

Activity of nickel molybdenum sulfide electrocatalyst as function of the ionomer in the ink formulation

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Supplementary Information

Reference electrode (Hg/HgO) calibration:

To calibrate the reference electrode, 40% Pt/C was deposited onto the same working electrode substrate described in the main text with a mass loading of 0.28 mg cm^{-2} . Initially CV analysis was performed between -0.93 and 0.40 V vs Hg/HgO in H_2 -saturated 1 M KOH at 100 mV s^{-1} until a reproducible profile in current density vs. potential plot was achieved. In the sequence, a new CV analysis was performed between -1.03 and $-0.83 \text{ V vs Hg/HgO}$ at 10 mV s^{-1} ; the result is presented in Figure S1. The average of potentials in which the curve crosses the value of 0 mA cm^{-2} in both anodic and cathodic directions was considered the theoretical potential of HOR/HER (0 V vs RHE). Based on this analysis, it was stated that for the reference electrode used during the experiments of this work, $-0.940 \text{ V vs Hg/HgO}$ is equivalent to 0 V vs RHE . Therefore, such value was used for all potential conversions towards V vs RHE unit.

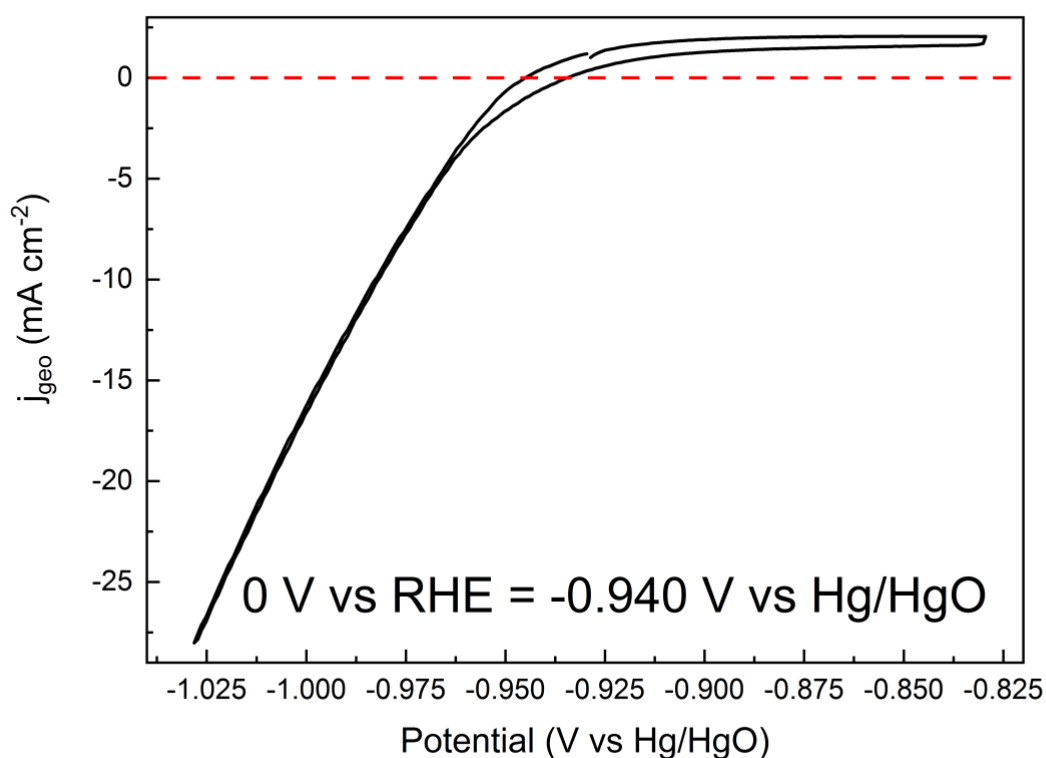


Figure S1 – CV of 40% Pt/C in H_2 -saturated 1 M KOH at 10 mV s^{-1} .

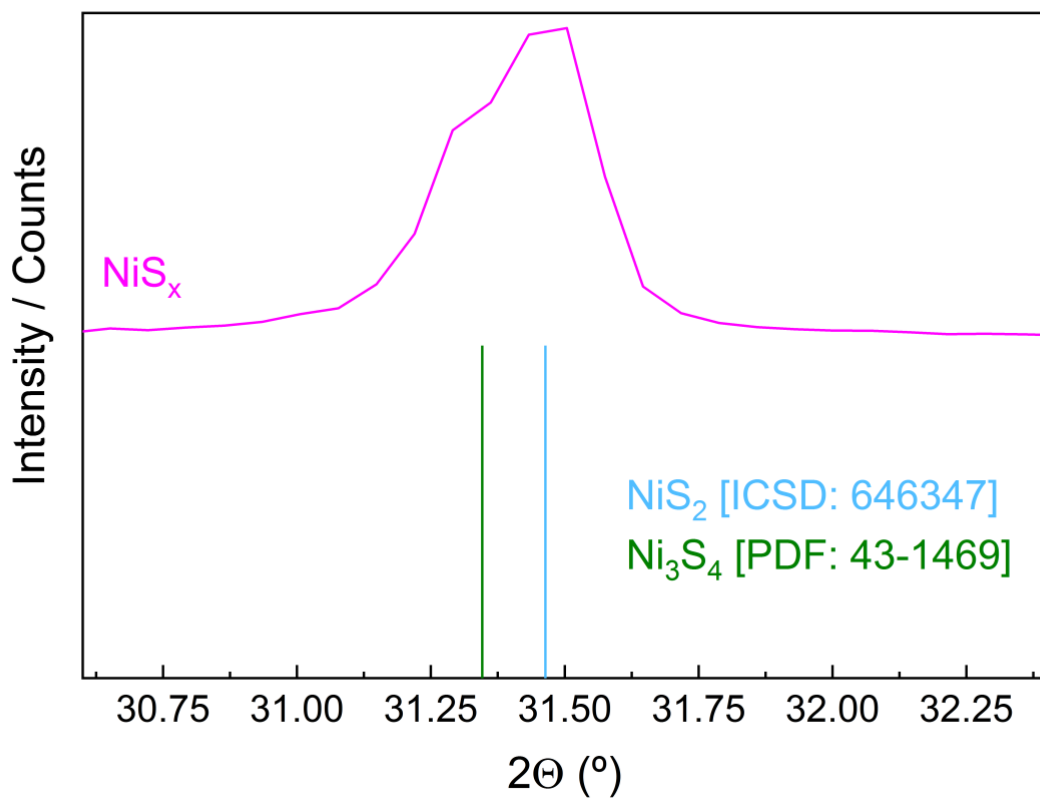


Figure S2 – X-ray diffractogram of NiS_x with a zoom in the region of the most intense peak.

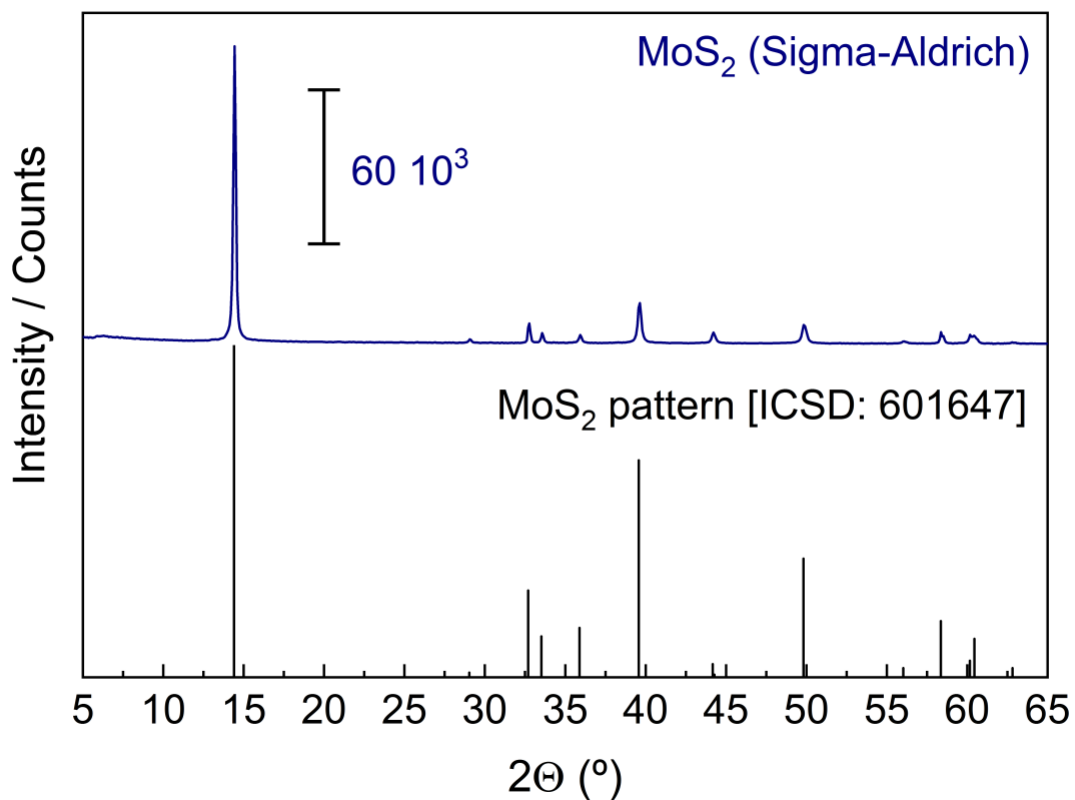


Figure S3 – X-ray diffractogram of a commercial MoS_2 powder supplied by Sigma-Aldrich.

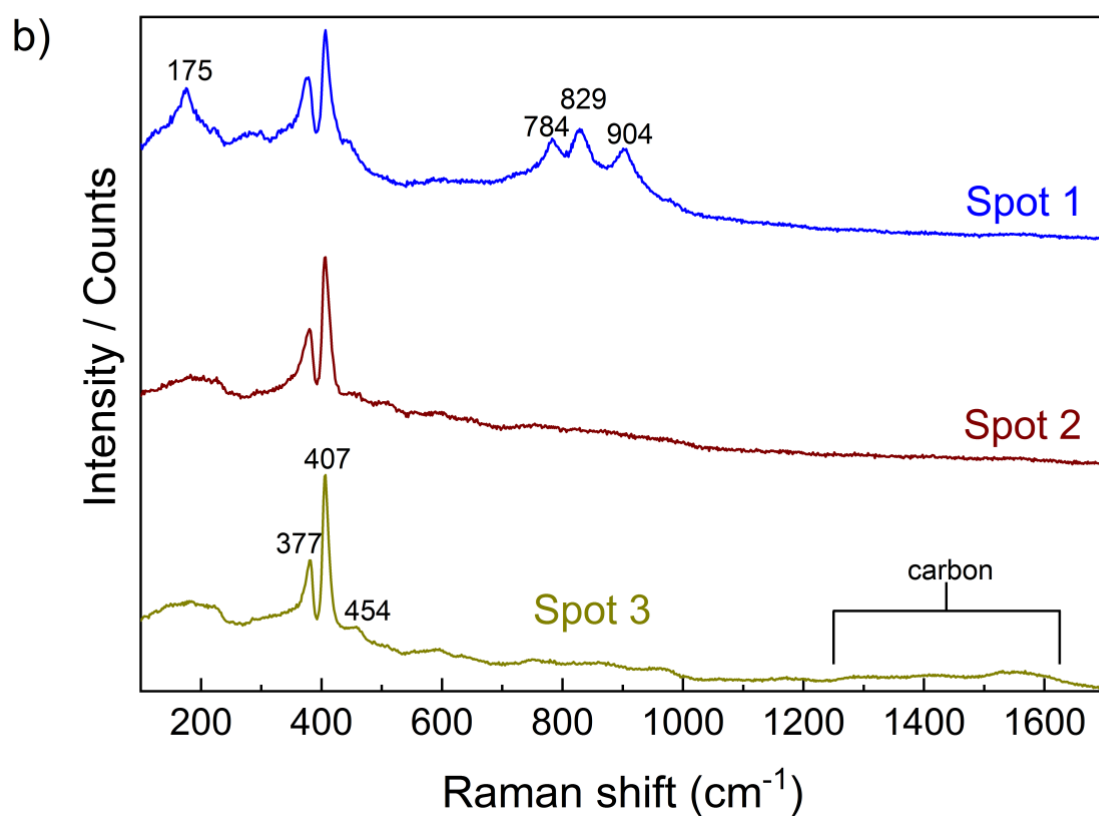
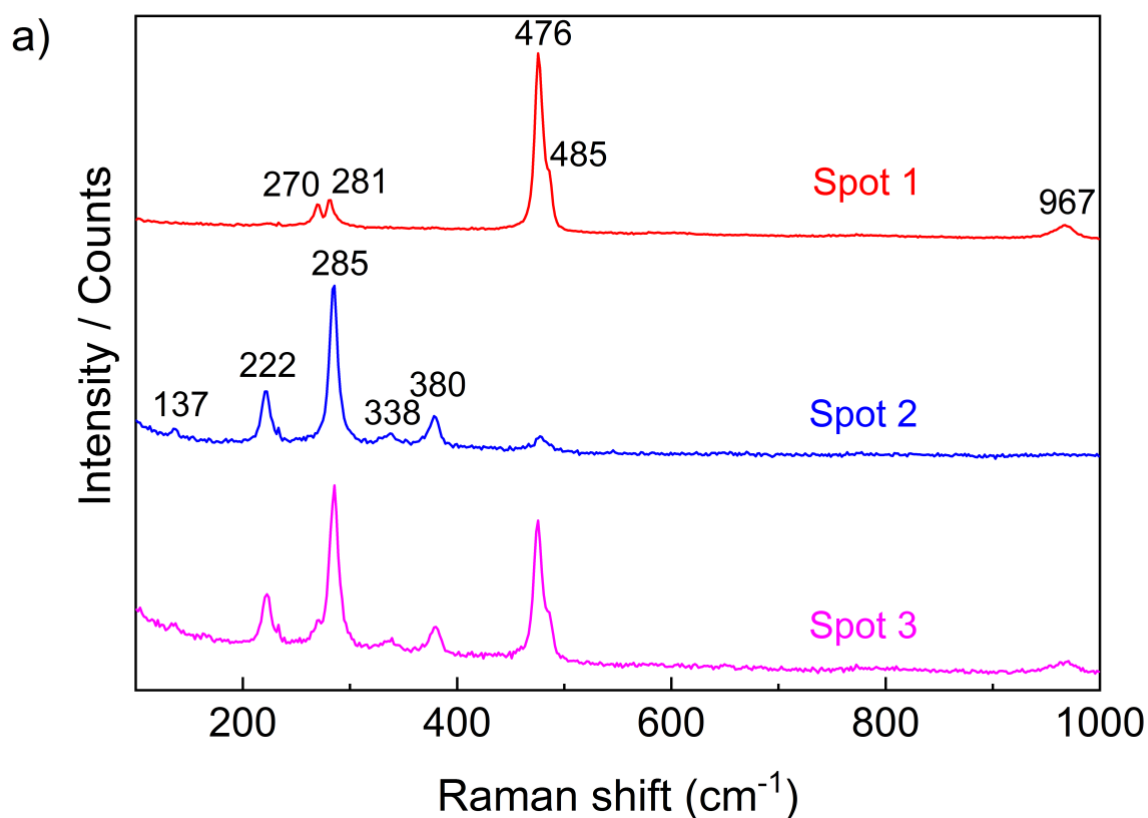
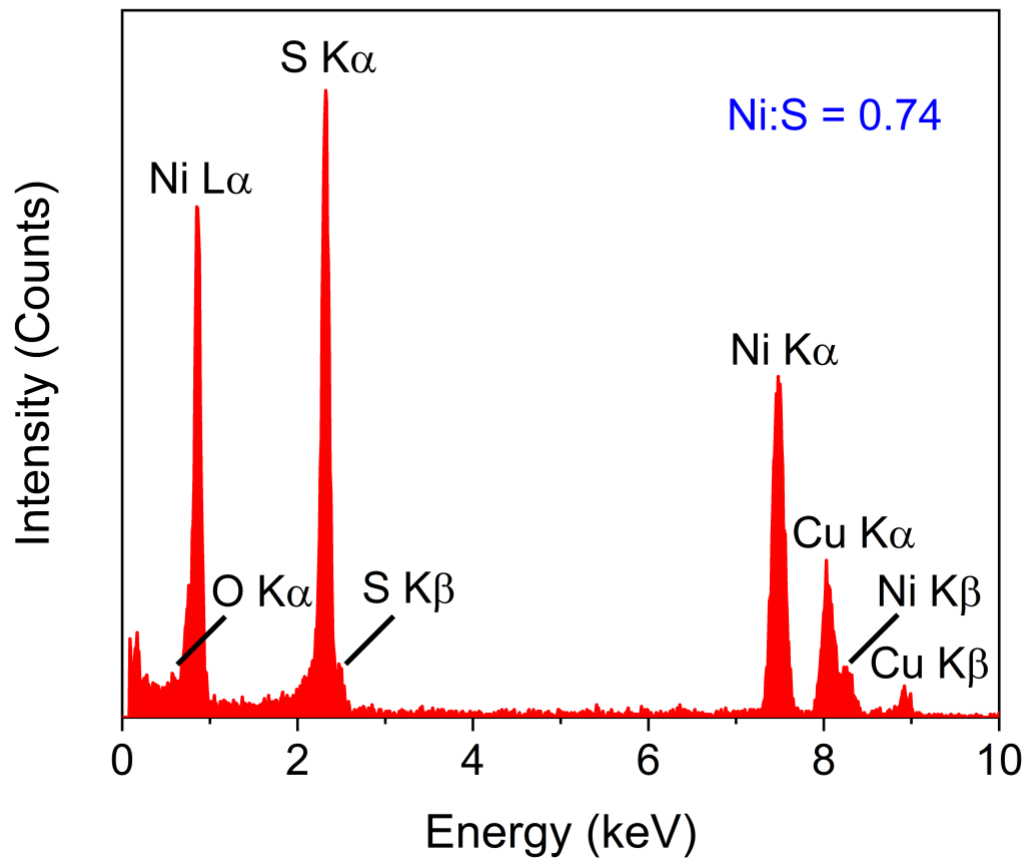


Figure S4 – Profiles obtained from the application of Raman spectroscopy analysis to different spots of (a) NiS_x and (b) MoS_x catalysts.

a)



b)

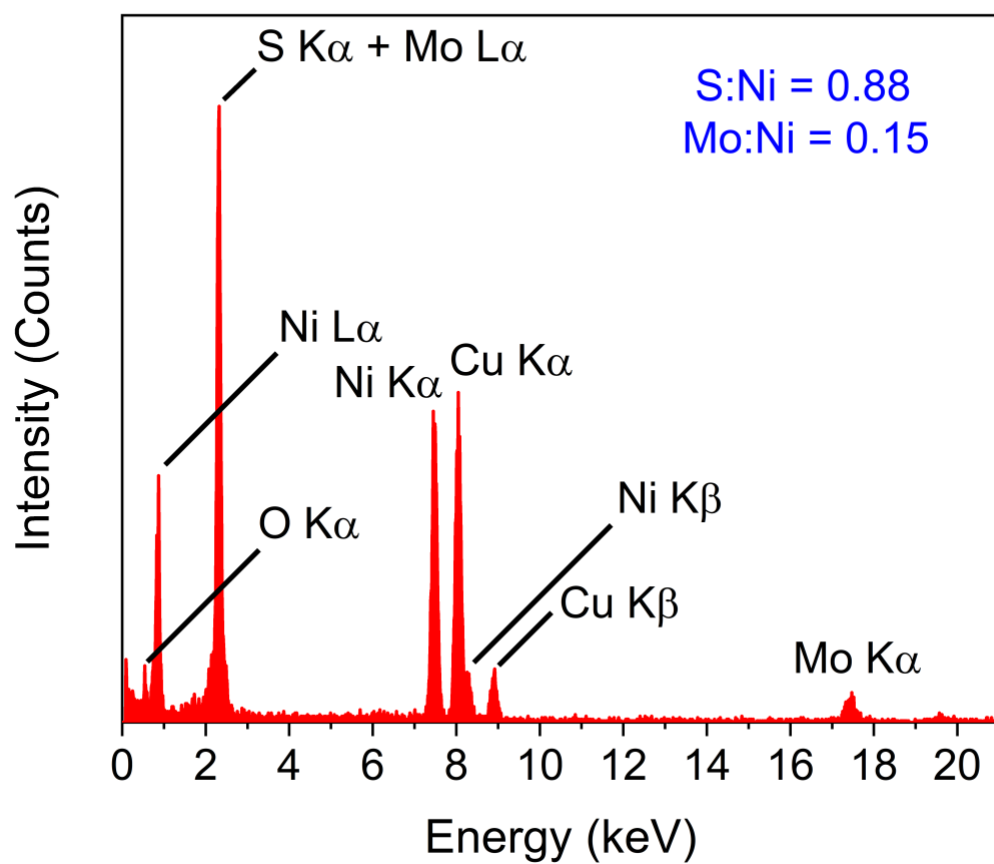


Figure S5 – EDS spectra of (a) NiS_x and (b) crystallized particles present in $Ni_{0.5}Mo_{0.5}S_x$, as illustrated in Figure 2i.

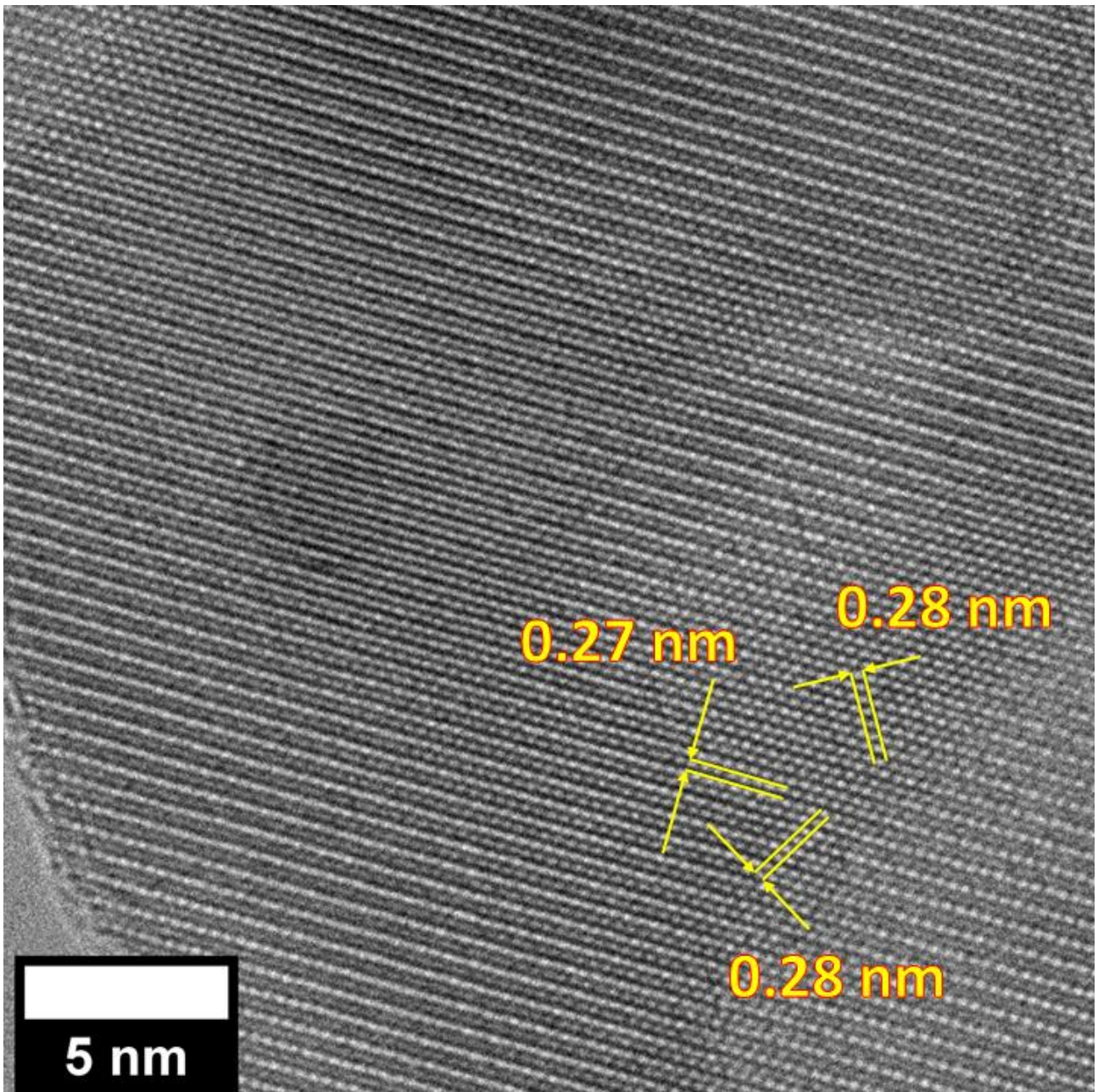


Figure S6 – HRTEM micrograph of NiS_x.

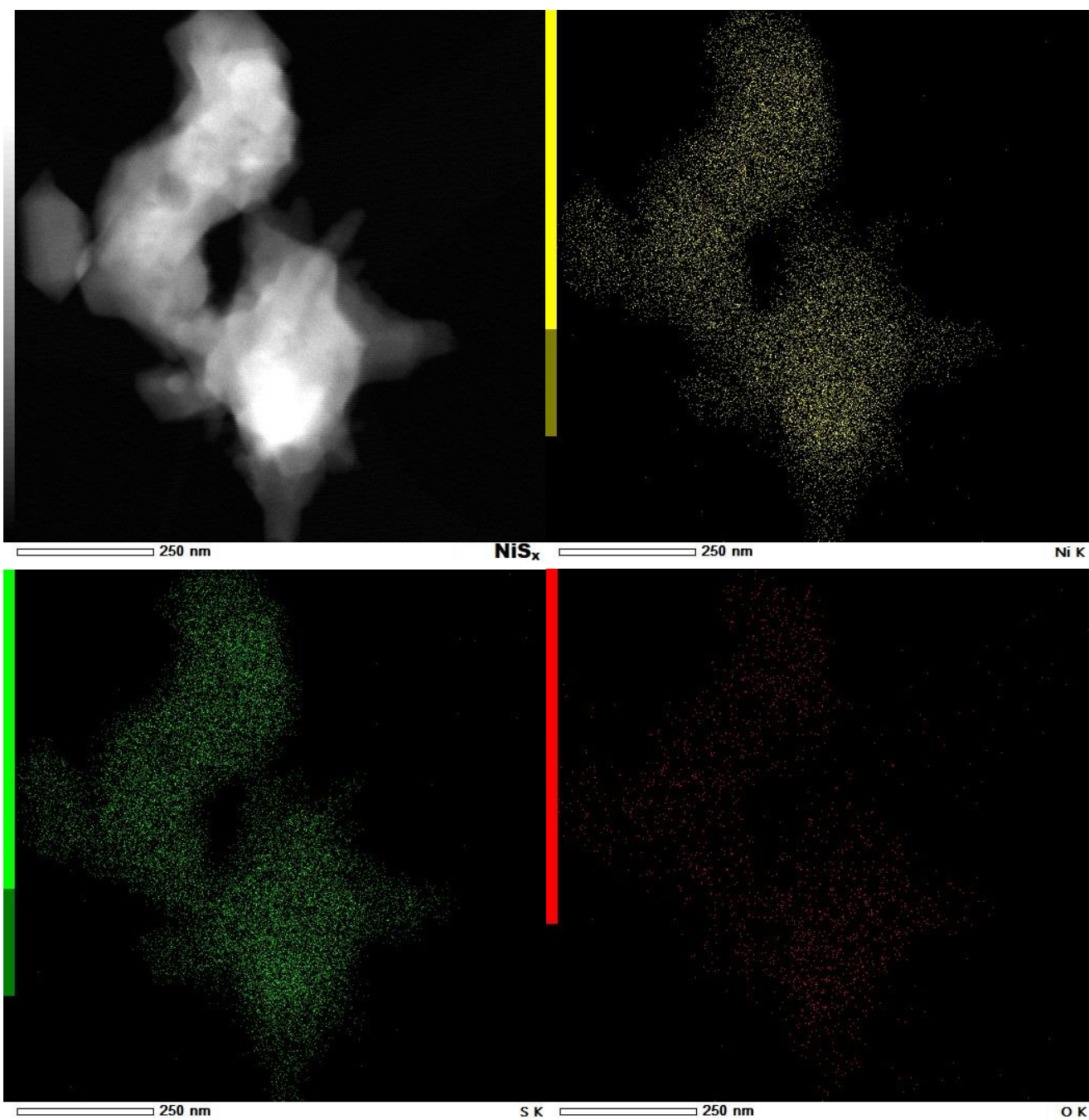


Figure S7 – Elemental mapping of NiS_x . Gray scale image represents the original figure, while the images in yellow, green and red were generated according to the spots where nickel, sulfur and oxygen, respectively, were identified.

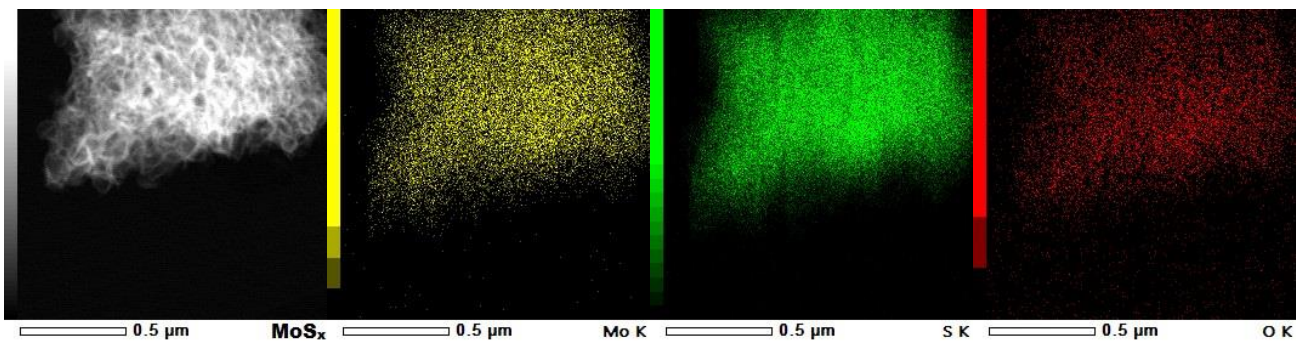
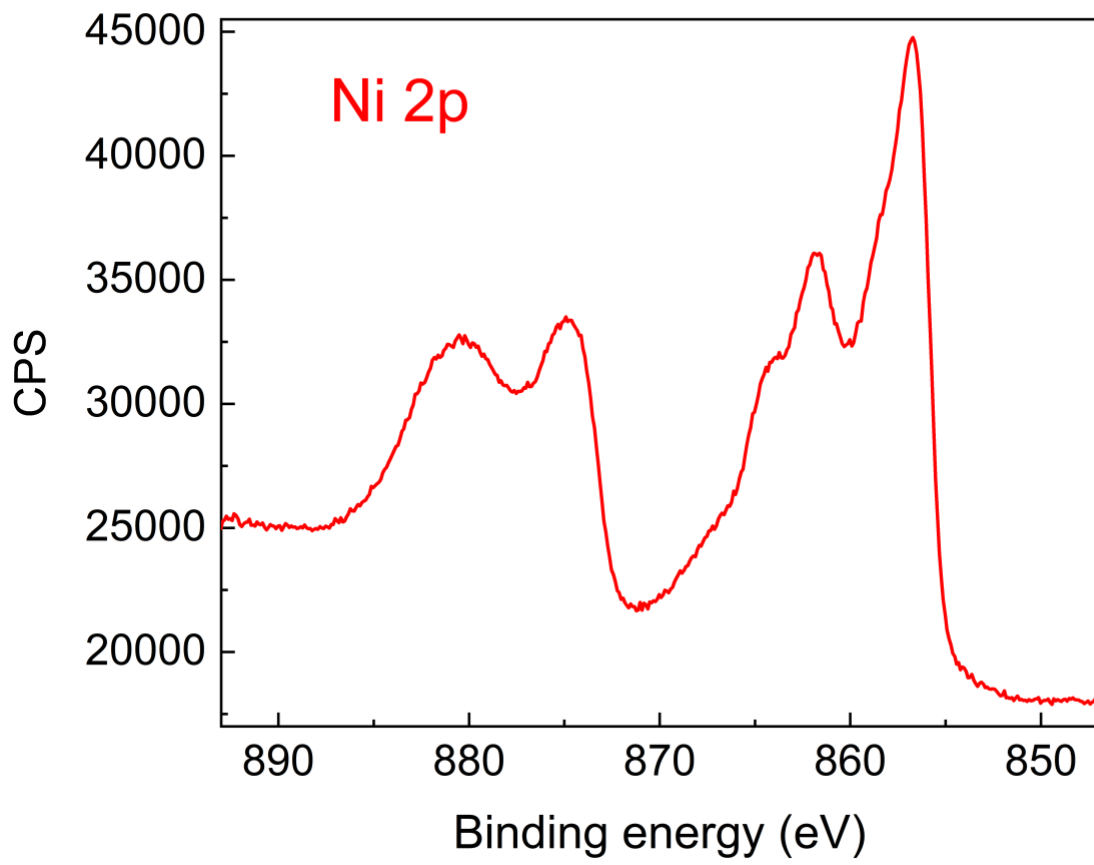


Figure S8 – Elemental mapping of MoS_x. Gray scale image represents the original figure, while the images in yellow, green and red were generated according to the spots where molybdenum, sulfur and oxygen, respectively, were identified.

a)



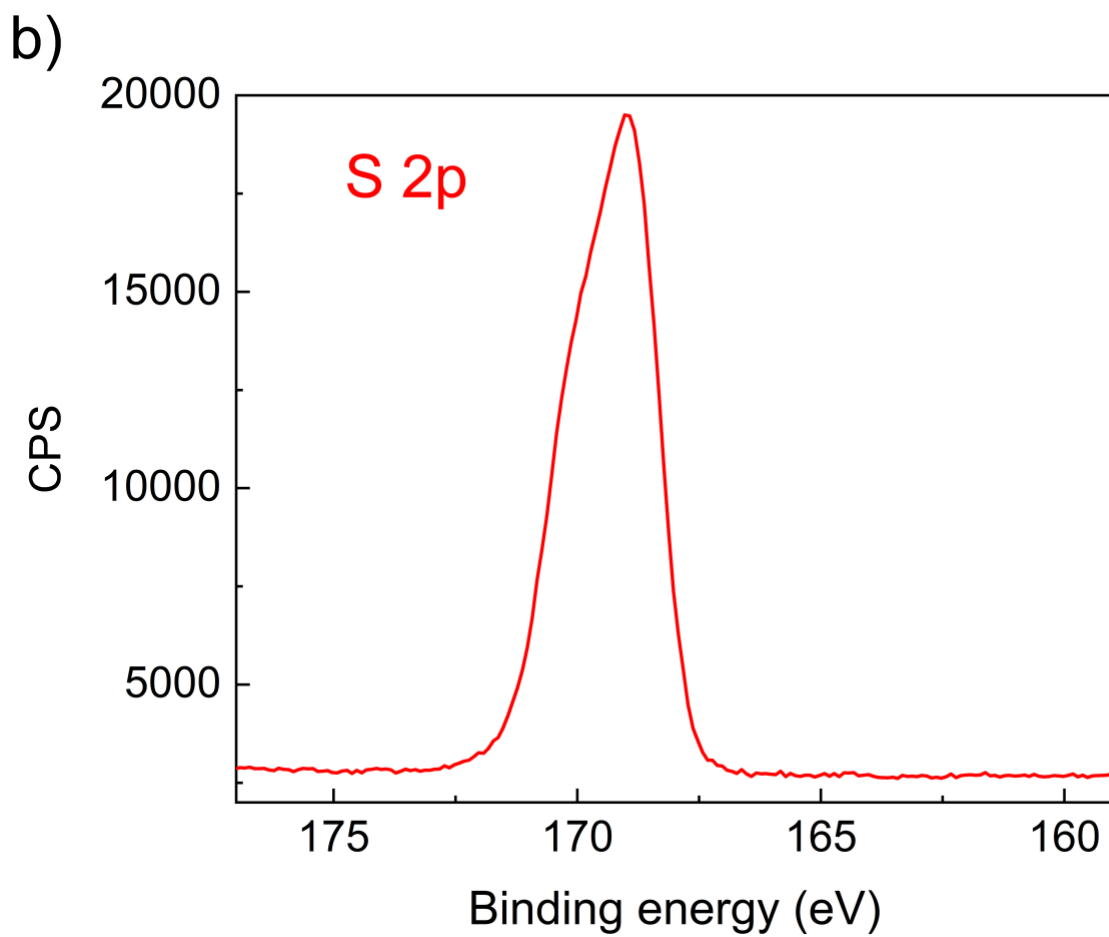


Figure S9 – (a) Ni 2p and (b) S 2p spectra of a commercial nickel sulfate heptahydrate.

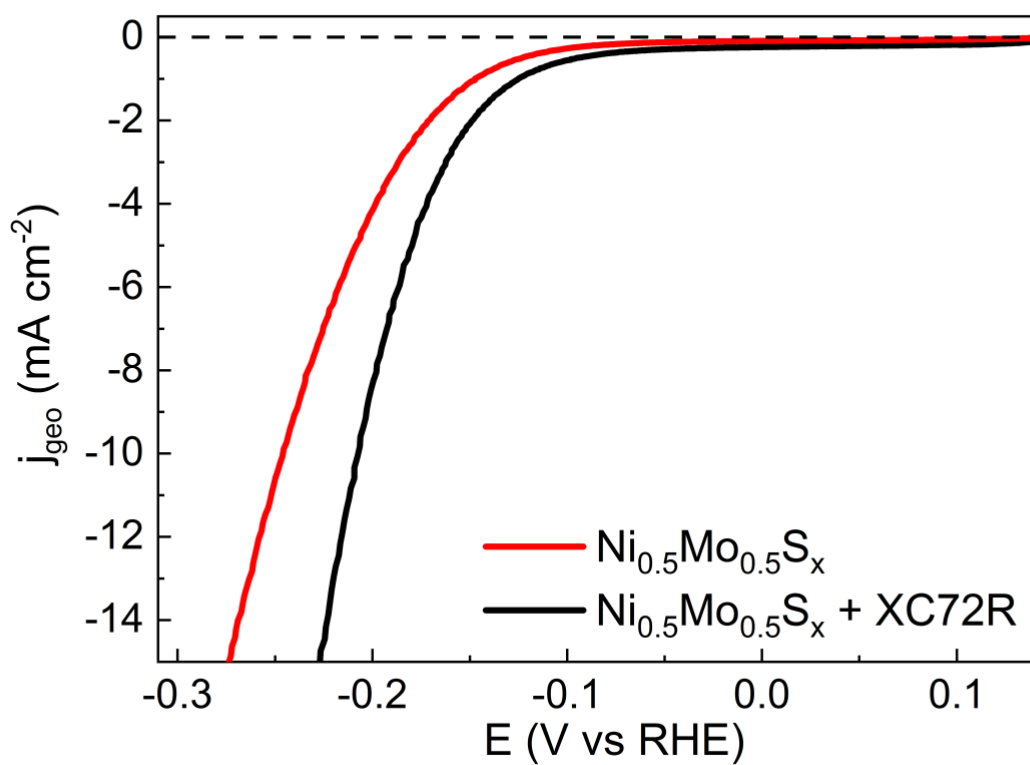


Figure S10 – Ohmic-drop compensated polarization curves obtained from the second scan of LSV technique analysis for $\text{Ni}_{0.5}\text{Mo}_{0.5}\text{S}_x$ and its physical mixture with Carbon Vulcan XC72R.

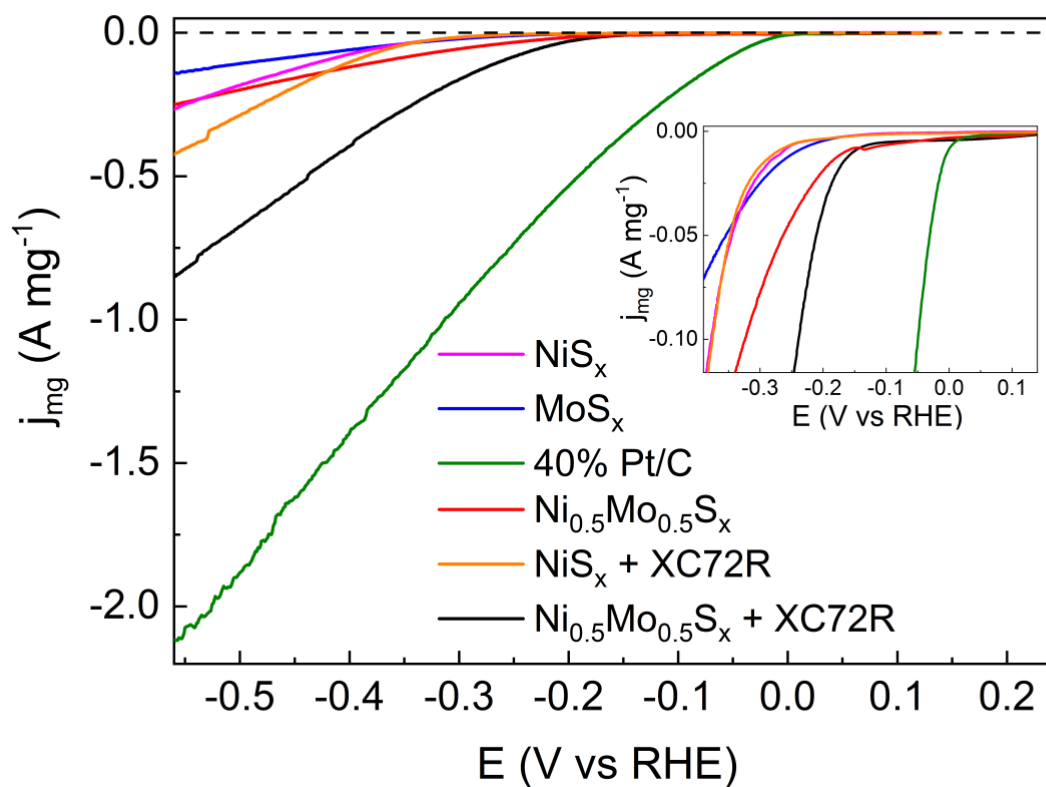
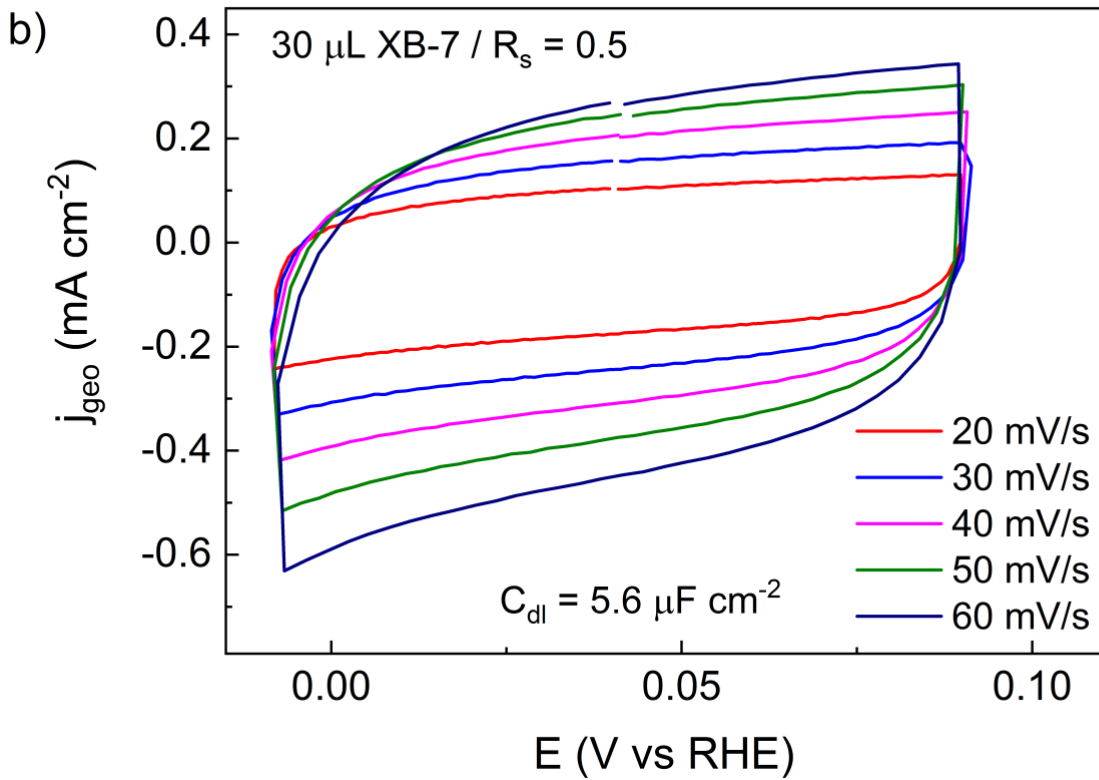
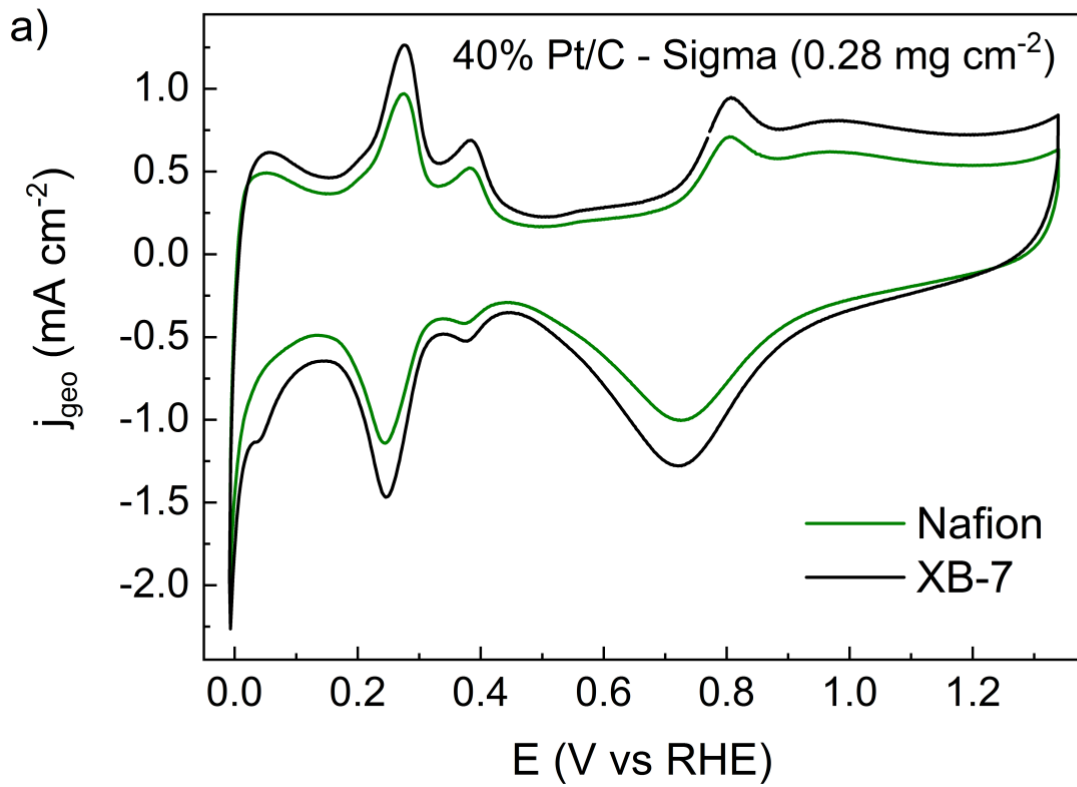


Figure S11 – Uncompensated polarization curves obtained by catalyst mass loading normalization. Inset: iR -drop compensated polarization curves at low current region.



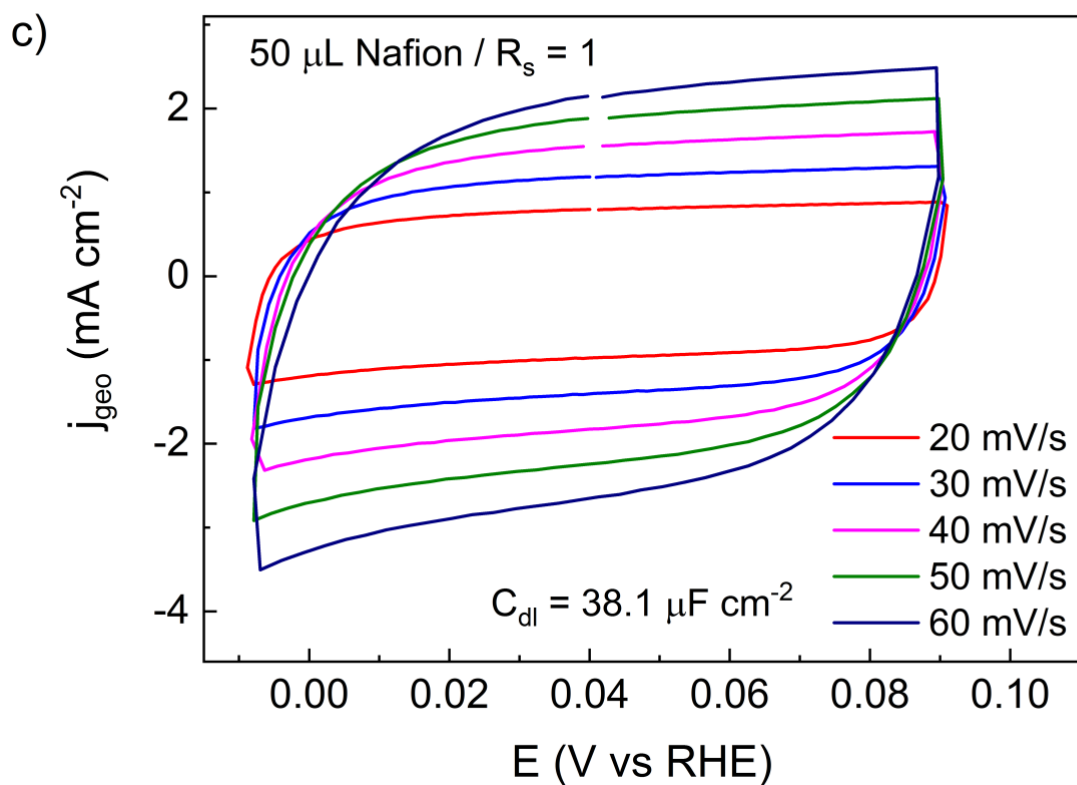


Figure S12 – CV analyses performed in N_2 saturated 1 M KOH for (a) 40% Pt/C in association with Nafion and XB-7 at 20 mV s^{-1} and $\text{Ni}_{0.5}\text{Mo}_{0.5}\text{S}_x$ obtained from inks containing (b) $30 \mu\text{L}$ of XB-7 and $R_s = 0.5$ and (c) $50 \mu\text{L}$ of Nafion and $R_s = 1$ at varying scan rates ($20\text{-}60 \text{ mV s}^{-1}$).