Supplementary Information (ESI)

Mapping the electrocatalytic activity of MoS_2 across its amorphous to crystalline transition

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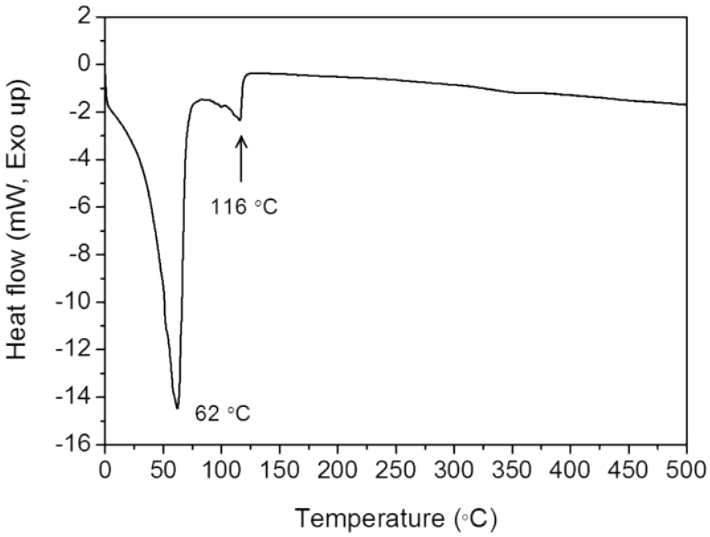

Fig. S1. DSC plot of the precursor solution, $(NH_4)_2MoS_4$ dissolved in anhydrous DMF measured at a scan rate of 5 °C/min. The endothermic peaks related to thermal decomposition are indicated.

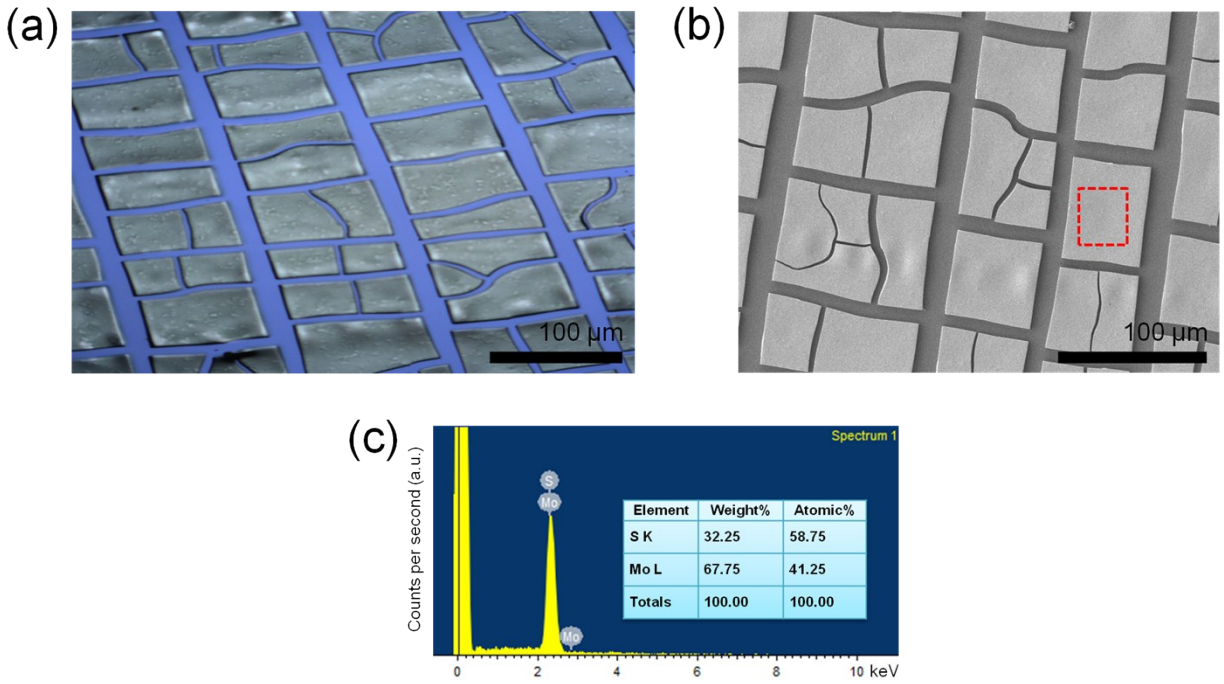

Fig. S2. (a) Optical microscopy and (b) SEM image of amorphous molybdenum sulfide flakes deposited on a Si/SiO_2 wafer after calcination under a flowing Ar ambient at 120°C. (c) Energy dispersive X-ray spectroscopy analysis of the region demarcated by dashed red lines in (b).

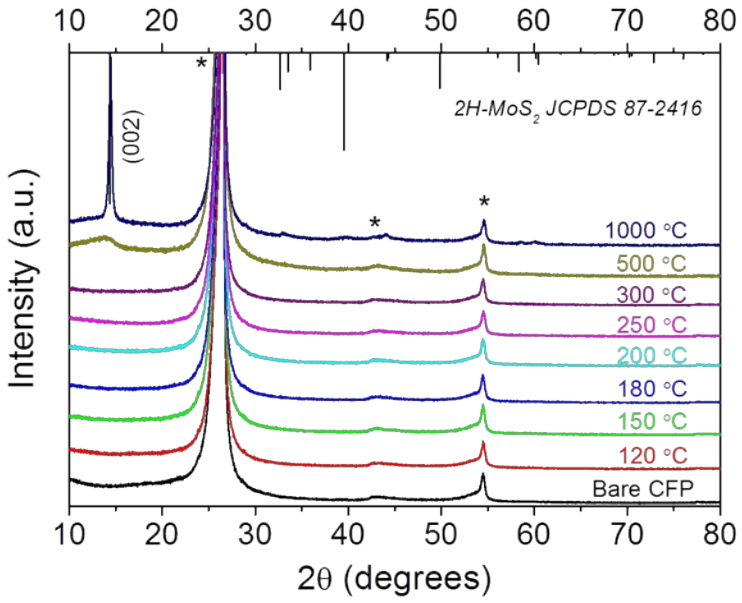

Fig. S3. XRD patterns of the molybdenum sulfides deposited on CFP and annealed under an argon ambient at temperatures from 120 to 1000 °C. The vertical bars indicate the reflections of 2H-MoS_2 (Joint Committee on Powder Diffraction Standards Card# 87-2416). The observed asterisked reflections correspond to that of the graphitized carbon fiber paper.

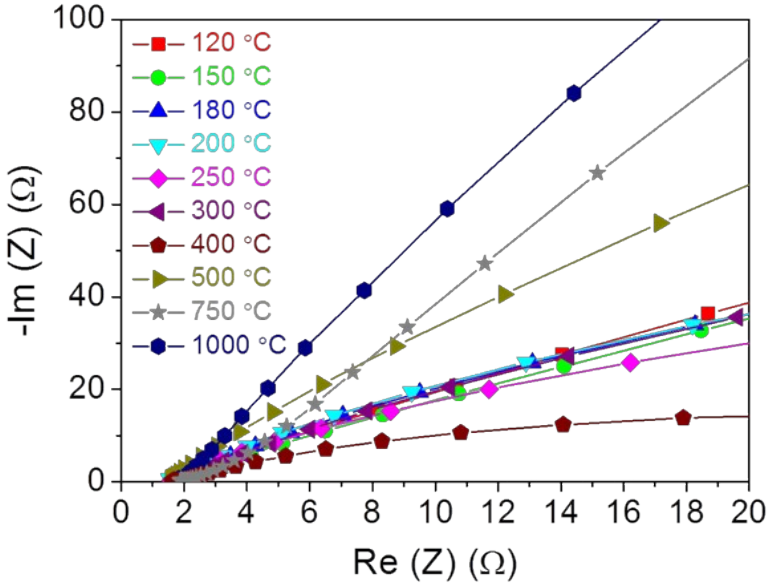

Fig. S4. Nyquist plots of the molybdenum sulfides formed upon annealing in the temperature range from 120—1000°C. The plots have been acquired at an open circuit potential from 200 kHz to 50 mHz using an AC amplitude of 25 mV. The series resistance components (R_s) have been measured to be about 1.6 Ω for all the molybdenum sulfide samples. Using these R_s values, the electrochemical overpotentials (η) measured in this work have been corrected by subtracting the ohmic drop (iR_s) as per: $\eta_{corr} = \eta - iR_s$.

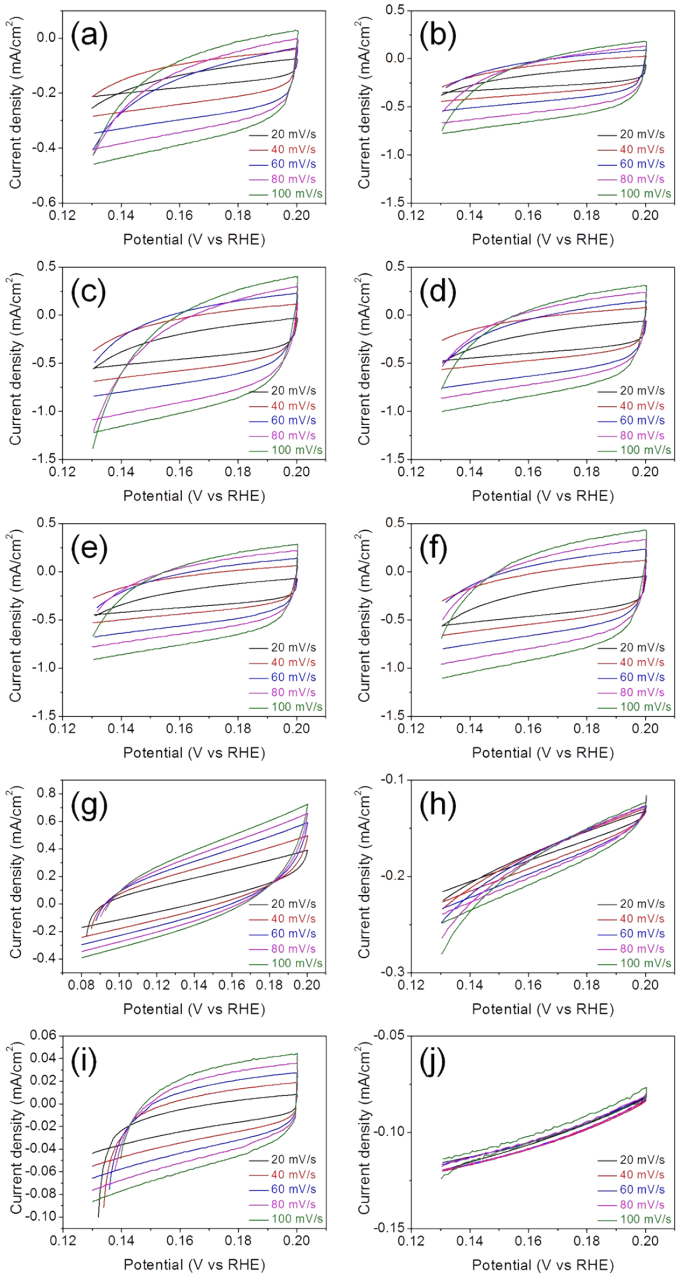

Fig. S5. Cyclic voltammograms acquired in the range between 0.13—0.20 V *vs.* RHE for molybdenum sulfide thin films cast onto CFP and annealed at different temperatures of (a) 120, (b) 150, (c) 180, (d) 200, (e) 250, (f) 300, (g) 400, (h) 500, (i) 750, and (j) 1000°C. The CV data have been acquired at rates of 20—100 mV/s.

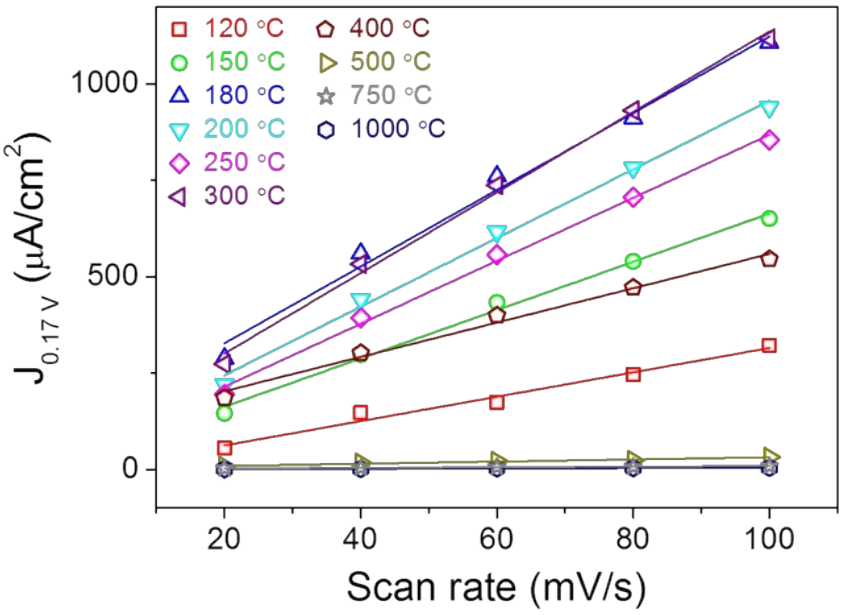

Fig. S6. The differential in current density ($\Delta j = j_a - j_c$) at 0.17 V *versus* RHE (in the non-Faradaic region) plotted as a function of the scan rate for molybdenum sulfide samples annealed at different temperatures. Each plot is fitted to a straight line to determine the C_{dl} values.

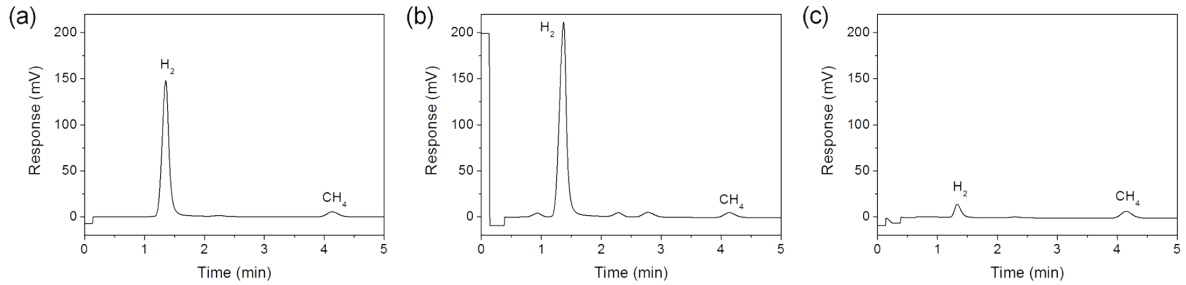

Fig. S7. Gas chromatogram of the generated H_2 with an injection volume of 1 mL CH_4 for samples annealed at (a) 150, (b) 300, and (c) 750°C.

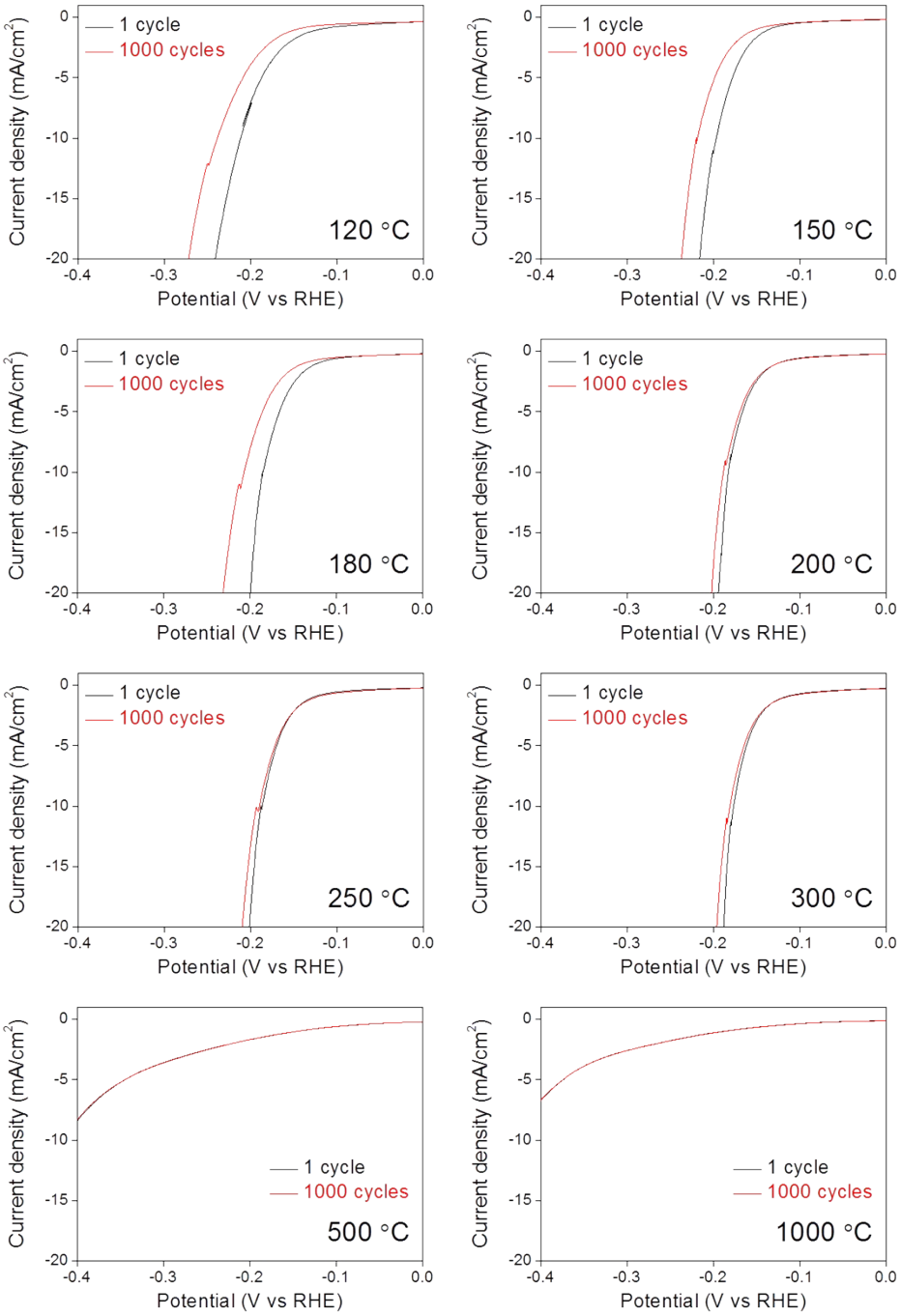

Fig. S8. Polarization curves of the molybdenum sulfides formed on CFP upon annealing at 120—1000°C before and after 1000 CV cycles between -0.2 and 0.2 V *versus* RHE at a scan rate of 100 mV/s.

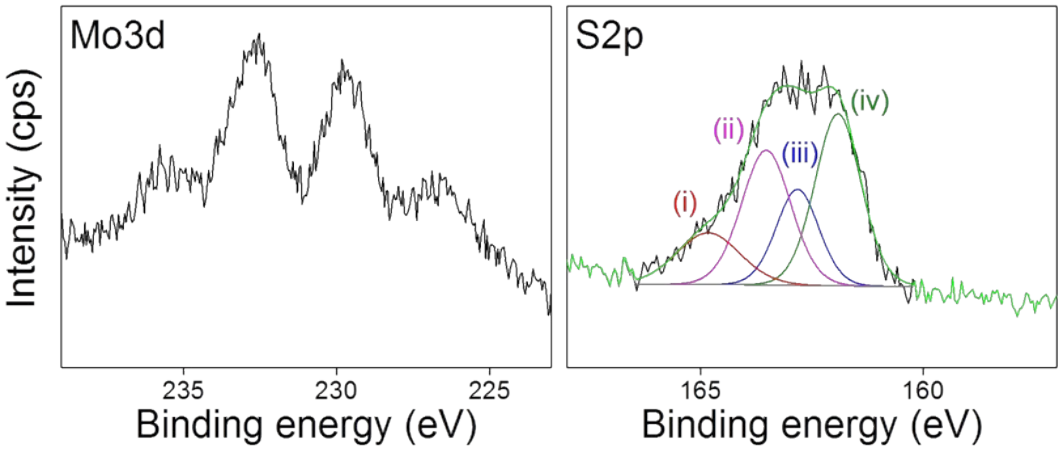

Fig. S9. XPS Mo 3d and S 2p spectra of the molybdenum sulfide prepared at 120°C after 1000 CV cycling. The S 2p spectra are deconvoluted to (i) $2p_{1/2}$ and (ii) $2p_{3/2}$ peaks for apical S^{2-} and/or bridging S_2^{2-} and to (iii) $2p_{1/2}$ and (iv) $2p_{3/2}$ peaks for unsaturated S^{2-} and/or terminal S_2^{2-}.