Electrochemical Surface Interrogation of a MoS₂ Hydrogen-Evolving Catalyst: In Situ Determination of the Surface Hydride Coverage and the Hydrogen Evolution Kinetics

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Supporting Information

ABSTRACT: The hydrogen evolution reaction (HER) on an electrodeposited a-MoS₂ electrode was investigated by a surface-selective electrochemical titration technique by application of surface interrogation scanning electrochemical microscopy. In a mildly acidic (pH 4.6) environment, the saturated surface hydride coverage of MoS₂ was determined to be 31%, much higher than that expected for a crystalline nanoparticle. The HER rate constant of a surface molybdenum atom was measured for the first time in situ to be 3.8 s⁻¹ at a 600 mV overpotential. At high Mo–H coverages, a change in the nature of the active sites was observed upon consumption of Mo–H by HER.

Much effort has been focused on developing earth-abundant alternative catalysts for the hydrogen evolution reaction (HER) to replace the current benchmark platinum. Molybdenum disulfide has been proposed as a candidate for replacing platinum as the HER catalyst because its hydrogen adsorption energy is similar to that of platinum. Many theoretical and experimental works suggest that the HER activity of MoS₂ would resemble that of a platinum surface. MoS₂ has a layered structure, and the HER active sites on a MoS₂ surface are known to be molybdenum-terminated edge sites, and the activity of such sites has been characterized by bulk electrochemical measurements. Recently, efforts to enhance the HER catalytic activity of MoS₂ have led to the development of electrodeposited MoS₂ catalysts, the selective exposure of the edge active sites, and the activation of the inactive atoms on the MoS₂ basal planes. Despite these experimental research efforts and many theoretical calculations, mechanistic study of the HER by MoS₂ remains predominantly based on Tafel plot analysis, the chemical activity and surface density of the proposed intermediate, molybdenum hydride, have not yet been measured experimentally. In the present Letter, we report a surface-selective electrochemical titration of an electrodeposited a-MoS₂ HER catalyst electrode, quantifying the surface molybdenum hydride coverage and the reactivity of the intermediate hydrides.

Surface-selective redox titration of the electrodeposited (nanocrystalline, unannealed) a-MoS₂ electrode was made possible by the implementation of surface interrogation scanning electrochemical microscopy (SI-SECM). This technique involves a redox messenger molecule (mediator) in solution, rendering it exclusively selective to surface atoms in direct contact with the solution. SI-SECM has been employed recently in evaluating the surfaces of catalysts such as the CoP and nickel–iron oxyhydroxide oxygen-evolving catalysts. The experimental setup is depicted in Scheme 1. In a SI-SECM experiment, two ultramicroelectrodes (UMEs, 12.5 μm radius Au disk, tip, and substrate) are placed in close proximity (2.4 μm) facing one another such that a species generated at the tip electrode (top, facing down) is quantitatively detected at the substrate (bottom, facing up); for setup details, refer to the Supporting Information. In this Letter, a 1.6 mM redox mediator (1,1′-ferrocenedimethanol; FcDM) in 0.1 M potassium phosphate buffer (pH 4.6) was used to titrate reduced intermediates on the substrate. The electrodeposited a-MoS₂ HER catalyst film (of thickness ca. 100 nm) was prepared onto the substrate electrode by published methods (see the Supporting Information and Figure S2 for details).

At the beginning of the SI-SECM experiments, the system is at the resting state with the molybdenums in the a-MoS₂, their Mo⁺ oxidation states and the FcDM in solution in its reduced form; therefore, no reaction occurs (Scheme 1A, left). The titrands (redox species of interest Mo=H, [MoS₂=H]²⁻) are generated by a reducing potential pulse to the substrate electrode (Scheme 1A, center), and the titration begins by generation of the titrant (FcDM⁺) at the tip electrode by an oxidizing potential step (Scheme 1A, right). The reaction between FcDM⁺ and the Mo=H will deliver a feedback current (until full consumption of the titrand) that is monitored at the tip electrode (Scheme 1C), integration over time of which

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should yield the surface density of Mo−H. Delaying a controlled amount of time (t\text{delay}) between titrand generation and titration will let protons in solution consume the Mo−H ([MoS2−H]\text{2−}) by HER during t\text{delay}, leading to decreased feedback current as a function of t\text{delay} (Scheme 1C). Analyzing the integrated charge as a function of t\text{delay} should yield the HER rate constant of Mo−H with protons. It is worth noting that the hydride formation on the surface of a-MoS2 is assumed based on a recent theoretical study.14

The redox titration chronoamperograms (CA) at the tip electrode are displayed in Figure 1. The feedback current increases as a function of applied potential to the substrate electrode, indicating that more active species were generated at further reducing potentials (investigation conducted in pH 4.6 phosphate-buffered water). The integrated charge densities arising from the CAs can be plotted as a function of the substrate potential to yield the redox titration curve shown in Figure 1; all potentials hereon are reported referenced to a 1 M Ag/AgCl electrode, and the E° for HER is −0.51 V on this scale. It is worth noting that in the a-MoS2 film employed in this work, a small fraction of MoS3 (or MoS2\text{+\text{x}}, x < 1) may be present. A small amount of charge from −0.65 to −0.8 V is attributed to the reduction of residual MoS3 in the film (see Figures 1 and S6).9 The titration curve reveals one redox event starting out at −0.82 V and plateauing between −1.02 and −1.12 V. This event is attributed to the formation of Mo−H (2 e− reduction of a MoS2 unit forming [MoS2−H]\text{2−}), which is usually thought to be the intermediate in the MoS2 HER.14

Molybdenum disulfide was first made popular for its use in hydrodesulfurization,26 and much theoretical and experimental work has followed studying the dissociative adsorption properties of H2 on MoS2.27,28 A common model is direct formation of Mo−H and S−H or formation of two S−H and then a reductive proton migration to a neighboring Mo, again yielding Mo−H and S−H.27,28 Molybdenum hydride is therefore an important intermediate in MoS2 HER because hydrogen evolution is the microscopic reverse of the H2 dissociative adsorption. The Mo−H is also highlighted as an intermediate in a recent theoretical paper, and the calculated Pourbaix diagram suggests that it would be present in the reaction conditions employed in this Letter.14 Following the formation of Mo−H, both theory and Tafel analysis predict a coupling of Mo−H with a water-stabilized proton to expel H2.8,9,14,18

The reduction event occurring from −0.82 to −1.12 V is therefore treated as a two-electron event, reducing MoS2 to [MoS2−H]\text{2−}. The quantification of the hydride coverage on a-MoS2 is more complicated than cases of quantitative one-electron events such as CoIII/II and NiIII/II.21−23 Therefore, in order to quantify the Mo−H density, a similar catalyst surface was adopted as a benchmark. The CoPi catalyst (nanocrystaline cobalt oxide) was evaluated at 270 μC/cm2.21,29 This charge density figure was used as that for full coverage of the Mo sites in MoS2. Taking into account the differences in the roughness factor between CoPi and a-MoS2 (2.3 and 6, respectively),29 the Mo−H coverages at −0.92 V (400 mV

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Scheme 1. (A) Titration Sequence, a (B) Reactions Occurring at the Tip−Substrate Gap during Titration, b and (C) Expected Titration Chronoamperograms in the Absence (black) and the Presence (red) of Surface Titrands. c

aResting at OCP (left), titrand generation by a reductive substrate pulse (center), and titration at the tip electrode (right). bTip generation of titrants, consumption of titrands (Mo−H) by titrants, and HER by Mo−H in the absence of titrants. cDelayed titration responses are displayed in green and purple. The reduction of titration currents is due to the consumption of surface titrands by the HER.
overpotential) and −1.12 V (600 mV overpotential) were 14 ± 1 and 31 ± 4%, respectively (see the Supporting Information for detailed calculations). The saturated hydride coverage of 31% at high overpotentials is surprisingly high for MoS2 because even for small nanoparticles (of size 25 nm), the molybdenum-terminated edge sites are estimated to be about 8% for crystalline MoS2;30 such a low active site density is said to be the main reason that MoS2 falls short of platinum.8 Moreover, hydride coverage of the 8% edge sites is known to be between 25 and 50%.3,8 Perhaps the enhanced HER catalysis by the electrodeposited (nanocrystalline, unannealed) material is due to an increased number of hydride-forming redox active sites.9,10

The Mo−H sites in the nanocrystalline electrodeposited α-MoS2 were indeed active for HER in pH 4.6 water, as evidenced by kinetic studies varying the tdelay in titration systematically (Figures 2 and S7). As seen in Figure 2, the titration feedback current arising from the reaction between the Mo−H and the FeDM+ redox messenger molecules decreased with increasing tdelay. Because the proton is in excess in the buffered solution (0.1 M in strength), a pseudo-first-order kinetic model can be applied (see the Supporting Information for detailed calculations). When the natural log of the Mo−H surface concentration was plotted against the decay time (Figure 2), the slope of the best-fit line was the kinetic rate constant for Mo−H in the HER. At −0.92 V, at which the Mo−H coverage is 14%, the HER rate constant k′ (equivalent to the turnover frequency; TOF) was 0.16 s−1. This TOF for a α-MoS2 active site is similar to that estimated from the exchange current at pH 0 (at E°, or zero overpotential);8 however, a direct measurement of the redox decay kinetics in situ is being reported for the first time here. Also, when H2 evolution was measured as a function of tdelay, the amount of evolved H2 agreed with the consumed amount of surface Mo−H, further reinforcing the mechanism involving Mo−H as an intermediate (see the Supporting Information and Figure S8 for details).
Observing $H_2$ evolution at open circuit as Mo–H was consumed seems to suggest some charge-storing ability of α-MoS$_2$ (Figure S8) because $H_2$ would not have been detected at open circuit if Mo–H behaved similar to an adsorbed hydrogen atom on a platinum surface. Stored charge in the α-MoS$_2$ delivered to the surface Mo–H presumably leads to $H_2$ evolution even at open circuit for a brief duration (until discharge, ca. 1 s).

A similar kinetic analysis was also performed at a higher overpotential at which the surface hydride coverage was 31%. The time dependence of the titration currents at −1.12 V overpotential at which the surface hydride coverage was 31% was measured at −0.92 V, pseudo-first-order kinetics with one slope for greater than two half-lives ($t_{1/2} = 4.3$ s for $k' = 0.16$; linear decay for 10 s; Figure 2), the ln[Mo] vs $t_{\text{delay}}$ plot at −1.12 V exhibited two linear regions with distinct $k'$ values; the first region spans from 0 s to approximately one half-life (0.18 s; Figure 3) with a $k'$ of 3.8 ± 1.2, and the second region is beyond the first half-life with a $k'$ of $0.06 \pm 0.10$ (Figure S9). Because the data do not fit second-order kinetics (Figure S10; theory also predicts Mo−H homocoupling to be unfavorable). It is logical to model this behavior as having a change in the active site after approximately one half-life. After approximately $55 \pm 13\%$ (uncertainty arising from the noncontinuous sampling of data; see Figure 3, $t_{\text{delay}}$ set at 0, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, and 10 s) loss of the Mo–H, the α-MoS$_2$ surface becomes much less potent of a HER catalyst. This model is also convincing because $k'$ at $t > 0.2$ s at −1.12 V is similar to that at −0.92 V, with one-half of the Mo–H lost from the 31% at −1.12 V, the hydride coverage should be similar to that at −0.92 V, 14%. In a practical operating situation where the electrode is constantly biased at the negative potential, the reaction rate will be similar to the initial $k'$ measured here (Figure 3), about four turnovers per atom per second.

In this work, we have studied the HER on an electrodeposited α-MoS$_2$ surface in a mildly acidic medium (pH 4.6). The saturated surface hydride coverage was determined to be 31%, much higher than that expected for a crystalline MoS$_2$ nanoparticle. The HER rate constant of a surface molybdenum atom was measured for the first time in situ, 0.16 and 3.8 s$^{-1}$, respectively, at −0.92 V (400 mV overpotential, 14% Mo–H coverage) and −1.12 V (600 mV overpotential, 31% Mo–H coverage). Some charge storage capability of α-MoS$_2$ was observed, as evidenced by $H_2$ evolution by Mo–H at open circuit until discharge.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b01276.

Electrode alignment and approach data, MoS$_2$ film deposition voltammogram, and capacitance measurement data (PDF)

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Notes

The authors declare no competing financial interest.

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**REFERENCES**


