Supporting information for:

Operando Spectroscopic Analysis of an Amorphous Cobalt Sulfide Hydrogen Evolution Electrocatalyst

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### Table S1. Comparison to other catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading</th>
<th>pH</th>
<th>Tafel Slope (mV/decade)</th>
<th>(j_0) (mA/cm(^2))</th>
<th>(\eta) at 2mA/cm(^2) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous CoS(^1)</td>
<td>79.6 µg/cm(^2)</td>
<td>7</td>
<td>93</td>
<td>.256</td>
<td>83</td>
</tr>
<tr>
<td>H(_2)-CoCat(^2)</td>
<td>59.8 µg/cm(^2)</td>
<td>7</td>
<td>140</td>
<td>.003</td>
<td>385</td>
</tr>
<tr>
<td>Ni(_3)P(^3)</td>
<td>1000 µg/cm(^2)</td>
<td>0</td>
<td>46</td>
<td>.033</td>
<td>100</td>
</tr>
<tr>
<td>MoS(_3) Film(^4)</td>
<td>5 µg/cm(^2)</td>
<td>0</td>
<td>40</td>
<td>1.3x10(^{-4})</td>
<td>170</td>
</tr>
<tr>
<td>Mo(_2)C Particles(^5)</td>
<td>32 µg/cm(^2)</td>
<td>0</td>
<td>56</td>
<td>.0038</td>
<td>190</td>
</tr>
<tr>
<td>MoS(_2)/MoO(_3)(^6)</td>
<td>60 µg/cm(^2)</td>
<td>0</td>
<td>50</td>
<td>6.9x10(^{-4})</td>
<td>190</td>
</tr>
<tr>
<td>Cu(_2)MoS(_4)(^7)</td>
<td>41.6 µg/cm(^2)</td>
<td>7</td>
<td>95</td>
<td>.040</td>
<td>210</td>
</tr>
<tr>
<td>MoN(^8)</td>
<td>41.6 µg/cm(^2)</td>
<td>1</td>
<td>54.5</td>
<td>.036</td>
<td>290</td>
</tr>
<tr>
<td>Amorphous MoSx(^9)</td>
<td>5-7 µm thick films</td>
<td>0.3</td>
<td>60</td>
<td>-</td>
<td>170</td>
</tr>
</tbody>
</table>
Figure S1. Control experiments demonstrate that in the cyclic voltammetry in a phosphate buffer in presence of 0.5 M thiourea only (A), no redox peaks appear. When thiourea is omitted and cyclic voltammetry is conducted in 5 mM cobalt chloride, an oxidation peak appears at -0.3 V vs. Ag/AgCl that has a slightly different shape than the CoSx electrodeposition oxidation peak and a smaller reduction peak appears at -0.5 V vs. Ag/AgCl.
Figure S2. Raman spectra of electrodes after CV cycles in the presence of thiourea (A) and cobalt chloride (B).
Figure S3. The redox peaks slightly increase in current with subsequent cyclic voltammetry cycles (A). A larger current increase occurs with the irreversible HER peak (B).
Figure S4. Raman spectra of powder standards
Figure S5. XPS of the CoSx film at normal incidence (A, B) and grazing incidence (C, D) reveal that oxygen is present throughout the depth of the CoSx film.
Figure S6. Overlaid cobalt K-edge data of the CoSx film and several reference compounds.
Figure S7. The integrated area under the cobalt L₃ edge is proportional to the oxidation state. The CoSₓ has an integrated L₃ area that most closely matches that of Co(II) compounds.
**Figure S8.** Comparison of the CoSx film under cathodic polarization to a CoS$_2$ standard shows that the two main new features at 400 cm$^{-1}$ and 290 cm$^{-1}$ closely correspond to that of CoS$_2$ $A_g$ and $E_g$ modes, respectively.
Figure S9. *In-Situ* cobalt L-edge data shows the rise of a satellite peak at 780 eV under cathodic polarization.
Figure S10. In-Situ sulfur K-edge data shows no significant changes under cathodic polarization.
Table S2. EXAFS fitting Parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>N</th>
<th>$R$ (Å)</th>
<th>$\sigma^2$</th>
<th>R%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSx – Ex Situ</td>
<td>$^{1}$Co-O</td>
<td>2.1 (1.4)</td>
<td>1.97 (.02)</td>
<td>.006 (.01)</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>$^{2}$Co-S</td>
<td>2.1 (1.1)</td>
<td>2.25 (.06)</td>
<td>.002 (.006)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{1}$Co-Co</td>
<td>6</td>
<td>3.09 (.23)</td>
<td>.0009 (.007)</td>
<td></td>
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<tr>
<td></td>
<td>$^{1}$Co-O</td>
<td>4</td>
<td>3.28 (.26)</td>
<td>.005 (.02)</td>
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<tr>
<td></td>
<td>$^{2}$Co-S</td>
<td>3</td>
<td>3.44 (.48)</td>
<td>.008 (.02)</td>
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<tr>
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<td>$^{2}$Co-S</td>
<td>1</td>
<td>3.69 (.55)</td>
<td>.008 (.02)</td>
<td></td>
</tr>
<tr>
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<td>$^{2}$Co-Co</td>
<td>6</td>
<td>3.87 (.21)</td>
<td>.018 (.006)</td>
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<tr>
<td>CoSx – In Situ</td>
<td>$^{1}$Co-O</td>
<td>0.8 (.3)</td>
<td>2.05 (.06)</td>
<td>.001 (.0003)</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>$^{2}$Co-S</td>
<td>5.2 (1.2)</td>
<td>2.24 (.42)</td>
<td>.007 (.006)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{2}$Co-S</td>
<td>1</td>
<td>3.51 (.47)</td>
<td>.02 (.04)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{2}$Co-S</td>
<td>1</td>
<td>3.76 (.51)</td>
<td>.02 (.04)</td>
<td></td>
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<tr>
<td></td>
<td>$^{2}$Co-Co</td>
<td>3.1</td>
<td>3.94 (.53)</td>
<td>.02 (.04)</td>
<td></td>
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</tbody>
</table>

* Indicates 1st shell path

1 Indicates path from CoO model structure

2 Indicates path from CoS$_2$ model structure

Standard deviations are indicated in parenthesis
Figure S11. Graphic representation the CoO crystal structure and of (A), 2\textsuperscript{nd} (B) and 3\textsuperscript{rd} (C) nearest neighbors to Cobalt that can act as primary single scattering paths. Cobalt atoms are displayed in blue and oxygen atoms are rendered in red.
Figure S12. Graphic representation the CoS$_2$ crystal structure and of (A), 2$^{nd}$ (B), 3$^{rd}$ (C), and 4$^{th}$ (D) nearest neighbors to Cobalt that can act as primary single scattering paths. Cobalt atoms are displayed in blue and sulfur atoms are rendered in yellow.
Figure S13. In-Situ EXAFS fit using only a CoS$_2$ model and a CoS$_2$ with a small fraction of oxide. Open circles indicate experimental data and solid lines indicate the fit. Incorporating a small oxide fraction yielded a lower misfit (1.3% vs. 8.5%), indicating that a small fraction of oxide still remains under HER operating conditions.
**Figure S14.** EXAFS data and fits in K-space, weight by $k^3$. Panel A represents the dry CoSx film and panel B represents the CoSx film under HER conditions. Gray open circles denote experimental data while the colored lines denote the fit.
Figure S15. EXAFS data and fits in R-space displayed in absolute magnitude as well as separated into real and imaginary components. Panel A represents the CoSx catalyst as made and panel B represents the CoSx catalyst under HER conditions.
**Figure S16.** Cross section of cell used in *in situ* cobalt L-edge XAS measurements. In this setup, electrolyte was continually recirculated to reduce any pressure buildup associated with H₂ formation under HER conditions.
**Figure S17.** Electrochemical cell used for *in situ* cobalt K-edge and sulfur K-edge XAS and EXAFS. The port at the bottom is used for the Ag/AgCl reference electrode and the Pt counter electrode is at the top. The sample of interest is pressed between the metal plate and PEEK cell and sealed with an O-Ring. Panels A and B represent the front and side views, respectively.
Figure S18. Multiple viewpoints of the CoSx tetra-nuclear model from figure 6 in the main text. Blue spheres represent cobalt atoms and yellow spheres represent sulfur atoms. Yellow bonds represent the bonds between bridging sulfurs.
Figure S19. CoSx clusters with 1 (A), 2(B), 3(C), 4(D), 5(E), and 6(F) cobalt nuclei. In reality, all six are likely to be present throughout the CoSx film to some extent as EXAFS fitting only yields average values of cobalt 2\textsuperscript{nd} shells. Yellow bonds represent the bonds between bridging sulfurs.
Figure S20. Multiple viewpoints of the CoSx in its bulk form. Blue spheres represent cobalt atoms and yellow spheres represent sulfur atoms. Yellow bonds represent the bonds between bridging sulfurs.
References