Electronic Supplementary Information

Fe, Co, and Ni Ions Promote the Catalytic Activity of Amorphous Molybdenum Sulfide Films for Hydrogen Evolution

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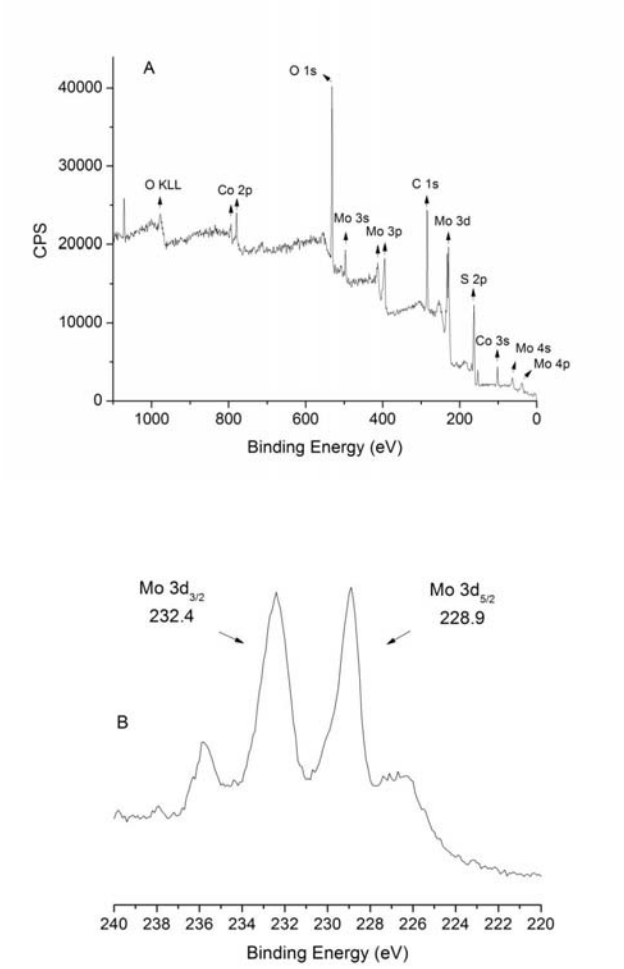


Figure S1. XPS spectrum of the cobalt-promoted molybdenum sulfide film on FTO-coated glass; survey spectrum **(A)** and Mo 3d region **(B)**.

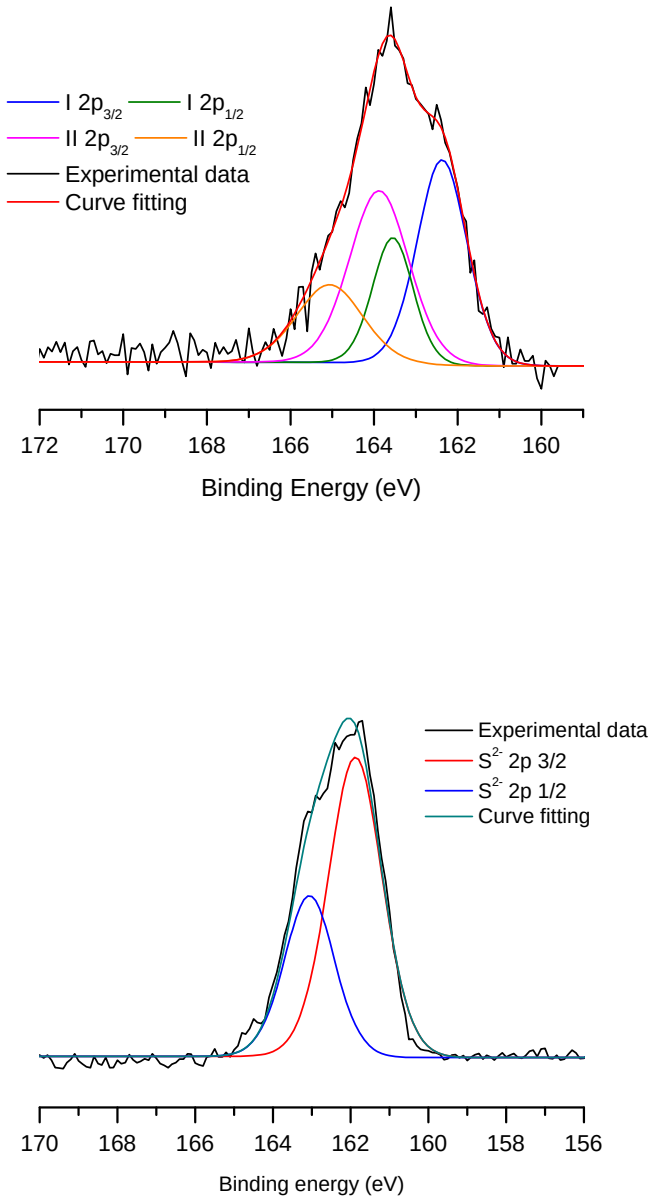


Figure S2. XPS sulfur 2p spectra of MoS_3 film before (top) and after (bottom) electrolysis.

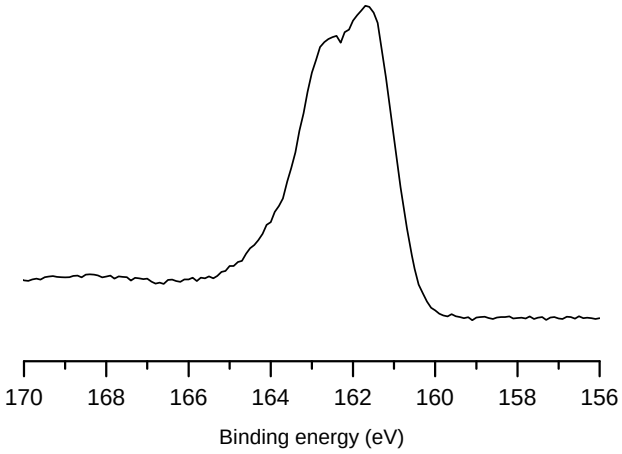


Figure S3. XPS sulfur 2p spectrum of Co-MoS_3 film after electrolysis at η = 200 mV for 5 minutes.

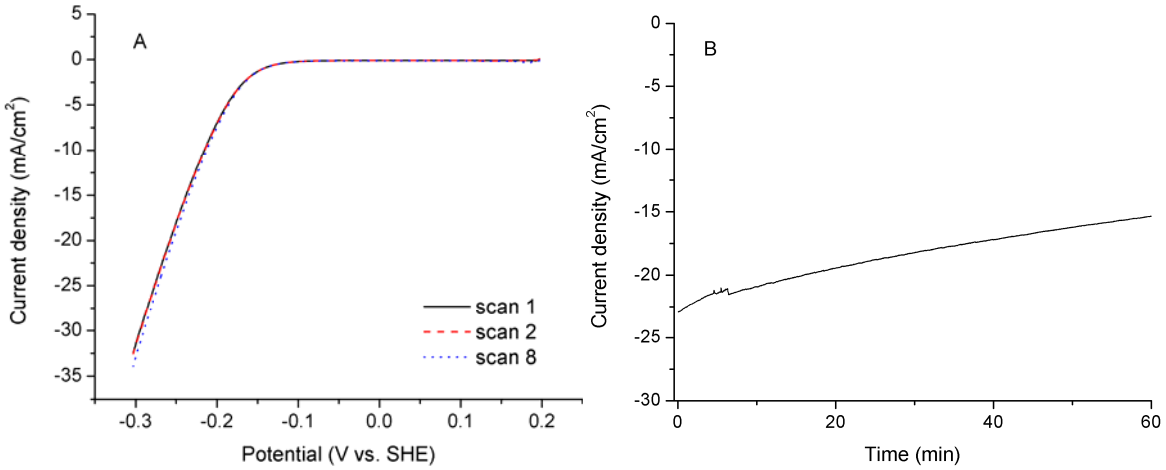


Figure S4. (A) Consecutive polarization curves of Co-promoted molybdenum sulfide film on glassy carbon at pH = 0 (scan rate: 5 mV/s). (B) Time course of the catalytic current during an electrolysis experiment at pH = 0 using a Co-MoS_3 film on glassy carbon (η = 200 mV). (Note: These measurements were done with different glassy carbon disk electrodes with different resistances. The slight decrease in current density is due to some mechanical damage of the film rather than the deactivation of catalyst. The mechanical damage can be seen in Fig. S7.)

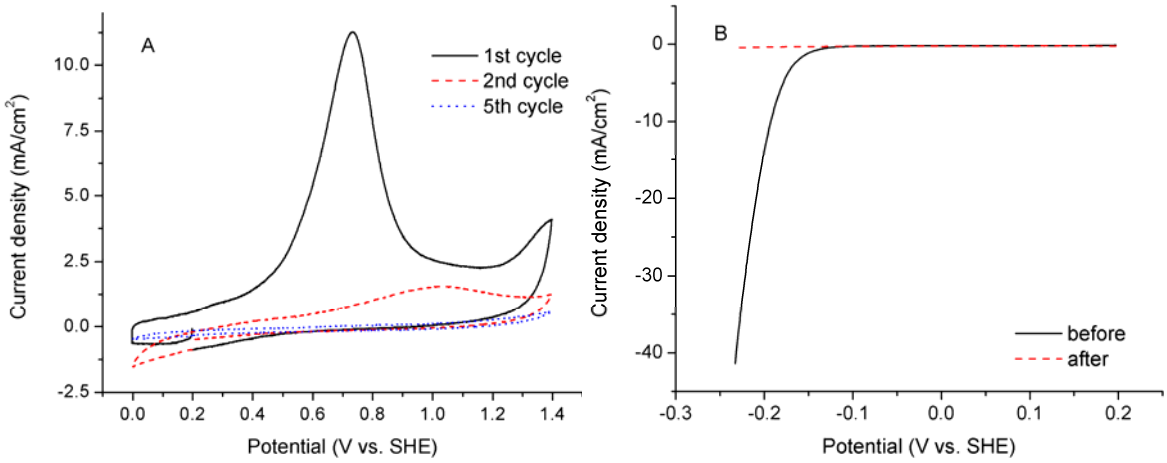
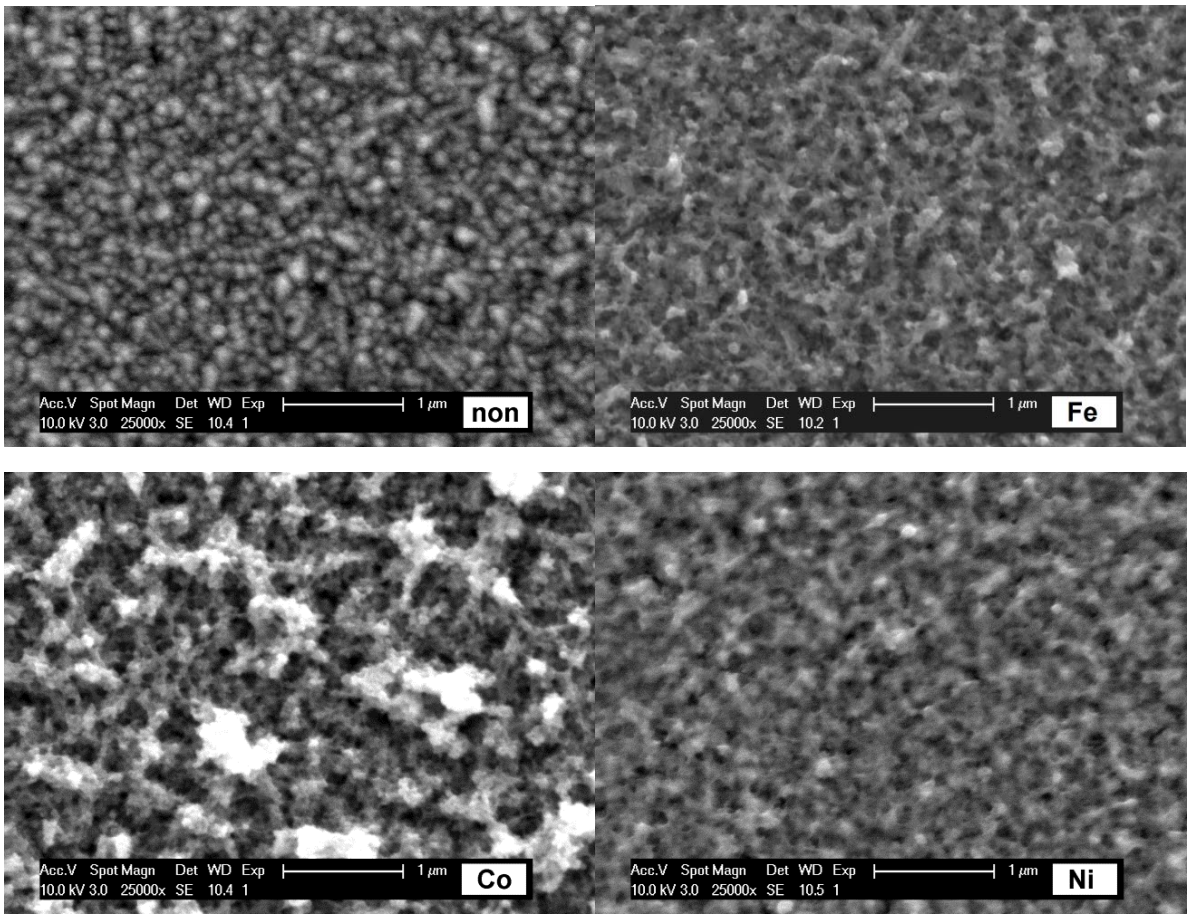


Figure S5. (A) Consecutive cyclic voltammograms at pH = 0 at positive potentials with a Co-MoS_3 film on glassy carbon (scan rate: 50 mV/s). (B) Polarization curves of the same electrode before and after the consecutive cyclic voltammetric measurements (scan rate: 5 mV/s).



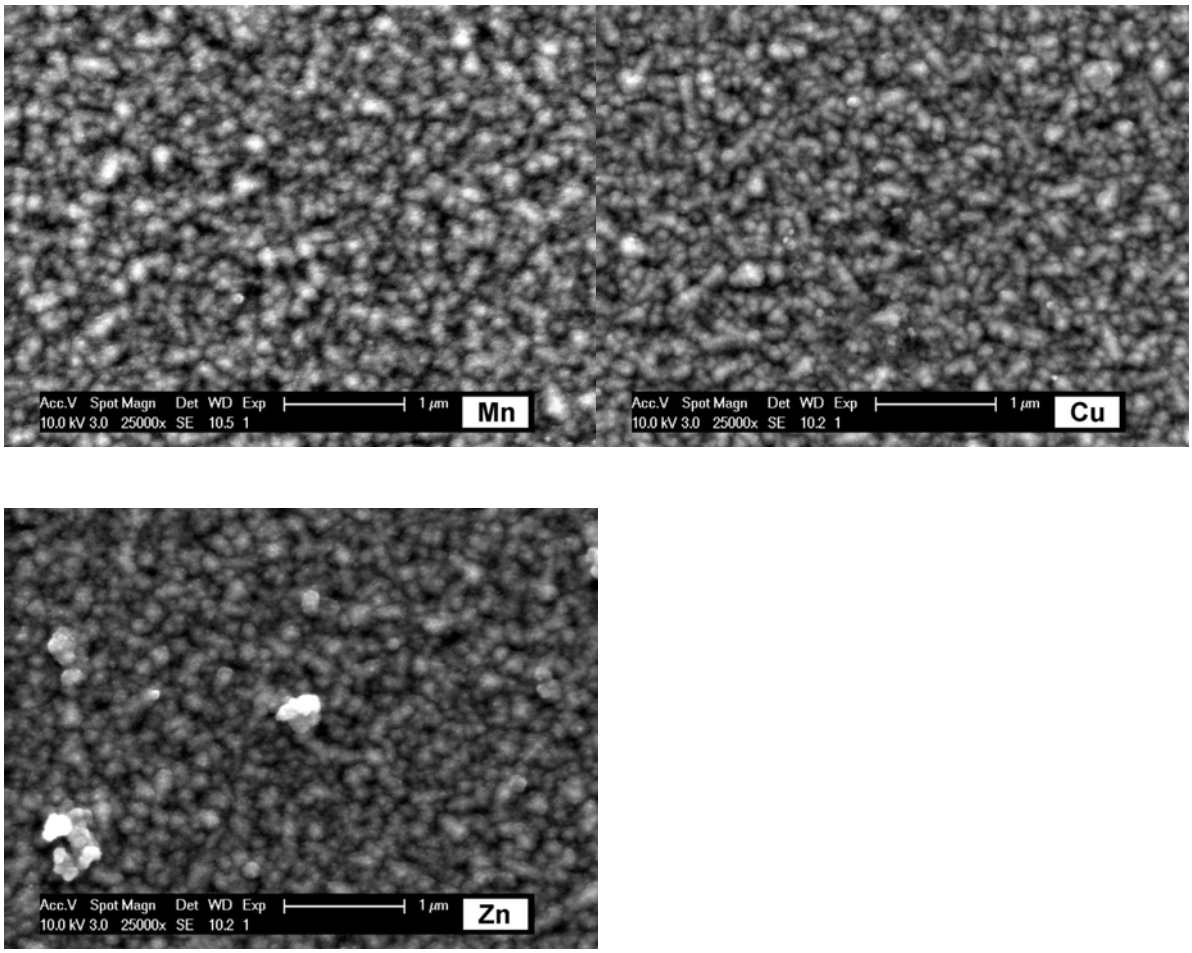


Figure S6. SEM images of unpromoted and M-promoted molybdenum sulfide films on FTO-coated glass. The M-promoted films were deposited in aqueous solutions of M^{2+} (0.67 mM) and MoS_4^{2-} (2 mM).

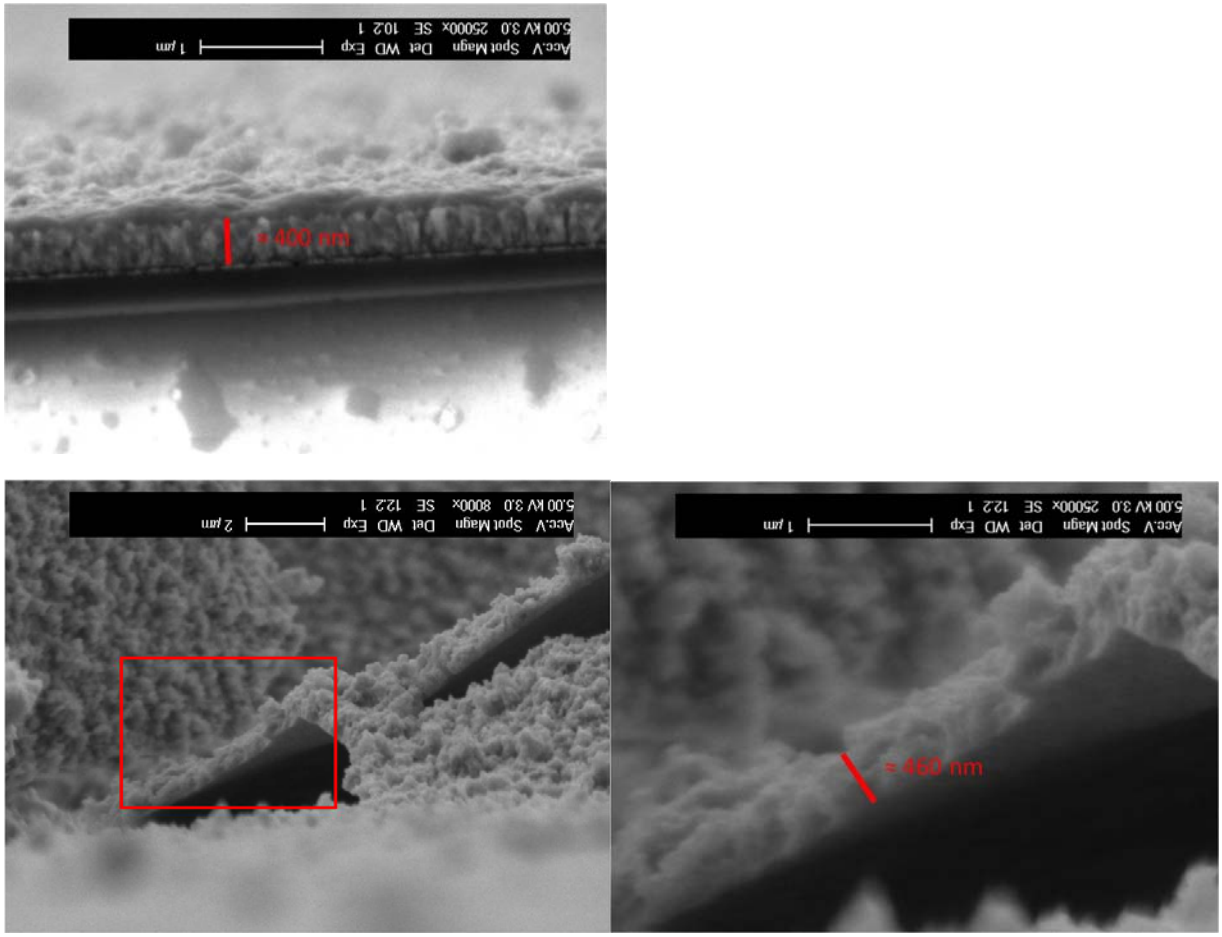


Figure S7. SEM images of cross-sections of Co promoted molybdenum sulfide film on FTO coated glass: cross-section of the whole electrode (deposited film – FTO – glass support) **(top)**; partially peeled off film **(bottom, left)**; zoom of bottom left image **(bottom, right)**. The distances were determined with the program *ImageJ 1.44p*.

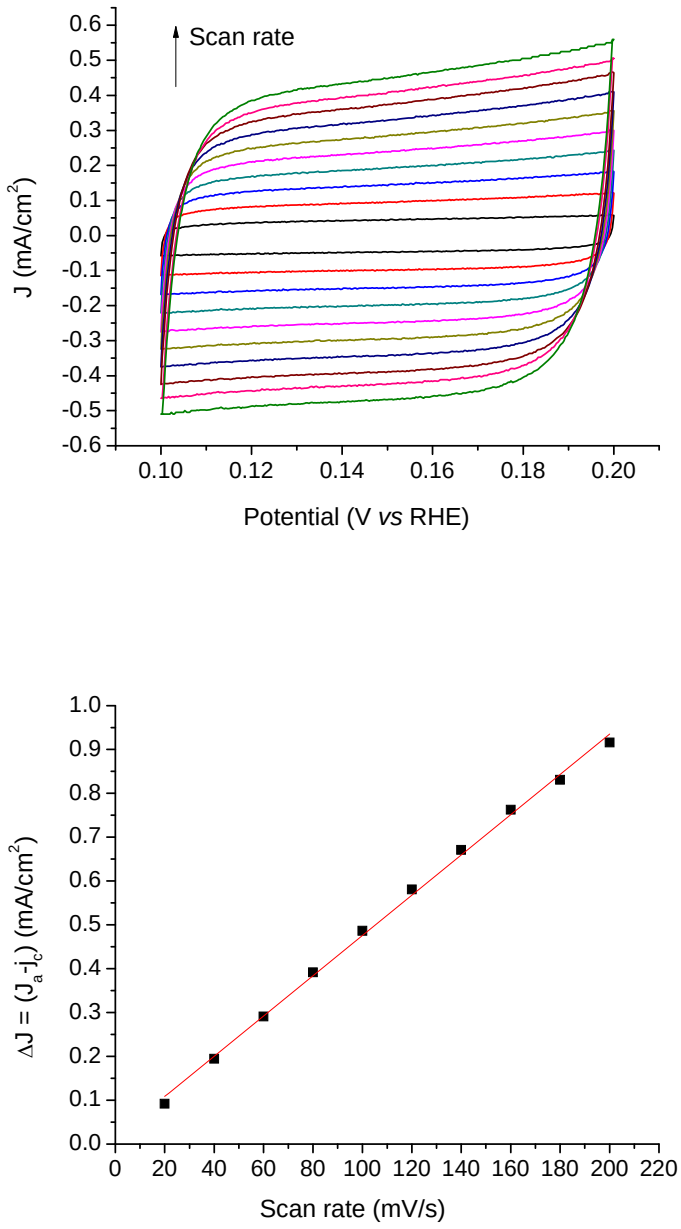


Fig. S8. Cyclic voltammograms at E = 0.1-0.2 V vs. RHE (left) and scan-rate dependence of the current density at E = 0.15 V vs. RHE (right) for the MoS_3 film on FTO in pH = 0.

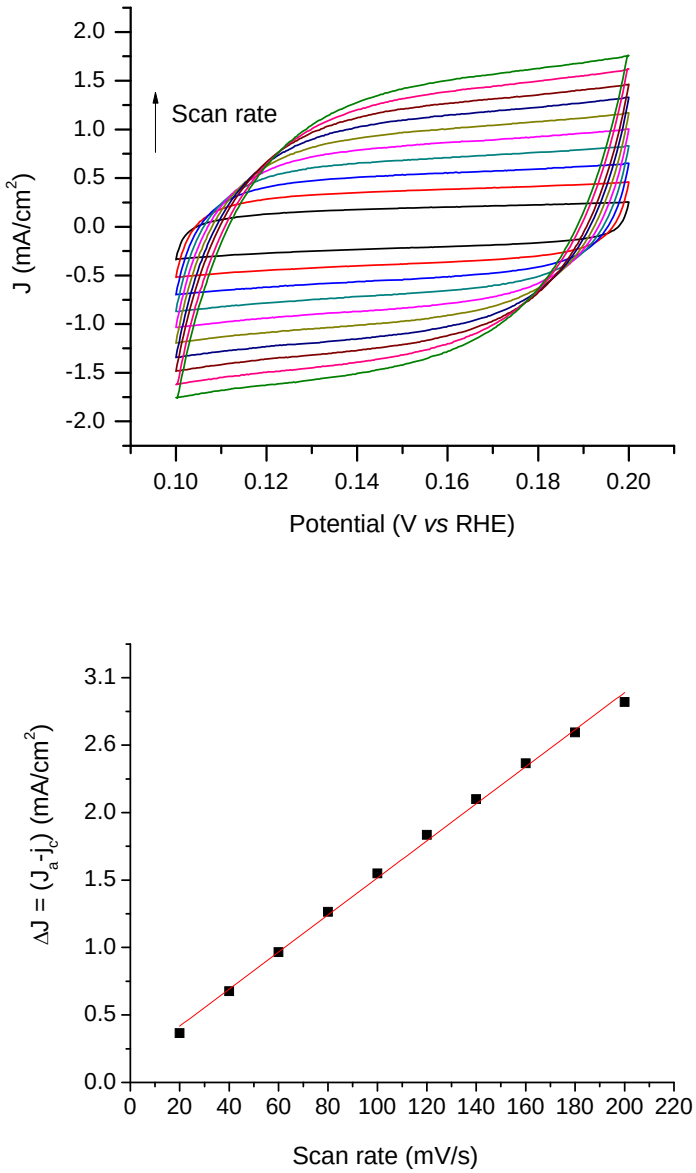


Fig. S9. Cyclic voltammograms at E = 0.1-0.2 V vs. RHE (left) and scan-rate dependence of the current density at E = 0.15 V vs. RHE (right) for the Fe-MoS_3 film on FTO in pH = 0.

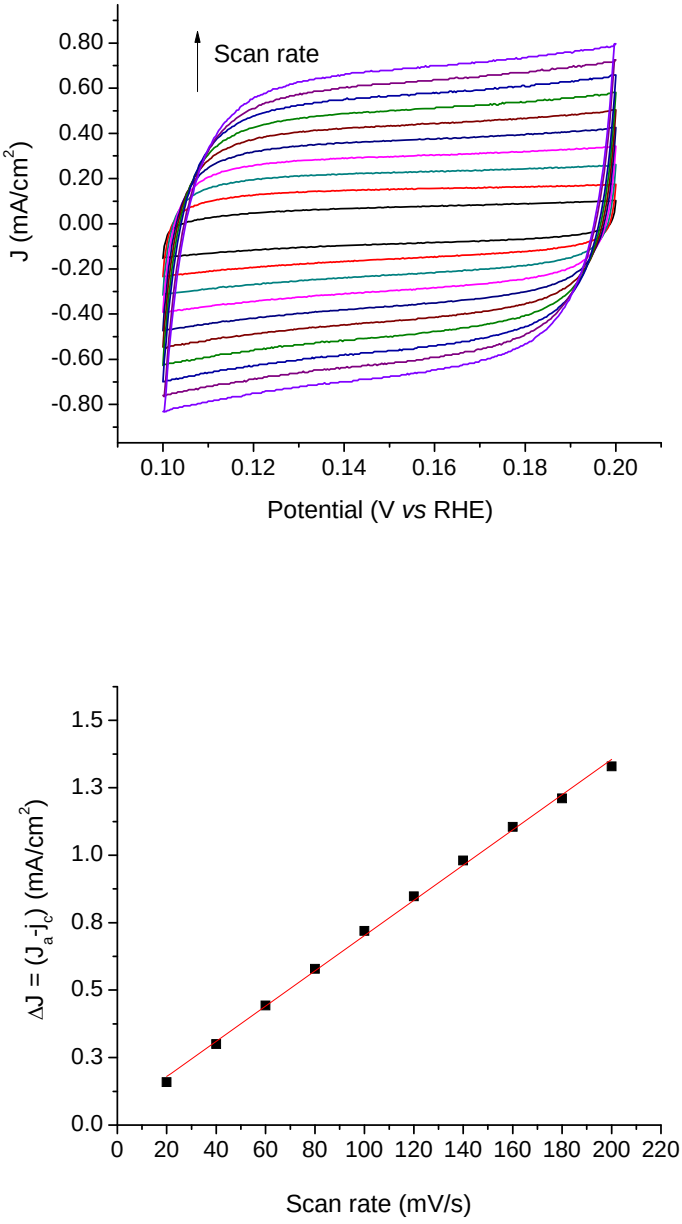


Fig. S10. Cyclic voltammograms at E = 0.1-0.2 V vs. RHE (left) and scan-rate dependence of the current density at E = 0.15 V vs. RHE (right) for the Ni-MoS_3 film on FTO in pH = 0.

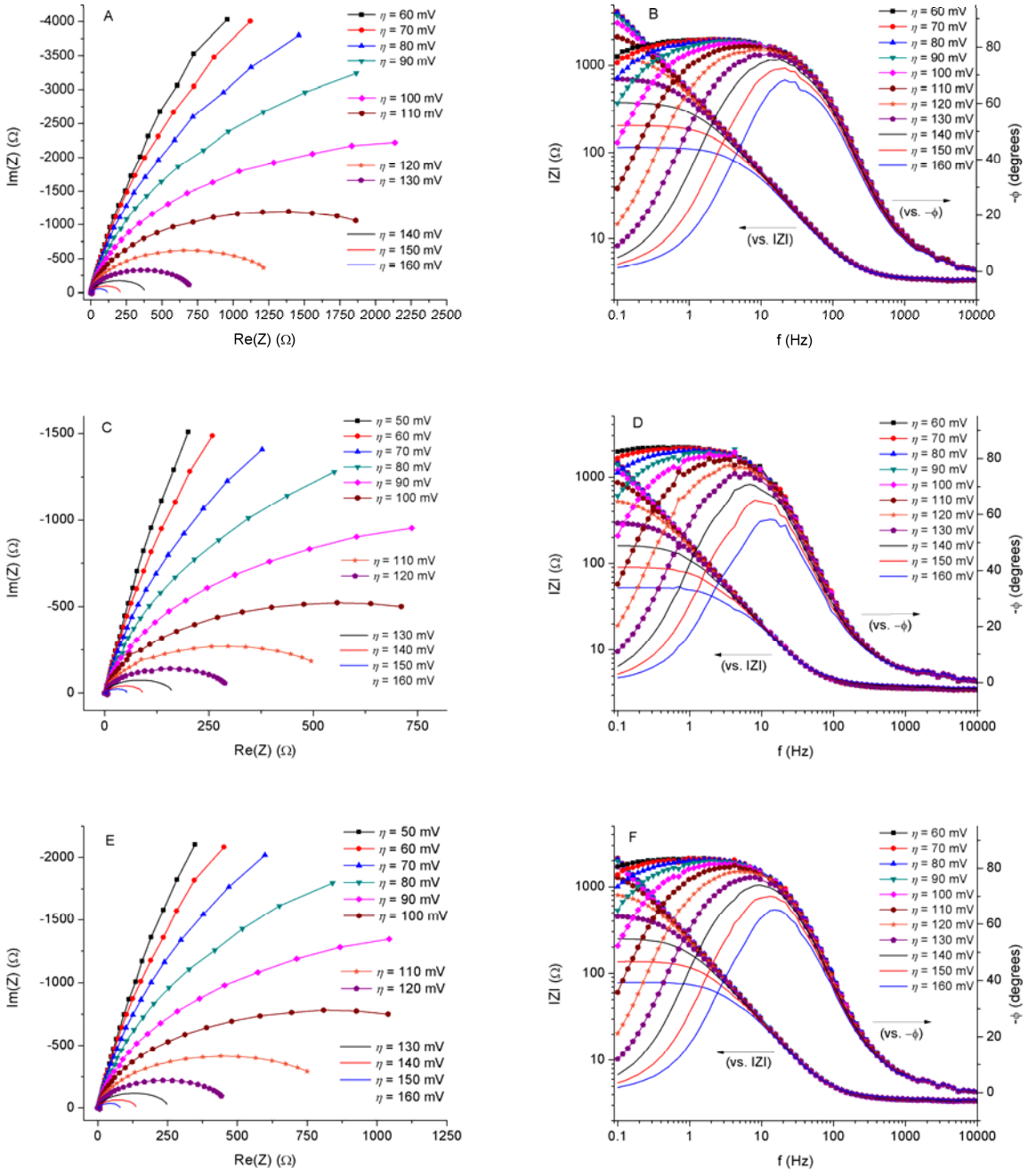


Figure S11. Nyquist and Bode plots showing EIS responses of non-promoted **(A, B)**, Fe **(C, D)**, and Ni **(E, F)** promoted molybdenum sulfide films on glassy carbon at various HER overpotentials at pH = 0.

Table S1. Values for R_s, R_{ct}, Q^{-1} and n obtained by fitting the EIS responses on unpromoted molybdenum sulfide film on glassy carbon at pH = 0 and the calculated values for C^*_{dl} for this film.

η (mV)	R_s (Ω)	R_{ct} (Ω)	Q^{-1} (F s^{n-1})	n (-)	C^*_{dl} (μF)
60	3.26E+00	3.67E+04	3.50E-04	9.31E-01	2.13E+02
70	3.25E+00	2.62E+04	3.48E-04	9.32E-01	2.12E+02
80	3.30E+00	1.60E+04	3.48E-04	9.33E-01	2.13E+02
90	3.26E+00	9.21E+03	3.48E-04	9.34E-01	2.15E+02
100	3.33E+00	4.97E+03	3.48E-04	9.35E-01	2.18E+02
110	3.35E+00	2.64E+03	3.48E-04	9.37E-01	2.21E+02
120	3.38E+00	1.37E+03	3.51E-04	9.39E-01	2.27E+02
130	3.40E+00	7.21E+02	3.53E-04	9.41E-01	2.33E+02
140	3.42E+00	3.81E+02	3.58E-04	9.44E-01	2.41E+02
150	3.44E+00	2.06E+02	3.66E-04	9.46E-01	2.49E+02
160	3.45E+00	1.14E+02	3.77E-04	9.45E-01	2.56E+02
		Average			2.27E+02
		Standard deviation			1.56E+01

Table S2. Values for R_s, R_{ct}, Q^{-1} and n obtained by fitting the EIS responses on Fe-promoted molybdenum sulfide film on glassy carbon at pH = 0 and the calculated values for C^*_{dl} for this film.

η (mV)	R_s (Ω)	R_{ct} (Ω)	Q^{-1} (F s^{n-1})	n (-)	C^*_{dl} (μF)
60	3.59E+00	3.08E+04	1.00E-03	9.48E-01	7.38E+02
70	3.42E+00	1.74E+04	1.00E-03	9.47E-01	7.31E+02
80	3.64E+00	8.36E+03	1.01E-03	9.47E-01	7.37E+02
90	3.71E+00	4.38E+03	1.00E-03	9.49E-01	7.41E+02
100	3.72E+00	2.21E+03	1.01E-03	9.51E-01	7.56E+02
110	3.71E+00	1.12E+03	1.02E-03	9.52E-01	7.70E+02
120	3.84E+00	5.80E+02	1.04E-03	9.53E-01	7.87E+02
130	3.82E+00	3.03E+02	1.05E-03	9.51E-01	7.93E+02
140	3.88E+00	1.59E+02	1.07E-03	9.57E-01	8.35E+02
150	3.89E+00	8.72E+01	1.12E-03	9.51E-01	8.40E+02
160	3.93E+00	4.98E+01	1.17E-03	9.43E-01	8.41E+02
		Average			7.79E+02
		Standard deviation			4.33E+01

Table S3. Values for R_s, R_{ct}, Q^{-1} and n obtained by fitting the EIS responses on Co-promoted molybdenum sulfide film on glassy carbon at pH = 0 and the calculated values for C^*_{dl} for this film.

η (mV)	R_s (Ω)	R_{ct} (Ω)	Q^{-1} (F s^{n-1})	n (-)	C^*_{dl} (μF)
60	3.49E+00	1.80E+04	7.99E-04	9.45E-01	5.69E+02
70	3.53E+00	1.14E+04	8.12E-04	9.46E-01	5.80E+02
80	3.66E+00	6.98E+03	8.17E-04	9.47E-01	5.90E+02
90	3.65E+00	4.08E+03	8.31E-04	9.46E-01	5.97E+02
100	3.58E+00	2.31E+03	8.36E-04	9.47E-01	6.05E+02
110	3.79E+00	1.26E+03	8.36E-04	9.49E-01	6.16E+02
120	3.68E+00	6.82E+02	8.52E-04	9.50E-01	6.29E+02
130	3.42E+00	3.67E+02	8.73E-04	9.48E-01	6.37E+02
140	3.58E+00	1.99E+02	8.86E-04	9.48E-01	6.47E+02
150	3.52E+00	1.10E+02	9.15E-04	9.46E-01	6.59E+02
160	3.49E+00	6.26E+01	9.35E-04	9.45E-01	6.70E+02
		Average			6.18E+02
		Standard deviation			3.30E+01

Table S4. Values for R_s, R_{ct}, Q^{-1} and n obtained by fitting the EIS responses on Ni-promoted molybdenum sulfide film on glassy carbon at pH = 0 and the calculated values for C^*_{dl} for this film.

η (mV)	R_s (Ω)	R_{ct} (Ω)	Q^{-1} (F s^{n-1})	n (-)	C^*_{dl} (μF)
60	3.29E+00	3.03E+04	6.99E-04	9.41E-01	4.79E+02
70	3.36E+00	1.82E+04	6.91E-04	9.44E-01	4.82E+02
80	3.10E+00	1.09E+04	6.91E-04	9.43E-01	4.76E+02
90	3.49E+00	5.89E+03	6.93E-04	9.46E-01	4.91E+02
100	3.45E+00	3.13E+03	6.99E-04	9.47E-01	4.97E+02
110	3.49E+00	1.69E+03	6.97E-04	9.49E-01	5.03E+02
120	3.53E+00	8.94E+02	6.97E-04	9.51E-01	5.12E+02
130	3.55E+00	4.74E+02	7.11E-04	9.50E-01	5.20E+02
140	3.52E+00	2.53E+02	7.21E-04	9.53E-01	5.36E+02
150	3.55E+00	1.37E+02	7.35E-04	9.52E-01	5.45E+02
160	3.58E+00	7.69E+01	7.53E-04	9.49E-01	5.46E+02
		Average			5.08E+02
		Standard deviation			2.60E+01

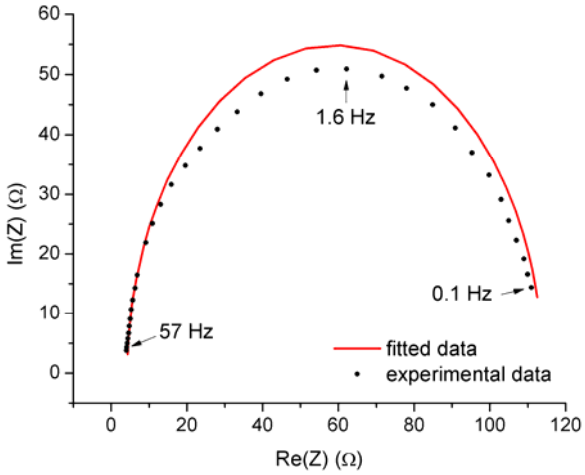


Figure S12. Nyquist plot showing the EIS response of Co-promoted MoS_3 film on glassy carbon at η = 150 mV and pH = 0. The black dots are experimental data and the red line is the fitted curve using an ideal capacitor instead of the CPE in the electrical equivalent circuit.

η (mV)	R_s (Ω)	R_{ct} (Ω)	C^*_{ideal} (F)
60	4.70E+00	8.67E+03	6.96E-04
70	7.26E+00	6.28E+03	7.46E-04
80	6.79E+00	4.34E+03	7.51E-04
90	8.81E+00	2.80E+03	7.77E-04
100	7.66E+00	1.77E+03	7.63E-04
110	5.88E+00	1.08E+03	7.34E-04
120	5.99E+00	6.40E+02	7.49E-04
130	6.50E+00	3.58E+02	7.78E-04
140	4.41E+00	1.99E+02	7.41E-04
150	4.28E+00	1.10E+02	7.57E-04
160	4.20E+00	6.27E+01	7.78E-04
	Average		7.52E-04
	Standard deviation		2.40E-05

Table S5. Values for R_s, R_{ct}, and C^*_{ideal} obtained by fitting the EIS responses on Co-promoted molybdenum sulfide film on glassy carbon at pH = 0, using an ideal capacitor instead of the CPE in the electrical equivalent circuit.