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Supporting Information: Sulfur Incorporation into NiFe Oxygen Evolution Electrocatalysts for Improved High Current Density Operation

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1 Additional Materials Characterization

TEM images (Figure S1) further show that instead of individual particles, both the NiFe and NiFeS exist as a nanoamorphous network. No crystalline structures were seen even at a scale of 20 μm. Meanwhile, x-ray diffractograms (Figure S1 inlays) of both catalysts shown no diffraction spots, thus indicating that both catalysts are indeed amorphous.

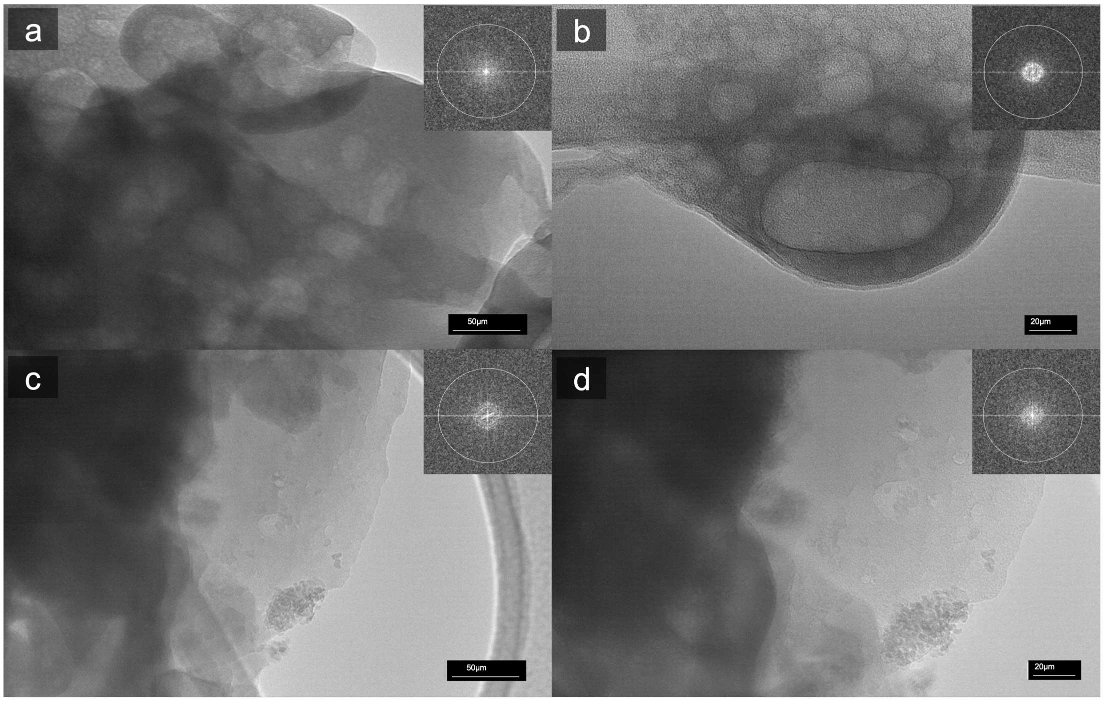

Figure S1. TEM and corresponding x-ray diffractograms of (a, b) NiFe and (c, d) NiFeS

Table S1 shows the mole percentages calculated from the XPS compositions for the NiFe and NiFeS. A 1:1 ratio between the Ni:Fe was anticipated for both electrocatalysts. However, while the NiFe catalyst resulted in close to the anticipated ratio, the NiFeS did not. For the NiFe catalyst, a 1.09:1 (26.89% Ni and 24.76% Fe) ratio between the Ni:Fe was measured. For the NiFeS catalyst, a 0.067:1 (2.59% Ni and 38.62% Fe) ratio between the Ni:Fe was measured.

Table S1. XPS Compositions of NiFe (left) and NiFeS (right)

Species	Mole %
Carbon	3.18
Oxygen	45.16
Iron	24.76
Nickel	26.89

Species	Mole %
Carbon	2.99
Oxygen	49.13
Sulfur	6.67
Iron	38.62
Nickel	2.59

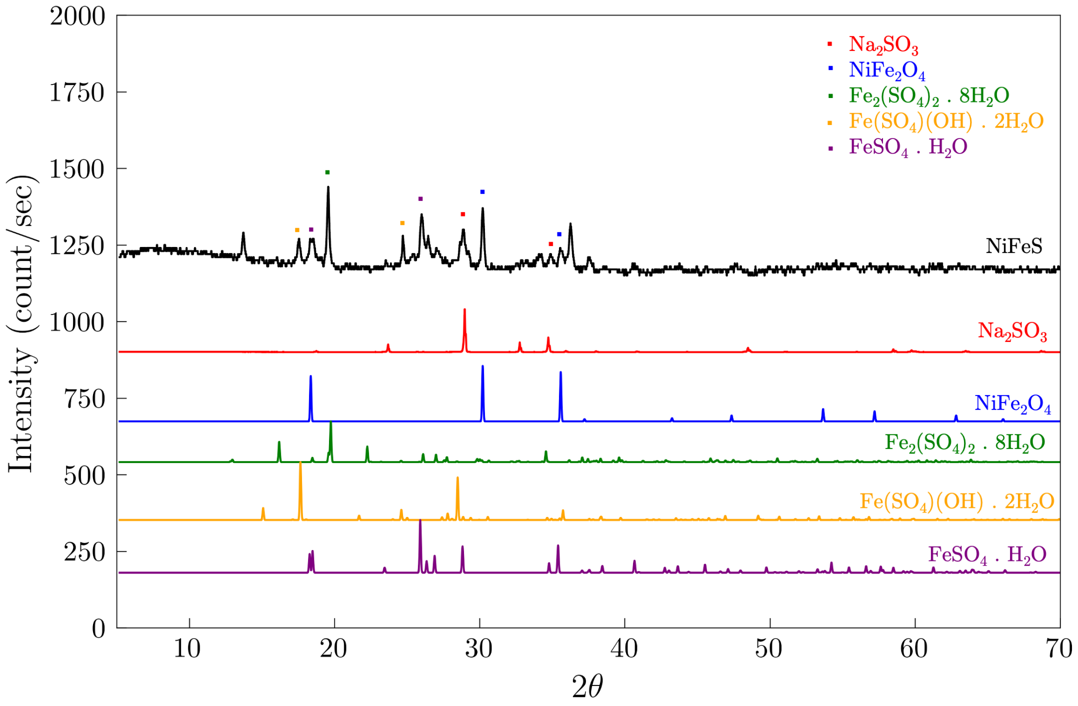

Figure S2. XRD Results for NiFeS

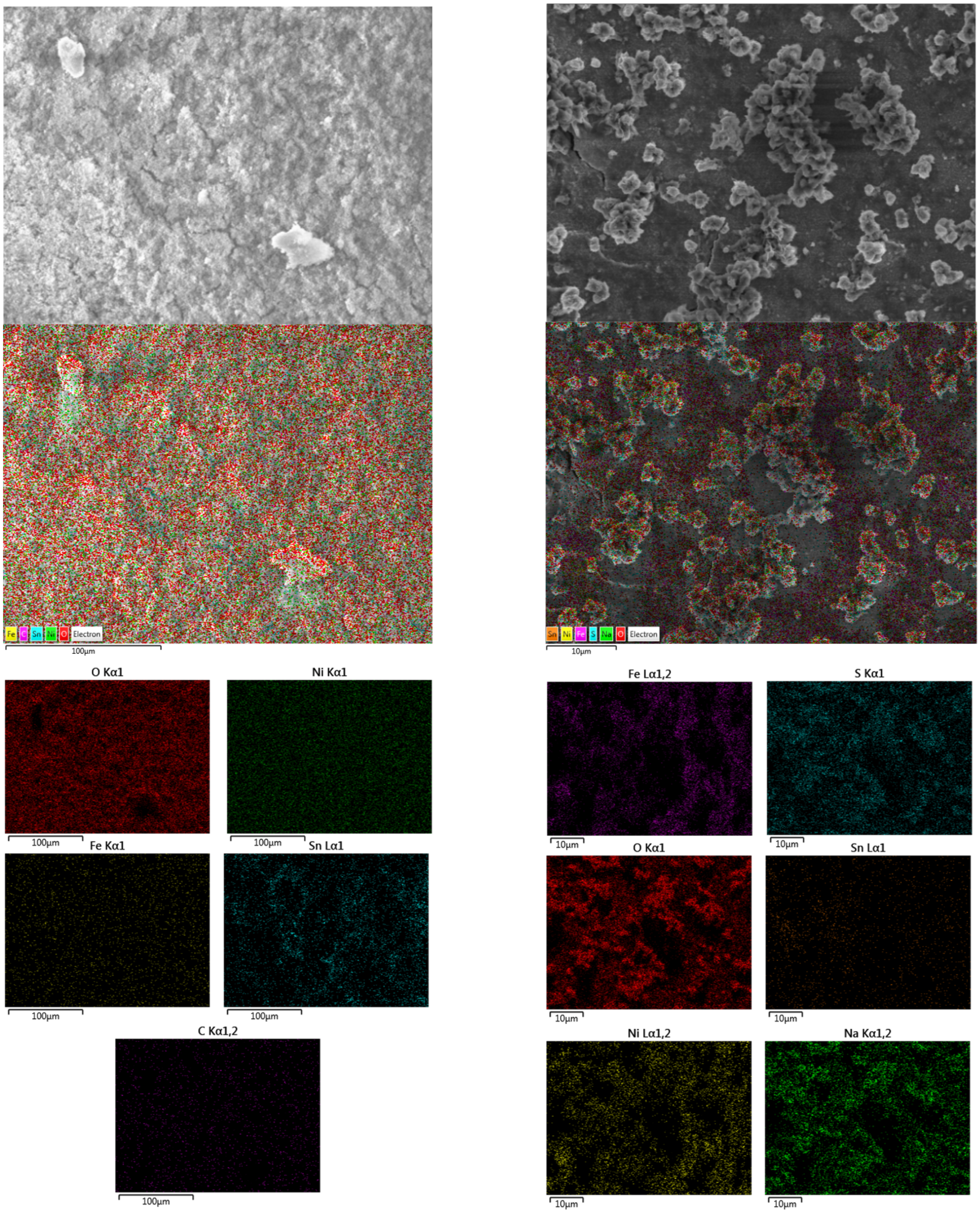

Figure S3. EDS data for NiFe (left) and NiFeS (right) including spectra, SEM image of region, and EDS elemental maps.

2 Additional Electrochemical Characterization

The following figures are additional data gathered while developing the NiFeS electrocatalyst. All cyclic voltammograms are corrected for the uncompensated resistance.

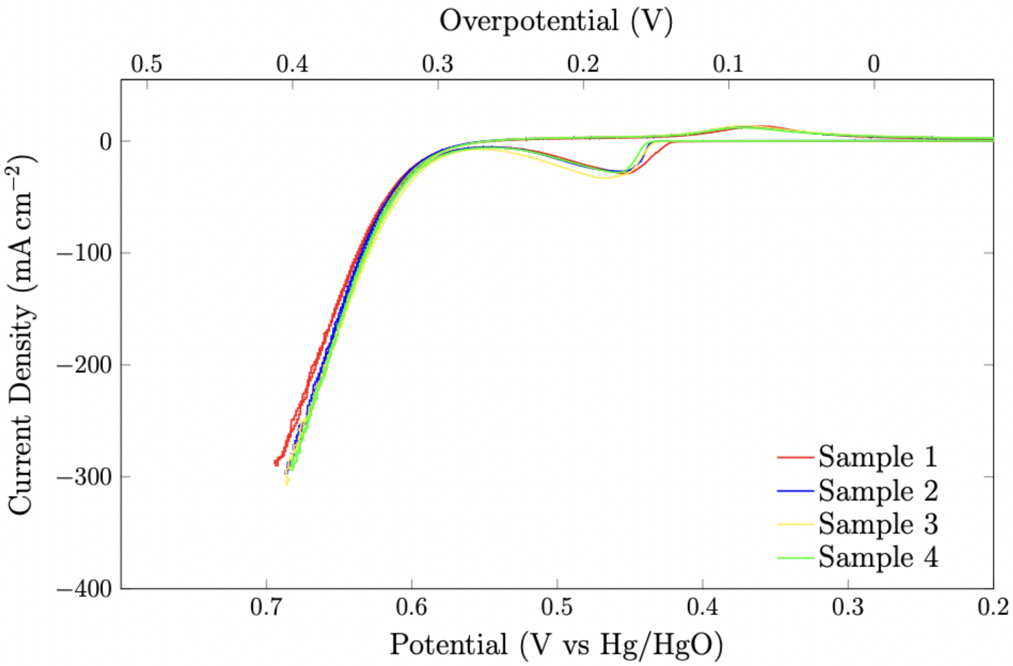

Figure S4. Replication cyclic voltammograms of NiFe on FTO support at a scan rate of 50 mV s^{-1}. All experiments were performed in 3M KOH and corrected for uncompensated resistance (R_Ω).

As seen from Figure S4 and Figure S5, both the NiFe and NiFeS catalysts demonstrate consistent results between replicate samples. The noise at high current densities of the NiFeS catalyst comes from the temporary blocking of nearby active sites by the increase in product formed.

Surface Interrogation - Scanning Electrochemical Microscopy (SI-SECM) experiments were performed as described in the main paper. Electrochemical reactivity maps (Figure S6) were performed in a 1000 - 1000 μm area with a step size of 20 μm at sample intervals of 0.1 s to locate the holes containing the catalyst. The GC tip was moved to the top of the hole before re-approaching close to the substrate.

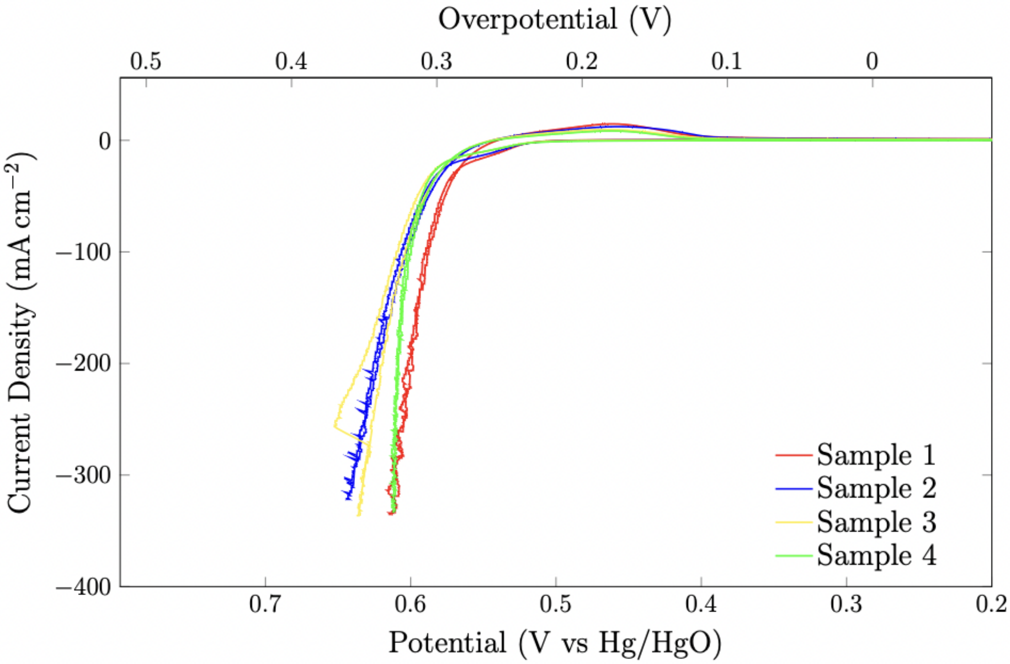

Figure S5. Replication cyclic voltammograms of NiFeS on FTO support at a scan rate of 50 mV s^{-1}. All experiments were performed in 3M KOH and corrected for uncompensated resistance (R_Ω).

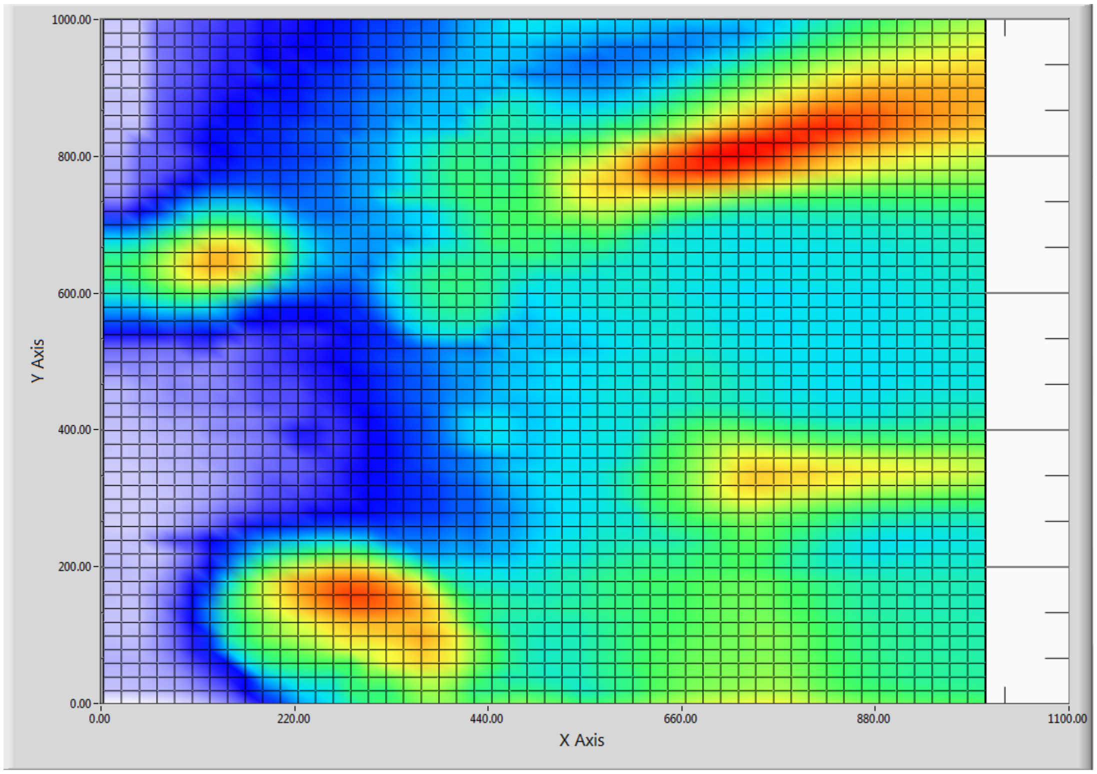

Figure S6. Constant height SECM map showing the holes in the masked FeNiS electrode to enable the SI-SECM experiment and avoid open circuit positive feedback.

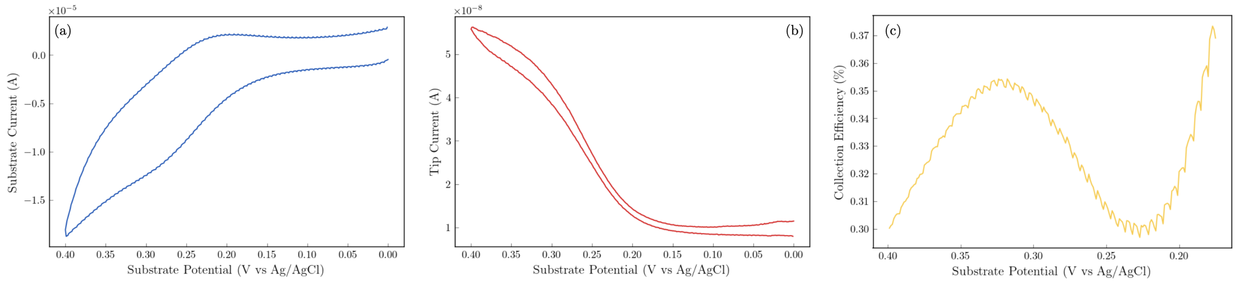

Figure S7. Substrate generation/tip collection SECM results to calibrate the collection efficiency on a NiFeS substrate electrode with a 200 µm Pt tip electrode in 0.5 mM ferrocene methanol with 0.1 M $NaNO_3$ supporting electrolyte. The potential of the substrate electrode was swept from 0 V to 0.4 V vs Ag/AgCl while the tip electrode was held constant at 0 V vs Ag/AgCl. (a) Substrate current as a function of substrate potential. (b) Tip current as a function of substrate potential. (c) Collection efficiency as a function of substrate potential.

In order to verify that the observed catalytic wave in the cyclic voltammetry experiments was the evolution of oxygen, substrate-generation/tip-collection SECM (SG/TC SECM) was performed. Here a 200 µm Pt disc electrode was placed in close proximity to the NiFeS catalytic electrode. Because the size of the SECM tip electrode is significantly smaller than the size of the NiFeS electrode, the collection efficiency of the SC/TC SECM experiment must be calibrated. To perform this calibration, cyclic voltammetry was performed in a 0.5 mM ferrocene methanol (with 0.1 M $NaNO_3$ supporting electrolyte) and the ferrocene/ferrocenium voltammogram on the NiFeS electrode is shown in Figure S7a. While holding the tip potential constant, the tip current is measured as a function of substrate potential as shown in Figure S7b. The ratio of the tip current to the substrate current is the collection efficiency as shown in Figure S7c. Here the collection efficiency was taken to be ca. 0.35 %, which is expected since the diameter of the tip electrode is ca. 200 µm and the diameter of the substrate electrode is ca. 3 mm.