Benchmarking the Activity, Stability, and Inherent Electrochemistry of Amorphous Molybdenum Sulfide for Hydrogen Production

Daniel Escalera-López, Zhiheng Lou, and Neil V. Rees*

Anodically electrodeposited amorphous molybdenum sulfide (AE-MoS\textsubscript{x}) has attracted significant attention as a non-noble metal electrocatalyst for its high activity toward the hydrogen evolution reaction (HER). The [Mo\textsubscript{3}S\textsubscript{13}]\textsuperscript{2−} polymer-based structure confers a high density of exposed sulfur moieties, widely regarded as the HER active sites. However, their intrinsic complexity conceals full understanding of their exact role in HER catalysis, hampering their full potential for water splitting applications. In this report, a unifying approach is adopted accounting for modifications in the inherent electrochemistry (EC), HER mechanism, and surface species to maximize the AE-MoS\textsubscript{x} electroactivity over a broad pH region (0−10). Dramatic enhancements in HER performance by selective electrochemical cycling within reductive (overpotential shift, η\textsubscript{HER} ≈ −350 mV) and electro-oxidative windows (η\textsubscript{HER} = −290 mV) are accompanied by highly stable performance in mildly acidic electrolytes. Joint analysis of X-ray photoelectron spectroscopy, Raman, and EC experiments corroborate the key role of bridging and terminal S ligands as active site generators at low pH, and reveal molybdenum oxysulfides (Mo\textsubscript{5}O\textsubscript{3}S\textsubscript{2}) to be the most active HER moiety in AE-MoS\textsubscript{x} in mildly acidic-to-neutral environments. These findings will be extremely beneficial for future tailoring of MoS\textsubscript{2} materials and their implementation in commercial electrolyzer technologies.

1. Introduction

Hydrogen, systematically praised as a candidate to substitute fossil fuels as an energy carrier in a carbon neutral economy, can be efficiently produced on demand and in a decentralized manner with (photo) electrochemical methods via the hydrogen evolution reaction (HER).\textsuperscript{[1−4]} Despite of being the best performing HER catalysts,\textsuperscript{[5,6]} noble metals such as Pt, Ir, and Pd are scarce and consequently hamper the viability of water electrolysis technologies. Hence earth-abundant materials, and notably transition metal dichalcogenides (TMDs) such as molybdenum disulfide (MoS\textsubscript{2}), have been extensively investigated as HER electrocatalysts.\textsuperscript{[7−11]}

The edge sites-driven hydrogen electroadsorption properties of TMDs\textsuperscript{[12,13]} have prompted the fabrication of amorphous molybdenum sulfide materials (MoS\textsubscript{x}) to minimize exposure of the electrocatalytically inert Mo\textsubscript{2} basal planes\textsuperscript{[14]} for multiple applications.\textsuperscript{[15−19]} A simple, yet scalable method to fabricate MoS\textsubscript{x} has been reported by substrate-insensitive electrodeposition from a [MoS\textsubscript{4}]\textsuperscript{2−} precursor\textsuperscript{[20,21]} and critical properties in MoS\textsubscript{x} materials such as film thickness,\textsuperscript{[22]} morphology,\textsuperscript{[23−26]} Mo:S stoichiometry,\textsuperscript{[27]} as well as incorporation of dopants\textsuperscript{[28−30]} or nanocomposite formation,\textsuperscript{[31−35]} have been easily tuned by experimental parameters.

For long-term electrocatalytic applications, however, HER activity and stability of TMDs are paramount. In crystalline MoS\textsubscript{2}, basal plane activation,\textsuperscript{[36−43]} edge site exposure,\textsuperscript{[44−53]} and metal doping/incorporation/intercalation\textsuperscript{[54−66]} are the most employed strategies.

In contrast, the [Mo\textsubscript{3}S\textsubscript{13}]\textsuperscript{2−} cluster-based polymeric structure of electrodeposited MoS\textsubscript{x}\textsuperscript{[67]} requires alternative approaches to maximize activity. In addition, the detailed HER mechanism as well as the true catalytically active sites are still under debate. Whilst pioneering studies on ambient pressure X-ray photoelectron spectroscopy (XPS) indicated the MoS\textsubscript{2} edge-like sites formed after MoS\textsubscript{3} phase transformation under in operando conditions responsible for the HER performance,\textsuperscript{[68]} in situ X-ray absorption spectroscopy experiments suggested terminal S\textsubscript{2−} ligands (S\textsubscript{2−}\textsubscript{terminal}) to be the proton acceptor sites,\textsuperscript{[69]} and more recently in situ Raman spectroscopy indicated these to be the electrochemically cleaved bridging S\textsubscript{2−} ligands (S\textsubscript{2−}\textsubscript{bridging}).\textsuperscript{[70]} Another study claimed that unsaturated Mo centers formed after cathodic dissolution of S\textsubscript{2−}\textsubscript{terminal} to be the true HER...
active sites.[71] Strikingly, very recent in situ Raman microscopy measurements at neutral pH values suggest the active sites to stem from an internal reorganization of bridging S$_{22}^{2-}$ bridging ligands to an S$_{22}^{2-}_{\text{terminal}}$ configuration yielding undercoordinated Mo-Mo sites which synergistically promoted the HER.[72]

Indeed, dramatic pH-dependent effects in crystalline MoS$_2$ HER performance, inherent electrochemistry and fluorescence have been reported.[73–76] Although preliminary pH studies on electrodeposited MoS$_x$ are available,[71,77] none have proposed a unified approach to maximize the HER electrocatalysis of electrodeposited MoS$_x$ accounting for modifications in pH-dependent surface properties. This is essential to successfully translate the efforts dedicated to MoS$_x$ into a commercially viable TMD electrolyzer with robust long-term water splitting performances.

In this study, we have conducted a thorough analysis of the inherent electrochemical features of electrodeposited MoS$_x$ within the pH 0–10 range, and proposed several electrochemical strategies to maximize their HER electrocatalysis. Our results not only show proof of reversible bridging S$_{22}^{2-}_{\text{bridging}}$ cleaving and irreversible terminal S$_{22}^{2-}_{\text{terminal}}$ dissolution at HER precatalytic potentials by combined analysis of the XPS and electrochemical data, but also the intimate dependence of experimental surface descriptors with the maximized/detrimental HER performances after electrochemical conditioning. Electrodeposited MoS$_x$ films activated in the pH 3–6 region presented the highest enhancements in HER activity (~400 mV positive shift in the HER overpotential) and extremely stable long-term performance under harsh testing conditions. Such extraordinary results are proposed to stem from the interplay between the stabilized, S-deficient molybdenum oxysulfide moieties and the modification of the HER mechanism in mildly acidic environments, providing invaluable information for the implementation of TMD-based proton-exchange membrane (PEM) electrolyzers.

2. Results and Discussion

2.1. Electrochemical Growth of Amorphous Molybdenum Sulfide

Preliminary electrochemical deposition studies were performed on Si/Ti/Au electrodes to evaluate the influence of experimental conditions (electrochemical setup, deposition parameters) on the growth of amorphous molybdenum sulfide (MoS$_x$) thin films. Both anodic (AE) and cathodic (CE) deposition conditions were investigated (full details are given in Section S2.1, Supporting Information), and it was found that AE-MoS$_x$ was the preferred material due to its higher deposition efficiency (~10 times more efficient) and reportedly improved HER properties as compared to CE-MoS$_x$.[27] AE-MoS$_x$ has been therefore utilized for the remainder of this report.

2.2. AE-MoS$_x$ Inherent Electrochemical Activity: HER Precatalytic Peaks

The AE-MoS$_x$ enhanced activity versus CE-MoS$_x$ has been related to the higher content of proton-accepting S sites and the multiple S moieties found in the [Mo$_3$S$_{13}$]$^{2-}$ cluster-based polymeric structure of the electrodeposit (representative schematic in Figure 1).[71]

Figure 1. Schematic of the coordination polymer structure of AE-MoS$_x$ based on the [Mo$_3$S$_{13}$]$^{2-}$ cluster unit. Sulfur ligand types labeled as follows: apical S$_2$ (S$_{\text{apical}}^{2-}$), blue; bridging S$_{22}^{2-}$ (S$_{\text{bridging}}^{2-}$), black; terminal S$_{22}^{2-}$ (S$_{\text{terminal}}^{2-}$), red; unsaturated S$_2$ (S$_{\text{unsat}}^{2-}$), green. S-deficient Mo-sites (AE-MoS$_x$ structural defects, referred as Mo$^{5+}$O$_x$S$_y$) represented by Mo$^{5+}$=O groups.
In order to shed light on the electrochemical activity of AE-MoS\textsubscript{x} films, comprehensive studies were conducted at different pHs, appropriately buffered to minimize any local pH changes that may affect the AE-MoS\textsubscript{x} inherent electrochemistry, morphology and/or surface species (see Section S2.2 in the Supporting Information for full details). Figure 2a shows a compilation of the hydrogen evolution linear sweep voltammograms (LSVs) recorded for 100 nm-thick AE-MoS\textsubscript{x} films at a voltage scan rate of 50 mV s\textsuperscript{−1} using different buffered electrolyte solutions in the 0–10 pH range after iR compensation. The redox processes responsible for these prewaves are irreversible, appearing only on the first scan, and are involved in the so-called irreversible ‘activation’ step which converts the S-rich AE-MoS\textsubscript{x} to the HER-active Mo\textsubscript{5}S\textsubscript{2} phase which presents a structure/stoichiometry closer to that of CE-MoS\textsubscript{x}.\[27,78] Separate experiments on bare Si/Ti/Au electrodes confirm they are surface-related and not due to species dissolved in the buffered electrolyte solutions (see the Supporting Information).

Figure 2b shows plots of their peak potential as a function of the pH, the gradients of which can be related via the Nernst equation to the relative numbers of protons and electrons involved in the electrochemical mechanism (proton-coupled electron transfer, PCET).

For the first reduction process, \(E_{\text{peak,1}}\) the gradient of \(-54\text{ mV dec}^{-1}\) is very close to the theoretical \(-59\text{ mV dec}^{-1}\) expected for redox processes involving an equivalent number of protons and electrons. Conversely, \(E_{\text{peak,2}}\) and \(E_{\text{peak,3}}\), found only in mildly acidic to alkaline pH conditions, present a \(-0\text{ mV dec}^{-1}\) and \(+21\text{ mV dec}^{-1}\) dependence, respectively. Thus, \(E_{\text{peak,2}}\) involves a reduction event in which no protons are involved, whereas \(E_{\text{peak,3}}\) is related to a PCET mechanism involving a two-electron : one proton ratio.

We therefore propose several potential candidates for the redox processes involved in each precatalytic feature. The in situ proof of S-S bond cleaving from S\textsubscript{2}\textendash bridging and S\textsubscript{2}\textendash terminal at potentials equivalent to that of \(E_{\text{peak,1}}\) leads us to ascribe the redox process occurring at \(E_{\text{peak,1}}\) to this process.\[90\] This involves a 2 H\textsuperscript{+} : 2e\textsuperscript{−} PCET reduction process (see reaction 1a), which would satisfy the approximate \(-59\text{ mV dec}^{-1}\) gradient experimentally observed.

\[
\text{Mo}^{IV}(\text{S\textendash S})_{\text{terminal}} + 2\text{H}^{+} + 2\text{e}^{-} \rightleftharpoons 2\text{Mo}^{IV} + \text{SH} \\ (1\text{a})
\]

However, the additional evidence of the removal of S\textsuperscript{2−\textendash terminal} ligands under HER operating conditions also suggests an alternative 2 H\textsuperscript{+} : 2e\textsuperscript{−} mechanism\[71\] this time leading to formation of unsaturated Mo\textsuperscript{4+} centers (see reaction 1b).

\[
\text{Mo}^{IV}[(\text{S\textendash S})_{\text{zeolite}}]^{1−} + 2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{Mo}^{IV} - \text{S}^{2−} + 2\text{HS}^{-} \text{ (1b)}
\]

While (1b) is an irreversible process, (1a) is an electrochemically reversible redox reaction. The degree of electrochemical reversibility/coexistence of these mechanisms and their implications in HER catalysis will be further investigated in Sections 2.5 and 2.6, respectively.

As for \(E_{\text{peak,2}}\) and \(E_{\text{peak,3}}\), their sole appearance at pH \(\geq 5\) might indicate that either (i) the species responsible are only formed at these pH values after (1a) and (1b) occur, or (ii) the species are unstable at pH \(\leq 5\) and consequently not present at the AE-MoS\textsubscript{x} surface until pH \(\geq 5\) values are achieved. Surface composition analysis of pristine AE-MoS\textsubscript{x} by XPS (see Figure S7, Supporting Information) suggests that the prepared films predominantly contain Mo\textsuperscript{6+} species, but Mo\textsuperscript{5+} oxysulfides and to a lesser extent MoO\textsubscript{3} are also present (Mo\textsuperscript{5+}: Mo\textsuperscript{6+}XPS relative ratios 75.4: 18.6: 6.0, Figure S7a, Supporting Information), giving Mo:S ratios of 1: 2.4 ± 0.2. Previous evidence suggests that the AE-MoS\textsubscript{x} undergoes a slow Mo\textsuperscript{5+} → Mo\textsuperscript{6+} transformation under atmospheric conditions\[25\] similar to that found in the (NH\textsubscript{4})\textsubscript{2}[MoS\textsubscript{4}] precursor\[79\]: this could partially occur between preparation and characterization of the Mo\textsubscript{5}S thin film. The presence of Mo\textsuperscript{5+}O\textsubscript{S}\textsubscript{2−} and MoO\textsubscript{3} at the outermost AE-MoS\textsubscript{x} pristine surface is key as their stability is pH-dependent: MoO\textsubscript{3} is well known to be unstable in acidic media\[80\] whereas Mo\textsuperscript{5+}O\textsubscript{S}\textsuperscript{2−} compounds are mostly soluble in acid unless structure-based properties confer enhanced stabilities.\[81\] Thus, the thermodynamically favored dissolution in acidic media eliminates their electrochemical contribution in electrolytes of pH \(\leq 5\)\[82\] leading us to hypothesis (ii) above. We propose, analogously to a previous report\[71\], \(E_{\text{peak,2}}\) to be due to the electrochemically assisted reduction of Mo\textsuperscript{5+}O\textsubscript{S}\textsubscript{2−} to Mo\textsuperscript{4+} species by reaction (2).

\[
\text{Mo}^{IV}O_{S_{2}} + 1\text{e}^{-} \rightarrow \text{Mo}^{IV}O_{S_{2}}S\text{ (2)}
\]

For \(E_{\text{peak,3}}\), the proton-generating nature of the redox reaction involved limits the potential events occurring as Mo or S reduction events are normally proton-depleting. We herein...
tentatively propose that Mo$^{4+}$O$_5$S$_3$ could further reduce at more cathodic potentials to form MoO$_2$ (reaction 3)

\[
\text{Mo}^{IV}\text{OS} + \text{Mo}^{IV}\text{OS}_4 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{MoO}_2 + 3\text{HS}^- + 1\text{H}^+ \quad (3)
\]

2.3. AE-MoS$_x$ Inherent Electrochemical Activity: HER Kinetics

It is crucial to monitor changes in the HER kinetics as a function of the pH, as provides insight into the HER mechanism and hence the electrocatalytic activity. Although previous reports describe almost unaltered Tafel slope values upon incremental MoS$_2$ loadings,[83] layer stacking,[80] and amorphous MoS$_x$ S:Mo stoichiometry,[78,84] the influence of the electrolyte pH is rarely documented.

We investigated this by analyzing the linear region of the $\eta$ versus $\log|i_{\text{comp}}|$ plot (i.e., Tafel plot, $b$) of iR-compensated LSVs acquired toward hydrogen evolving potentials, over a set of independent repeated measurements at the different buffered electrolytes studied. Figure 3a compiles the Tafel plots of bare Si/Ti/Au (as control) substrates and AE-MoS$_x$ thin films, the latter in the presence and absence of 1500 rpm stirring, to identify potential contributions of both substrate and mass transport in the obtained values.

A plateau in the $0 \leq \text{pH} \leq 3$ range, followed by an overall increase in the Tafel slope ($b$) values with pH, was found for both Si/Ti/Au substrates and AE-MoS$_x$ films. While $b$ seems independent on the presence of AE-MoS$_x$ up to pH 5, Si/Ti/Au substrates exhibit slightly higher values in neutral to alkaline environments. Although the exact HER pathway on bare Au is still under debate,[85] recent investigations in acid electrolytes have found two characteristic Tafel slope values at low ($b \approx 68 \pm 5$ mV dec$^{-1}$) and high current densities ($b \approx 120 \pm 2$ mV dec$^{-1}$) due to hydrogen surface diffusion effects,[86,87] converging to a Tafel slope of $b \approx 120$ dec$^{-1}$ in alkaline environments.[88] AE-MoS$_x$ films tested under stirring gave Tafel slopes with lower dispersion compared to their quiescent counterparts ($b \approx 65 \pm 10$ mV dec$^{-1}$ in the 0 \leq \text{pH} \leq 3 range closer to theoretical Volmer–Heyrovsky $b \approx 40$ mV dec$^{-1}$ as reported for AE-MoS$_x$ in acid). For further discussion of Tafel slope variations before and after stirring, see Section S2.3 (Supporting Information).

The Si/Ti/Au substrate, particularly in acidic conditions, seems to govern the experimental Tafel slopes obtained after MoS$_x$ modification across the 0–10 pH range: supporting working electrodes of different nature[86,89] and morphology[90] yielded analogous results in previous HER experiments.

As regards the Tafel slope versus pH trend, recent studies on AE-MoS$_x$ by Dubouis et al. using sulfuric acid in the $0 \leq \text{pH} \leq 4$ range[77] suggests that for pH $\leq 2$ the HER mechanism operated by the electroreduction of the hydronium ion ($\text{H}_3\text{O}^+ + 1\text{e}^- \rightarrow 1/2\text{H}_2 + \text{H}_2\text{O}$), while for pH $\geq 3$ the HER occurred via the water reduction/splitting mechanism ($\text{H}_2\text{O} + 1\text{e}^- \rightarrow 1/2\text{H}_2 + \text{OH}^-$).

This implies that $b$ should be pH-insensitive for pH $\leq 2$, whereas $b$ should increase at pH $> 3$ due to increasingly lower proton concentrations yielding the proton electroadsorption rate-limiting step (i.e., Volmer step, $b \approx 120$ mV dec$^{-1}$) to govern the HER performance, as previously reported for noble metal surfaces.[92–95]. Despite using electrolytes with different spectator species and ionic strengths, this trend is also found for our AE-MoS$_x$ results under stirring: within the $0 \leq \text{pH} \leq 2$ range, Tafel slopes are almost constant $b \approx 65 \pm 10$ mV dec$^{-1}$, whilst at pH $> 2$ they increase approximately linearly yielding $b \approx 120$ mV dec$^{-1}$ at pH 5.

For neutral to alkaline pHs, however, $b$ exceeds 120 mV dec$^{-1}$: since electron transfer coefficients in mildly acidic to alkaline conditions are reported to be almost pH independent,[96] mass transport limitations (i.e., proton depletion at the electrode interface) and surface species will necessarily play a role on the HER kinetics. Indeed, molybdenum oxides such as MoO$_3$ and MoO$_2$, stable in neutral to alkaline environments, exhibited Tafel slopes as high as $b \approx 160$ mV dec$^{-1}$ and $b \approx 200$ mV dec$^{-1}$, respectively in $0.5 \text{M} \text{H}_2\text{SO}_4$.[97] Thus, we believe that the presence such MoO$_x$ surface species at these mid-pH values with different HER active site kinetics, along with the partial exposure of the underlying Au substrate due to AE-MoS$_x$ instability, could explain the Tafel slopes observed.

This pH-dependence on the Tafel slope, HER mechanism, and surface species consequently supports the AE-MoS$_x$ LSVs found under stirring after iR and Nernstian compensation (Figure 3b). As found by Dubouis et al., LSVs in the $0 \leq \text{pH} \leq 2$ range fully overlap due to invariant Tafel slope and HER kinetics, whereas for pH $> 3$ the HER mechanism and Tafel slope modification result in nonoverlapping, negatively shifted LSVs toward higher pH values.

![Figure 3](image-url)
2.4. AE-MoS$_x$ Inherent Electrochemical Activity: Electro-Oxidation

Next, we investigated the electro-oxidative processes of the 100 nm thick AE-MoS$_x$ films. For pristine AE-MoS$_x$, an LSV from +0 V to 1.2 V (vs SCE) reveals a broad anodic feature, in the 0.2–1.1 V voltage range, with its peak at +0.7 V when tested in a 0.5 m H$_2$SO$_4$ electrolyte (Figure 4a). Plotting the electro-oxidation band peak potential as a function of the pH gives an experimental gradient of $\sim 27$ mV dec$^{-1}$, which closely matches the $\sim 29.5$ mV dec$^{-1}$ theoretical Nernstian slope characteristic of a 1 H$^+$: 2e$^-$ PCET electro-oxidation mechanism (Figure 4b), in agreement with literature results for crystalline MoS$_2$ materials ascribed to the oxidation of the Mo$^{4+}$ moieties to Mo$^{6+}$.[74,98] To the best of our knowledge, our investigation is the first to experimentally support the 1 H$^+$: 2e$^-$ PCET electro-oxidation mechanism for pristine AE-MoS$_x$ (detailed discussion of the electrochemical features is provided in Section S2.4, Supporting Information).

To gain further insight on the implications of the complex electro-oxidation mechanism, ex situ Raman spectra of the electro-oxidized AE-MoS$_x$ films were recorded (Figure S10, Supporting Information), and showed changes to several Raman-active vibrations: 1) the v(Mo=Mo) band at $\sim 201$ cm$^{-1}$ sharpens and increases its relative intensity, 2) the v(Mo=S) band at $\sim 358$ cm$^{-1}$ sharpens to the detriment of the remaining v(Mo=S) bands, and undergoes a redshift to $\sim 354.8$ cm$^{-1}$, 3) the out-of-plane A$_{1g}$ mode appears at $\sim 404$ cm$^{-1}$, with relative intensities higher than those found for the in-plane E$_{2g}$ mode at $\sim 380$ cm$^{-1}$ and 4) additional Raman modes appear at $\sim 341$ (faint), 490 (strong), and 730 (strong) cm$^{-1}$, respectively. This indicates that electro-oxidation irreversibly changes the morphology of the cluster-based AE-MoS$_x$ structure: the Raman signal intensity sharpening in features 1–3) inform that the resulting structure comprises morphologies with predominance of those vibration modes. As for 4), we believe that the weakening and disappearance of v(Mo=S) and v(S=S)$_{\text{terminal}}$ vibration modes, respectively, are responsible for the 341 and 490 cm$^{-1}$ bands. Additionally, the 730 cm$^{-1}$ band should correspond to the partial oxidation of Mo$^{4+}$ sites, as this vibration is not far away from the one expected for Mo=O ($\sim 880$ cm$^{-1}$). Thus, we conclude that the 1 H$^+$: 2e$^-$ PCET electro-oxidation mechanism for pristine AE-MoS$_x$ primarily involves the disappearance of S$_2^{2\text{-terminal}}$ and the formation of partially oxidized molybdenum sites.

To investigate the effect of reducing (i.e., HER) potentials on these electro-oxidative features, anodic voltammetry was recorded after one LSV toward HER potentials (from 0.7 to $\sim$1.2 V vs SCE, scan rate 50 mV s$^{-1}$). The anodic LSV showed differences compared to that performed on pristine AE-MoS$_x$: for pH = 7 (see Figure S11, Supporting Information), two well-resolved peaks can be identified, the first ($E_{\text{peak, I}}$) at $\sim$0.16 V and the second ($E_{\text{peak, II}}$) at $\sim$0.29 V (partially overlapped at other buffered electrolytes). These are equivalent to those previously found for AE-MoS$_x$ being oxidatively stripped after applying a cathodic scan to HER potentials.[78,99] In stark contrast with the electro-oxidative behavior found for pristine AE-MoS$_x$, this suggests that electrochemical conditioning to hydrogen evolving potentials alters the electro-oxidation mechanism.

It was previously hypothesized that scanning to anodic potentials, first selectively oxidized weakly Mo-bound low XPS binding energy unsaturated S$^{2-}$ (S$_2^{2\text{-terminal}}$) and S$_2^{2\text{bridge}}$, respectively. However, neither the pH-dependence of these reactions nor the electrochemical reversibility of reaction (1a) triggered by the initial LSV scan toward HER potentials were taken into consideration when proposing these reactions. To gather insight on these redox processes, we elucidated the pH-dependence of the post-LSV AE-MoS$_x$ electro-oxidative features (Figure 5a) by plotting the electro-oxidation peak potentials versus the electrolyte pH for both $E_{\text{peak, I}}$ (Figure 5b) and $E_{\text{peak, II}}$ (Figure 5c) after Gaussian peak deconvolution. For $E_{\text{peak, I}}$, a $\sim$56 ± 4 mV dec$^{-1}$ dependence was observed between pH 2 and pH 8. This is in excellent agreement with a widely established 1 H$^+$: 1e$^-$ (or subsequent multiples) PCET electro-oxidation mechanism. However, this does not satisfy the widely established 1 H$^+$: 2e$^-$ PCET mechanism under which the irreversible electro-oxidation of MoS$_2$ materials to Mo$^{6+}$ is reported to proceed, as this would give a theoretical Nernstian slope of $\sim$29.5 mV dec$^{-1}$.[74,98,100]

Thus, an alternative electro-oxidation event precedes the complete electrochemical oxidation of the AE-MoS$_x$ thin film. Analysis of the voltammetric features found after cycling the post-LSV AE-MoS$_x$ at variable voltage windows indicates that the electro-oxidation event responsible for $E_{\text{peak, I}}$ can only be found when AE-MoS$_x$ has undergone cathodic cycling past the

![Figure 4](image-url)  
**Figure 4.** a) Anodic stripping voltammogram of freshly deposited AE-MoS$_x$ films recorded from 0 to 1.2 V versus SCE in 0.5 m H$_2$SO$_4$. b) Plot of AE-MoS$_x$ electro-oxidation peak potential versus buffered electrolyte pH showing a gradient of $-27$ mV dec$^{-1}$. Scan rate: 50 mV s$^{-1}$.
precatalytic peak $E_{\text{peak}, 1}$ (Figure S12, Supporting Information). Given the electrochemical reversibility of reaction (1a), we preliminarily suggest the electro-oxidation event $E_{\text{peak}, 1}$ to be the reinstatement of the previously cleaved $\text{S} = \text{S}$ bond in $\text{S}_2^2\text{−}$ bridging and/or $\text{S}_2^2\text{−}$ terminal ($2 \text{H}^+: 2\text{e}^- \text{PCET mechanism}$).

$$2\text{Mo}^{IV} + \text{SH} \rightleftharpoons \text{Mo}^{IV} (\text{S-S}_{\text{br}}) + \text{Mo}^{IV} + 2\text{H}^+ + 2\text{e}^- \quad (4a)$$

However, the partial corrosion of the previously cleaved $\text{S}_2^2\text{−}$ bridging and/or $\text{S}_2^2\text{−}$ terminal sites giving $\text{MoO}_2$ also satisfies a close-to $1 \text{H}^+: 1\text{e}^- \text{PCET electro-oxidation mechanism}$, and thus cannot be discarded.

$$\text{Mo}^{V} + 6\text{H}_2\text{O} \rightarrow \text{MoO}_4^{2−} + 3\text{H}_2\text{O} + 6\text{H}^+ + 11\text{e}^- \quad \text{(acidic pH)}$$
$$\text{Mo}^{V} - 6\text{H}_2\text{O} \rightarrow \text{MoO}_4^{2−} + 3\text{H}_2\text{O} + 13\text{H}^+ + 11\text{e}^- \quad \text{(neutral pH)} \quad (4b)$$

As for $E_{\text{peak}, II}$, a clear $-117 \pm 17 \text{ mV dec}^{-1}$ gradient is found at neutral to alkaline pHs ($7 \leq \text{pH} \leq 10$). This satisfies a $2 \text{H}^+: 1\text{e}^- \text{PCET mechanism}$: based on the thermodynamic instability seen for Mo species at positive potentials in alkaline environments,$[82]$ we suggest the electro-oxidation of $\text{MoO}_2$ to the soluble $\text{MoO}_4^{2−}$ anion to be the reaction taking place.

$$\text{MoO}_2 + 2\text{H}_2\text{O} \rightarrow \frac{1}{2} \text{MoO}_4^{2−} + 4\text{H}^+ + 2\text{e}^- \quad (5)$$

In acidic pH, $E_{\text{peak}, II}$ presents a slightly positive gradient of $+14 \pm 5 \text{ mV dec}^{-1}$. This clearly deviates from the $1 \text{H}^+: 2\text{e}^- \text{PCET mechanism}$ generally ascribed to $\text{MoS}_2$ electrodissolution, and would theoretically imply a $1 \text{ proton-depleting, 3 electron-generating PCET mechanism}$. This informs of a complex electro-oxidation mechanism which cannot be unambiguously described by one specific redox process. The most likely final electro-oxidation products are, according to thermodynamic stability, the acid-unstable $\text{MoO}_3$ (pH $\leq 1$) and the solution-soluble $\text{HMoO}_4^{−}$ ($1 \leq \text{pH} \leq 7$).[82,101]

### 2.5. AE-$\text{MoS}_x$ Inherent Electrochemical Activity: Electrochemical Conditioning

Having in mind the inherent electrochemical features found for AE-$\text{MoS}_x$, we proceeded to evaluate the impact of several voltammetric pretreatments on pristine thin films. These not only intend to identify an optimal activation step to maximize the AE-$\text{MoS}_x$ thin film HER activities, but also to corroborate the redox mechanisms proposed previously. For such purpose, a combined use of electrochemical techniques, ex situ Raman and ex situ XPS measurements were used to correlate positive/negative electrocatalytic effects with modifications in surface morphology and/or species.

Multiple activation pretreatments can be chosen by tuning the electrochemical parameters: in our study cyclic voltammetry is chosen over potentiostatic preconditioning procedures because of the need to monitor any electrochemical modifications of the redox features during preconditioning. Although AE-$\text{MoS}_x$ operate in reductive potentials under HER conditions, ex situ XPS acquired after electrochemical conditioning will enable to correlate generated/electrodissolved surface
species and their immediate impact to the HER, which would be misguidedly ascribed if samples were to be measured after HER operation due to irreversible precatalytic redox processes as previously mentioned. Conditioning procedures considered were: reductive, oxidative and reductive-oxidative (for further details, see Section 4 and Section S2.5 in the Supporting Information). For perspective purposes, a compilation of the electrochemical performance of AE-MoS\textsubscript{x} thin films with respect to other MoS\textsubscript{2}-based HER catalysts is shown in Table S1 (Supporting Information).

For the electro-oxidation treatment (Figure S12a, Supporting Information), no electro-oxidative peaks are observed, but these peaks can be found for both oxidative-reductive treatments (Figures S12c,d, Supporting Information). This suggests that the species responsible for the electro-oxidation features $E_{\text{peak,I}}$ and $E_{\text{peak,II}}$ only arise after the AE-MoS\textsubscript{x} thin films have been previously cycled past the precatalytic wave $E_{\text{peak,1}}$ at cathodic potentials. Thus, we believe that the cathodic prewave is indispensable for $E_{\text{peak,I}}$ to occur and vice-versa: this would initially support our claims that $E_{\text{peak,1}}$ corresponds to the electrochemically reversible S–S bond cleaving/dissolution and reductive (Figure S14, Supporting Information) cyclic pretreatments along with their respective XPS spectra. For the oxidative-reductive voltammograms, it was observed that $E_{\text{peak,1}}$ split into two peaks after continuous cycling irrespective of the electrolyte pH (Figure 6a). For AE-MoS\textsubscript{x} cycled in a pH 6 electrolyte (Figure 6b), the initially broad precatalytic peak found at $E_{\text{peak,1}} \approx -0.68$ V for the first scan decomposed into $E_{\text{peak,III}} \approx -0.53$ V and $E_{\text{peak,IV}} \approx -0.64$ V. Peak III current density decreased, and peak position shifted positively upon cycling, whereas peak IV emerged as cycling progressed. Plotting of the pH-dependent $E_{\text{peak,III}}$ and $E_{\text{peak,IV}}$ position in the 0–10 pH range for the 50th oxidative-reductive cathodic scan (Figure 6c) showed that both peaks presented a Nernstian gradient close to $-59$ mV dec\textsuperscript{-1} ($E_{\text{peak,III}} \approx -52 \pm 1$ mV dec\textsuperscript{-1}, $E_{\text{peak,IV}} \approx -49 \pm 1$ mV dec\textsuperscript{-1}), consequently leading to an almost constant peak separation. This satisfies the 2 H\textsuperscript{+}: 2e\textsuperscript{-} PCET reduction mechanism under which the S–S bond cleaving/dissolution is suggested to occur.

Finally, we compared the relative peak current intensities of $E_{\text{peak,III}}$ and $E_{\text{peak,IV}}$ to the relative abundance of the S\textsubscript{2}\textsuperscript{-} components found in XPS after electrochemical testing. Amorphous MoS\textsubscript{2} materials are deconvoluted with two S 2p\textsubscript{3/2} spin-orbit doublets (see Figure S7b, Supporting Information): for pristine AE-MoS\textsubscript{x} these correspond to a “low binding energy” doublet ascribed to both S\textsubscript{2}\textsuperscript{-} bridging and S\textsubscript{2}\textsuperscript{-} terminal given by reactions (1a) and (1b), and $E_{\text{peak,1}}$ to the reverse reaction (4a).

2.5.1. AE-MoS\textsubscript{x} Electrochemical Conditioning by Oxidative-Reductive and Reductive Cycling: EC, Raman, and XPS Analysis

To further corroborate this, we analyzed the voltammetric profiles of both oxidative-reductive (Figure S13, Supporting Information) and reductive (Figure S14, Supporting Information) cyclic pretreatments along with their respective XPS spectra. For the oxidative-reductive voltammograms, it was observed that $E_{\text{peak,1}}$ split into two peaks after continuous cycling irrespective of the electrolyte pH (Figure 6a). For AE-MoS\textsubscript{x}, cycled in a pH 6 electrolyte (Figure 6b), the initially broad precatalytic peak found at $E_{\text{peak,1}} \approx -0.68$ V for the first scan decomposed into $E_{\text{peak,III}} \approx -0.53$ V and $E_{\text{peak,IV}} \approx -0.64$ V. Peak III current density decreased, and peak position shifted positively upon cycling, whereas peak IV emerged as cycling progressed. Plotting of the pH-dependent $E_{\text{peak,III}}$ and $E_{\text{peak,IV}}$ position in the 0–10 pH range for the 50th oxidative-reductive cathodic scan (Figure 6c) showed that both peaks presented a Nernstian gradient close to $-59$ mV dec\textsuperscript{-1} ($E_{\text{peak,III}} \approx -52 \pm 1$ mV dec\textsuperscript{-1}, $E_{\text{peak,IV}} \approx -49 \pm 1$ mV dec\textsuperscript{-1}), consequently leading to an almost constant peak separation. This satisfies the 2 H\textsuperscript{+}: 2e\textsuperscript{-} PCET reduction mechanism under which the S–S bond cleaving/dissolution is suggested to occur.

Finally, we compared the relative peak current intensities of $E_{\text{peak,III}}$ and $E_{\text{peak,IV}}$ to the relative abundance of the S\textsubscript{2}\textsuperscript{-} components found in XPS after electrochemical testing. Amorphous MoS\textsubscript{2} materials are deconvoluted with two S 2p\textsubscript{3/2} spin-orbit doublets (see Figure S7b, Supporting Information): for pristine AE-MoS\textsubscript{x}, these correspond to a “low binding energy” doublet ascribed to both S\textsubscript{2}\textsuperscript{-} terminal and S\textsubscript{2}\textsuperscript{-} unsat with 2p\textsubscript{3/2} and 2p\textsubscript{1/2} binding energies of 161.7 ± 0.1 eV and 162.9 ± 0.1 eV, and a “high binding energy” doublet ascribed to both S\textsubscript{2}\textsuperscript{-} bridging and apical S\textsubscript{2}\textsuperscript{-} (S\textsuperscript{2}\textsuperscript{-}apical) with 2p\textsubscript{3/2} and 2p\textsubscript{1/2} binding energies of 163.0 ± 0.1 eV and 164.2 ± 0.1 eV.[67,102] An excellent correlation
between relative atomic abundance of the $S_{2\text{-terminal}}^{\text{unsat}}/S_{2\text{-apical}}^{\text{unsat}}$ and $S_{2\text{-bridging}}^{\text{bridging}}/S_{2\text{-apical}}^{\text{apical}}$ components after electrochemical conditioning and the relative $E_{\text{peak,III}}/E_{\text{peak,IV}}$ current intensity at the 50th scan was found, respectively, in the 0–7 pH range (see Table S2, Supporting Information).

For alkaline pHs, the electrochemical oxidation of the MoS$_x$ film by (4b) along with the thermodynamic instability of its reaction products driven by reaction (5) results in overall thin film dissolution and oxidation of $S_x^{\text{−}}$ components to $SO_x^{\text{−}}$ which prevents any quantitative XPS analysis. This led us to ascribe $E_{\text{peak,III}}$ and $E_{\text{peak,IV}}$ to the electrochemical cleaving of the S–S bond from $S_{2\text{-terminal}}^{\text{2-terminal}}$ and $S_{2\text{-bridging}}^{\text{bridging}}$. This is in good agreement with the inherent bonding strengths of $S_{2\text{-terminal}}^{\text{2-terminal}}$ and $S_{2\text{-bridging}}^{\text{bridging}}$: the Raman vibration of $S_{2\text{-terminal}}^{\text{2-terminal}}$ $\nu(S-S)_{\text{terminal}}$ $\approx$ 516 cm$^{-1}$, appears at lower wavenumbers (i.e., softer binding energy) than that of $S_{2\text{-bridging}}^{\text{bridging}}$ $\nu(S-S)_{\text{bridging}}$ $\approx$ 555 cm$^{-1}$, indicates that $S_{2\text{-terminal}}^{\text{2-terminal}}$ is more prone to undergo electrochemical cleaving at lower overpotentials than $S_{2\text{-bridging}}^{\text{bridging}}$. The excellent correlation between electrochemical and ex situ XPS data supports the use of the latter versus in situ XPS, technically challenging and not available in most research facilities.

The higher content of the “high binding energy” $S_{2\text{-bridging}}^{\text{bridging}}/S_{2\text{-apical}}^{\text{apical}}$ component versus the “low binding energy” $S_{2\text{-terminal}}^{\text{2-terminal}}/S_{2\text{-unsat}}^{\text{unsat}}$ after oxidative-reductive cycling (averaged $S_{2\text{-terminal}}^{\text{2-terminal}}/S_{2\text{-unsat}}^{\text{unsat}}$ $S_{2\text{-bridging}}^{\text{bridging}}/S_{2\text{-apical}}^{\text{apical}}$ ratio of 35.65 vs 46.54 as found in pristine AE-MoS$_x$) along with the $E_{\text{peak,III}}$ current intensity decay upon continuous cycling suggests that S–S cleaving in $S_{2\text{-terminal}}^{\text{2-terminal}}$ proceeds by the cathodic dissolution mechanism (1b) along with electro-oxidative dissolution (4b), the former favored by successive cycling due to the increasingly more positive $E_{\text{peak,III}}$ position. For $E_{\text{peak,IV}}$, the conversion of $S_{2\text{-bridging}}^{\text{bridging}}$ to $S_{2\text{-unsat}}^{\text{unsat}}$ appears to be partially reversible as in both oxidative-reductive and reductive cycling, the $E_{\text{peak,IV}}$ current intensity decreases steadily but the peak is still well resolved. In stark contrast, at the electrochemical cycling voltage region the HER pre-catalytic feature is almost irreversible: after the first scan, $E_{\text{peak,1}}$ current decreases substantially or is almost negligible (see Figures S12b and S14, Supporting Information). Interestingly, the relative $S_{2\text{-terminal}}^{\text{2-terminal}}/S_{2\text{-unsat}}^{\text{unsat}}$ $S_{2\text{-bridging}}^{\text{bridging}}/S_{2\text{-apical}}^{\text{apical}}$ XPS ratio is almost unchanged with respect to pristine AE-MoS$_x$ after reductive cycling across the 0–10 pH range (averaged 49.51 over 0–10 pH results vs initial 46.54, Table S3, Supporting Information). This can be well understood if $S_{2\text{-bridging}}^{\text{bridging}}$ and $S_{2\text{-terminal}}^{\text{2-terminal}}$ cleaving selectively undergo mechanisms (1a) and (1b), respectively. The freshly formed $S_{2\text{-unsat}}^{\text{unsat}}$ moieties after $S_{2\text{-bridging}}^{\text{bridging}}$ cleaving compensate the loss of $S_{2\text{-terminal}}^{\text{2-terminal}}$ in the XPS S 2P$_{3/2}$/2P$_{1/2}$ components, keeping their relative ratio balanced.

Investigation of the Raman spectra recorded for samples after having undergone oxidative-reductive and reductive electrochemical conditionings (Figures S15 and S16, Supporting Information) present multiple similarities. The gradual decrease toward higher pH values of both $\nu(S-S)_{\text{terminal}}$ and $\nu(S-S)_{\text{bridging}}$ Raman modes as compared to $\nu(S_{\text{apical}}^{\text{Mo}}-\text{Mo})$, which ultimately disappear in neutral to alkaline pHs, corroborates the electrochemical cleaving of $S_{2\text{-terminal}}^{\text{2-terminal}}$ and $S_{2\text{-bridging}}^{\text{bridging}}$ moieties at hydrogen pre-catalytic potentials. It is also observed that both $\nu(\text{Mo}−\text{Mo})$ and $\nu(\text{Mo}−\text{S})$ vibration bands in the 150–225 cm$^{-1}$ and 285–360 cm$^{-1}$ wavenumber range, respectively, become increasingly unresolved toward higher pH values to ultimately become a broad band: this indicates the loss of the cluster-like structure as found in pristine AE-MoS$_x$. The lack of any $\nu(\text{Mo}−\text{Mo})$ and $\nu(\text{Mo}−\text{S})$ band sharpening, contrary to that found for pristine films’ electro-oxidation, suggests that morphological restructuring under these electrochemical conditioning protocols is less severe.

Interestingly, the $\nu(S_{\text{apical}}^{\text{Mo}}-\text{Mo})$ vibrational band seems to split into two additional peaks: one redshifted ($\approx$437 cm$^{-1}$, sharp and intense) and another one blueshifted ($\approx$483 cm$^{-1}$), the latter poorly defined toward higher pHs. Tran and co-workers suggested that $S_{2\text{-terminal}}^{\text{2-terminal}}$ dissolution under hydrogen evolving conditions modified the Mo$_x$ cluster geometry ultimately red-shifting the $\nu(S_{\text{apical}}^{\text{Mo}}-\text{Mo})$ vibration. Indeed, the fact that these bands selectively arise upon reductive cycling within the pre-catalytic peak $E_{\text{peak,1}}$ voltage region informs us that this redox process is indeed directly responsible for the emerging Raman modes. The initial $\nu(S_{\text{apical}}^{\text{Mo}}-\text{Mo})$ vibration is greatly diminished, but still present at pH 0, which clearly indicates that the band at $\approx$437 cm$^{-1}$ is a indeed new Raman vibration arising from a weaker $S_{\text{apical}}^{\text{Mo}}$ bond. Accordingly, we believe that the band at $\approx$437 cm$^{-1}$ corresponds to a Mo–S–Mo vibration arising after $S_{2\text{-bridging}}^{\text{bridging}}/S_{2\text{-apical}}^{\text{apical}}$ cleavage, similar to the $\nu(\text{Mo}−\text{S}−\text{Mo})$ stretching mode found for CE-MoS$_x$ (425 cm$^{-1}$). This would support previous reports which suggested a morphological conversion of CE-MoS$_x$ to CE-MoS$_x$ under HER potentials due to S loss and S–S bond cleavage. In the case of the band at $\approx$483 cm$^{-1}$, as already discussed for the pristine electro-oxidation Raman scenario, it is hypothesized to be originated by partially cleaved $S_{2\text{-terminal}}^{\text{2-terminal}}$ moieties: ultimately this band disappears after full dissolution of $S_{2\text{-terminal}}^{\text{2-terminal}}$ moieties.

As for the Mo$^{4+}$–Mo$_2$O$_3$S$_4$; Mo$^{6+}$ XPS relative photoemission ratios, no clear trend can be found neither for the oxidative-reductive nor for the reductive CV conditioning treatments as a function of the pH.

Analysis of Raman and XPS ex situ data for AE-MoS$_x$ samples conditioned by electro-oxidative cycling (see Section S2.5.2 in the Supporting Information for full details) confirms the electrochemical evidence that in acidic pH values the overall Mo$_x$S$_x$ electro-oxidation is governed by the $S_{2\text{-terminal}}^{\text{2-terminal}}/S_{2\text{-unsat}}^{\text{unsat}}$ electrode dissolution (4b) accompanied by a steady Mo$^{4+}$/Mo$^{6+}$ conversion, whereas in mildly acidic to alkaline pHs the Mo$_x$S$_x$ electro-oxidation mostly proceeds by the prominent Mo$_x$O$_{y/z}$ electro-dissolution.

2.6. AE-MoS$_x$ Activity After Electrochemical Conditioning: Descriptors for Enhanced HER Electrocatalysis

After gathering understanding regarding the implications of the electrochemical cycling pretreatments on the inherent morphology and oxidation state on AE-MoS$_x$ samples, we proceeded to evaluate their impact on the HER electrocatalysis. Figure 7 shows representative LSVs (iR compensated) of AE-MoS$_x$ samples before/after undergoing reductive electrochemically conditioned treatments at pH 0, 3, 6, and 9, respectively. It can be clearly concluded, by comparing the overpotentials required to achieve HER current densities of $\approx$2.5 mA cm$^{-2}$ ($\eta_{\text{HER}}$ = $\eta_{\text{initial}} - \eta_{\text{final}}$), a figure of merit attainable at the HER overpotential window monitored for all
pH values in this study, that the electrochemical conditioning treatments performed do have an effect on the HER electrocatalysis. Samples conditioned at very acidic pHs (pH 0) present the faintest modification in their performance; at mildly acidic conditions (pH 3) their overall effect is negative, whilst in quasi-neutral conditions (pH 6) there is a substantial enhancement in the HER electrocatalysis. Finally, for alkaline conditions (pH 9), the electrochemical conditionings studied are again detrimental for the HER electrocatalysis. In an attempt to correlate any modification in HER electrocatalysis with physical properties of the AE-MoS₂ samples, we plotted \( \eta_{\text{HER}} \) as a function of the most commonly used HER descriptors in the amorphous MoS₂ literature across the studied pH range according to their XPS relative abundance: “high binding energy” \( S^{2-}_{\text{apical}}/S^{2-}_{\text{apical}} \), \( Mo^{4+} \), \( S^{2-}/S^{2-} \)-\( Mo^{4+} \) ratio (only including unoxidized Mo and S surface species), and total S:Mo ratio (accounting for oxidized Mo and S surface species).

For samples undergoing the “electro-oxidation” cycling (Figure 8), there is a clear correlation between the HER electrocatalysis and the relative surface content of \( S^{2-}_{\text{apical}}/S^{2-}_{\text{apical}} \) and \( Mo^{4+} \) species. Surprisingly, the samples which presented enhanced HER electrocatalysis were the ones which presented lower \( Mo^{4+} \) and \( S^{2-}_{\text{apical}}/S^{2-}_{\text{apical}} \) species contents, and vice versa. This contradicts recent reports which correlated higher hydrogen turnover frequencies with incremental \( S^{2-}_{\text{apical}}/S^{2-}_{\text{apical}} \) species and \( Mo^{4+} \) contents.\(^{[78]}\) This leads us to believe that partially oxidized, undercoordinated Mo moieties generated during electro-oxidation present promoted HER activities compared to the untreated AE-MoS₂ cluster-like structure, somehow involving the generation of more active \( S^{2-}_{\text{terminal}}/S^{2-}_{\text{unsat}} \) moieties.

For samples treated by the “oxidation-reduction” cycling (Figure S18, Supporting Information), no clear trend can be found for the \( S^{2-}_{\text{bridging}}/S^{2-}_{\text{apical}} \) and \( Mo^{4+} \) species relative surface content, but it seems to be present in the \( S^{2-}/S^{2-} : Mo^{4+} \) ratio instead: higher sulfide contents lead to improved HER activity and vice versa. The well-established proton-accepting role of sulfur sites in MoS₂ electrocatalysis supports this experimental trend.\(^{[13,104]}\) Finally, the AE-MoS₂ samples electrochemically conditioned by “reductive” cycling (Figure 9) present HER electrocatalytic properties correlating with “high binding energy” \( S^{2-}_{\text{bridging}}/S^{2-}_{\text{apical}} \) and \( S^{2-}/S^{2-} : Mo^{4+} \) ratio (the latter to a minor extent): higher sulfide contents and lower \( S^{2-}_{\text{bridging}}/S^{2-}_{\text{apical}} \) promoted HER on AE-MoS₂. This trend is very valuable as it informs that not only sulfur is the main HER active site triggered under selective cathodic preconditioning, but also that the simultaneously electrochemically induced \( S^{2-}_{\text{bridging}} \) cleaving and \( S^{2-}_{\text{terminal}} \) dissolution leads to unsaturated \( S^{2-}_{\text{unsat}} \) moieties which are ultimately the proton-accepting sites.

It is also noteworthy to compare the maximum positive/negative electrocatalytic effects obtained as a function of the electrochemical preconditioning employed, giving an order as follows: reductive (from \(-350 \) to \(+250 \) mV) > electro-oxidative (from \(-290 \) to \(+210 \) mV) > oxidative-reductive (from \(-220 \) to \(+150 \) mV). Hence, selective electrochemical cycling within the precatalytic HER and electro-oxidative windows, trigger electrochemically driven AE-MoS₂ surface restructuring that
govern the HER performance, namely, $S_{22}^{-}$ bridging cleaving and $S_2^{-}$ terminal dissolution, and partially oxidized undercoordinated Mo moieties generation, respectively. Analogous enhancements on crystalline MoS$_2$ were found upon reductive electrochemical treatments, initially allocated to lower chalcogen-to-metal ratios exposing more Mo-edge sites$^{[100]}$ and later ascribed to the basal plane activation by formation of S vacancies below $-1$ V versus RHE.$^{[42]}$ For oxidative-reductive conditioning, the partial electrochemical reversibility of the aforementioned phenomena limits their impact on the HER electrocatalysis, as their generation

Figure 8. Summary of $\eta_{\text{HER}}@2.5$ mA cm$^{-2}$ as a function several AE-MoS$_x$ descriptors across the 0–10 pH range after electro-oxidative AE-MoS$_x$ conditioning: a) “high binding energy” $S_{22}^{-}$ bridging/$S_2^{-}$ apical content, b) Mo$^{4+}$ content, c) $S_2^{-}/S_{22}^{-}$:Mo$^{4+}$ ratio, and d) total S:Mo ratio. At% units correspond to relative XPS percentages within the Mo 3d and S 2p deconvoluted components.

Figure 9. Summary of $\eta_{\text{HER}}@2.5$ mA cm$^{-2}$ as a function several AE-MoS$_x$ descriptors across the 0–10 pH range after reductive AE-MoS$_x$ conditioning: a) “high binding energy” $S_{22}^{-}$ bridging/$S_2^{-}$ apical content, b) Mo$^{4+}$ content, c) $S_{2}^{-}$/$S_{22}^{-}$:Mo$^{4+}$ ratio, and d) total S:Mo ratio. At% units correspond to relative XPS percentages within the Mo 3d and S 2p deconvoluted components.

at anodic/cathodic regions will be inevitably followed by their partial depletion/reinstatement at the opposite voltage range.

In addition to this, specific pH ranges can be identified where the AE-MoS$_x$ surface is either insensitive or dramatically affected by the electrochemical conditioning methods employed. Samples preconditioned at pH 4 present the lowest overpotential modifications (reductive: $-10$ mV, electro-oxidative: $-15$ mV, oxidative-reductive: $+30$ mV), whereas those conditioned at pH 6 (reductive: $-350$ mV, electro-oxidative: $-290$ mV, oxidative-reductive: $-220$ mV) and pH 9 (reductive: $+250$ mV, electro-oxidative: $+210$ mV, oxidative-reductive: $+150$ mV) present the most positive and negative impact on HER electrocatalysis, respectively. These provide insight on specific pH regions under which AE-MoS$_x$ activity and/or stability may be exploited for long-term operating conditions.

Thus, we can conclude that monitoring of specific HER descriptors across the whole pH spectrum, specifically those related to sulfide moieties ($S_2^{2-}$bridging/$S_2^{2-}$apical and $S_2^{2-}$/S$_2^{2-}$:Mo$_{4+}$ ratio), allow the correlation of the experimental hydrogen electrocatalysis observed with surface-dependent AE-MoS$_x$ properties.

2.7. AE-MoS$_x$, Long-Term HER Performance: Stability and Accelerated Durability Testing

Assessment of the stability and durability of HER catalysts is paramount for their implementation in commercial PEM electrolyzer stacks. However, recent reports have highlighted that no standardized stability test protocol has been adopted in the HER field to evaluate electrocatalytic lifetimes.$^{[105,106]}$ For oxygen evolution electrocatalysts, however, several benchmarking tests have been proposed, most of them comprising chronopotentiometric measurements to monitor catalyst stability (with durations not less than 2 h)$^{[107]}$ and continuous potential cycling at high voltage scan rates. The latter have proven to give representative information on electrocatalyst durability at shorter timescales, comparable to that obtained at PEM electrolyzer average lifetimes (50 000 h)$^{[108]}$. Here we opted to evaluate pristine AE-MoS$_x$ hydrogen evolution stability and durability across the 0–10 pH range by recording, under 1500 rpm stirring, chronopotentiograms of 12 h duration at a constant cathodic current density of $-10$ mA cm$^{-2}$ (HER benchmarking current density),$^{[109]}$ and by acquiring 3000 cyclic voltammograms at 100 mV s$^{-1}$ scan rate with a cathodic voltage limit set to attain a maximum current density of $-10$ mA cm$^{-2}$.

A compilation of the 12 h stability test results is shown in Figure 10a,b. At very acidic environments ($0 \leq$ pH $\leq 2$) a significant upward increase in both initial ($t = 0 \pm 10$ min) and final ($t = 12$ h $\pm 10$ min) HER overpotentials was found toward higher pH values. It is widely established that transition metal sulfides dissolve in acidic media under HER operating conditions due to sulfur atoms loss.$^{[110,111]}$ This property is key in AE-MoS$_x$, as the electrochemically induced $S_2^{2-}$bridging cleaving and $S_2^{2-}$terminal dissolution at cathodic potentials, despite of

Figure 10. a) Representative chronopotentiograms recorded during AE-MoS$_x$ HER stability measurements (12 h galvanostatic electrolysis at $j_{geom} = -10$ mA cm$^{-2}$). b) Averaged ($\pm 10$ min) initial (green) and final (red) overpotentials to sustain $j_{geom} = -10$ mA cm$^{-2}$ for 12 h. c) Initial (blue) and final (orange) HER $\eta_{HER}@$ [5 mA cm$^{-2}$] obtained during accelerated durability testing on AE-MoS$_x$ (3000 CVs, 100 mV s$^{-1}$). Values with * indicate approximate overpotentials due to experimental currents not achieving $-5$ mA cm$^{-2}$ at the evaluated voltage window. d) Summary of $\eta_{HER}@$ [5 mA cm$^{-2}$] as a function Mo$_{5+}$O$_x$S$_y$ relative XPS content across the 0–10 pH range after accelerated durability testing.
the inevitable sulfur loss, are responsible for the generation of the $S^2\text{MoS}_x$ HER active sites. At pH 2, we suspect that the high AE-MoS$_x$ instability, along with the dissolution of the Au electrode layer promoted by the high chloride concentration in the buffered electrolyte (found after physical inspection of the samples' surfaces), explain the dramatic HER overpotential increase. Surprisingly, in mildly acidic conditions (3 ≤ pH ≤ 6) the AE-MoS$_x$ samples present almost unchanged HER performances, slightly improved at pH 4 values (≈167 mV lower average overpotential) and to a lesser extent at pH 6 (≈45 mV lower average overpotential). Finally, for neutral-to-alkaline environments (7 ≤ pH ≤ 10), the HER continuous performance seems almost constant in neutral pHs (7–8) whereas it clearly worsens in alkaline pHs (9–10), with starting overpotentials increasingly higher toward higher pHs. As mentioned previously, the increasingly higher inherent thermodynamic instability of AE-MoS$_x$ toward alkaline environments supports the worsened HER performance observed.

Upon analysis of the overall initial HER overpotential trends, it is of particular relevance that both the 3 ≤ pH ≤ 5 and pH 7 regions break the generally upward trend: these might represent pH environments of AE-MoS$_x$ improved electrochemical activity and stability.

A compilation of the accelerated durability cycling testing for $\eta_{HER}$$[$5 mA cm$^{-2}$] across the 0–10 pH range is shown in Figure 10c (for representative cycling voltammograms, see Figure S19, Supporting Information). The experimental trends are in good agreement those obtained for chronopotentiometry experiments: acidic (0 ≤ pH ≤ 2) and neutral-to-alkaline (7 ≤ pH ≤ 10) pH environments present increased HER overpotentials after voltammetric cycling, significantly higher in the alkaline scenario. However, AE-MoS$_x$ tested in mildly pH conditions (3 ≤ pH ≤ 6), contrary to chronopotentiometry experiments, present enhanced HER electrocatalytic activities. This supports previous experimental evidence that, under these pH conditions, AE-MoS$_x$ HER electrocatalysis does not only seem more favorable (maximized HER activities after electrochemical conditioning for pH 6) but can also be sustained under short duty and accelerated durability testing conditions.

Ex situ Raman (Figure 11) and XPS spectroscopy measurements after accelerated durability tests provide insight on their origin. Compared to pristine AE-MoS$_x$, both $v$(Mo−Mo) and $v$(Mo−S) vibration bands in the 150–225 and 285–360 cm$^{-1}$ wavenumber range, respectively, become increasingly unresolved toward higher pH values leading to their complete disappearance in favor of a broad band from pH 4 upward. Hence, the previously well-defined AE-MoS$_x$ cluster-based structure is irreversibly modified after accelerated HER operation conditions. Analogously, the $v$(S$_{apical}$−Mo), $v$(S−S)$_{terminal}$, and $v$(S−S)$_{bridging}$ vibrations found at 447, 516, and 555 cm$^{-1}$ in pristine thin films, respectively, undergo substantial modifications.

As previously reported for AE-MoS$_x$ undergoing reductive electrochemical preconditioning, in acidic environments (0 ≤ pH ≤ 3), the signal intensities of $v$(S−S)$_{terminal}$ and $v$(S−S)$_{bridging}$ gradually decreased at increasing pH values, the former completely disappearing at pH 1 and the latter blueshifting and ultimately only observed as a shoulder up to pH 3. Analogously, the $v$(S$_{apical}$−Mo) vibrational band splits into two additional peaks: one redshifted (≈437 cm$^{-1}$, ascribed to Mo−S−Mo vibration similar to those found for CE-MoS$_x$ and another one blueshifted (≈483 cm$^{-1}$, ascribed to partially cleaved S$_2^{2−}$ terminal moieties), the latter poorly defined toward upward pHs. From mildly acidic to neutral pHs (4 ≤ pH ≤ 7), the Mo=O (≈880 cm$^{-1}$) and Mo(=O)$_2$ (≈960 cm$^{-1}$) vibrations steadily surfacing in acidic pHs govern the Raman spectra, leaving the unresolved (Mo−Mo) and (Mo−S) bands in the 100–600 cm$^{-1}$ overlapped as a shoulder. Finally, the thermodynamic instability of surface molybdenum oxides in alkaline environments implies the dissolution of Mo$_2$O$_3$, species responsible for Mo=O and Mo(=O)$_2$ vibrations, which ultimately justifies the resurfacing of (Mo−Mo) and (Mo−S) bands from nondissolved MoS$_x$.

Component analysis of ex situ XPS spectra on the freshly tested samples shows no clear trend involving the previously employed HER descriptors (see Figure S20,
Supporting Information). However, when plotting the oxygen-incorporated MoO$_3$:O$_{S_y}$ relative surface content along with the $\eta_{\text{HER}}$ [5 mA cm$^{-2}$] across the 0–10 pH range (Figure 10d), a clear positive correlation between enhanced HER performances and MoO$_{4}$:O$_{S_y}$ contents was found: at pH 6, where the MoO$_{4}$:O$_{S_y}$ relative surface content is found to be the highest (±36.7 ± 3.6 at%), the biggest HER overpotential shift is also achieved (≈−220 mV). As stated in Section 2.2, the presence of $E_{\text{peak,2}}$ and $E_{\text{peak,3}}$ at pH $\geq$ 5 supported the instability of MoO$_{4}$:O$_{S_y}$ in acidic environments, which is in good agreement with the results obtained in both Raman (faint Mo=O and Mo(=O)$_2$ vibration intensities) and XPS measurements (MoO$_{4}$:O$_{S_y}$ contents lower after electrochemical testing than as-prepared AE-MoS$_x$; <18±2.0 at%) for samples tested in acidic electrolytes. Remarkably, at pH values higher than 4 (i.e., when the HER electrocatalysis is greatly enhanced), the intense Mo=O and Mo(=O)$_2$ vibrations allocated to molybdenum oxide species as well as the sharp increase in oxygen-containing MoO$_{4}$:O$_{S_y}$ surface species indicate a convergence between oxygen incorporation in the AE-MoS$_x$ film and enhanced HER electrocatalysis.

Thus, this leads us to the conclusion that the most active HER AE-MoS$_x$ phase involves, under hydrogen evolving conditions, the formation of oxygen-incorporated (i.e., sulfur deficient) MoO$_{5}^{-}$:O$_{S_y}$ species. As the undeniable role of S$_2^{\text{unsat}}$:bridging and S$_2^{\text{unsat}}$:terminal in the HER catalysis has been proven in this study, their selective electrochemical cleaving lead, respectively, to unsaturated sulfur (reaction 1a) and molybdenum (reaction 1b) sites. We hypothesize, accordingly, that both phenomena synergistically assist in the generation of the HER active sites. Indeed, a very recent report has correlated enhanced hydrogen electrocatalysis in amorphous MoS$_x$ materials at neutral pH values with an internal reorganization of a bridging S$_2^{\text{bridge}}$:bridging ligand to an S$_2^{\text{unsat}}$:terminal configuration by in situ Raman measurements.$^{[72]}$ This reorganization in the Mo$_y$-thio cluster-like structure was proposed to yield undercoordinated Mo–Mo sites which synergistically promoted the HER. However, the S$_2^{\text{unsat}}$:terminal dissolution found in this study supported by electrochemical, Raman, and XPS experiments leads us to believe that the bridging S$_2^{\text{bridge}}$:bridging ligand adopts an S$_2^{\text{unsat}}$:unsat configuration instead.

The AE-MoS$_x$ electrolycatalysis under hydrogen evolution conditions is then proposed to operate as follows. In acidic pH values (0 ≤ pH < 4), the predominant HER active sites are those comprising S$_2^{\text{unsat}}$:terminal formed after S$_2^{\text{unsat}}$:bridging cleaving as unsaturated Mo sites (although more active to the HER) will be prone to oxy(hydro)xide formation by hydration and subsequently present thermodynamic instability. On the other hand, in mildly acidic to neutral pHs (4 ≤ pH < 7), the unsaturated Mo$^+$ as found in MoO$_{5}^{-}$:O$_{S_y}$ species will no longer dissolve in the electrolyte, compensating for the S$_2^{\text{unsat}}$:loss and opening an alternative HER route similar to that proposed by Tran et al.$^{[74]}$ At this stage we must also take into account the variations of the inherent HER kinetics across the studied pH range to understand their interplay with the proposed active sites. At 0 ≤ pH ≤ 2, where the AE-MoS$_x$ HER mechanism is expected to undergo by H$_2$O$_2$ electroreduction, we believe that the cleaved S$_2^{\text{bridge}}$:bridging moieties (which act as proton-accepting sites, as suggested by in operando Raman studies) are the HER active sites. At higher pH values, as HER electrocatalysis should operate by the water reduction/splitting mechanism, we believe that the freshly cleaved S$_2^{\text{unsat}}$:bridging moieties are less electrocatalytically active, and only when MoO$_{5}^{-}$:O$_{S_y}$ species are thermodynamically stable at the surface (pH > 4) the HER can be successfully catalyzed. As previous in operando studies suggest an absence of v(Mo–H) at hydrogen evolving potentials, we believe that the HER mechanism on MoO$_{5}^{-}$:O$_{S_y}$ species necessarily involves the protonation of the Mo=O moieties through O–H bond cleavage and sequential electron transfer. Finally, at neutral to alkaline pHs (7 ≤ pH ≤ 10), the instability of both S$_2^{\text{unsat}}$:unsat and MoO$_{5}^{-}$:O$_{S_y}$ leads to the prominent formation of solution soluble molybdenum oxides with worsened HER kinetics.

### 3. Conclusion

This study has explored the impact of electrolyte pH on the inherent and HER electrochemistry of electrodeposited AE-MoS$_x$ films and its implications in long term operation conditions. Analysis of the precatalytic HER features along with EC and XPS using buffered electrolytes have corroborated the simultaneous cleaving of S$_2^{\text{bridge}}$:bridging and S$_2^{\text{unsat}}$:terminal dissolution along with a proposed reduction of MoO$_{5}^{-}$:O$_{S_y}$ species to MoO$_2$ only observed in the 5 ≤ pH ≤ 10 range.

The previously reported distinctive EC-dependent electro-oxidation features have been rationalized using PCET theory, demonstrating a modification in the complex electro-oxidation mechanism. Pristine AE-MoS$_x$ satisfies a 1 H$^+$:2e$^-$ PCET across the studied pH range ascribed to the oxidation of the Mo$^+$ moieties to Mo$^6+$ analogous to crystalline MoS$_2$, whereas HER preconditioned AE-MoS$_x$ presents two distinct electro-oxidation behaviors. In acidic electrolyte this cannot be unambiguously understood: XPS and Raman investigations suggest a mechanism comprising overall S$_2$:terminal/S$_2$:unsat electro-dissolution accompanied by a gradual Mo$^{6+}$/Mo$^{4+}$ conversion to generate MoO$_x$ species. In the 7 ≤ pH ≤ 10 range, it seems to operate by a sequential 1 H$^+$:1e$^-$ PCET arising from partial reinstatement of previously cleaved S$_2$:bridge$^-$:bridge$^-$ ligands and S$_2$:terminal liga$^-$ dissolution, followed by a 2 H$^+$:1e$^-$ PCET corresponding to the oxidation of MoO$_x$ to MoO$_{2^+}$. Electrochemical conditioning by cycling within reductive/ electro-oxidative/oxidative-reductive voltage results in pronounced changes in the HER performance giving an order of $|\eta_{\text{HER}}|@2.5$ mA cm$^{-2}$ enhanced/detrimental electrocatalytic effects as follows: reductive (from −350 to +250 mV) > electro-oxidative (from −290 to +210 mV) > oxidative-reductive (from −220 to +150 mV). The pH ranges responsible for the most enhanced and detrimental performances are 4 ≤ pH ≤ 6 and 8 ≤ pH ≤ 10, respectively. The triggered surface modifications mainly consisted of S$_2$:bridge$^-$:bridge$^-$ cleaving and S$_2$:terminal dissolution (reduction) and partially oxidized undercoordinated Mo sites generation with predominance of S$_2$:terminal/S$_2$:unsat moieties (electro-oxidative). Raman spectra analysis corroborated the reductive S$_2$:bridge$^-$:bridge$^-$ cleaving and S$_2$:terminal dissolution (suppressed vibration modes under reductive potentials), identifying additional bands here ascribed to partially cleaved S moieties.

Finally, 12 h constant current hold and accelerated cyclic voltammetry experiments revealed that AE-MoS$_x$ films, contrary
to conventional testing conditions reported in literature, retain their initial activity and provide more stable performances in the 3 ≤ pH ≤ 5 range. Combined analysis of XPS and Raman measurements suggest the oxygen-containing, S-deficient MoO\textsubscript{5}O\textsubscript{3}S\textsubscript{4} surface species as the responsible sites for the HER catalysis in this range. Although cleaved S\textsuperscript{2}− bridging ligands generating S\textsuperscript{2−}\textsubscript{unst} proton-accepting sites explain the HER activity of AE-MoS\textsubscript{x} in acidic electrolytes, the thermodynamic stability of MoO\textsubscript{5}O\textsubscript{3}S\textsubscript{4} species along with the water reduction HER mechanism satisfied in mildly acidic to alkaline electrolytes explain the key role of MoO\textsubscript{5}O\textsubscript{3}S\textsubscript{4}. The pivotal knowledge gathered from our pH-dependent benchmarking experiments, we believe, will enable to accelerate the deployment TMD-based electrolyzers and shed light into understanding the interplay between surface properties and electroactivity maximization for other earth-abundant HER materials.

4. Experimental Section

Electrochemical Measurements: Electrochemical measurements on electrodeposited MoS\textsubscript{x} thin films were made in a three-electrode configuration using a PC-controlled PGSTAT128N potentiostat (Metrohm Autolab B.V., Netherlands) with a thermostatted cell (295 ± 2K). MoS\textsubscript{x} thin film-modified Si (1 mm)/Si thermal oxidation layer (1 mm)/Ti (10 mm)/Au (100 nm) substrates prepared by sputtering deposition and mechanical dicing (5 × 15 mm, IMB-CNM, Universitat Autoboma de Barcelona, Spain) were used as working electrodes. A saturated calomel electrode (SCE, BAS Inc., Japan) and a bright Pt mesh (Alfa Aesar, U.K.) were used as reference and counter electrodes, respectively. To prevent possible platinum contamination onto the pristine MoS\textsubscript{x}, thin films, the Pt counter electrode was encapsulated in a glass tube with a fitted junction.

Electrolytes employed for pH-controlled inherent electrochemistry and HER measurements were prepared as follows. For pH=0, a 0.5 m H\textsubscript{2}SO\textsubscript{4} (95% v/v, Fisher Scientific) acid solution was employed. pH 1–2 solutions were obtained by mixing aliquots of 0.2 m HCl (37% v/v ACS, Sigma-Aldrich) and 0.2 m KCl (anhydrous, ACS ≥ 99%, Sigma-Aldrich) electrolytes. pH 3–6 buffered electrolytes were obtained by mixing varying volumes of 0.1 m citric acid monohydrate (ACS ≥ 99%, Sigma-Aldrich) and 0.1 m sodium citrate dihydrate (≥99% FG, Sigma-Aldrich) solutions. The phosphate buffered saline (PBS) pH 7 electrolyte was prepared by mixing 6.15 mL of a 1 m potassium phosphate dibasic trihydrate (≥99%, for molecular biology, Sigma-Aldrich), and 3.85 mL of a 1 m potassium phosphate monobasic (≥99%, for cell culture, Sigma-Aldrich). Finally, pH 8–10 buffered electrolytes were prepared by mixing 0.5 m sodium tetraborate (anhydrous, BioUltra ≥ 99%, Sigma-Aldrich) with 0.1 m HCl (for pH 8–9) or 0.1 m NaOH (ACS ≥ 97%, pellets, Sigma-Aldrich) (for pH 10). All electrolytes were brought to volume in 100 mL volumetric flasks with ultrapure water (Millipore Milli-Q Direct 8, resistivity not less than 18.2 MΩ cm), testing their final pH using a 3-point calibrated Mettler-Toledo FiveEasy FE20 pH bench meter coupled to a Mettler-Toledo LE438 pH electrode (Greifensee, Switzerland). Oxygen-free conditions during electrochemical experimentation were achieved after purging the EC cell with N\textsubscript{2} (Oxygen-free grade, Sigma-Aldrich) and maintaining by applying a positive N\textsubscript{2} atmosphere above the electrolyte surface. All electrochemical glassware was cleaned overnight by use of a dilute solution of KMnO\textsubscript{4} (ACS ≥ 99%, Sigma-Aldrich) in concentrated H\textsubscript{2}SO\textsubscript{4} (≥95% analytical grade, Fisher Scientific) followed by thorough rinsing with ultrapure water.

pH-dependent inherent electrochemical activity of as-prepared electrodeposited MoS\textsubscript{x} thin films was evaluated by acquiring one cyclic voltammogram from 0.7 to −1.2 V versus SCE. For MoS\textsubscript{x}, activation pretreatment studies, a 50 cyclic voltammogram protocol was employed, where both anodic and cathodic limits were modified based on the inherent electrochemical features observed in the voltammogram of the as-prepared sample. Three main pretreatments were investigated: electro-oxidative (lower voltage selected close to OCP values, upper voltage selected past the electro-oxidation features), oxidative-reductive (lower voltage selected past the first cathodic prewave peak, upper voltage selected past the electro-oxidation features) and reductive (lower voltage selected past the first cathodic prewave peak, upper voltage selected close to OCP values). Linear sweep voltammograms (E\textsubscript{anodic} = E\textsubscript{SCE} + 0.059 pH, to E\textsubscript{cathodic} = −1.2 V − 0.059 pH) and electrochemical impedance spectroscopy measurements (voltage range: 0.1 V to −1.4 V versus SCE, 200 mV steps, frequency range: 10\textsuperscript{−2}–10\textsuperscript{−1} Hz, voltage amplitude = 10 mV) were recorded before and after the activation pretreatment step to account for modifications in both HER activities and iR compensation corrections.

For long-term potentiodynamic durability testing, an initial linear sweep voltammogram was recorded from 0.7 to −1.2 V versus SCE on as-prepared MoS\textsubscript{x} thin films under 1500 rpm exeried by a magnetic stirring bar controlled by a stirring plate to establish the anodic and cathodic limits. The upper voltage limit was selected close to OCP values, whereas the cathodic limit was selected to achieve HER geometric current densities of −10 mA cm\textsuperscript{−2}. Under these conditions, 3000 cyclic voltammograms were recorded at 1500 rpm and positive N\textsubscript{2} pressure for all the electrolytes tested at a voltage scan rate of 100 mV s\textsuperscript{−1}. For stability measurements, a 12 h chronopotentiometry experiment was set to monitor the overpotential required to sustain a constant HER geometric current density of −10 mA cm\textsuperscript{−2}, with experimental conditions equivalent to those used for potentiodynamic experiments (1500 rpm, positive N\textsubscript{2} pressure).

All electrochemical experiments were repeated no less than three times to ensure reproducibility.

Preparation of Amorphous MoS\textsubscript{x}, Thin Films: Amorphous MoS\textsubscript{x} thin films were deposited onto Si/Ti (10 nm)/Au (100 nm) substrates by electrochemical deposition from a freshly prepared, deaerated electrolyte solution containing 2 × 10\textsuperscript{−1} m (NH\textsubscript{4})\textsubscript{2}Mo\textsubscript{4}O\textsubscript{2} (99.97% trace metal analysis, Sigma-Aldrich) and 0.1 m NaClO\textsubscript{4} (ACS ≥ 98%, Sigma-Aldrich). In this setup, a double-junction saturated Ag/AgCl reference electrode (Sigma-Aldrich) and a bright Pt mesh counter electrode (Alfa Aesar, UK) were employed. Analogously to HER experiments, the Pt counter electrode was encapsulated in a glass vial with a fitted junction to prevent Pt redeposition onto the deposited MoS\textsubscript{x} thin films. A deposition area on Si/Ti/Au chips (5 × 5 mm\textsuperscript{2}) was selectively exposed to the electrolyte by insulating the remaining working electrode surface with hydrophobic PTFE tape. Electrodeposition was carried out with neither rotation nor N\textsubscript{2} bubbling to prevent alterations in the deposition rate from the effects of convection. Preliminary deposition rate studies were performed by depositing MoS\textsubscript{x} thin films at various charge densities. Anodic electrodeposition (AE) was performed at a constant voltage of +0.1 V versus Ag/AgCl, while cathodic electrodeposition (CE) was performed at −1 V versus Ag/AgCl. MoS\textsubscript{x} thin film thickness versus charge density plots (Figure S3, Supporting Information) were obtained after three independent height profile measurements of each MoS\textsubscript{x}-modified sample using a Dektak TSF surface Profilometer (Veeco, USA). For inherent electrochemistry and HER experiments on AE-MoS\textsubscript{x}, an approx. thickness of 100 nm (33.7 mC cm\textsuperscript{−2}) was employed in all samples, assuming a 100% Faradaic deposition efficiency.

Physical Characterization of Amorphous MoS\textsubscript{x}, Thin Films: X-ray photoelectron spectroscopy (XPS) measurements were performed in a Thermo Scientific K-Alpha system (Thermo Scientific, UK) as well as in a Kratos AXIS ULTRA system (Kratos, UK): both used a microfocused monochromatic aluminum X-ray source (Al K\textalpha, 1486.6 eV, 12 kV), a charge neutralizer filament to prevent surface charging, and working pressures below 5 × 10\textsuperscript{−9} mbar. Three independent and nonoverlapping XPS analysis positions were acquired, using spot sizes of 400 × 800 µm (Thermo Scientific) and 0.5 mm\textsuperscript{2} (Kratos), on each MoS\textsubscript{x} sample mounted on a clean stainless steel plate. For low resolution survey spectra, 150 eV (Thermo Scientific)/80 eV (Kratos) pass energies and 0.4 eV (Thermo Scientific)/0.5 eV (Kratos) step sizes were employed (dwell time: 10 ms), whereas for high-resolution spectra pass energies
and step sizes of 40 eV (Thermo Scientific)/20 eV (Kratos) and 0.1 eV were selected (dwell time: 100 ms). All high-resolution spectra were energy-corrected to the adventitious C 1s peak set to 284.6 eV, and processed using the CASA XPS software (version 2.3.18PR1.0). For peak-deconvolution, Shirley backgrounds and Gaussian-Lorentzian (30) lineshapes were selected. Mo 3d spectra were fitted by applying a 3:2 area ratio constraint and 3.1 eV separation on the 3d5/2:3/2 spin-orbit doublets, whereas S 2p spectra were fitted by applying a 2:1 area ratio constraint and 1.2 eV separation on the 2P1/2:3/2 spin-orbit doublets.[30,112,113]

Raman spectroscopy measurements were conducted on a Renishaw inVia Raman microscope (Renishaw, UK) using a 532 nm laser and an interchangeable 50 cm−1 low pass filter (Renishaw, UK) previously calibrated by the 520 cm−1 peak found in a Si wafer standard. Low resolution survey spectra were recorded in the 100–2500 and 100–1200 cm−1 wavelength ranges by three cumulative acquisitions of 30 s were employed. In all cases, two nonoverlapping regions were investigated per MoS2 thin film sample, using a 20x objective lens and 10% laser power. Higher magnification lenses at the selected laser power and exposure times lead to lased-induced MoS2 crystallization as reported by Nguyen et al.[99]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank the EPSRC for support through funding for the Centre for Doctoral Training in Fuel Cells and their Fuels (D.E.L., N.V.R., EP/ G037116/1 and EP/L015749/1). The authors would also like to thank Dr. Francisco Javier del Campo and Dr. Joaquima Lopez Garcia at the IMB-CNM (CSIC) for the preparation of the Si/Ti/Au electrodes used in this work, and Dr. Jacqueline K. Deans at the Centre for Chemical and Materials Analysis (School of Chemistry, University of Birmingham) for support during Raman spectroscopy measurements. X-ray photoelectron spectra were obtained at the National EPSRC XPS Users’ Service (NEXUS) at Newcastle University, and EPSRC Mid-Range Facility, and at the Nanoscale and Microscale Research Centre (NMRC) at the University of Nottingham by Dr. Emily Smith.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

active sites, benchmarking, hydrogen evolution, molybdenum sulfide, pH

Received: August 21, 2018
Revised: October 10, 2018
Published online:

[1] A. Tatin, J. Bonin, M. Robert, ACS Energy Lett. 2016, 1, 1062.
[2] S. Chu, Y. Cui, N. Liu, Nat. Mater. 2017, 16, 16.
[3] J. A. Turner, Science 2004, 305, 972.
[4] S. Ardo, D. Fernandez Rivas, M. A. Modestino, V. Scholze Greiving, F. F. Abdi, E. Alarcon Llado, V. Artero, K. Ayers, C. Battaglia, J.-P. Becker, D. Bederat, A. Berger, F. Buda, E. Chinello, B. Dam, V. Di Palma, T. Edvinsson, K. Fujii, H. Gardeniers, H. Geerlings, S. M. H. Hashemi, S. Haussener, F. Houle, J. Huskens, B. D. James, K. Konrad, A. Kudo, P. P. Kuntur, D. Lohse, B. Mei, E. L. Miller, G. F. Moore, J. Muller, K. L. Orchard, T. E. Rossier, F. H. Saadi, J.-W. Schüttauf, B. Seger, S. W. Sheehan, W. A. Smith, J. Spurgeon, M. H. Tang, R. van de Krol, P. C. K. Veskberg, P. Wieserik, Energy Environ. Sci. 2018, 11, 2768.
[5] P. Quaino, F. Juarez, E. Santos, W. Schmickler, Beilstein J. Nanotechnol. 2014, 5, 846.
[6] D. Strmcič, P. P. Lopes, B. Genorio, V. R. Stamenkovic, N. M. Markovic, Nano Energy 2016, 29, 29.
[7] U. Gupta, C. N. R. Rao, Nano Energy 2017, 41, 49.
[8] Q. Ding, B. Song, P. Xu, S. Jin, Chem 2016, 1, 699.
[9] X. Yue, Q. Zhang, W. Wang, H. Cao, Q. Yang, L. Fu, Adv. Energy Mater. 2017, 7, 1.
[10] C. (Rose) Zhu, D. Gao, J. Ding, D. Chao, J. Wang, Chem. Soc. Rev. 2018, 47, 4332.
[11] D. Voiry, J. M. Chhouwalla, Adv. Mater. 2016, 28, 6197.
[12] T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Horch, I. Chorkendorff, Science 2007, 317, 100.
[13] B. Hinnemann, P. Moses, J. Bonde, K. P. Jørgensen, J. H. Nielsen, S. Horch, I. Chorkendorff, J. K. Nørskov, J. Am. Chem. Soc. 2005, 127, 5308.
[14] C. L. Bentley, M. Kang, F. Marder, F. Li, M. Walker, J. Zhang, P. R. Unwin, Chem. Sci. 2017, 8, 6583.
[15] L. Gong, S. C. Haur, J. Mater. Chem. C 2017, 5, 2090.
[16] M. Ruhul Amin, M. Anower Hossain, Y. Zakaria, R. Amin, ACS Appl. Mater. Interfaces 2018, 10, 13509.
[17] R. Ding, Y. Liu, M. Wang, L. Qin, X. Cui, C. Wang, L. Wang, B. Lv, Electrochim. Acta 2017, 248, 20.
[18] X. Hai, W. Zhou, K. Chang, H. Pang, H. Liu, L. Shi, F. Ichihara, J. Ye, J. Mater. Chem. A 2017, 5, 8591.
[19] A. Y. Lu, X. Yang, C. C. Tseng, S. Min, S. H. Lin, C. L. Hsu, H. Li, H. Idriss, J. L. Kuo, K. W. Huang, L. J. Li, Small 2016, 12, 5530.
[20] R. N. Bhattacharya, C. Y. Lee, F. H. Pollak, D. M. Schleich, J. Non-Cryst. Solids 1987, 91, 235.
[21] D. Bélanger, G. Lapereière, B. Marsan, J. Electroanal. Chem. 1993, 437, 165.
[22] D. Merki, S. Fierro, H. Vrubel, X. Hu, Chem. Sci. 2011, 2, 1262.
[23] D. W. Redman, J. Kim, J. Stevenson, M. J. Rose, J. Mater. Chem. A 2016, 4, 7027.
[24] Q. G. Han, X. Shang, S. S. Lu, B. Dong, X. Li, Y. R. Liu, W. H. Hu, J. Bin Zeng, Y. M. Chai, C. G. Liu, Int. J. Hydrogen Energy 2017, 42, 5132.
[25] D. W. Redman, M. J. Rose, K. J. Stevenson, Langmuir 2017, 33, 9354.
[26] S. Murugesan, A. Akkineni, B. P. Chou, M. S. Glaz, D. A. Vanden Bout, K. J. Stevenson, ACS Nano 2013, 7, 8199.
[27] H. Vrubel, X. Hu, ACS Catal. 2013, 3, 2002.
[28] S. M. Tan, M. Pumera, ACS Appl. Mater. Interfaces 2017, 9, 41955.
[29] X. Chia, N. A. A. Sutrisnoh, M. Pumera, ACS Appl. Mater. Interfaces 2018, 10, 8702.
[30] D. Merki, H. Vrubel, L. Rovelli, S. Fierro, X. Hu, Chem. Sci. 2012, 3, 2515.
[31] M. Shang, H. Qi, C. Du, H. Huang, S. Wu, J. Zhang, W. Song, Sens. Actuators, B 2018, 266, 71.
[32] J. H. Kim, H. Kim, J. Kim, H. J. Lee, J. H. Jang, S. H. Ahn, J. Power Sources 2018, 392, 69.
[33] Z. Liu, X. Zhang, B. Wang, M. Xia, S. Gao, X. Liu, A. Zavabeti, J. Z. Ou, K. Kalantar-Zadeh, Y. Wang, J. Phys. Chem. C 2018, 122, 12589.
[34] F. Scaglione, Y. Xue, F. Celegato, P. Rizzi, L. Battezzati, J. Mater. Sci. 2018, 53, 12388.
[96] S. Haghighat, J. M. Dawlaty, J. Phys. Chem. C 2016, 120, 28489.
[97] N. Mohamad Latiff, L. Wang, C. C. Mayorga-Martinez, Z. Sofer, A. C. Fisher, M. Pumera, Nanoscale 2016, 8, 16752.
[98] J. Bonde, P. G. Moses, T. F. Jaramillo, J. Norskov, I. Chorkendorff, Faraday Discuss. 2008, 140, 219.
[99] D. N. Nguyen, L. N. Nguyen, P. D. Nguyen, T. V. Thu, A. D. Nguyen, P. D. Tran, J. Phys. Chem. C 2016, 120, 28789.
[100] X. Chia, A. Ambrosi, Z. Sofer, J. Luxa, M. Pumera, ACS Nano 2015, 9, 5164.
[101] V. S. Saji, C. W. Lee, ChemSusChem 2012, 5, 1146.
[102] J. C. Dupin, D. Gonbeau, I. Martin-Litas, P. Vinatier, A. Levasseur, Appl. Surf. Sci. 2001, 173, 140.
[103] G. C. Stevens, T. Edmonds, J. Catal. 1975, 37, 544.
[104] C.-H. Lee, S. Lee, Y.-K. Lee, Y. C. Jung, Y.-I. Ko, D. C. Lee, H.-I. Joh, ACS Catal. 2018, 8, 5221.
[105] P. C. K. Vesborg, B. Seger, I. Chorkendorff, J. Phys. Chem. Lett. 2015, 6, 951.

[106] M. Ledendecker, J. S. Mordschein, O. Kasis, S. Geiger, D. Göhl, M. Schalenbach, A. Zeradjanin, S. Cherevko, R. E. Schaak, K. Mayrhofer, Angew. Chem., Int. Ed. 2017, 56, 9767.
[107] C. C. L. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo, J. Am. Chem. Soc. 2013, 135, 16977.
[108] C. Spöri, J. T. H. Kwan, A. Bonakdarpour, D. P. Wilkinson, P. Strasser, Angew. Chem., Int. Ed. 2017, 56, 5994.
[109] J. D. Benck, T. R. Hellstern, J. Kibsgaard, P. Chakthranont, T. F. Jaramillo, ACS Catal. 2014, 4, 3957.
[110] N. Q. Tran, V. Q. Bui, H. M. Le, Y. Kawazoe, H. Lee, Adv. Energy Mater. 2018, 8, 1702139.
[111] Y. Sun, C. Liu, D. C. Grauer, J. Yano, J. R. Long, P. Yang, C. J. Chang, J. Am. Chem. Soc. 2013, 135, 17699.
[112] H. W. Wang, P. Skeldon, G. E. Thompson, Surf. Coat. Technol. 1997, 91, 200.
[113] W. Grunert, A. Y. Stakhnev, R. Feldhaus, K. Anders, E. S. Shpiro, K. M. Minachev, J. Phys. Chem. 1991, 95, 1323.