Evidence from In Situ X-Ray Absorption Spectroscopy for the Involvement of Terminal Disulfide in the Reduction of Protons by an amorphous Molybdenum Sulfide Electrocatalyst.

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Supplementary Information

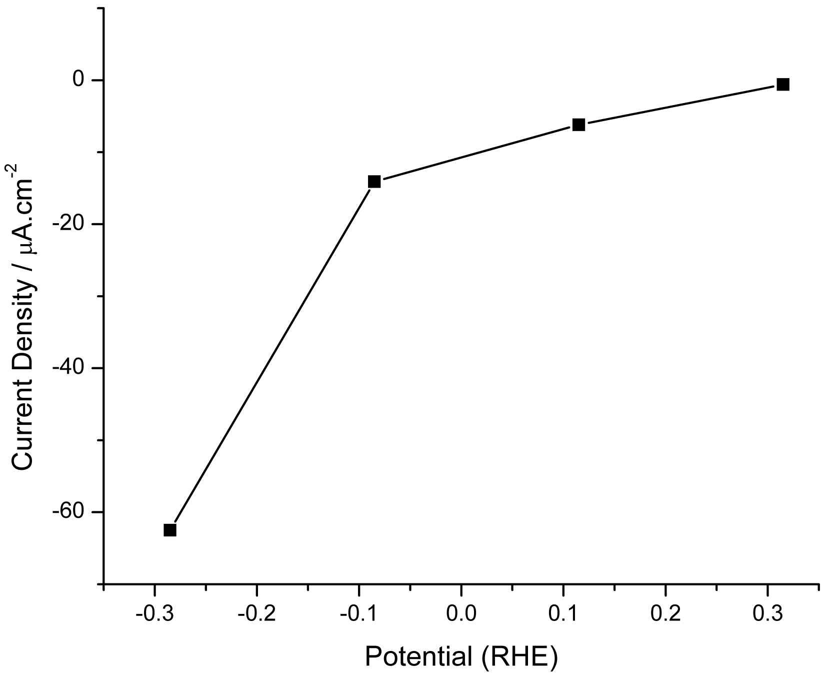

Figure S1. Current density as a function of potential applied on the MoS_x film during *in situ* XAS measurements. Room temperature, pH = 2, nitric acid.

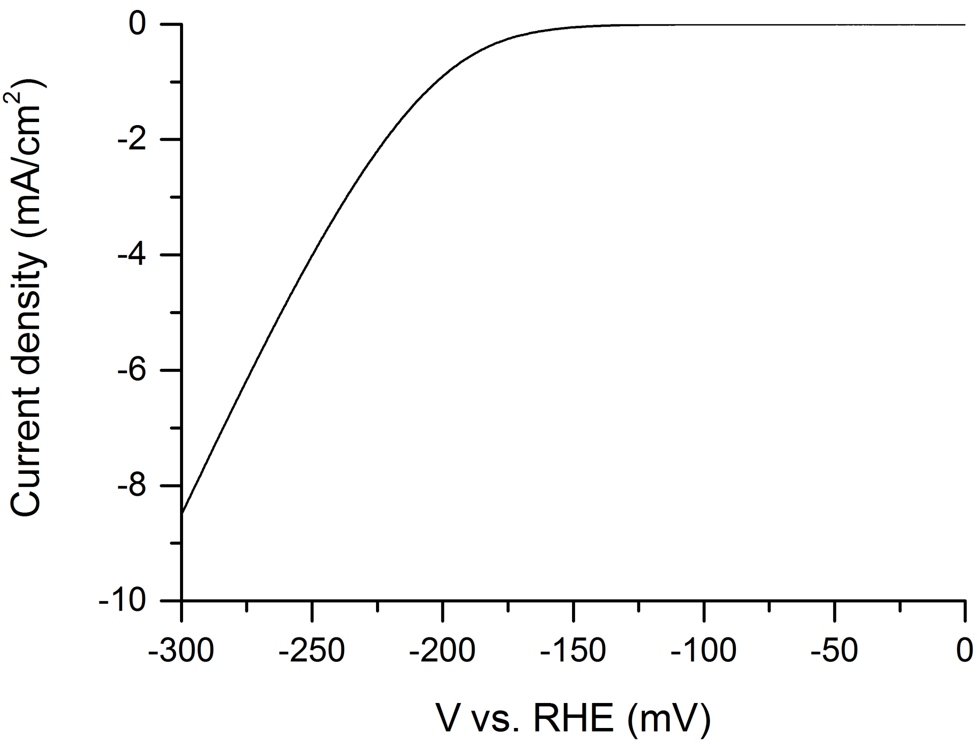

Figure S2. polarization curve of the MoS_x film on a rotating disk carbon electrode at pH = 2; scan rate = 2 mV/s, rotating speed = 4500 rpm.

X-ray absorption data analysis details

EXAFS curve fitting was performed with Artemis and IFEFFIT software using *ab initio*-calculated phases and amplitudes from the program FEFF 8.2. These *ab initio* phases and amplitudes were used in the EXAFS equation:

$$\chi(k) = S_0^2 \sum_j \frac{N_j}{kR_j^2} f_{eff_j}(\pi, k, R_j) e^{-2\sigma_j^2 k^2} e^{-2R_j/\lambda_j(k)} \sin(2kR_j + \phi_{ij}(k))$$

The neighboring atoms to the central atom(s) are divided into j shells, with all atoms with the same atomic number and distance from the central atom grouped into a single shell. Within each shell, the coordination number N_j denotes the number of neighboring atoms in shell j at a distance of R_j from the central atom. $f_{eff_j}(\pi, k, R_j)$ is the *ab initio* amplitude function for shell *j*, and the Debye-Waller term $e^{-2\sigma_j^2 k^2}$ accounts for damping due to static and thermal disorder in absorber-backscatterer distances. The mean free path term $e^{-2R_j/\lambda_j(k)}$ reflects losses due to inelastic scattering, where $\lambda_j(k)$ is the electron mean free path. The oscillations in the EXAFS spectrum are reflected in the sinusoidal term, $\sin(2kR_j + \varphi_{ij}(k))$ where $\varphi_{ij}(k)$ is the *ab initio* phase function for shell *j*. S_0^2 is an amplitude reduction factor due to shake-up/shake-off processes at the central atom(s). The EXAFS equation was used to fit the experimental data using *N, R*, and the EXAFS Debye-Waller factor (σ^2) as variable parameters. For the energy (eV) to wave vector (k, Å^{-1}) axis conversion, E_0 was defined as 20010 eV and the S_0^2 value was fixed to 0.84. All fits were performed in the R space.

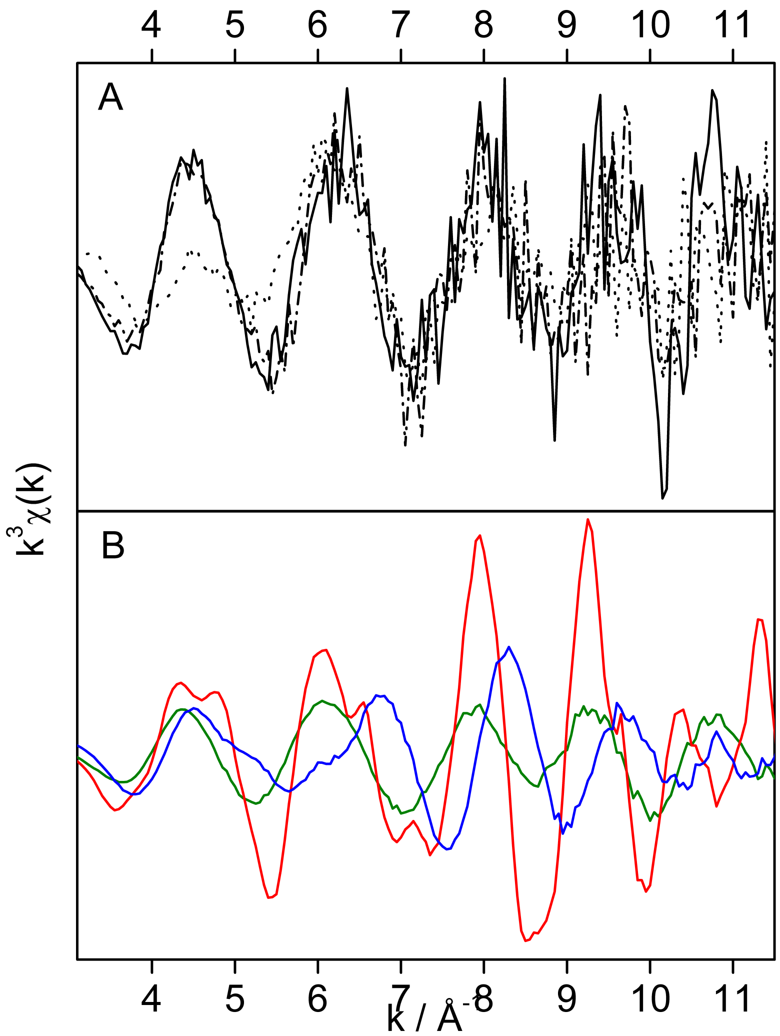

Figure S3. Panel A: k^3-weighted EXAFS signal for the as prepared MoS_x film (dotted black) and poised at +0.3 (plain black) and -0.3 V (dash-dot black). Panel B: k^3 weighted EXAFS signal of Mo_3S_4 (blue) MoS_3, (plain green) and MoS_2 (red).

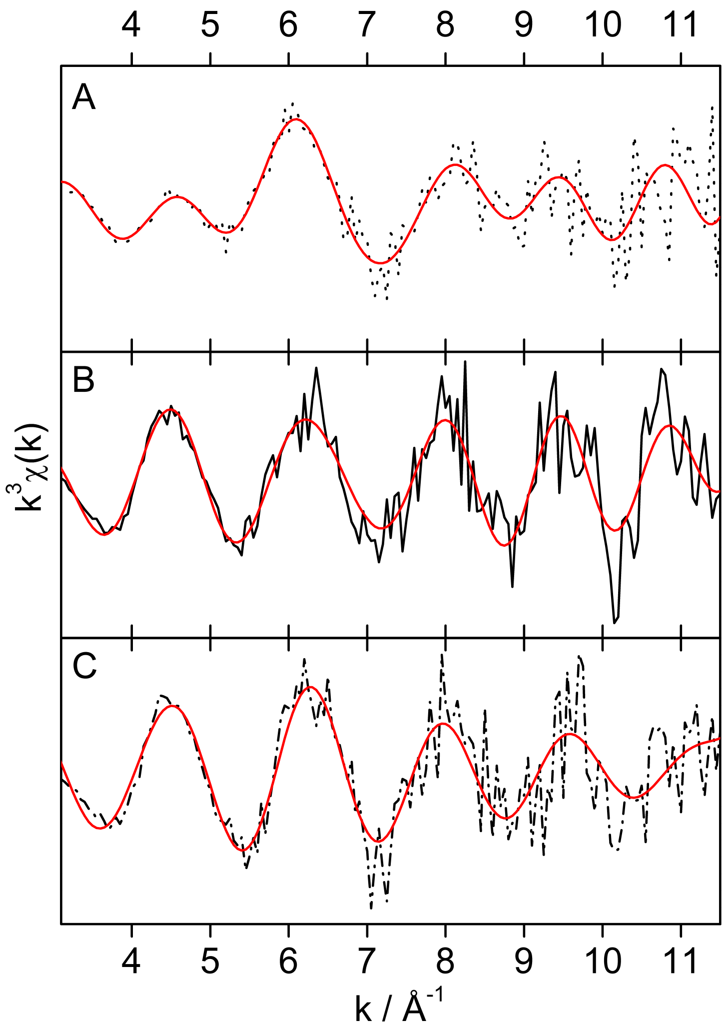

Figure S4. k^3-weighted EXAFS data (black) and fit (red) for the as prepared MoS_x film, (A, dotted black) poised at 0.3V (B, plain black) and at -0.3V (C, dash-dot black).

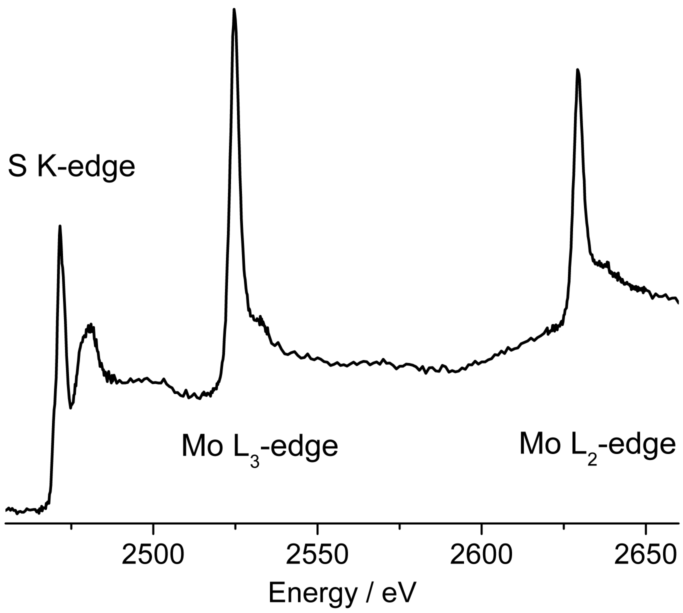

Figure S5. Combined sulfur K-edge and Molybdenum L_3- and L_2-edge spectra of the as prepared MoS_x film. The spectrum is normalized to the L_2 edge jump. When used separately, each spectrum is normalized to its own edge jump and its own pre-edge is subtracted.