

Supplementary Information for

Facile Solvent-Free Synthesis of Metal Thiophosphates and Their Examination as Hydrogen Evolution Electrocatalysts

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Table S1. M-P-S crystal structure information

Compound	Unit Cell & Space Group (number)	Lattice Parameters	Cell Volume ($\text{\AA}^3$)	Ref.
FePS ₃	Monoclinic C2/m (12)	$a = 5.95 \text{ \AA}$; $b = 10.30 \text{ \AA}$ $c = 6.72 \text{ \AA}$; $\beta = 107.16^\circ$	393.43	[1]
CoPS ₃	Monoclinic C2/m (12)	$a = 5.90 \text{ \AA}$; $b = 10.22 \text{ \AA}$ $c = 6.66 \text{ \AA}$; $\beta = 107.17^\circ$	383.71	[1]
NiPS ₃	Monoclinic C2/m (12)	$a = 5.81 \text{ \AA}$; $b = 10.07 \text{ \AA}$ $c = 6.63 \text{ \AA}$; $\beta = 106.98^\circ$	371.23	[2]
Cu ₃ PS ₄	Orthorhombic Pmn21 (31)	$a = 7.28 \text{ \AA}$; $b = 6.34 \text{ \AA}$ $c = 6.08 \text{ \AA}$	280.43	[3]

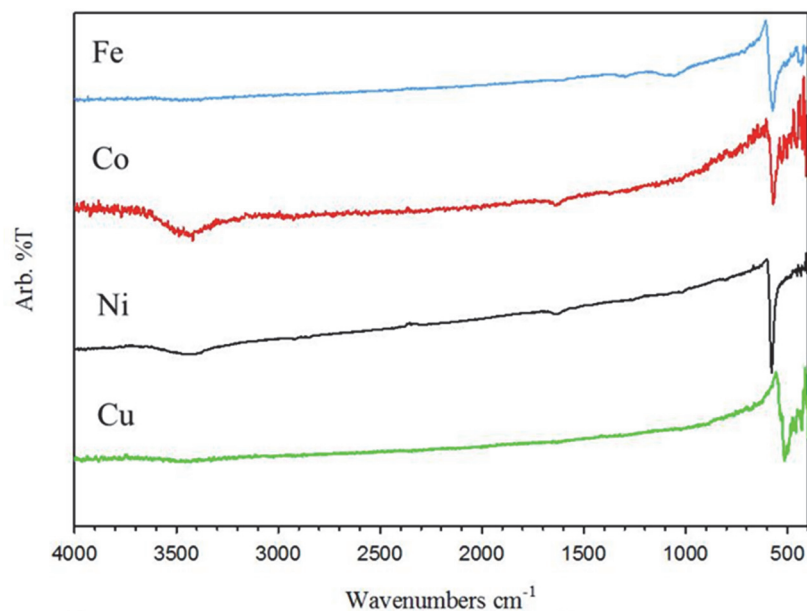


Figure S1. FT-IR data on KBr pressed pellets containing M-P-S samples synthesized from MCl_x and P+S reaction products. Broad adsorbed water peaks on KBr are at $\sim 3400 \text{ cm}^{-1}$ and $\sim 1600 \text{ cm}^{-1}$. The black colored MPS₃ samples absorb across the entire spectrum. The MPS₃ samples have an intense peak at $570 - 580 \text{ cm}^{-1}$ region consistent with P-S stretching vibrations.

Table S2. Summary of estimated M-P-S band gaps calculated from solid-state DRS absorption data.

Products	Onset Abs. (nm)	Est. Band Gap (eV)	Literature Band Gap (eV)
FePS₃ (P+S)	760	1.63	1.50 [4]
FePS₃ (P₂S₅ + P)	780	1.59	1.50 [4]
CoPS₃ (P+S) (contains CoP_{0.5}S_{1.5})	940	1.32	1.40 [5-6]
CoPS₃ (P₂S₅ + P)	745	1.66	1.40 [5-6]
NiPS₃ (P+S) (contains NiS₂)	915	1.36	1.60 [4]
NiPS₃ (P₂S₅ + P)	740	1.68	1.60 [4]
Cu₃PS₄ (P+S)	520	2.38	2.36 [7]
Cu₃PS₄ (P₂S₅ + P)	525	2.36	2.36 [7]

Table S3. Magnetic data for M-P-S samples. The spin only cases assume high spin M²⁺ for MPS₃.

Products	M ⁿ⁺ , d ⁿ , spin-only μ_B (BM)	Lit. values μ_B (BM) [8]	Experimental χ_M ($\times 10^{-3}$) cm ³ /mol	Experimental μ_B (BM) ¹
FePS₃ (P+S)	Fe ²⁺ , d ⁶ , 4.90	4.94	10.3	4.98
FePS₃ (P₂S₅ + P)	Fe ²⁺ , d ⁶ , 4.90	4.94	11.7	5.28
CoPS₃ (P+S) (contains CoP_{0.5}S_{1.5})	Co ²⁺ , d ⁷ , 3.87	4.93	3.34	2.87
CoPS₃ (P₂S₅ + P)	Co ²⁺ , d ⁷ , 3.87	4.93	5.87	3.02
NiPS₃ (P+S) (contains NiS₂)	Ni ²⁺ , d ⁸ , 2.83	3.90	1.79	2.10
NiPS₃ (P₂S₅ + P)	Ni ²⁺ , d ⁸ , 2.83	3.90	2.00	2.23
Cu₃PS₄ (P+S)	Cu ⁺ , d ¹⁰ , 0.00	diamagnetic	-0.076	0.46
Cu₃PS₄ (P₂S₅ + P)	Cu ⁺ , d ¹⁰ , 0.00	diamagnetic	-0.020	0.48

1) magnetic moment calculated after diamagnetic corrections to measured molar susceptibility.

Table S4. Comparison of thermochemical and reaction product info for phosphorus and sulfur reactions with metal halides.[9-10] Reactions were run in evacuated ampoules to 500 °C using stoichiometrically balanced reactions to produce PCl₃ or S₂Cl₂ byproducts.

Reaction	Target Product	ΔH_{rxn} (kJ/mol)	XRD results
FeCl ₃ + P	FeP ₂	-113	FeP ₂
CoCl ₂ + P	CoP ₃	-83	CoP ₃
NiCl ₂ + P	NiP ₂	-19	NiP ₂
CuCl ₂ + P	CuP ₂	-95	CuP ₂
FeCl ₃ + S	FeS ₂	+189	NR, FeCl ₂ -H ₂ O
CoCl ₂ + S	Co ₂ S ₃	+296	NR, CoCl ₂ -6H ₂ O
NiCl ₂ + S	NiS ₂	+158	NR, NiCl ₂
CuCl ₂ + S	CuS	+145	NR, CuCl

NR = no detectable reaction

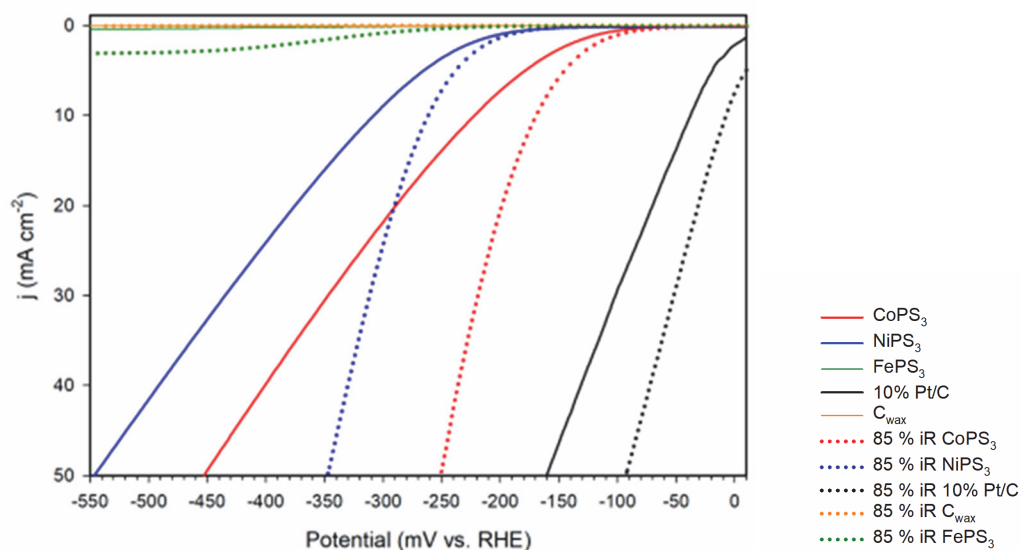


Figure S2. Overlay graph of representative LSV data for MPS₃, Pt/C, and C_{wax} in 0.5 M H₂SO₄ with and without 85% iR compensation. Curves with dashed lines have 85% iR instrument correction applied.

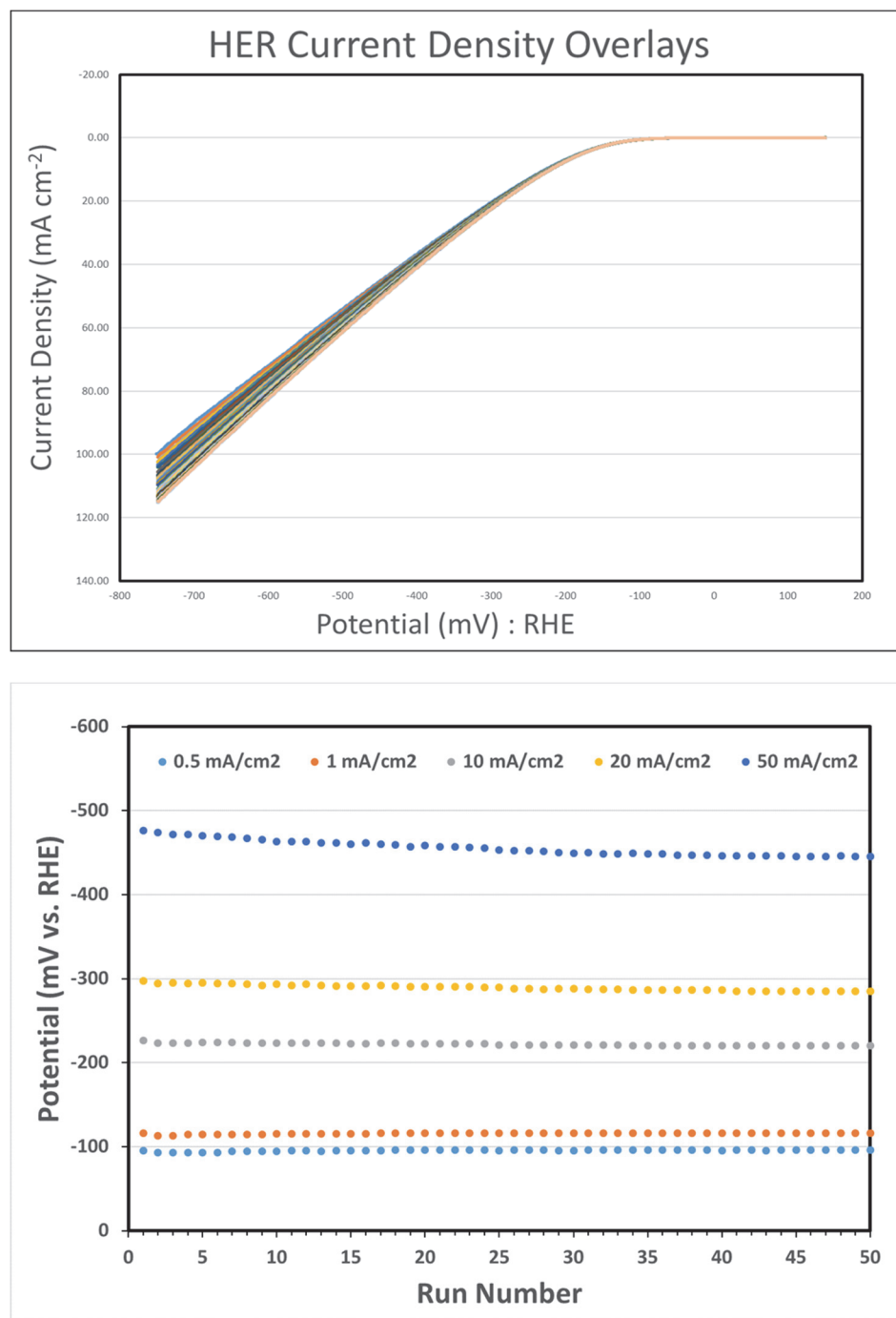


Figure S3A. Overlay LSV graphs (top) for 50 runs using CoPS₃ catalyst in 0.5 M H₂SO₄ (5 mV/s scan rate, graphite counter, no iR compensation). Bottom plot shows applied potentials required to achieve specific mA/cm² values in each LSV run that is in the LSV overlay plot.

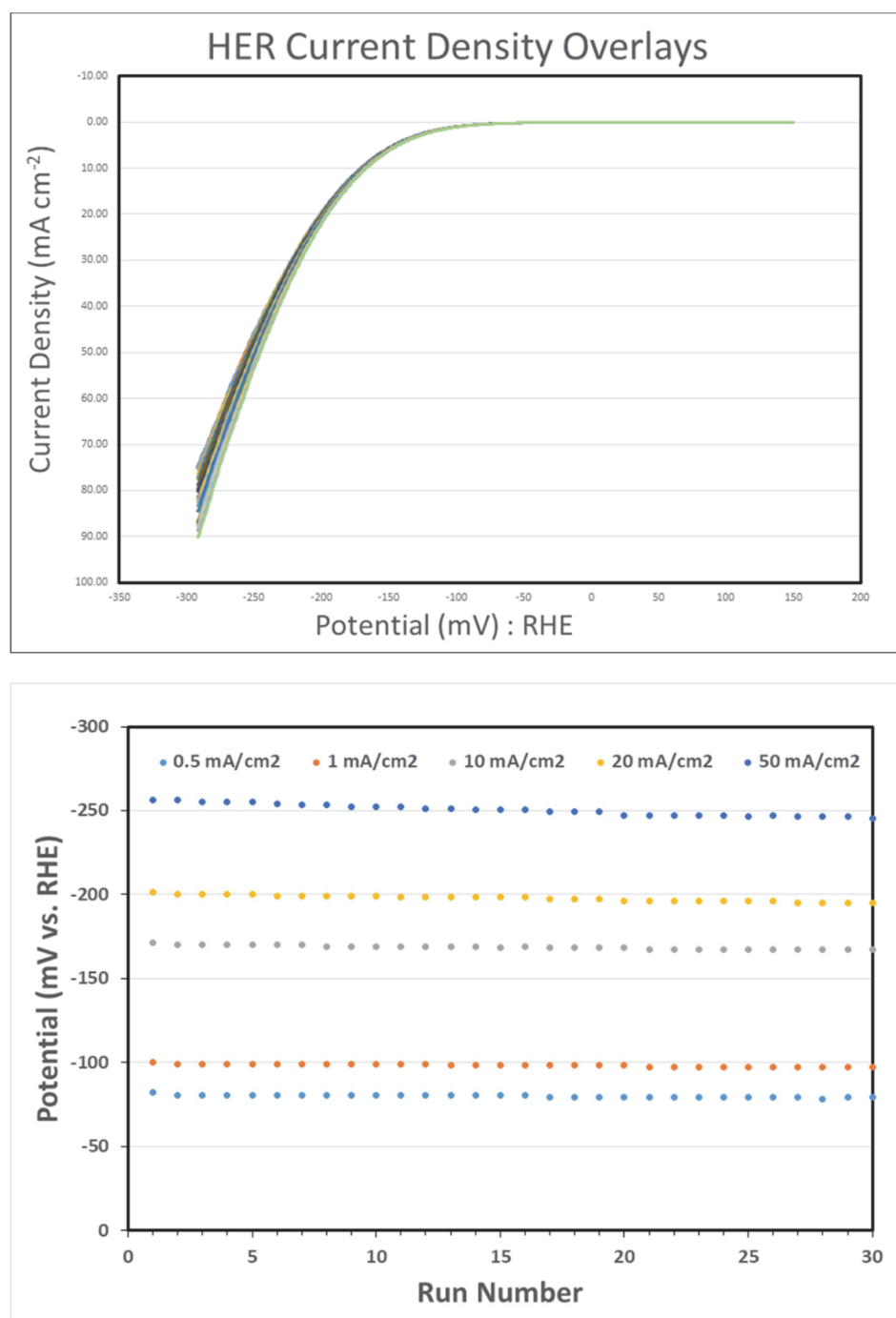


Figure S3B. Overlay LSV graphs (top) for 30 runs using CoPS₃ catalyst in 0.5 M H₂SO₄ (5 mV/s scan rate, graphite counter, 85% iR compensation, R_{cell} = 64 Ω). Bottom plot shows applied potentials required to achieve specific mA/cm² values in each LSV run that is in the LSV overlay plot.

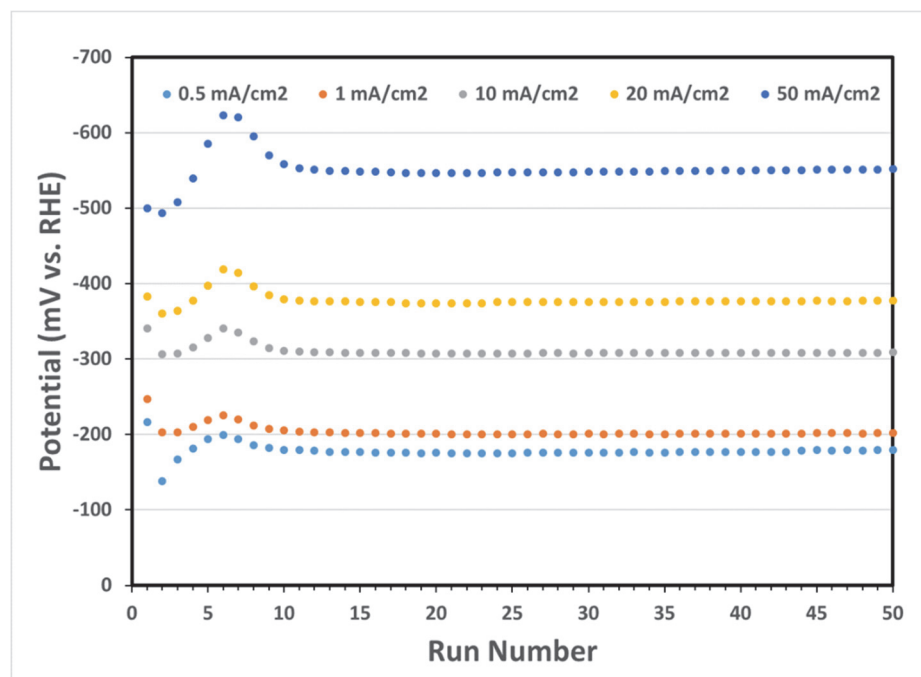
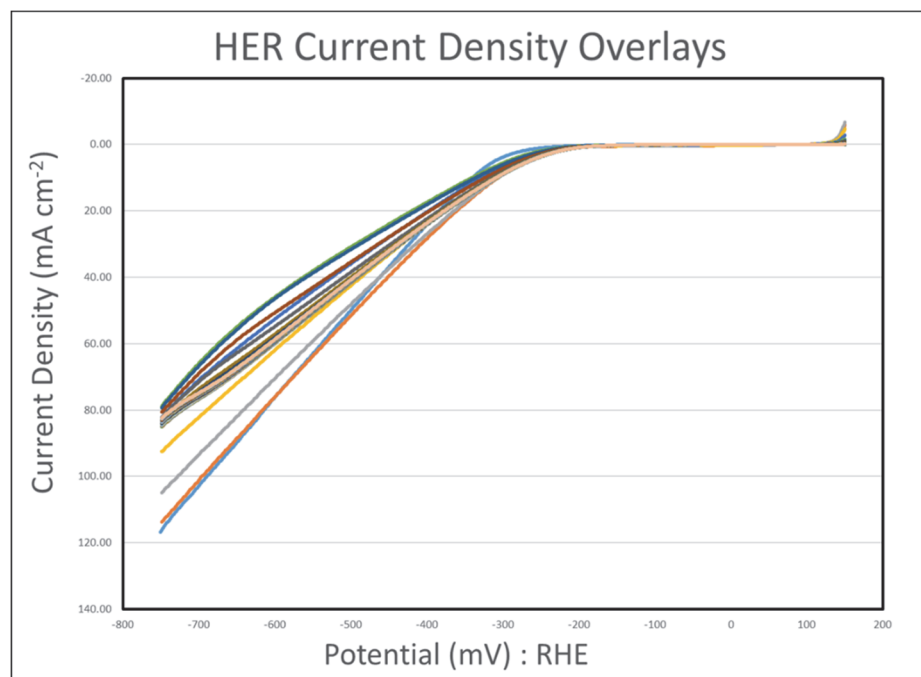


Figure S4A. Overlay LSV graphs (top) for 50 runs using NiPS₃ catalyst in 0.5 M H₂SO₄ (5 mV/s scan rate, graphite counter, no iR compensation). Bottom plot shows applied potentials required to achieve specific mA/cm² values in each LSV run that is in the LSV overlay plot.

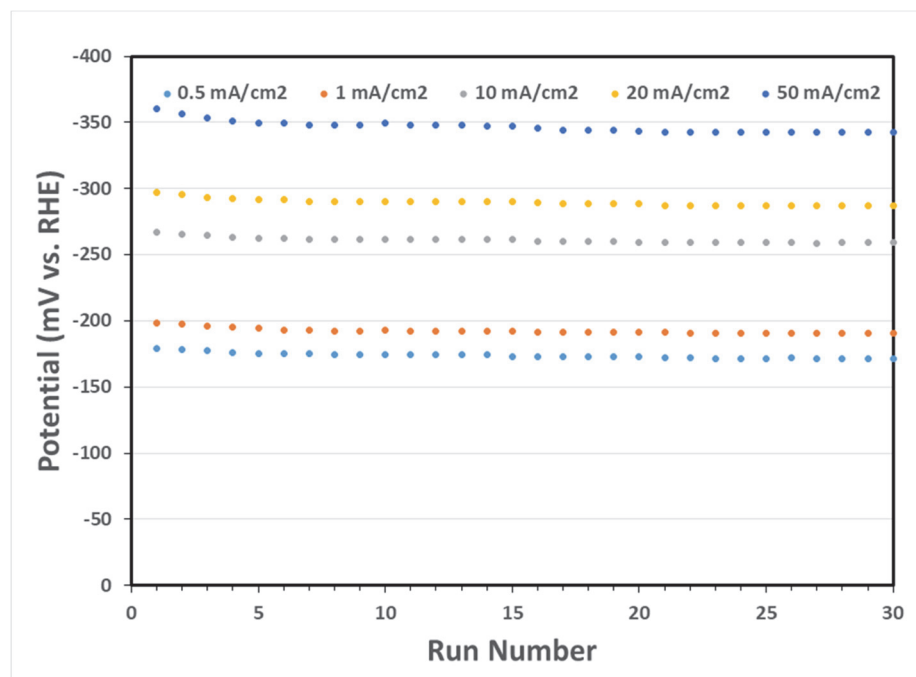
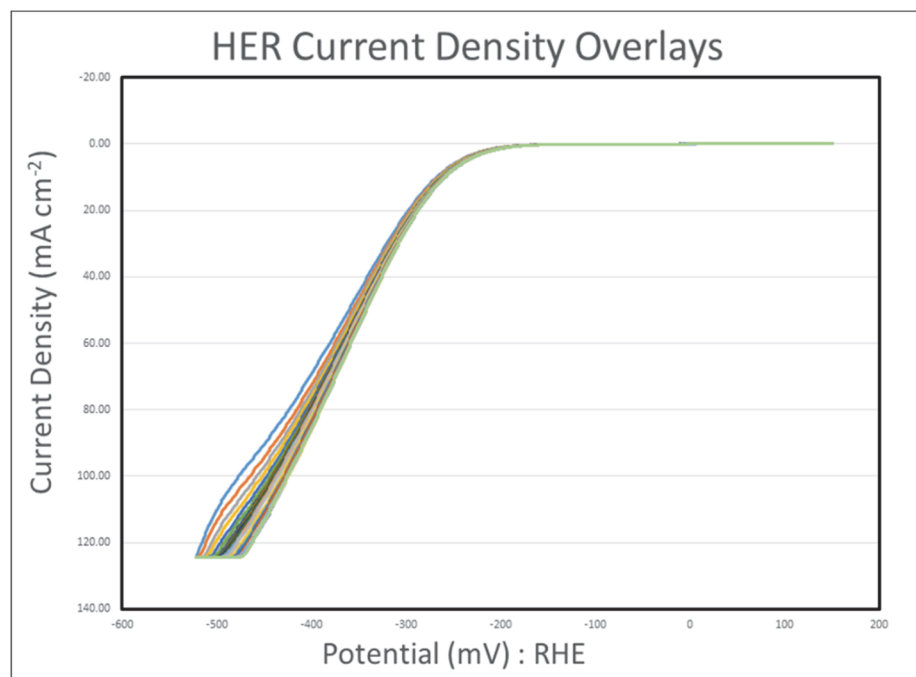


Figure S4B. Overlay LSV graphs (top) for 30 runs using NiPS₃ catalyst in 0.5 M H₂SO₄ (5 mV/s scan rate, graphite counter, 85% iR compensation, R_{cell} = 68 Ω). Bottom plot shows applied potentials required to achieve specific mA/cm² values in each LSV run that is in the LSV overlay plot.

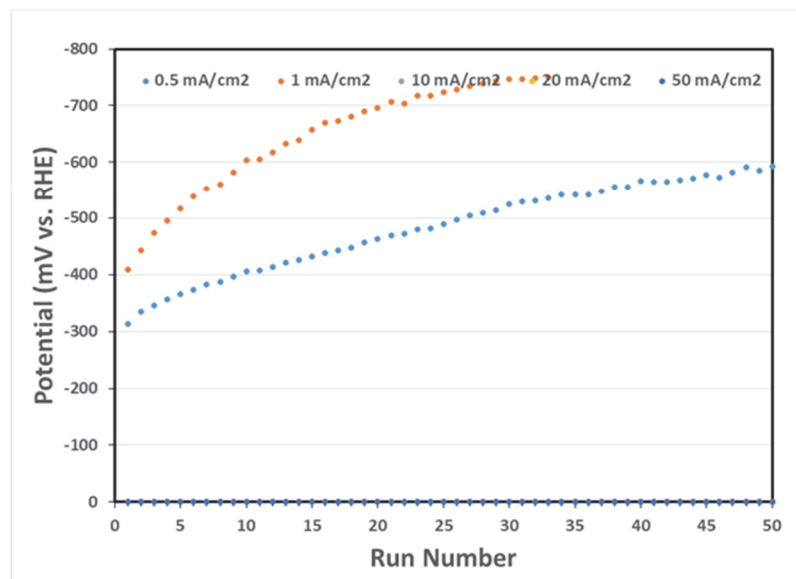
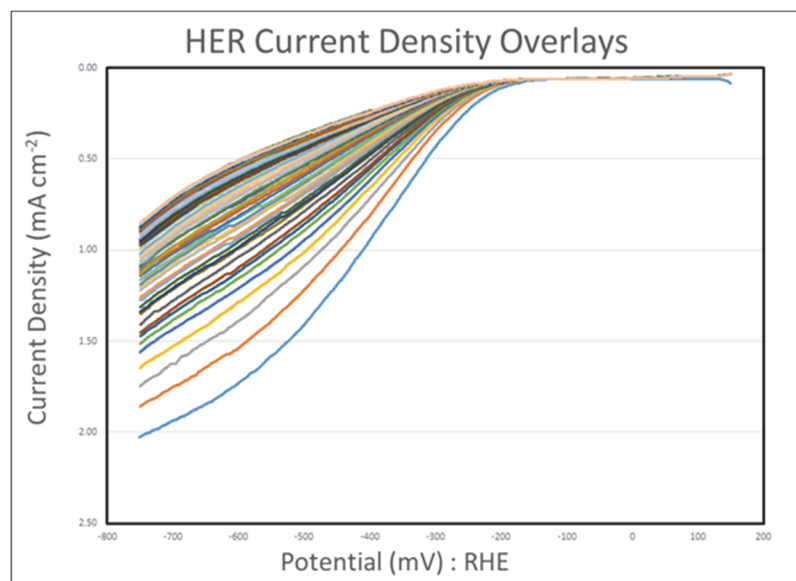


Figure S5A. Overlay LSV graphs (top) for 50 runs using FePS₃ catalyst in 0.5 M H₂SO₄ (5 mV/s scan rate, graphite counter, no iR compensation). Bottom plot shows applied potentials required to achieve specific mA/cm² values in each LSV run that is in the LSV overlay plot.

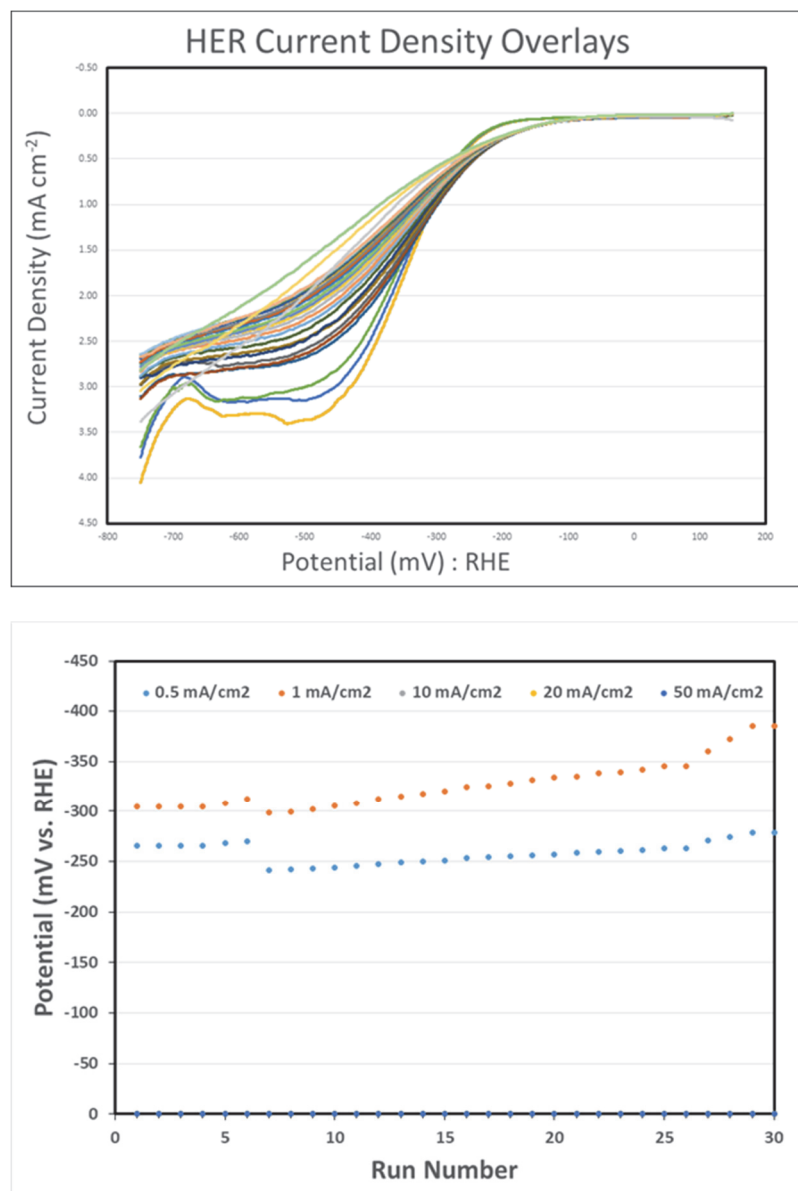


Figure S5B. Overlay LSV graphs (top) for 30 runs using FePS_3 catalyst in 0.5 M H_2SO_4 (5 mV/s scan rate, graphite counter, 85% iR compensation, $R_{\text{cell}} = 350 \, \Omega$). Bottom plot shows applied potentials required to achieve specific mA/cm^2 values in each LSV run that is in the LSV overlay plot.

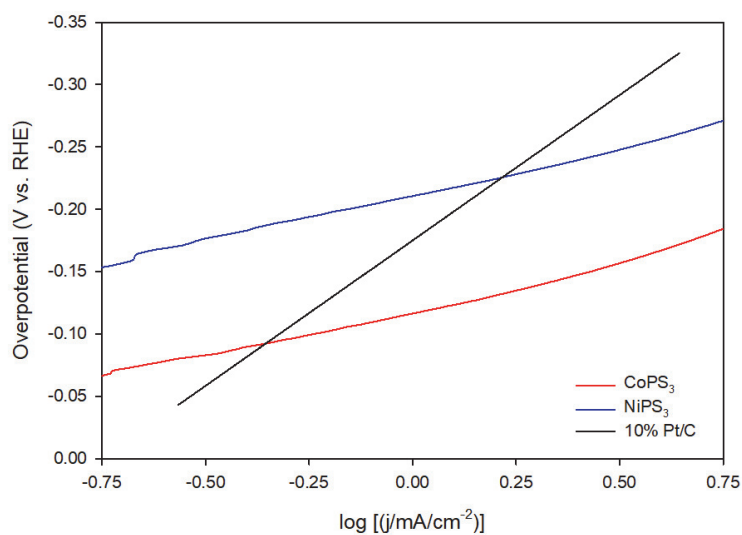
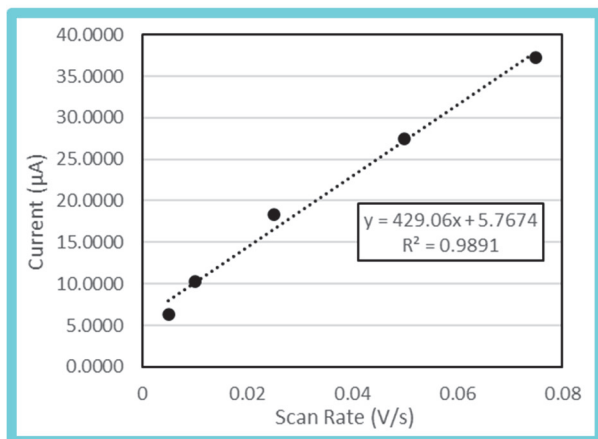
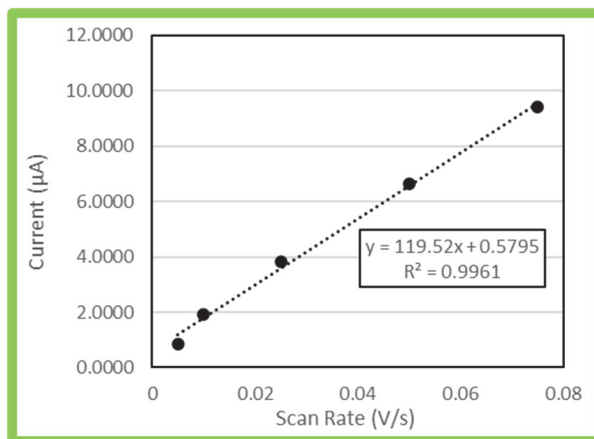


Figure S6. Representative Tafel graphs for CoPS₃, NiPS₃, and Pt/C powders. Data from 50 LSV runs overlay well with these graphs and deviations from the mean are reported in Table 3 of the main paper. Linear regression equations for these data are: CoPS₃ ($y = -0.071x - 0.1173$, $R^2 = 0.9971$), NiPS₃ ($y = -0.0858x - 0.2006$, $R^2 = 0.9987$), and 10% Pt/C ($y = -0.0492x + 0.0202$, $R^2 = 0.9983$)

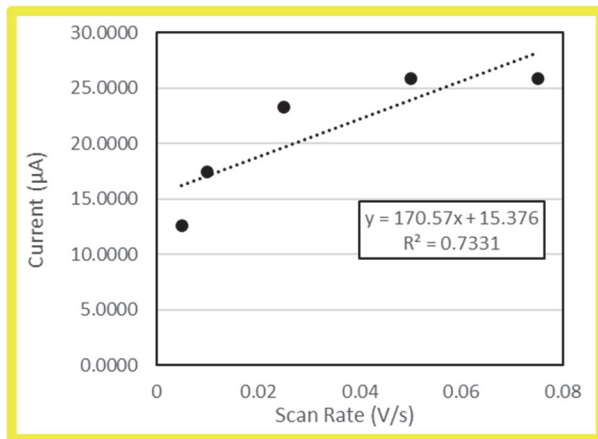
CoPS₃, 300 mV, ECSA 6.1 cm²



NiPS₃, 470 mV, ECSA 1.7 cm²



FePS₃, 450 mV, ECSA 2.4 cm²



10%Pt/C, 250 mV, ECSA 26.9 cm²

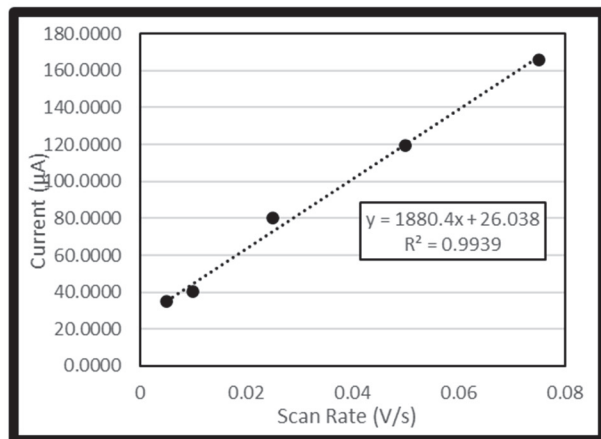


Figure S7. Analysis of scan rate data from CV runs used to calculate ECSA values in Table 3.

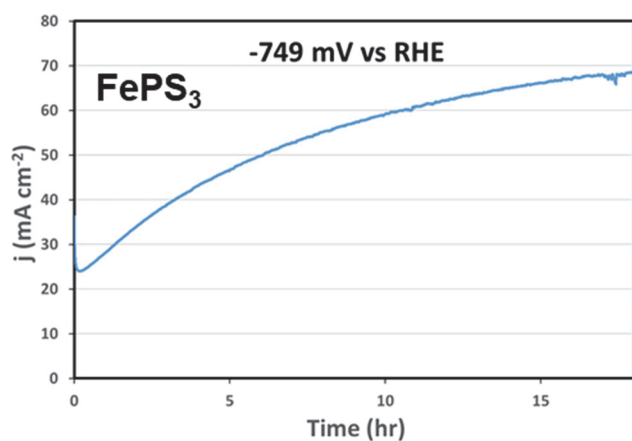
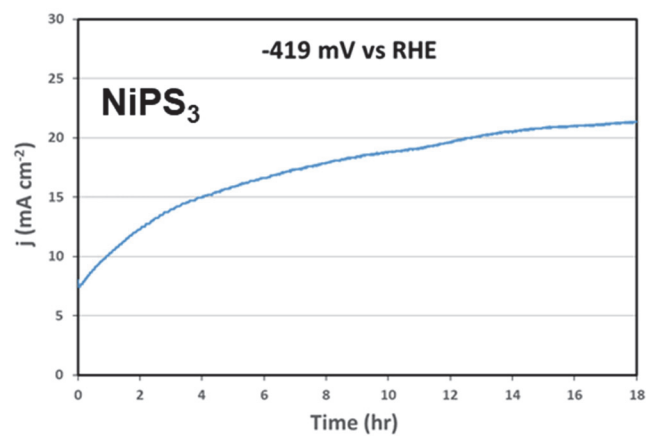
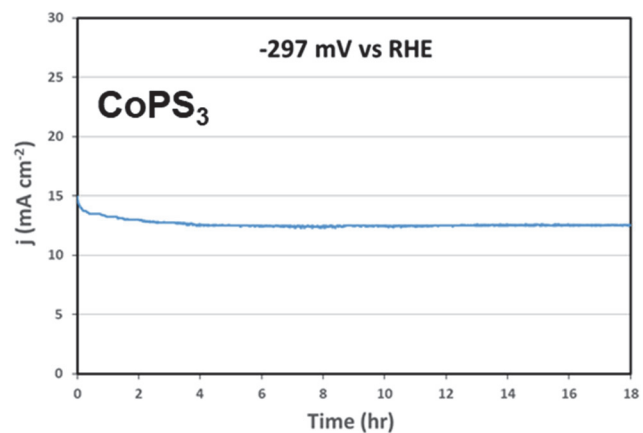


Figure S8. 18-hr chronoamperometry (CA) HER data for MPS₃ (0.5 M H₂SO₄, platinum counter, no iR compensation): CoPS₃ top, NiPS₃ middle, FePS₃ bottom. Constant applied potential values for experiment is listed in each graph.

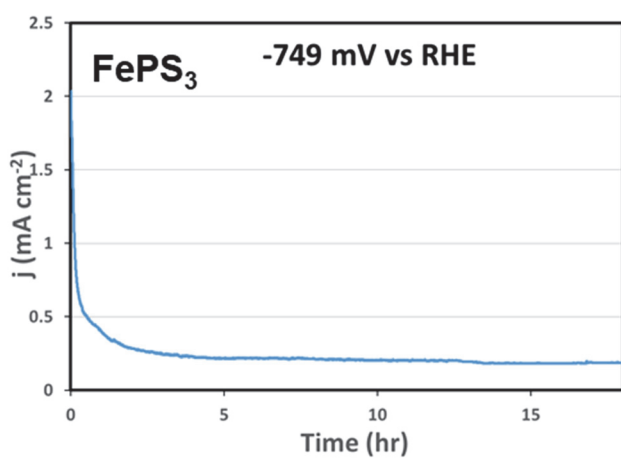
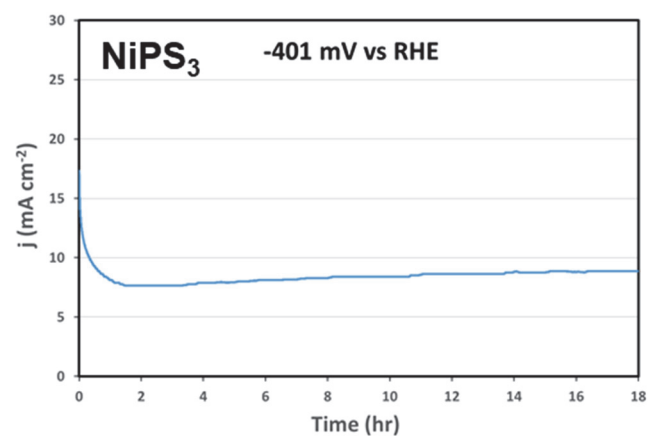
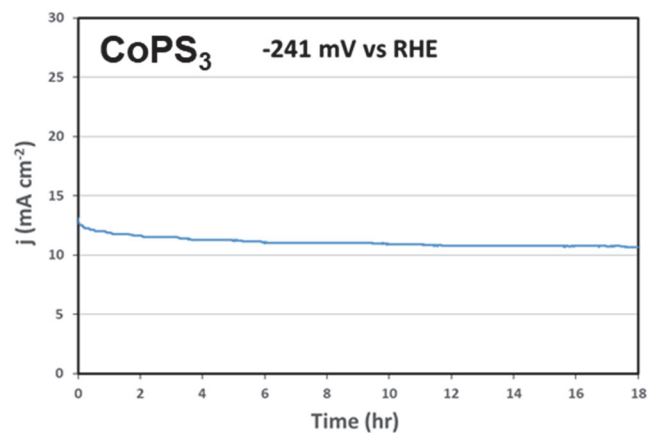


Figure S9. 18-hr chronoamperometry (CA) HER data for MPS₃ (0.5 M H₂SO₄, graphite counter, no iR compensation): CoPS₃ top, NiPS₃ middle, FePS₃ bottom. Constant applied potential values for experiment is listed in each graph.

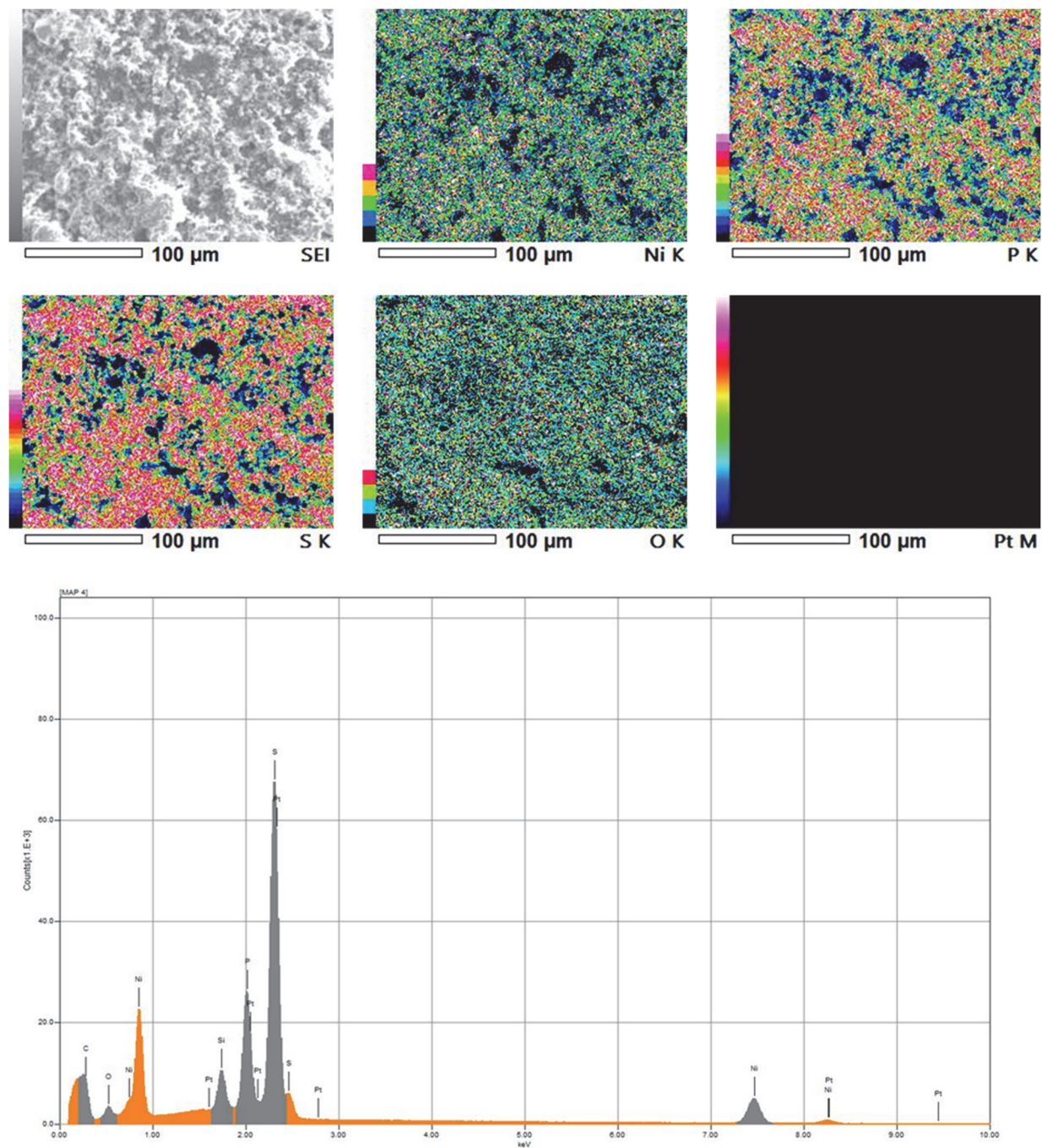


Figure S10A. Microprobe elemental mapping and semiquantitative surface analysis of NiPS₃ particles embedded on C_{wax} tips after 18-hour CA experiments using a platinum CE. The colors in each microprobe image reflect relative intensity of that surface detected element. To the left of each graph is its legend of increasing elemental content represented by different colors: pink>red>orange>yellow>green>blue>black.

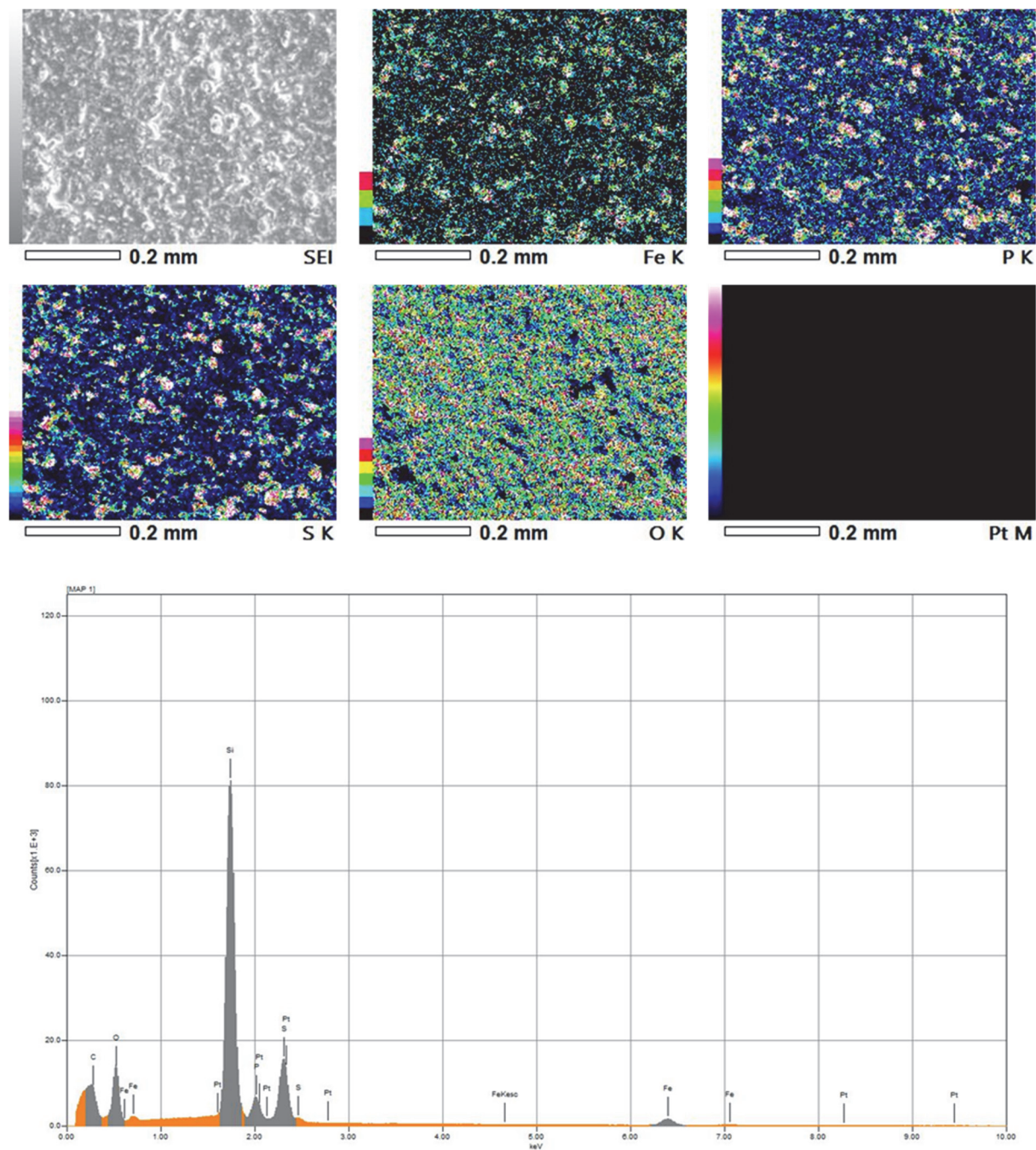


Figure S10B. Microprobe elemental mapping and semiquantitative surface analysis of FePS₃ particles embedded on C_{wax} tips after 18-hour CA experiments using a platinum CE. The colors in each microprobe image reflect relative intensity of that surface detected element. To the left of each graph is its legend of increasing elemental content represented by different colors: pink>red>orange>yellow>green>blue>black.

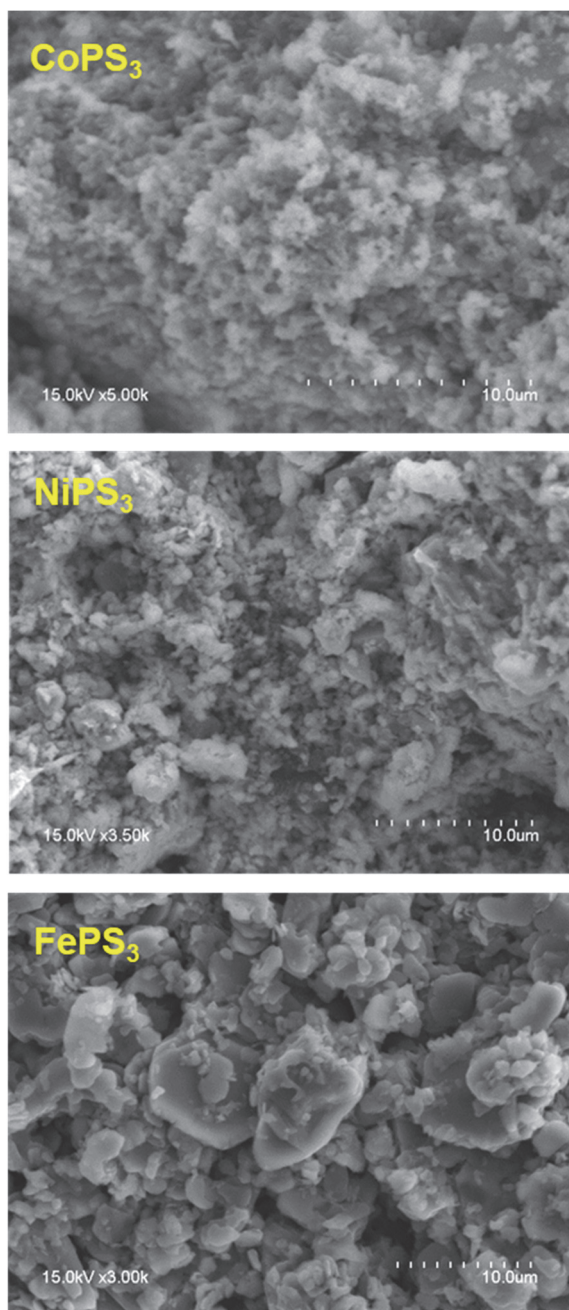


Figure S11. SEM images of MPS_3 materials embedded on the C_{max} electrode surface after 18-hour HER CA experiment in 0.5 M H_2SO_4 .

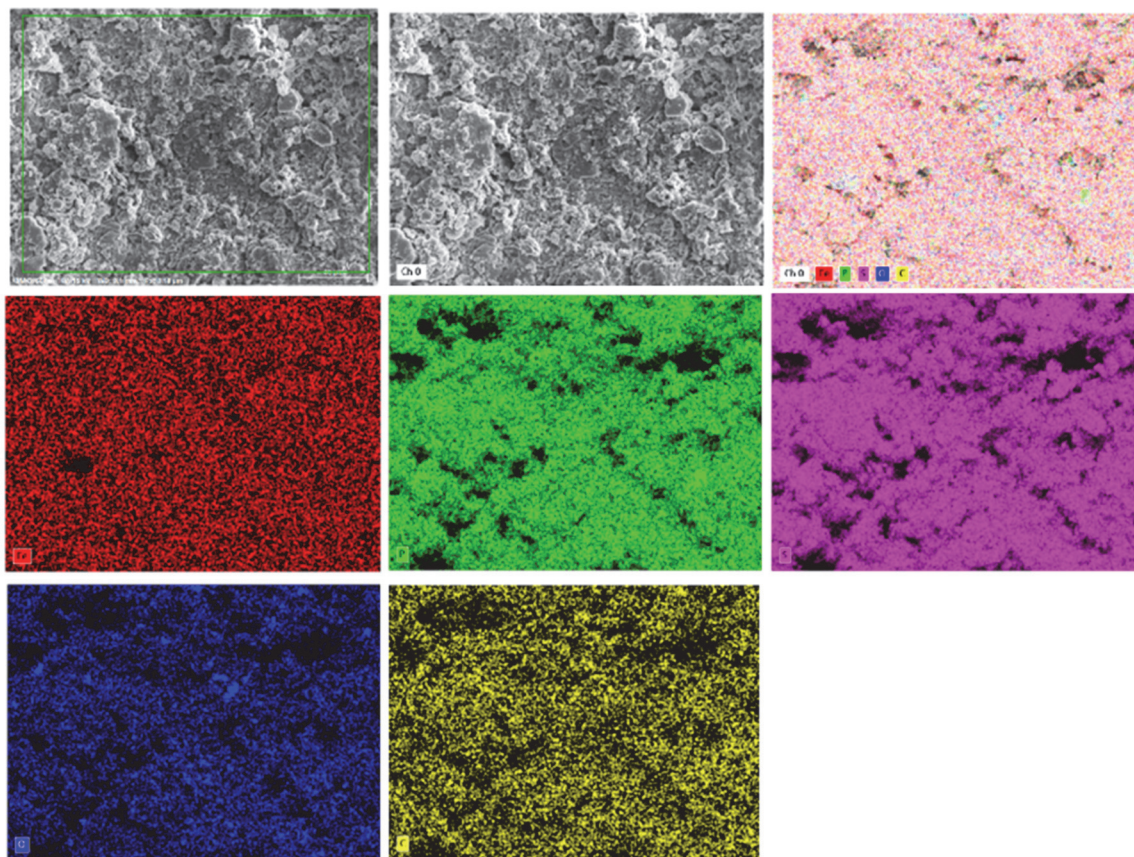


Figure S12A. EDS elemental mapping of FePS_3 particles embedded on C_{wax} tips after 18-hour CA experiments using a graphite CE. Semiquantitative elemental analysis gives $\text{Fe/P/S} = 1/1.1/2.8$. Scale bar in top left SEM image is 40 μm long.

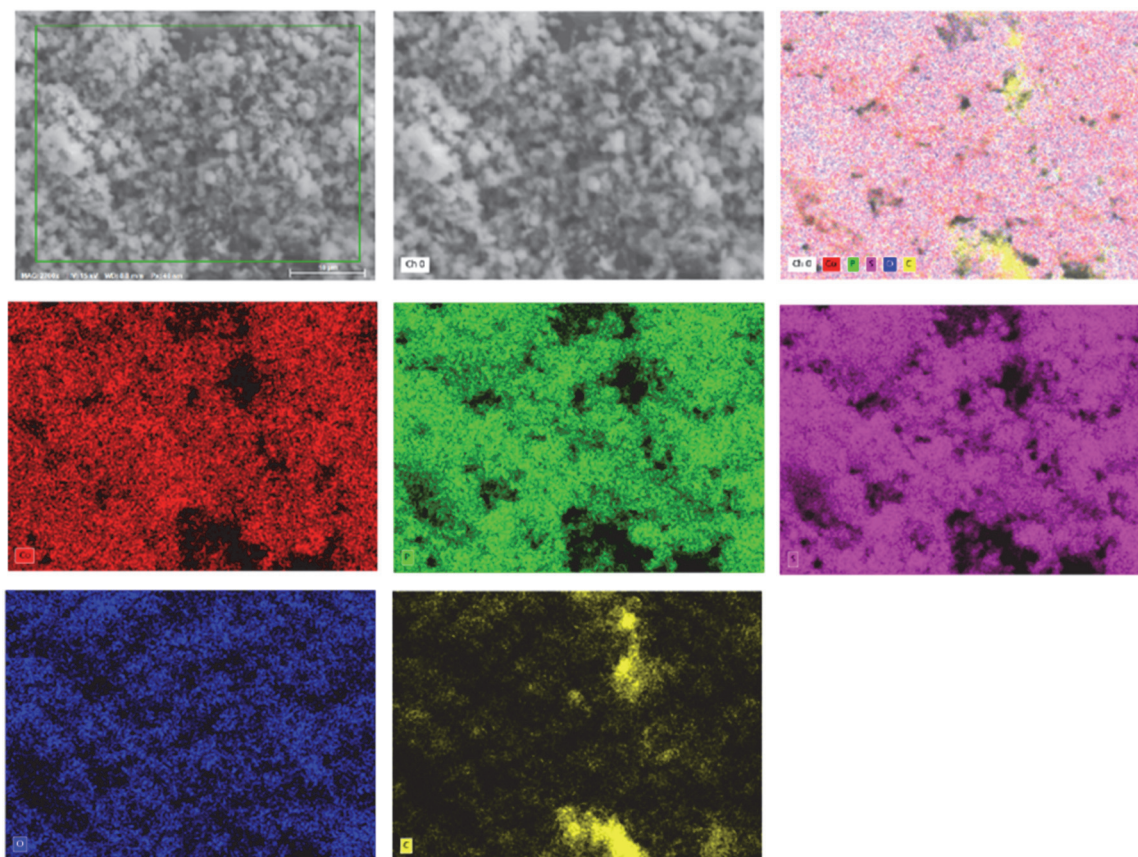


Figure S12B. EDS elemental mapping of CoPS_3 particles embedded on C_{wax} tips after 18-hour CA experiments using a graphite CE. Semiquantitative elemental analysis gives $\text{Co/P/S} = 1/1.2/3.3$. Scale bar in top left SEM image is 10 μm long.

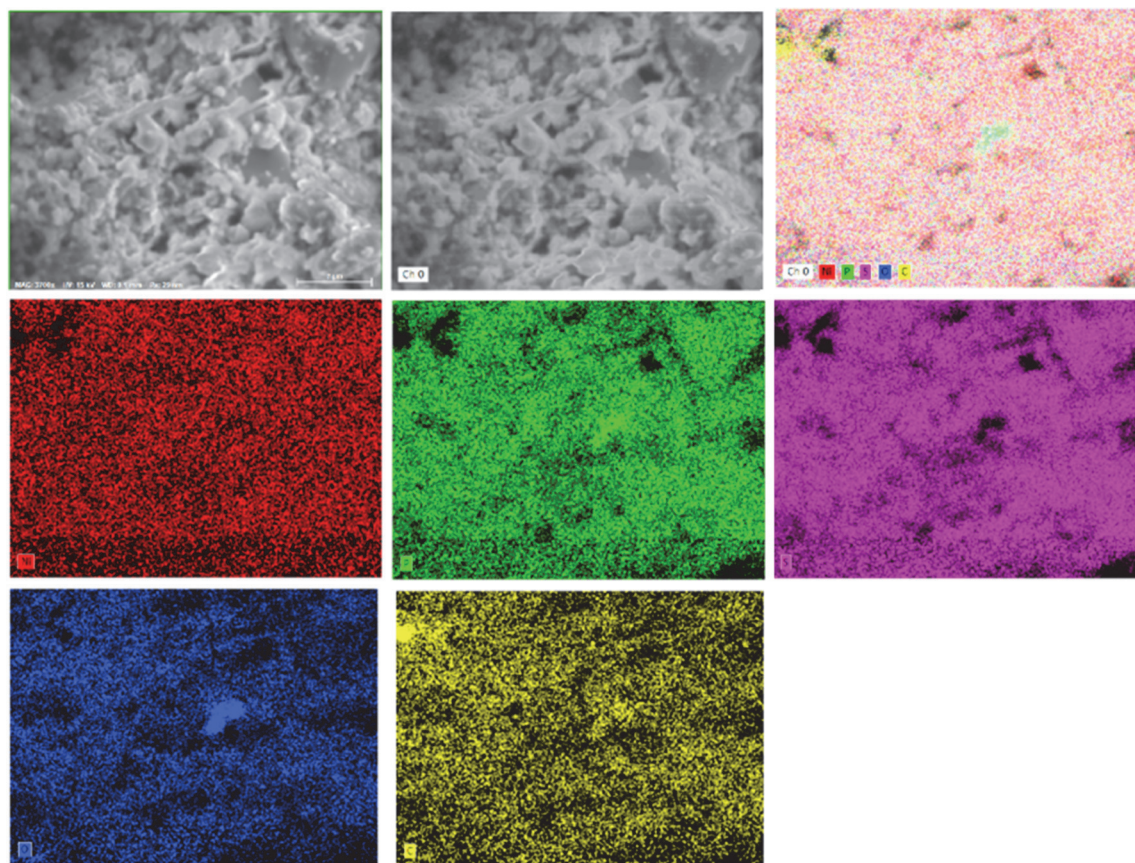


Figure S12C. EDS elemental mapping of NiPS_3 particles embedded on C_{wax} tips after 18-hour CA experiments using a graphite CE. Semiquantitative elemental analysis gives $\text{Ni/P/S} = 1/1/2.6$. Scale bar in top left SEM image is 7 μm long.

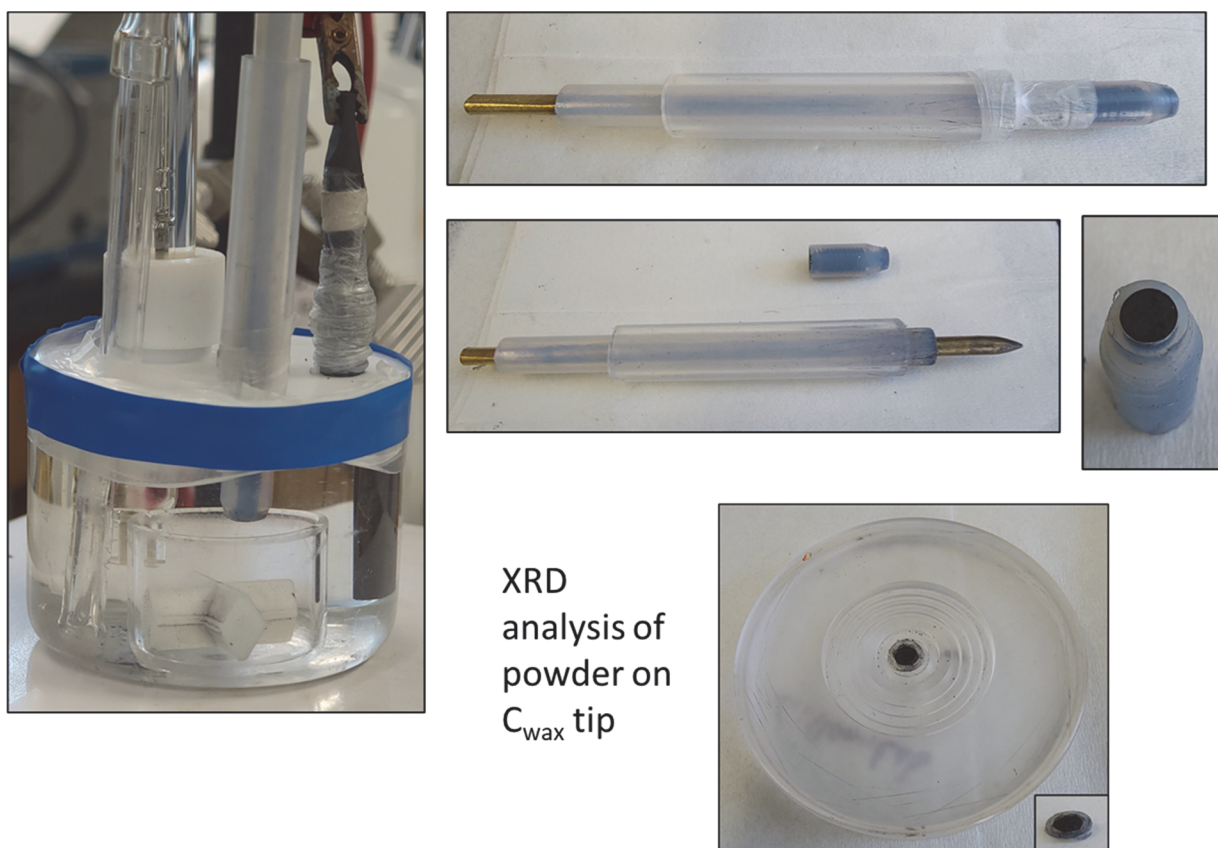


Figure S13. Electrochemical cell setup (top left) and images of C_{wax} electrode assembly and example of cut tips used for XRD analysis.

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