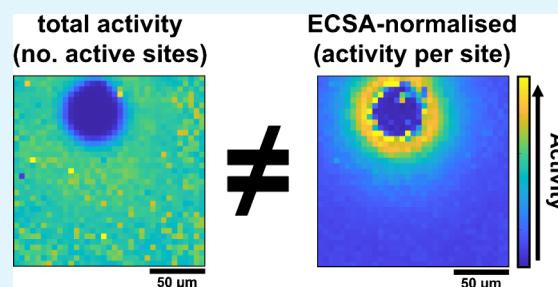
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ABSTRACT: Amorphous molybdenum sulfide (a-MoS_x) is a promising candidate to replace noble metals as electrocatalysts for the hydrogen evolution reaction (HER) in electrochemical water splitting. So far, understanding of the activity of a-MoS_x in relation to its physical (e.g., porosity) and chemical (e.g., Mo/S bonding environments) properties has mostly been derived from bulk electrochemical measurements, which provide limited information about electrode materials that possess microscopic structural heterogeneities. To overcome this limitation, herein, scanning electrochemical cell microscopy (SECCM) has been deployed to characterize the microscopic electrochemical activity of a-MoS_x thin films (ca. 200 nm thickness), which possess a significant three-dimensional structure (i.e., intrinsic porosity) when produced by electrodeposition. A novel two-step SECCM protocol is designed to quantitatively determine spatially resolved electrochemical activity and electrochemical surface area (ECSA) within a single, high-throughput measurement. It is shown for the first time that although the highest surface area (e.g., most porous) regions of the a-MoS_x film possess the highest total activity (measured by the electrochemical current), they do not possess the highest specific activity (measured by the ECSA-normalized current density). Instead, the areas of highest specific activity are localized at/around circular structures, coined “pockmarks”, which are tens to hundreds of micrometers in size and ubiquitous to a-MoS_x films produced by electrodeposition. By coupling this technique with structural and elemental composition analysis techniques (scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy) and correlating ECSA with activity and specific activity across SECCM scans, this work furthers the understanding of structure–activity relations in a-MoS_x and highlights the importance of local measurements for the systematic and rational design of thin film catalyst materials.

KEYWORDS: scanning electrochemical cell microscopy, SECCM, electrocatalysis, hydrogen evolution reaction, HER, molybdenum disulfide, MoS₂



INTRODUCTION

Hydrogen (H₂) production is essential in the modern world, serving as a critical component in many industrial processes.^{1,2} As global efforts toward a sustainable future have increased, hydrogen's use has extended into a promising fossil fuel replacement; however, its production is still dominated by the steam reforming of fossil fuels.^{2–4} Water electrolysis and photoelectrochemical water splitting are promising alternatives to produce green hydrogen, both utilizing hydrogen evolution reaction (HER) catalysts on the (photo)cathode to boost performance.^{4–6} Platinum is the most effective HER catalyst,^{6,7} particularly in acidic media; however, its rarity and cost have led to extensive research into competitive earth-abundant alternatives. Crystalline molybdenum disulfide (MoS₂) is a leading nonprecious metal candidate,^{8–10} but its synthesis often requires difficult and expensive conditions including

ultrahigh vacuum, high temperatures, and a corrosive/toxic H₂S precursor.^{11,12}

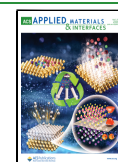
Amorphous molybdenum sulfide (a-MoS_x) is faster, easier, and cheaper to produce, using electrodeposition of a [MoS₄]^{2–} precursor at ambient temperatures and pressures to synthesize catalytically active thin films adhered to a range of possible (semi)conductive substrates.^{11–13} a-MoS_x films show high catalytic activities and long-term stability under high catalytic turnover in acidic media, a particularly attractive property for use with commonly unstable cathode materials, acting as a

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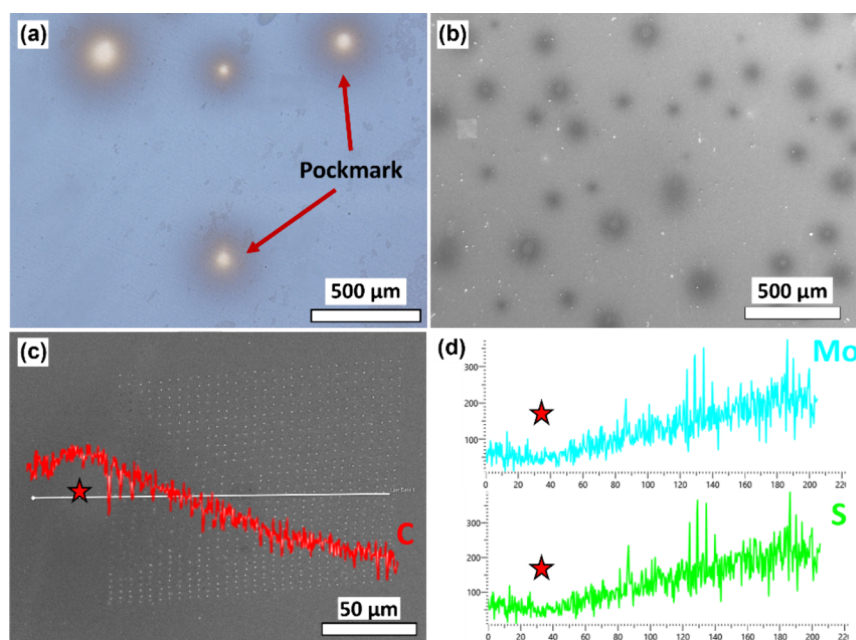


Figure 1. (a) Optical image of the as-deposited a-MoS_x thin film. (b) SEM image of the pockmarked a-MoS_x thin film surface. (c) SEM image of a pockmark and residues from an SECCM scan, overlay: (red line) carbon linescan signal measured by EDX, (red star) center of the pockmark. (d) Mo and S signals from the same EDX linescan measurement, with red stars at the *x* position of the pockmark center, as marked in panel c.

dual-function protective coating and electrocatalyst layer.^{14–16} The suitability of production via scalable coating methods that can be tuned by deposition conditions and supporting working electrode nanostructures makes a-MoS_x an ideal candidate for large-scale HER catalysis.^{17,18}

Despite the great promise of a-MoS_x, the origin of its high catalytic activity, as well as the structure–activity relations and surface spatial heterogeneity of a-MoS_x, is underexplored.^{17,19–21} In fact, the exact structure of a-MoS_x—and therefore the possible bonding environments of the S atoms—is still under debate.²² Experimental and theoretical studies have identified that the HER activity of a-MoS_x samples is intimately linked to the S types present, making this information vital to aid in the systematic design of high-performance a-MoS_x catalysts.^{23–27} Further, there is a consensus within the literature that thicker a-MoS_x films show higher activity; however, such measurements are taken macroscopically only and have not been fully rationalized.^{17,18}

Scanning electrochemical cell microscopy (SECCM) is an emerging technique for characterizing the structure–activity relationships of functional electromaterials.^{28–31} In SECCM, a local electrochemical cell is formed when the meniscus (droplet) protruding from the end of an electrolyte-filled micro/nanopipette tip is contacted with the surface of a suitable working electrode (WE).³² In this way, electrochemical measurements can therefore be performed at nanoscale locations within a confined area.³³ Scanning a grid of such measurements produces electrochemical maps and/or movies that can be compared with colocated structural or morphological information to reveal how local electrochemical properties relate to structure, for example, in catalytic thin films,^{20,34} nanoparticles,^{19,35} photoactive semiconductors,^{36,37} battery materials,³⁸ and polycrystalline metals, in the context of catalysis³⁹ and corrosion.^{40–42}

To date, SECCM is most commonly used on relatively flat (nonporous) surfaces, where the area of surface residue left behind after each measurement (termed the meniscus or

droplet “footprint”) is representative of the working area of the electrochemical cell, and can be used to convert the measured currents to (geometric) current densities.^{32,43} Indeed, this approach has been used to great success to characterize the HER activity of 2H-MoS₂ and related crystalline transition metal dichalcogenides.^{20,44–47} However, as alluded to above, a-MoS_x is often deployed with greater relative thickness than 2H-MoS₂, and as a result, it may possess significant porosity. When porosity is introduced, the two-dimensional “footprint” approach outlined above is no longer accurate because of the additional wetting dimension of the electrochemical cell into the film during measurement. Under these conditions, it is difficult to quantify the area of measurement and thus estimate the specific activity (related to surface area-normalized current density), although a semiquantitative approach was recently proposed in an SECCM study on thin (<15 nm), featureless, topographically flat films of a-MoS_x.¹⁷

Herein, a new SECCM scanning protocol is developed and applied to a porous, high surface area a-MoS_x thin film (~200 nm in thickness) to quantitatively measure and compare local porosity–activity relationships across a structurally heterogeneous surface. It is shown for the first time that although the highest surface area (e.g., most porous) regions of the a-MoS_x film possess the highest total activity (measured by the current), they do not possess the highest specific activity (measured by the surface area-normalized current density). Instead, the areas of highest specific activity are localized at/around circular structures, coined “pockmarks”, which are 10s to 100s μm in size and are ubiquitous to a-MoS_x films produced by electrodeposition. Expansion of SECCM applications to include highly nanostructured and porous materials is key to realizing its full potential as a characterization tool in (electro)materials development.

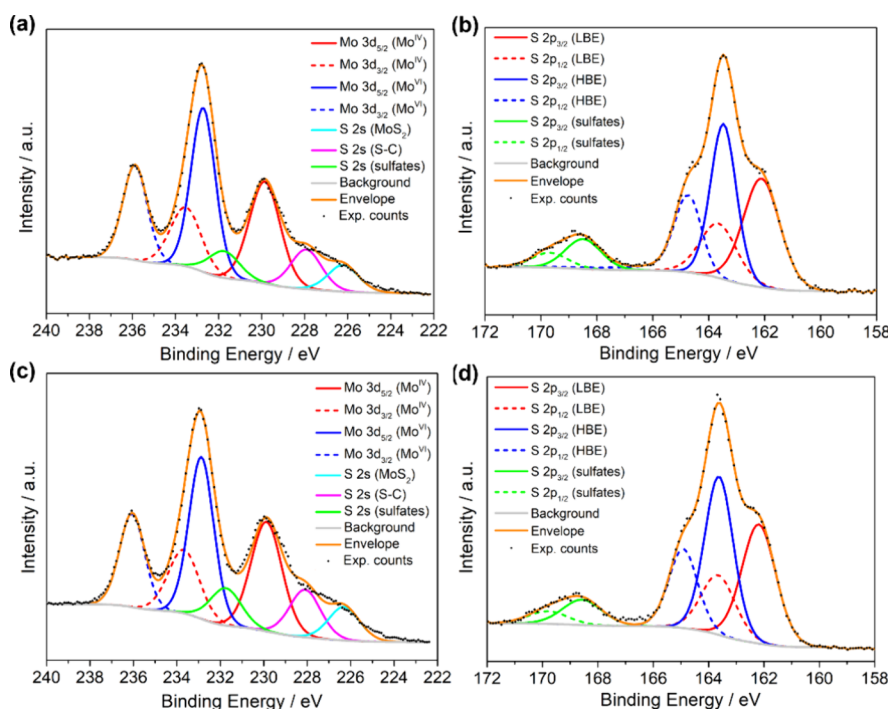


Figure 2. High-resolution XPS spectra of an a-MoS_x thin film electrode for a nonpockmarked area: (a) Mo 3d and (b) S 2p and pockmarked area: (c) Mo 3d and (d) S 2p.

RESULTS AND DISCUSSION

Physical Characterization of a-MoS_x Thin Films. a-MoS_x thin films were fabricated by electrodeposition onto a macroscopic glassy carbon (GC) electrode using a method modified from a previous report (Supporting Information (SI), Figure S1).¹⁷ Preliminary studies (not shown) demonstrated that the film deposition parameters (e.g., oxidative/reductive limits, number of voltammetric cycles, precursor concentration) all affected the macroscopic activity of the deposited a-MoS_x films, in agreement with previous reports.^{13,17,18} Herein, a protocol of 30 cycles sweeping between −1.2 and 0.1 V vs Ag/AgCl (3.4 M KCl) at a scan rate of 50 mV s^{−1}, with an 8 mM [(NH₄)₂MoS₄] precursor and 0.1 M LiClO₄ supporting electrolyte solution, was settled upon for further study.

The protocol described above produces a-MoS_x films of ~200 nm thickness (measured using SECCM, see SI, Figure S2), which, as shown in Figure 1a, were superficially “flat” and contained circular blemishes across the otherwise homogeneous surface, herein denoted as “pockmarks”. Pockmarks formed consistently with varying distributions in all of the repeated depositions. The pockmark formation must therefore be intrinsic to the film growth, possibly as a result of H₂ bubble formation during deposition, and not simply due to an unclean or rough GC surface. Scanning electron microscopy (SEM) images of the sample confirm the visibility of pockmarks under both optical and electron microscopy (Figure 1b), and energy dispersive X-ray spectroscopy (EDX), measured as a linescan across a single pockmark, revealed increasing C content and decreasing Mo/S content toward the pockmark center followed by the reverse effect away from the center (Figure 1c,d). This observation suggests a thinning and/or decreasing density of the film at the pockmark, revealing more of the underlying GC substrate. Note that there were no identifiable Mo/S elemental ratio variations between the pockmarked and nonpockmarked areas at the sensitivity of EDX.

To further investigate possible chemical (i.e., composition and/or structure) variations, X-ray photoelectron spectroscopy (XPS) analysis was employed to characterize both non-pockmarked and pockmarked areas (Figure 2a,b and c,d, respectively). Note that this a-MoS_x thin film sample had previously been used for SECCM scanning (*vide infra*). All peak positions and relative abundances can be found in the SI (Table S1). Survey spectra, C 1s spectra, and O 1s spectra are also presented in the SI (Figure S3). For the Mo 3d spectra (Figure 2a,c), the signals arising from Mo^{IV} (~229.9 eV (3d_{5/2}) and ~233.5 eV (3d_{3/2})) represent MoS₂ and MoS₃, which make up the a-MoS_x film as shown in eqs S1 and S2. Note that it has been identified by previous reports that all Mo centers within MoS₃ occur in the 4+ oxidation state, with a composition corresponding to Mo^{IV}(S^{2−})(S₂^{2−}).^{11,18,48,49} Mo^{VI} signals (~232.8 eV (3d_{5/2}) and ~236.0 eV (3d_{3/2})) therefore originate from surface MoO₃, revealing that significant surface oxidation has occurred (Mo^{IV}/Mo^{VI} ratio of 0.79 and 0.84 for nonpockmarked and pockmarked areas, respectively) from passive air exposure and/or SECCM measurements.^{11,18} Evidence of MoO₃ is also present as a signal in the O 1s spectra (~530.8 eV, Figure S3b,e). Previous studies have shown that S 2p signals from XPS analysis remain relatively unaffected from surface oxidation.^{11,18} In Figure 2c,d, S 2p signals are denoted as low binding energy (LBE, ~162.2 eV (2p_{3/2}) and ~163.7 eV (2p_{1/2})), representing unsaturated S^{2−} and/or terminal S₂^{2−}, or high binding energy (HBE, ~163.5 eV (2p_{3/2}) and ~164.9 eV (2p_{1/2})), for apical S^{2−} and/or bridging S₂^{2−}.⁴¹ Distinguishing between the two types of S present at each BE is difficult.⁵⁰ Surface sulfates are also present (~168.5 eV (2p_{3/2}) and ~169.8 eV (2p_{1/2})), consistent with a partially oxidized a-MoS_x surface.^{11,18}

Overall comparison of XPS spectra for the nonpockmarked and pockmarked areas shows little variation in the surface chemical structures and compositions. Linking the surface

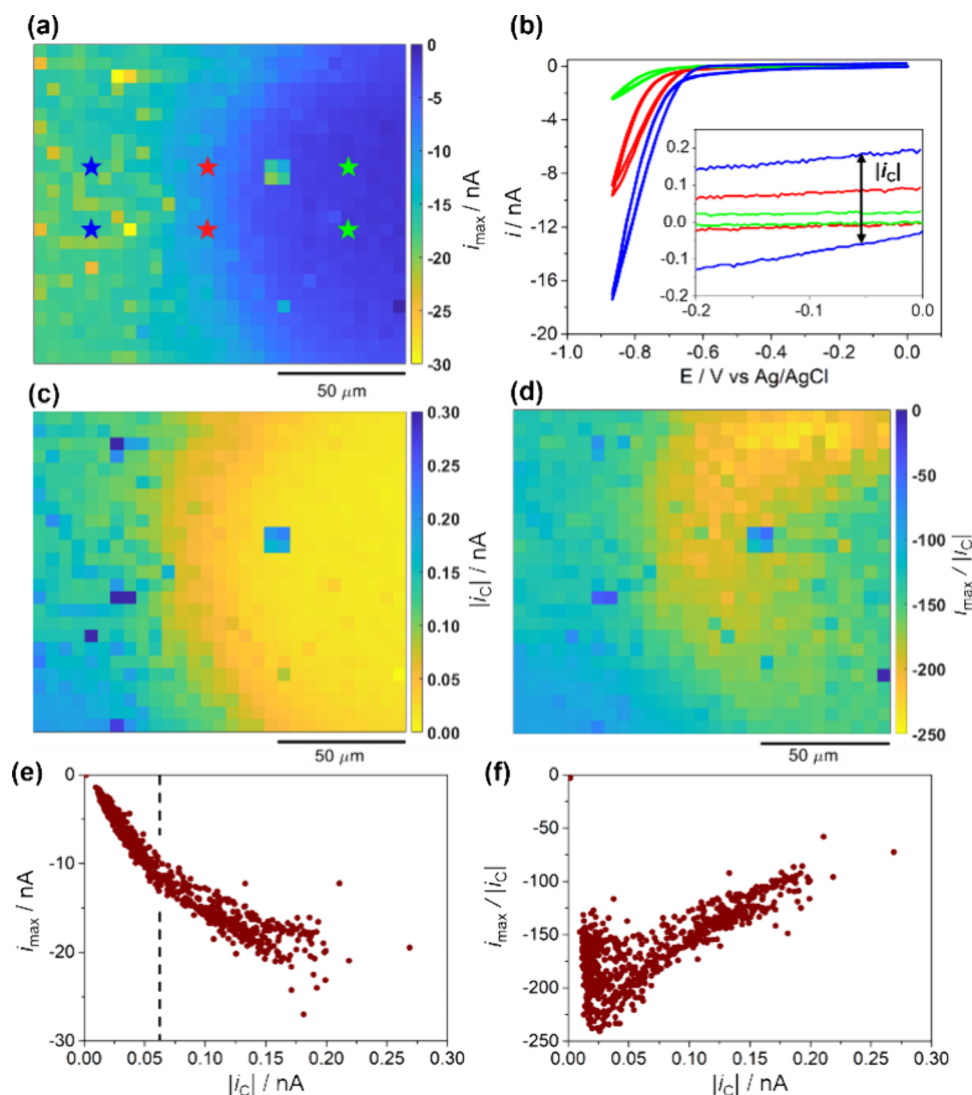


Figure 3. (a) Max electrochemical activity ($i_{\max}$) map (extracted at -0.87 V vs Ag/AgCl from Movie S1) recorded in a 31×26 pixel grid ($5 \mu\text{m}$ hopping distance), with approximately half the scan covering a pockmarked region (low activity region on the right) of the a-MoS_x film. (b) CVs from pixels in panel a, correspondingly marked with green, red, or blue stars; inset shows a zoomed view of the nonfaradaic regions and the measurement of $|i_c|$. (c) $|i_c|$ map. (d) Surface area-normalized activity map ($i_{\max}/|i_c|$, unitless). Plots of (e) $i_{\max}$ vs $|i_c|$ and (f) $i_{\max}/|i_c|$ vs $|i_c|$. Note that in panels e and f, each point represents a single pixel shown in panels a, c, and d.

structure analysis here with the morphology and elemental analyses within Figure 1, pockmarks are concluded to be ubiquitous and present chemical structures and compositions similar to those of the rest of the electrodeposited a-MoS_x film.

Semiquantitative Specific Activity Analysis with Standard Voltammetric Hopping Mode SECCM.

SECCM was deployed in voltammetric hopping mode to probe the local electrocatalytic activity of the as-prepared porous a-MoS_x thin film for the HER. Operational principles and detailed experimental conditions for SECCM can be found in the Experimental Section. Initial SECCM scans were taken over a pockmarked area with a standard cyclic voltammetric hopping mode protocol⁵¹ to produce a spatially resolved electrochemical movie, as shown in SI, Movie S1. The electrochemical current–potential (i – E) data were then used to construct a map of maximum catalytic current ($i_{\max}$; i.e., the current corresponding to a potential of -0.87 V vs Ag/AgCl, the cathodic limit of CVs), as shown in Figure 3a. Note that the $i_{\max}$ values appear to be exceptionally high for the used

probe diameter; i.e., -16 nA corresponds to a geometric current density of ~ 2 A cm⁻², normalized to a probe tip area of $\sim 0.8 \mu\text{m}^2$. It is important to note that SECCM does not suffer from bubble (H₂) formation due to efficient gas transport across the gas/liquid/solid three-phase interface, and therefore, complications usually associated with such high current densities are not present here.⁵² Given that the films are superficially flat (e.g., Figure 1a,b), the high geometric current density values are indicative of a highly porous, high electrochemical surface area (ECSA) a-MoS_x morphology, explored in detail below.

Consulting Figure 3a, $i_{\max}$ values decrease from ca. -16 to -2 nA from the nonpockmarked (yellow) to pockmarked (dark blue) area, indicating decreased apparent activity within the pockmark, the same conclusion that would be reached through conventional macroscopic (bulk) electrochemical measurements if the pockmark structure was able to be isolated. However, because the film possesses significant porosity (*vide infra*), it is important to analyze the specific

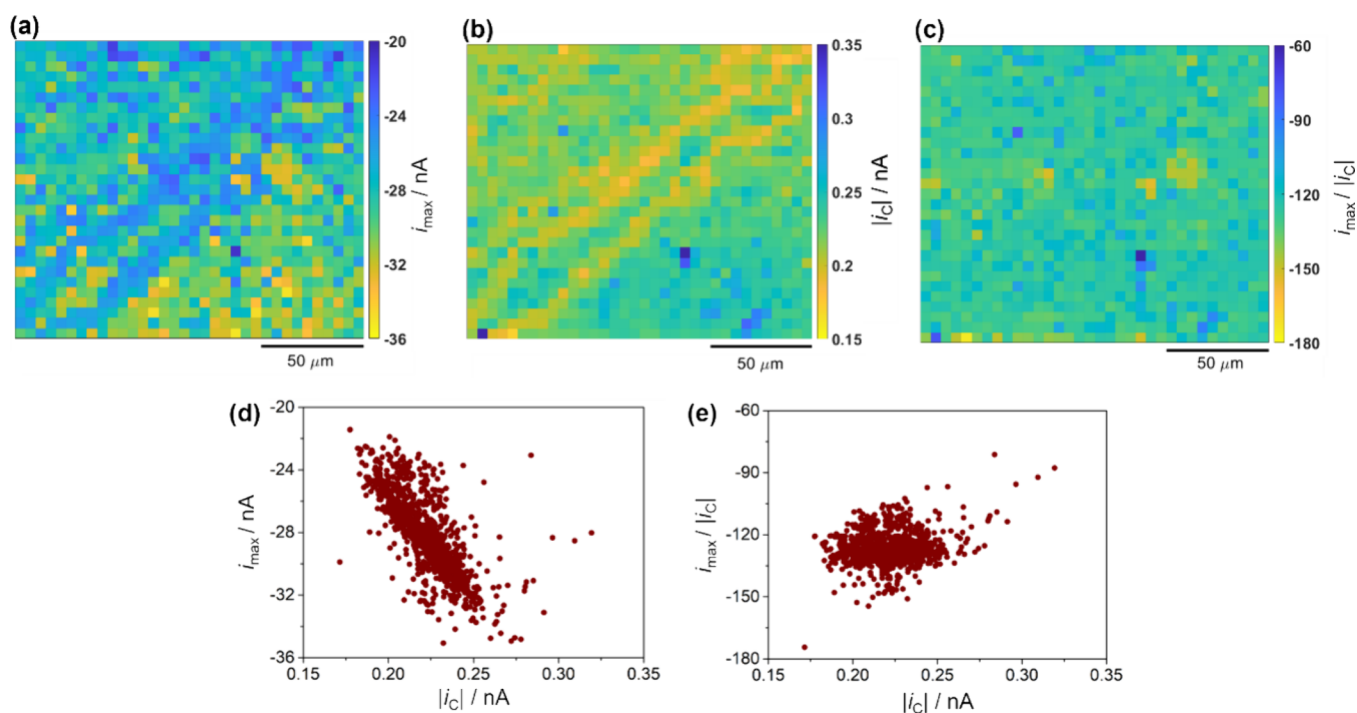


Figure 4. (a) Max electrochemical activity ($i_{\max}$) map (extracted at -0.87 V vs Ag/AgCl from Movie S3) recorded in a 36×36 pixel grid ($5 \mu\text{m}$ hopping distance) across a nonpockmarked region of the a-MoS_x film. (b) $|i_C|$ map. (c) Surface area-normalized activity map ($i_{\max}/|i_C|$, unitless). Plots of (d) $i_{\max}$ vs $|i_C|$ and (e) $i_{\max}/|i_C|$ vs $|i_C|$. Note that in panels d and e, each point represents a single pixel shown in panels a, b, and c.

activity (i.e., activity per site, indicated by the surface area-normalized current density, j) instead of the total activity of all sites (i.e., indicated by the measured current, i) within the SECCM meniscus cell. Figure 3b presents representative individual cyclic voltammograms (CVs) extracted from the indicated pixels, which also clearly exhibit a decreasing catalytic current from nonpockmarked to outer pockmarked to inner pockmarked regions. In fact, the CVs exhibit an increased current magnitude from pockmarked to nonpockmarked areas across the entire potential range, including in the potential regions where only nonfaradaic current is flowing (e.g., 0 to -0.2 V vs Ag/AgCl; details on the reference electrode used herein are available in the Experimental Section).

In this potential region, the capacitive current (termed $|i_C|$ herein, see Figure 3b) can be measured,⁵³ which is proportional to the ECSA of the a-MoS_x thin film, and can therefore be used as a surface area normalization parameter. The value of $|i_C|$, extracted for every pixel in the scan at -0.05 V vs Ag/AgCl (Figure 3c), shows the same pattern of reactivity as the HER catalytic current; i.e., there is a gradual decrease of $|i_C|$ crossing from the nonpockmarked to pockmarked area. In principle, $|i_C|$ can be converted into ECSA through a known specific capacitance value (i.e., $60 \mu\text{F cm}^{-2}$ for an atomically smooth MoS₂ surface, previously reported⁵⁴). However, such an approach assumes that the electrical double layer behaves as an ideal capacitor (i.e., $|i_C| \propto \nu$, where ν = voltammetric scan rate, and approaches 0 A at $\nu = 0 \text{ V s}^{-1}$), which is often not the case. This limitation will be overcome by performing measurements at many different ν values, as discussed below, but for now, $|i_C|$ will be treated as a semiquantitative normalization factor for the ECSA.

Division of the current (e.g., $i_{\max}$) by $|i_C|$ for all pixels across the scan, representing normalizing a measured current with the ECSA, yields a semiquantitative, unitless, specific electro-

chemical activity map, as shown in Figure 3d (extracted from Movie S2). Interestingly, normalizing the current in this way causes a switching of the highest activity regions. The pockmark, particularly the outer region, now consistently exhibits the most negative $i_{\max}/|i_C|$ values, signifying greater HER activity, on a per-site basis. This is a significant finding and is thought to arise from either of the following two possibilities: (i) The nonpockmarked areas of the a-MoS_x film are more porous and therefore exhibit greater $i_{\max}$ values due to the significantly greater number of active sites accessed during each local SECCM measurement; however the pockmarked region, while appearing to be less active on a total measured current basis, contains active sites with a greater activity per-site, possibly due to a difference in the a-MoS_x structure and/or elemental composition. From Figures 1 (EDX) and 2 (XPS) previously discussed, the elemental composition (Mo/S ratio) of the amorphous (i.e., no long-range order) a-MoS_x is relatively constant, and the surface chemistry of the two regions has little variation. Additionally, a previous correlative SECCM/XPS study by Bentley et al.¹⁷ on a thinner (<15 nm), featureless, topographically flat a-MoS_x film showed no substantial evidence for a spatially dependent chemical structure. It is therefore unlikely that there are any microscopic structural or compositional variations within the two areas that would change the activity per site to cause this spatially heterogeneous catalytic activity observation. (ii) The per-site activities of the two regions are identical; however, the high porosity of nonpockmarked a-MoS_x leads to mass transport limitations arising from high proton (H^+) consumption within the porous structure, which cannot be readily replenished because of the high tortuosity of the structure. Another possibility is the buildup of gaseous H_2 arising from restricted removal of catalysis product within the highly developed film, which blocks active sites and prevents the full utilization of the

ECSA for HER catalysis. In either case, sites buried deep in the film (i.e., near the GC/a-MoS_x interface) become limited by the availability of H⁺ and/or the buildup of H₂ product, and as a result, an apparent per-site activity lower than the true value is measured.

A plot of $i_{\max}$ against $|i_{\text{cl}}|$ for all pixels within the SECCM scan, shown in Figure 3e, demonstrates how a-MoS_x film utilization changes with ECSA. Two distinct linear regions are seen in the plot (marked with a dashed line), indicating the presence of two distinct behaviors within the film, corresponding to nonpockmarked and pockmarked areas. The linear region at lower $|i_{\text{cl}}|$ values (i.e., $|i_{\text{cl}}| < 0.06$ nA) represents the pockmarked area, with a steeper gradient signifying a greater ability to utilize its ECSA for electrocatalysis and therefore higher specific activity (i.e., a-MoS_x has greater activity gain with increasing ECSA). Conversely, at higher $|i_{\text{cl}}|$ values (i.e., $|i_{\text{cl}}| > 0.06$ nA), representing the nonpockmarked areas, there are less correlation with $|i_{\text{cl}}|$ and a shallower gradient, demonstrating a diminished ability of the film to utilize its ECSA for HER electrocatalysis. Interestingly, the two linear regions switch at a distinct point of ca. $|i_{\text{cl}}| \approx 0.06$ nA, which, when comparing to the $|i_{\text{cl}}|$ map in Figure 3c, occurs within the outer regions of the pockmarked area (i.e., where the $i_{\max}/|i_{\text{cl}}|$ values are largest in magnitude, Figure 3d).

Another way to demonstrate the diminishing specific activity with increasing ECSA is to plot $i_{\max}/|i_{\text{cl}}|$ vs $|i_{\text{cl}}|$, as shown in Figure 3f. This plot interestingly reveals a volcano-type relationship that peaks at an $|i_{\text{cl}}|$ value of ca. 0.02 nA, at which point the apparent specific activity is the highest. Below the peak $|i_{\text{cl}}|$ value, the specific activity appears to rapidly fall off with decreasing $|i_{\text{cl}}|$ (i.e., steep slope), which may be due to the a-MoS_x film becoming too thin and (eventually) approaching the behavior of the catalytically inactive GC support (*vide infra*). Above the peak $|i_{\text{cl}}|$ value, the specific activity falls off more gently (i.e., shallow slope), again signifying a decreasing ability of a-MoS_x to utilize its ECSA for HER electrocatalysis, likely due to the tortuous nature of the porous film. Such a “sweet spot” between specific activity and ECSA has rarely been reported and is critically important to maximize material utilization in thin film electrodes for electrocatalytic water splitting and beyond (explored below).

To understand whether the specific activity vs ECSA trends are unique to the pockmarked areas of a-MoS_x or are generally applicable, an analogous scan was carried out on an entirely nonpockmarked area of the film, as shown in Movie S3. The electrochemical i - E data were then used to construct the map of $i_{\max}$ shown in Figure 4a. It is important to note that the overall activity varies from film-to-film and even from area-to-area on a given a-MoS_x thin film. Thus, although the magnitudes of the measured currents may vary between individual scan areas, it is the trends within a given scan area that are important, as discussed below.

Consulting Figure 4a, it is clear that even the nonpockmarked areas of the a-MoS_x are not uniformly active, consistent with a previous study,¹⁷ with distinct areas of low (top-left) and high (bottom-right) activity separated by two diagonal lines of low activity running from bottom-left to top-right. Comparing Figure 4a to the corresponding $|i_{\text{cl}}|$ map, Figure 4b, demonstrates that the lower activity regions do indeed coincide with the areas of lower ECSAs (i.e., lower $|i_{\text{cl}}|$ values). Unlike the pockmarked area above (Figure 3) however, these inhomogeneities seemingly vanish upon surface area normalization, as shown in the $i_{\max}/|i_{\text{cl}}|$ map shown in

Figure 4c (extracted from Movie S4). A plot of $i_{\max}$ vs $|i_{\text{cl}}|$, Figure 4d, reveals a linear relationship, this time with a single region (slope), consistent with the nonpockmarked area of the scan shown in Figure 3, as the $|i_{\text{cl}}|$ values are well above the high/low specific activity threshold value of ~ 0.06 nA identified in Figure 3e. A plot of $i_{\max}/|i_{\text{cl}}|$ vs $|i_{\text{cl}}|$, Figure 4d, reveals a relatively concentrated cluster of values with no overall trend, centered between $i_{\max}/|i_{\text{cl}}|$ values of -100 to -150 and $|i_{\text{cl}}|$ values 0.18 to 0.26 nA (i.e., corresponding to the “flattening” region of Figure 3f), as expected for an area of the surface only containing sites with relatively equal specific activities.

Overall, the results in Figures 3 and 4 highlight that local differences in the overall activity of the a-MoS_x film can be largely explained by differences in the ECSA based on the relationship of $i_{\max}$ with $|i_{\text{cl}}|$ (i.e., larger $|i_{\text{cl}}|$ = larger ECSA = more active sites = higher overall activity). To further illustrate this point, mean and relative standard deviation (RSD) values for $i_{\max}$, before and after surface area normalization, are reported in Figure 5. In both Figures 3 and 4, the RSD values

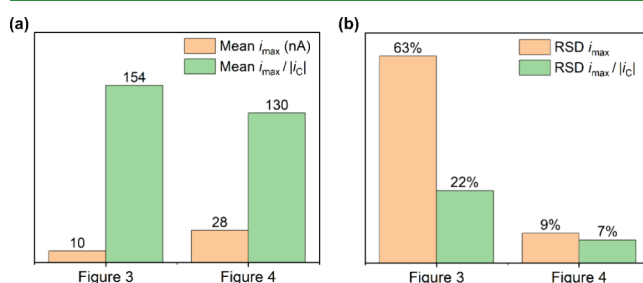


Figure 5. (a) Mean $i_{\max}$ values (reported as absolute $i_{\max}$) and (b) relative standard deviation (RSD) for data from scans presented in Figure 3 (an area with a pockmark) and Figure 4 (a nonpockmarked area).

are significantly reduced after normalization because of the mitigation of any inhomogeneity in ECSA across the film, which effectively “blends” the unique surface features. Figure 3, which contains a pockmark, exhibits much higher RSD values than Figure 4, which does not contain a pockmark, both before (63 vs 9%) and after (22 vs 7%) normalization, as expected when two different specific activity regimes are present. The switching of the highest (specific) activity regions after normalization is also evident in the mean values; the nonpockmarked scan (Figure 4) possesses a greater mean $i_{\max}$ value initially (-28 vs -10 nA) due to the increased higher total activity of the nonpockmarked area but a lower mean $i_{\max}/|i_{\text{cl}}|$ value after normalization (-130 vs -154) due to the lower activity per site (specific activity).

Calculating Local ECSA and Catalytic Activity with a Scanning Protocol. As alluded to above, the ECSA can be calculated from $|i_{\text{cl}}|$ and a known specific capacitance (C_s) value via the following relationships:

$$C_{\text{DL}} = \frac{|i_{\text{cl}}|}{2\nu} \quad (1)$$

$$\text{ECSA} = \frac{C_{\text{DL}}}{C_s} \quad (2)$$

where C_{DL} is the double layer capacitance. Performing this conversion from a single measurement point is strictly only possible if the electrical double layer behaves as an ideal

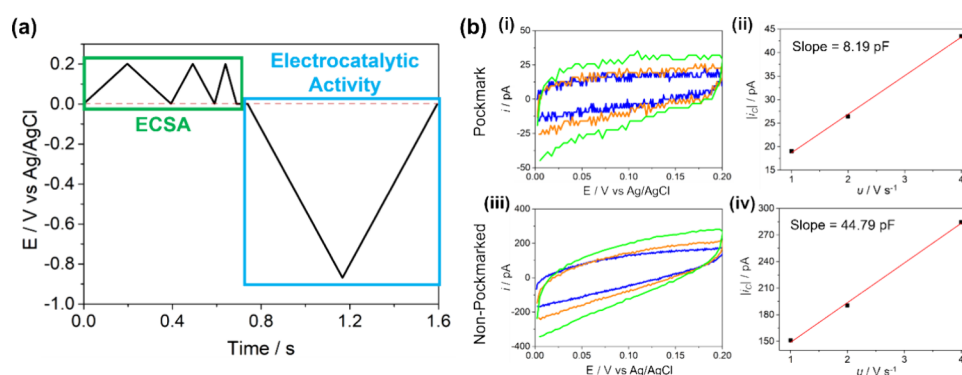


Figure 6. (a) Program design used for data collection for both ECSA and catalytic activity characterization in a single SECCM hop measurement. (b) ECSA data collection and calculation for pixels on (i, ii) and off (iii, iv) a pockmark, containing cyclic voltammograms from three different scan rates (1, 2, and 4 V s⁻¹) in the nonfaradaic potential range 0 to 0.2 V vs Ag/AgCl (i, iii) and the subsequent $li_c|$ vs v plots where the double layer capacitance is calculated quantitatively from the slope of the linear regression line (ii, iv).

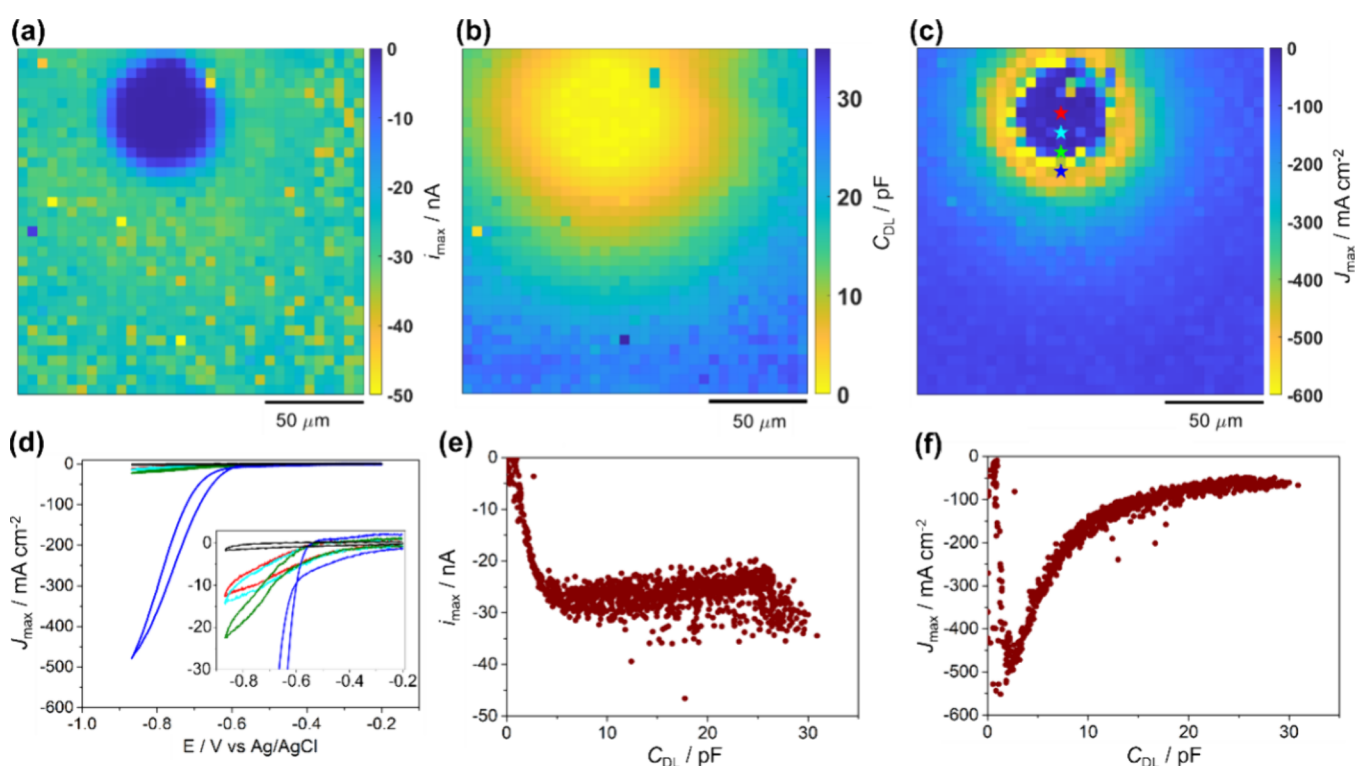


Figure 7. (a) Max electrochemical activity ($i_{\max}$) map (extracted at -0.87 V vs Ag/AgCl from Movie S5) recorded in a 35×35 pixel grid ($5 \mu\text{m}$ hopping distance) partially covering a pockmark (low activity region at top). (b) Double layer capacitance (C_{DL}) map. (c) Max surface area-normalized current density map ($J_{\max}$). (d) Representative CVs starting inside the outer pock region and toward the center of the pockmark (marked by color-matched stars on panel c). Black CV represents an identical measurement taken on pristine GC. Plots of (e) $i_{\max}$ vs C_{DL} and (f) $J_{\max}$ vs C_{DL} . Note that in panels e and f, each point represents a single pixel shown in panels a, c, and d.

capacitor (i.e., $li_c|$ approaches 0 A at 0 V s⁻¹), which is rarely observed in practice.^{55,56} To overcome this limitation, it is commonplace to take a series of i - E measurements at different v values and then estimate C_{DL} from the slope of a $li_c|$ vs v plot, as per eq 1. In this way, any nonidealities can potentially be identified (e.g., a nonlinear $li_c|$ vs v plot) or ignored (e.g., a nonzero intercept, where $li_c| = 2C_{\text{DL}} \cdot v + \text{constant}$).

With these considerations in mind, a new SECCM protocol was designed to obtain quantitative data using a true ECSA measurement instead of $li_c|$, the E - t waveform of which is shown in Figure 6a. During each hop of the SECCM experiment, the E - t waveform includes an ECSA measurement component (shown in green) in addition to the

electrocatalytic activity component (shown in light blue). All measurements must occur on a “per-hop” basis (i.e., without retraction of the probe tip between the ECSA and electrocatalytic activity components); thus, high v values were used to avoid prolonged scan times. ECSA is calculated by plotting $li_c|$, measured from CVs in a potential range where only nonfaradaic processes occur, versus v , as per eqs 1 and 2.

The ECSA component therefore must include a minimum of three distinct CVs, spanning exclusively a potential range where no faradaic processes occur (0 to 0.2 V vs Ag/AgCl, herein) and each with a different v (1, 2, and 4 V s⁻¹, herein). Following a short equilibration time (25 ms, herein), the electrocatalytic activity scan then takes place over the

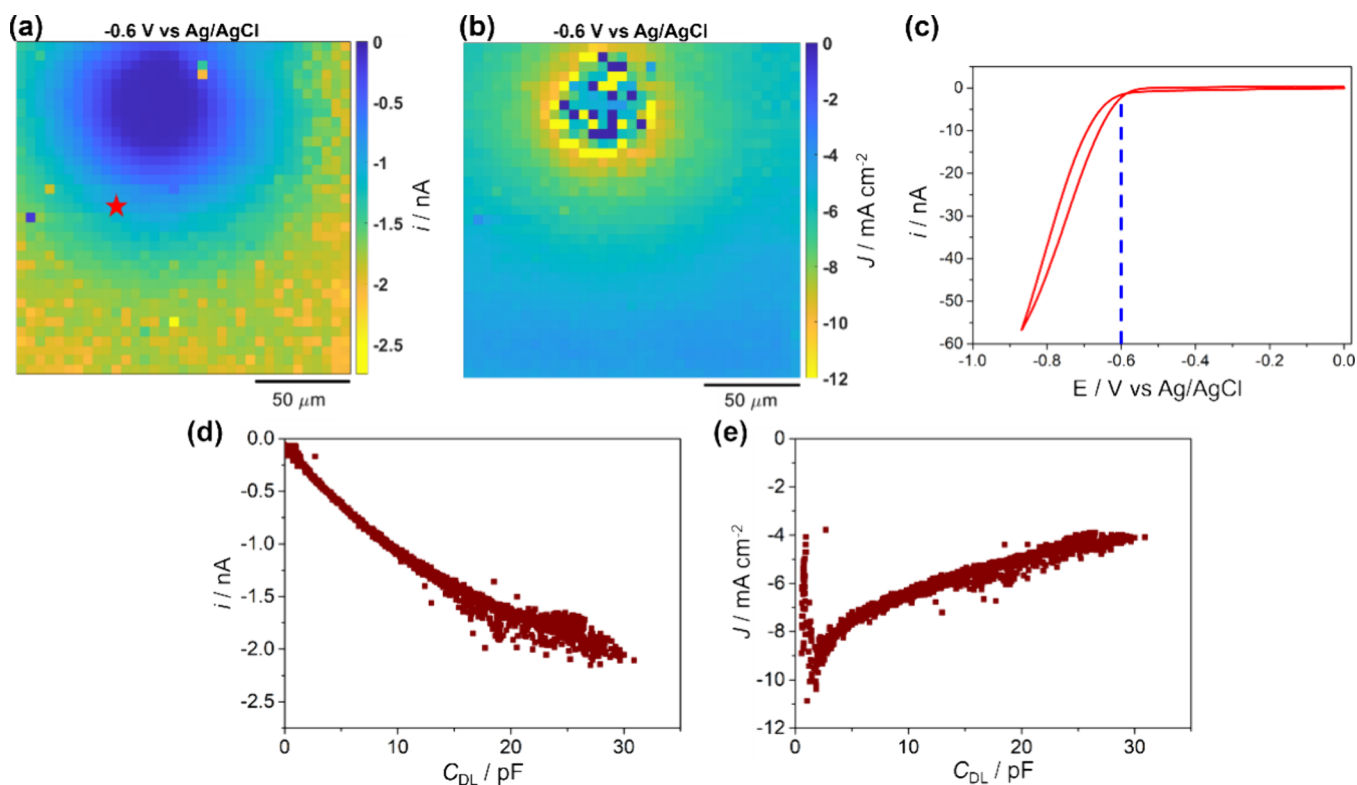


Figure 8. (a) Electrochemical activity (i) map extracted at -0.6 V vs Ag/AgCl from Movie S5; the same scan as in Figure 7. (b) Surface area-normalized current density (J) map extracted at -0.6 V vs Ag/AgCl from Movie S6. (c) CV from one pixel within the scan (marked with a red star). The blue dashed line identifies HER onset. Plots of (d) i vs C_{DL} and (e) J vs C_{DL} . Note that in panels d and e, each point represents a single pixel shown in panels a and b and Figure 7b.

appropriate range of potentials (0 to -0.87 V vs Ag/AgCl, herein) before tip retraction and movement to the next “hop” of the scan. In this way, electrochemical maps and movies of i , C_{DL} , and surface area-normalized current density (J) can then be produced by using the data from a single SECCM scan (i.e., $J = i/\text{ECSA}$). Figure 6b presents the ECSA measurements (i.e., CV and corresponding plot of $|i_c|$ vs v) from two individual hops of an SECCM scan obtained from pockmarked and nonpockmarked areas of the a-MoS_x thin film. The CVs obtained from both areas exhibit excellent signal-to-noise ratios and strong linear correlations between $|i_c|$ vs v (r^2 values of 0.998 and 0.996 in the pockmarked and nonpockmarked areas, respectively). From the slopes of 8.2 and 44.8 pA·s V⁻¹ (pF), C_{DL} values of 4.1 and 22.4 pF are calculated, corresponding to ECSA values of 6.8 and 37 μm^2 , respectively.⁵⁴ Note that these ECSA values are significantly larger than the geometric area of the tip of the used probe ($\sim 0.8 \mu\text{m}^2$) and, given the superficially flat appearance of the films (e.g., Figure 1a,b), must reflect the high porosity of electrodeposited a-MoS_x (i.e., roughness factor, $\text{RF} = A_{\text{ECSA}}/A_{\text{geometric}} = 9$ on the pockmarked region and 47 on the nonpockmarked region, where A = area). For comparison, an analogous protocol was performed in bulk with a macroscopic a-MoS_x/GC electrode, as shown in Figure S4.

Quantitative Specific Activity Analysis with the New ECSA/Electrocatalytic Activity Protocol. The new SECCM protocol was used to quantify the relationship between ECSA and HER electrocatalytic activity on a pockmarked area of a-MoS_x. An electrochemical movie of the electrocatalytic component of the experiment (Figure 6a, light blue box), an optical image of the SECCM scan area, and SEM images of

scanned nonpockmarked and pockmarked regions are shown in the SI (Movie S5 and Figures S5a and S6, respectively). The electrochemical i – E data were then used to construct the map of i_{max} shown in Figure 7a. In agreement with Figure 3 above, the pockmarked region exhibits significantly less “apparent” electrocatalytic activity than the nonpockmarked region, which itself shows uniformly large currents (e.g., $i_{\text{max}} \approx -30$ nA, comparable to Figure 4). A map of C_{DL} was constructed from the ECSA component (Figure 6a, green box) of the experiment, as shown in Figure 7b. Again, consistent with the semiquantitative maps of $|i_c|$ above (Figures 3c and 4b), C_{DL} is considerably lower on the pockmarked (<5 pF) compared to the nonpockmarked (>10 pF) areas, indicating that the former possesses a significantly lower ECSA. The clear and significant increase in ECSA measured moving out from the pockmarked into the nonpockmarked region and the ECSA value within the nonpockmarked region being too large to simply be due to surface roughness strongly support the proposal of a porous structure. In fact, the SEM images of the film surface (Figure S6) show the a-MoS_x film appearing featureless and smooth, demonstrating that the unambiguously measured increased ECSA must come from subsurface features (i.e., porosity).

Combining that data in Movie S5 (SI) and Figure 7b and taking the reported C_s value of 60 $\mu\text{F cm}^{-2}$,⁵⁴ an electrochemical movie of J is presented in the SI (Movie S6). The electrochemical J – E data were then used to construct the map of maximum surface area-normalized current density (J_{max}) shown in Figure 7c. In agreement with Figure 3 above, the relative activities of the pockmarked and nonpockmarked regions “flip” after surface area normalization of the current,

with the outer regions of the pockmarked areas exhibiting the largest $J_{\max}$ values (ca. -500 mA cm^{-2}) compared to the nonpockmarked areas (ca. -100 mA cm^{-2}), representing a remarkable 5-fold difference in specific activity across the probed area. Interestingly, in Figure 7c, $J_{\max}$ falls off toward the center of the pockmarked area, again suggesting that there is a minimum a-MoS_x film thickness required to achieve efficient electrocatalysis (in agreement with the volcano-shaped $i_{\max}/|i_{\text{Cl}}|$ vs $|i_{\text{Cl}}|$ in Figure 3f, explored further below).

Plotting $i_{\max}$ vs C_{DL} (i.e., analogous to the $i_{\max}$ vs $|i_{\text{Cl}}|$ plots in Figures 3e and 4d) reveals a two-region linear plot (Figure 7e, analogous to Figure 3e). At $C_{\text{DL}} < 5 \text{ pF}$, associated with the pockmarked area of the scan (i.e., yellow pixels in Figure 7b), $i_{\max}$ (activity) changes linearly with C_{DL} (ECSA). At $C_{\text{DL}} > 5 \text{ pF}$, associated with the nonpockmarked areas of the scan (i.e., blue pixels in Figure 7b), $i_{\max}$ enters a flattened ("saturated") region, where activity ($i_{\max}$) no longer scales with C_{DL} (ECSA). Such a property has not been observed in SECCM before and suggests that, at a certain thickness or porosity, the a-MoS_x film can no longer be utilized further for HER catalysis, carrying important implications for the application of these films in water electrolysis (*vide infra*).

Plotting $J_{\max}$ vs C_{DL} (i.e., analogous to the $i_{\max}/|i_{\text{Cl}}|$ vs $|i_{\text{Cl}}|$ plots in Figures 3f and 4e) shows a trend similar to that discussed for Figure 3f: a volcano-type relationship that peaks at a C_{DL} value of ca. 3 pF , at which point the apparent specific activity is the highest. At $C_{\text{DL}} < 3 \text{ pF}$, $J_{\max}$ rapidly falls off with decreasing C_{DL} (e.g., moving from the outer regions toward the center of the pockmarked area in Figure 7b), again supporting the notion that there is a lower limit on the thickness of the a-MoS_x film that is required to support efficient HER electrocatalysis. Plotting the CVs extracted at the lowest C_{DL} values (i.e., center of the pockmarked area in Figure 7) reveals behavior that approaches that of the naked GC support electrode (Figure 7d). At $C_{\text{DL}} > 3 \text{ pF}$, $J_{\max}$ initially falls off rapidly with increasing C_{DL} before flattening out and asymptotically approaching a value of ca. -50 mA cm^{-2} (Figure 7f). This again highlights that the a-MoS_x is less able to use its ECSA for HER electrocatalysis at large C_{DL} values, meaning that film utilization decreases with increasing mass loading. Similar trends were found in additional pockmarked and nonpockmarked example scans, as shown in Figures S9 and S11.

Hitherto, $i_{\max}$ and $J_{\max}$ obtained at the switching potential of the CVs (i.e., -0.87 V vs Ag/AgCl), have been used as proxies for total activity and specific activity, respectively. As alluded to above, at this potential, the rate of HER is high (e.g., geometric current densities $>2 \text{ A cm}^{-2}$ in the most active/porous parts of the film), and therefore, the rates of H⁺ consumption and H₂ production are also relatively high. To test whether the apparent decrease in specific activity is related to restricted (tortuous) mass transport of H⁺ and/or H₂ within the porous film structure, the same set of analyses was performed at a lower driving force (i.e., less negative potential or smaller overpotential; kinetically limited). This is possible because individual equipotential frames can be extracted from the generated electrochemical movies at any potential within the voltammetric sweep range.

The i and J maps that were extracted from Movies S5 and S6, respectively, at $E = -0.6 \text{ V}$ vs Ag/AgCl are shown in Figure 8a,b, respectively. Consulting a representative CV from the scan area (Figure 8c), it is clear that -0.6 V vs Ag/AgCl lies near the "onset potential" (E_{on}) of the HER on a-MoS_x. At E_{on} ,

the pockmark feature in the i map (Figure 8a, ca. 30 pixels or $150 \mu\text{m}$ in diameter) appears to spread out further than that seen in the corresponding $i_{\max}$ map (Figure 7a, ca. 15 pixels or $75 \mu\text{m}$ in diameter). In the J map (Figure 8b), the same switching of activity for the outer pockmark region is present as was seen for $J_{\max}$ (Figure 7c), although some pixels within the inner pockmark region now show particularly high specific activities, whereas others show low activities (significantly lower than the specific activity within the nonpockmarked area).

Plotting i at -0.6 V vs Ag/AgCl vs C_{DL} , shown in Figure 8d, results in no apparent "saturation" in i at higher C_{DL} values, as seen for the analogous $i_{\max}$ vs C_{DL} plot (Figure 7e). In fact, the plot appears to exhibit two approximately linear regions with different slopes (ca. intercept at a C_{DL} of 13 pF), as seen in Figure 3e for the plot of $i_{\max}$ vs $|i_{\text{Cl}}|$, corresponding to distinct regions of "low" and "high" C_{DL} (i.e., pockmarked and nonpockmarked areas, respectively). This confirms that the apparent saturation in a-MoS_x activity with ECSA seen in Figure 7e most likely arises from higher rates of HER resulting in mass transport limitations, causing H⁺ consumption to outweigh replenishment and/or higher H₂ production causing an increase in "blocked" active sites within the areas of the film with the highest ECSA values (e.g., nonpockmarked regions), hence resulting in lower measured currents. Finally, plotting J at -0.6 V vs Ag/AgCl vs C_{DL} , shown in Figure 8e, also shows a volcano-like relationship that peaks at a C_{DL} value of $\sim 3 \text{ pF}$; however, in this case, the difference between the "peak" activity (ca. -10 mA cm^{-2}) and activity at large ECSA values (ca. -5 mA cm^{-2}) is only 2-fold compared to 5-fold for $J_{\max}$ (Figure 7f). This confirms that the apparent drop-off in specific activity at larger ECSA values is less severe at lower rates of H₂ production (i.e., smaller driving force or overpotential), again suggesting that the origin of this phenomenon is likely to be the restricted mass transport of H⁺ and/or H₂ within the most porous (or thickest) areas of the a-MoS_x film.

Broader Implications of the Data and Further Applications of the New SECCM Protocol. Porous electrodes find extensive use across a range of disciplines integral to the modern world, including batteries,⁵⁷ electrocatalysis,⁵⁸ and photocatalysis.¹⁴ Despite this, there is a notable lack of functional techniques to measure and understand "real" active surface area (e.g., ECSA) on a local (spatially resolved) level. This work is a significant advancement in fulfilling this gap in material characterization, contributing toward a deeper understanding of electrode behavior and optimization.

The crucial difference between the observed activity and specific activity for an electrocatalyst has been made clear. The volcano-type relationship observed for specific activity relative to C_{DL} (ECSA) in Figure 7 identified a peak C_{DL} value of ca. 3 pF (a low C_{DL} compared to that of a nonpockmarked area) with steep drop-offs on either side. The area of the film corresponding to this C_{DL} range is within the outer region of the pockmark, which had relatively low activity for the $i_{\max}$ electrochemical map. The specific activity measured using this protocol identifies the optimum C_{DL} for high activity per site; however, an equivalent homogeneous film with a C_{DL} of entirely 3 pF would show lower overall activity, as the total current ($i_{\max}$) is increased for higher C_{DL} . Instead, the specific activity at 3 pF can be considered the specific activity "potential" of the nonpockmarked region compared to its actual (ca. 5- to 10-fold lower) specific activity. If this high surface area (C_{DL}) nonpockmarked region possessed this peak

specific activity, the total activity of the film would dramatically increase. Identification of the limiting factor for specific activity using this protocol enables modifications to be made that mitigate the negative impact. For example, in this case, the limiting factor was suggested as the mass transport of H^+ ions and/or H_2 gas through the more extensive porous morphologies; hence, one solution could be creating mesopore “highways” throughout the structure to promote faster and less hindered mass transport.

More generally, this new protocol can be applied to any nonflat thin film that would previously have been unsuitable for local characterization by SECCM. The ambiguity between specific surface features and areas of different surface area (C_{DL}) in electrochemical activity movies has been eliminated, and clear distinctions can now be made. This development is crucial for deployment on thin films made for application and/or at later stages of development and readiness. For example, thin films for electrocatalysis and photocatalysis are often highly nanostructured and porous to increase surface area while also possessing significant structural complexity from doping or use of multimetallic hybrid materials.¹⁴ The protocol described here could be used to unambiguously identify the activities of the range of surface features present and therefore gain a deeper understanding toward overall optimization.

CONCLUSIONS AND OUTLOOK

A two-step SECCM protocol was designed and applied to quantitatively determine and correlate the local ECSA and electrochemical activity of electrocatalytic electrode materials within a single high-throughput measurement. Application to highly porous, a-MoS_x thin films, which intrinsically possess ubiquitous “pockmark” surface features, revealed an “activity switching” upon normalization of electrochemical current with ECSA, with pockmarks flipping from the apparent least active surface regions (measured by i_{max}) to the most active (measured by J_{max}). These activity differences could not be explained by structure or elemental composition differences (i.e., EDX and XPS) and were concluded through analysis of SECCM data to be due to the restricted mass transport of H^+ into and/or H_2 gas out of the extensive porous structure, limiting the rate of HER catalysis within the high surface area, nonpockmarked regions of a-MoS_x. Plots of i_{max} and J_{max} vs C_{DL} were produced to identify distinct activity–porosity regimes, which coincided with the pockmarked and nonpockmarked areas of a-MoS_x, as well as the critical C_{DL} (ECSA) point of transition between each regime. An optimized C_{DL} (ECSA) value with respect to specific activity (J) for the film could therefore be identified, a crucial outcome for application in the systematic development of (electro)catalytic thin films.

Overall, heterogeneity within a porous a-MoS_x thin film has been quantitatively investigated on the microscale for the first time, deepening the understanding of electrochemical activity trends previously inferred from macroscopic measurements. This work extends the possible application of SECCM further into (electro)materials science, with employment onto highly porous and/or nanostructured thin films now possible, furthering the capabilities of systematic device design to rationalize optimal material structures, morphologies, and compositions.

EXPERIMENTAL SECTION

Chemical Reagents and Electrode Materials. Ammonium tetrathiomolybdate $[(NH_4)_2MoS_4]$, Sigma-Aldrich, 99.97% trace metal

analysis], lithium perchlorate trihydrate ($LiClO_4 \cdot 3H_2O$, Sigma-Aldrich), sulfuric acid (H_2SO_4 , Sigma-Aldrich, ACS Reagent, 95–98%), and potassium chloride (KCl, 99.5%, Sigma-Aldrich) were used as supplied by the manufacturer. All aqueous solutions were prepared with ultrapure deionized (DI) water (resistivity = 18.2 MΩ·cm at 25 °C, Direct-Q Water Purification System, Milli-Q, USA).

A glassy carbon (GC) substrate was purchased from Goodfellow (UK), polished with slurries of 1.0 μm diamond (ProSciTech, Australia) and 0.05 μm alumina (Buehler, USA), then washed thoroughly with acetone and ethanol, followed by sonication for 15 min in ethanol, and subsequently dried over a stream of N_2 , prior to use. An AgCl-coated Ag wire, prepared by the electrochemical oxidation of the Ag wire (Goodfellow, UK; thickness, 0.125 mm; purity, 99.99%) surface in a solution of saturated KCl, was used as the quasi-reference counter electrode (QRCE). These QRCEs have previously been shown to possess a stable potential of 0.25 ± 0.02 V vs Ag/AgCl (3.4 M KCl) in acidic media, which drift by less than 2 mV on the time scale of a typical SECCM scan (e.g., 1 h).⁵⁹ Note that unless otherwise stated, all potentials herein are referenced to the Ag/AgCl QRCE scale.

a-MoS_x Electrodeposition. An electrodeposition bath was prepared by dissolution of 0.1 M $LiClO_4$ and 8 mM $(NH_4)_2MoS_4$ in DI water. The a-MoS_x thin film was deposited using a three-electrode electrochemical cell [platinum auxiliary electrode (AE), leakless Ag/AgCl reference electrode (RE, 3.4 M KCl, eDAQ, Australia), and 1 × 1 cm GC plate working electrode (WE)] connected to an EmStat 4S potentiostat (PalmSens). Cyclic voltammetry was performed using 30 potential cycles within a range of −1.2 to 0.1 V vs Ag/AgCl (3.4 M KCl) and a voltammetric scan rate of 0.05 V s^{−1}. Immediately after deposition, the GC/a-MoS_x electrode was removed from the solution, gently rinsed with ultrapure water, and then dried in air before testing. The resulting thin films contained small but visible pockmarks.

Probe Fabrication. To prepare the SECCM probes, borosilicate capillary tubes (BF100-S0-10, Sutter Instruments, USA; outer diameter 1.0 mm; inner diameter 0.5 mm; length 100 mm) were pulled to form micropipettes (ca. 1 μm tip diameter) using a two-stage capillary gravity puller (PC-100, NARISHIGE Group, Japan) with first-stage parameters of heat 63.3, weight 0, and slider 9 and second-stage parameters of heat 51.7, weight 0, and slider 4.5. The resulting micropipette was then filled with 0.5 M H_2SO_4 solution and equipped with an Ag/AgCl QRCE, rendering it ready for use.

Scanning Electrochemical Cell Microscopy. SECCM was carried out on a home-built scanning electrochemical probe microscope based on a previously reported setup.^{29,31,33,52} This consisted of a three-axis piezoelectric stage (200 × 200 × 200 μm range, Nano-3D200, MadCityLabs, USA) with a micropipette attached such that the tip was positioned above the electrode region of interest. The location of the tip with respect to the surface was adjusted with a micropositioner (9064-XYZ-M, Newport, USA) prior to the experiment.

The GC/a-MoS_x WE was attached to an SEM stub (SEM pin stubs, Microscopy Solutions Pty. Ltd., Australia) using conductive double-sided copper tape (Agar Scientific, UK) before being placed in a polypropylene container (Lock&Lock, South Korea) that served as an atmosphere-controlled environmental cell, as previously reported.⁶⁰ To this cell was attached a gas inlet port (Omnifit Connector, Kinesis, UK) that enabled the supply of N_2 to the cell, and a circular hole of ~4 mm in the top of the lid enabled the approach of the micropipette while maintaining a positive flow of gas through the cell. The N_2 was passed through a bubbler containing DI water to humidify the gas before passing through a variable area flow meter (Brooks Instrument, USA) to maintain a constant supply (~100 cm³ min^{−1}) and eventually being delivered to the cell via PVC tubing. Two circular holes (~2 cm) were drilled into the lid and replaced with cover glass (thickness: 0.13–0.17 mm, dimensions: 24 × 50 mm²) to supply the surface with light and provide an optical pathway for viewing of the micropipette tip and surface using an optical camera (AxioCam ERc 5s, ZEISS, Germany) fitted with a magnification lens (44 mm/3.00× InfiniStix, Infinity USA). All instrumentation was

placed on an optical breadboard on which the positioner, environmental cell, and camera were mounted, and the breadboard was attached to a vibration isolation stage (25BM-8, Minus K Technology, USA). The vibration isolation stage with attachments was placed in an aluminum Faraday cage lined internally with acoustic insulation foam (RS PRO, UK).

Before beginning the SECCM experiment, an electrical connection was made to the Ag/AgCl QRCE in the tip and the SEM stub housing the GC/a-MoS_x electrode. This latter connection fed to a variable-gain low-noise current amplifier (DLPCA-200, FEMTO, Germany). The tip was then moved to the desired position before closing the Faraday cage and programming the experiment in LabVIEW (National Instruments, USA) with dedicated Warwick electrochemical scanning probe microscopy (WEC-SPM) software, publicly available via academic license from <https://warwick.ac.uk/fac/sci/chemistry/research/electrochemistry/wec-spm/>.

The SECCM experiment was conducted in the voltammetric hopping mode with the tip repeatedly approaching the surface in a grid pattern to obtain spatially resolved electrochemical information (Figure S12).⁶¹ At each location, the tip was approached toward the surface at 5 $\mu\text{m s}^{-1}$, with an applied potential (E_{app}) on the QRCE of 0 V with respect to the ground until the electrolyte meniscus protruding from the tip contacted the surface, inducing a double-layer charging current. When this charging current exceeded ± 12 pA, the approach was stopped. It should be noted that because the potential was applied at the QRCE and not the surface, the surface is at a potential opposite to that of the QRCE ($E_{\text{surf}} = -E_{\text{app}}$), and all quoted potentials herein will be quoted relative to the surface.

For the initial ECSA determination, three CVs were measured with a potential range from 0 to -0.2 V versus Ag/AgCl with scan rates of 1, 2, and 4 V s^{-1} . To measure electrochemical activity, the potential was held at -0.2 V versus Ag/AgCl for 25 ms, and a fourth CV was measured with a potential range from -0.2 to -0.87 V versus Ag/AgCl and scan rate of 2 V s^{-1} . High voltammetric scan rates were chosen to ensure a reasonable scanning time scale (1–3 h) and minimize the risk of artifacts such as QRCE contamination and/or drift associated with prolonged scan times.⁶² Finally, the tip was moved away from the surface before being moved to the next location (with a hopping distance of 5 μm), with the above process being repeated until a measurement was taken at the full grid of positions. Positioning of the probe was constantly monitored, and the z-piezo position at each hop location was used to generate a topographical map of the scan area. Throughout the experiment, the current at the a-MoS_x surface (i_{surf}) was recorded every 4 μs and averaged 256 times, giving a data acquisition rate of $(256 + 1) \times 4 = 1028$ μs per data point. The data acquisition was handled by an FPGA card (NI USB-7855R, National Instruments, USA), which sat between the LabVIEW interface and the SECCM instrument. Raw data were processed in the MATLAB environment (MathWorks, USA).

Complementary Surface Analysis. Optical microscopic imaging was performed on an Axiolab 5 microscope (ZEISS, Germany) with a range of fitted objectives (5, 10, 20, and 50 $\times$). Images were collected via an attached Axiocam 105 color (ZEISS, Germany) optical camera. Post scan colocation and imaging were obtained by field emission scanning electron microscopy (JEOL JSM-7001F FEGSEM), and elemental analysis was performed by energy dispersive X-ray spectroscopy (EDX, Oxford Instruments AZtec X-ray analysis system and 80 mm^2 SDD).

X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific Nexsa Surface Analysis System equipped with a hemispherical analyzer. The incident radiation was monochromatic Al K α X-rays (1486.6 eV) at 72 W (6 mA and 12 kV, 100 $\times$ 100 μm^2 spot). Survey (wide) and high-resolution (narrow) scans were recorded at analyzer pass energies of 150 and 50 eV and step sizes of 1.0 and 0.1 eV, respectively. The base pressure in the analysis chamber was less than 5.0×10^{-9} mbar. A low-energy dual-beam (ion and electron) flood gun was used to compensate for surface charging. Data processing was carried out using the Advantage V5 software, and the energy calibration was referenced to the main line of C 1s at 284.8 eV. Smart background was used for curve fitting.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.4c06308>.

Electrodeposition reactions and CVs (Figure S1); measurement of a-MoS_x thin film topography by SECCM (Figure S2); O 1s and C 1s high-resolution XPS spectra and binding energies and atomic percentages for Mo 3d and S 3p (Figure S3, Table S1); macroscopic activity and ECSA-normalized activity measurements (Figure S4); optical and SEM images of residual footprints from each probe tip retraction within scans (Figures S5 and S6); electrochemical activity scans on a-MoS_x with three consecutive CVs for each hop (Figure S7); ECSA data collection and calculation on GC (Figure S8); additional ECSA-normalized SECCM scan containing a pockmark, and frames from the movie taken at HER onset (Figures S9 and S10); ECSA-normalized SECCM scan over a nonpockmarked area (Figure S11); and SECCM apparatus schematic (Figure S12) (PDF)

Electrochemical movies of current (i), normalized current, and current density (J) obtained from -MoS_x (ZIP)

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Notes

The authors declare no competing financial interest.

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