Supporting Information

Electrocatalytic Hydrogen Evolution from Molybdenum Sulfide–Polymer Composite Films on Carbon Electrodes

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Deposition of a MoS_x film onto a naked carbon electrode and polarization curve for the resulting C|MoS_x film modified electrode in acidic aqueous electrolyte

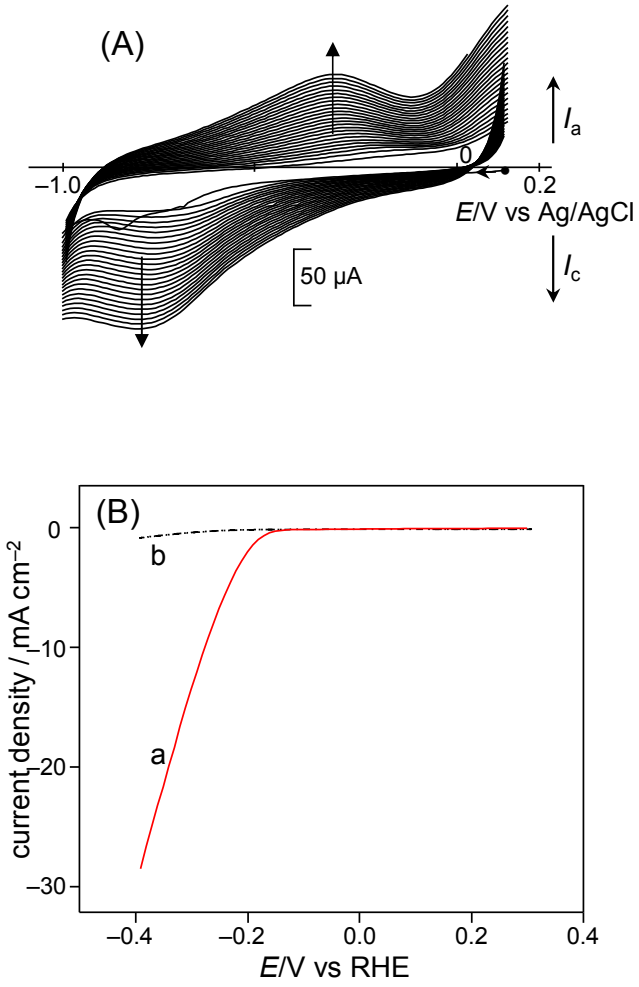

Figure S1. (A) Deposition of a MoS_x film on a glassy carbon disc electrode (3 mm diameter) by repeated cyclic voltammetry scans (25 cycles) in a 10 mM aqueous solution of $(NH_4)_2MoS_4$ containing 0.1 M $NaClO_4$, pH 6.6; scan rate 50 mV s^{-1}.

(B) Curve a: polarization curve recorded with the C|MoS_x film modified electrode prepared in (A), in 0.5 M aqueous H_2SO_4 (pH 0.3); curve b: curve recorded at a naked carbon disc electrode; scan rate 20 mV s^{-1}.

Redox features for MoS_4^{2-} in acetonitrile electrolyte

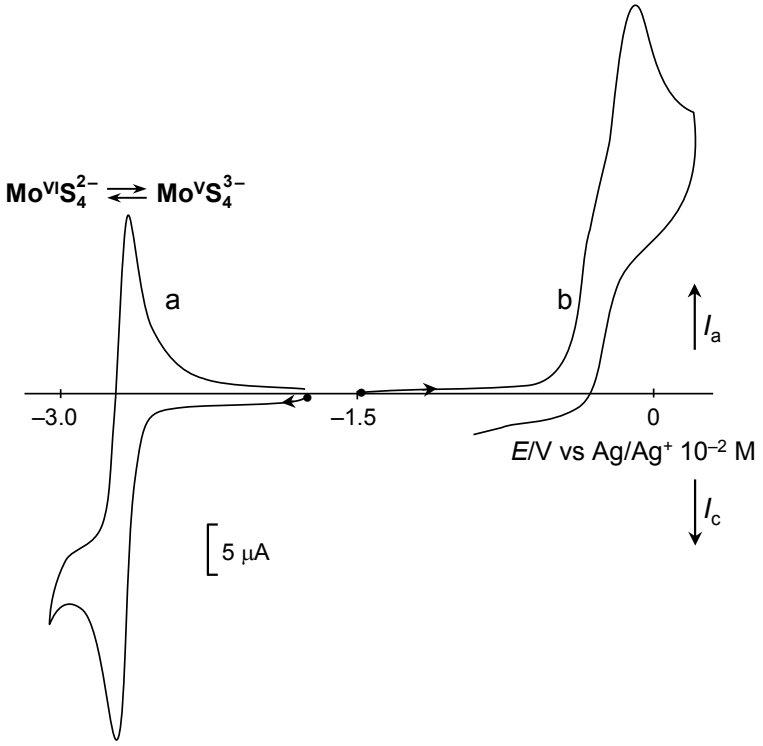

Figure S2. CV curve obtained at a 3 mm diameter carbon disc electrode in CH_3CN containing 2.7 mM $(Et_4N)_2MoS_4$ and 0.1 M TBAP; scan rate 50 mV s^{-1}

Electroreductive deposition of MoS_x into a poly1 film, following the incorporation $MoS_4 2-$ from an aqueous solution, and polarization curve recorded with the resulting C|poly1-MoS_x modified electrode in acidic aqueous electrolyte

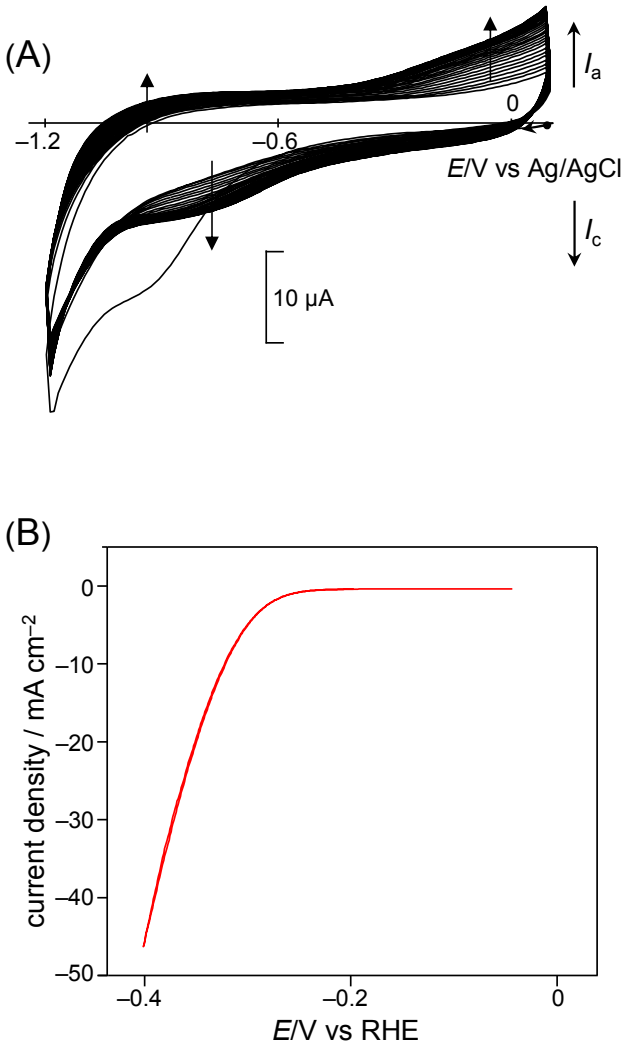

Figure S3. (A) Electroreductive precipitation of MoS_x into a poly(pyrrole-alkylammmonium) film, by repeated cyclic voltammetry scans in a 0.1 M $NaClO_4$ aqueous solution (pH 6) at a C|poly**1** modified electrode (3 mm diameter; $\Gamma_{N+} = 8\times10^{-8}$ mol cm^{-2}) previously soaked for 10 min in a 10 mM aqueous solution of $(NH_4)_2MoS_4$; scan rate 50 mV s^{-1}. (B) Polarization curve recorded in 0.5 M H_2SO_4 (pH 0.3) with the C|poly**1**-MoS_x modified electrode prepared in A; scan rate 20 mV s^{-1}.

Deposition of MoS_x into a poly1 film under various electrochemical conditions, and polarization curves recorded with the resulting C|poly1-MoS_x modified electrodes in acidic aqueous electrolyte

Carbon electrodes modified with poly**1** films have been soaked for 10 min in an $(NH_4)_2MoS_4$ aqueous solution, then were treated under different electrochemical conditions, including potential cycling in the negative potential region, anodic electrolysis at 0.1 V, and cathodic electrolysis at –1.0 V. The catalytic activity towards proton reduction of the C|poly**1**-MoS_x modified electrodes synthesized by these different conditions was then evaluated from the polarization curves recorded in acidic electrolyte (Figure S4).

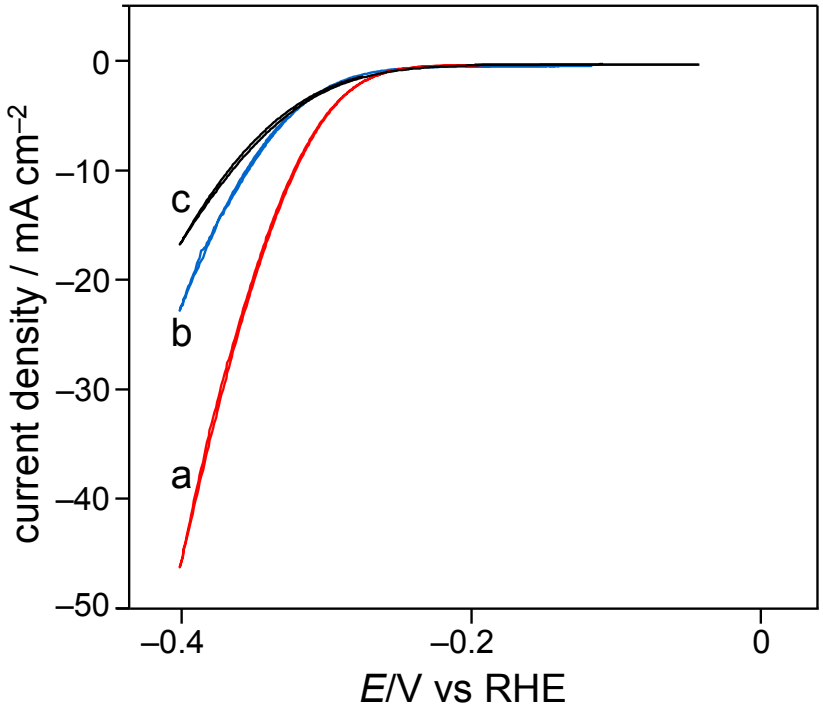

Figure S4. Polarization curves recorded in aqueous H_2SO_4 (pH 0.3) at C|poly**1**-MoS_x modified electrodes prepared under various conditions; scan rate 20 mV s^{-1}; the electrodes (3 mm diameter; Γ_{N+} = 8×10^{-8} mol cm^{-2}) were previously soaked for 10 min in a 10 mM aqueous solution of $(NH_4)_2MoS_4$, then transferred to aqueous 0.1 M $NaClO_4$ (pH 6) and treated under different electrochemical conditions; electrode (a): repeated scans (25 cycles; scan rate 20 mV s^{-1}) over the 0.1 V to –1.2 V potential range; electrode (b): reduction at constant applied potential (–1.0 V) for 10 min; electrode (c): oxidation at applied potential (0.1 V) for 7 min.

Current-time curves for HER at various poly1-MoS_x modified carbon foam electrodes

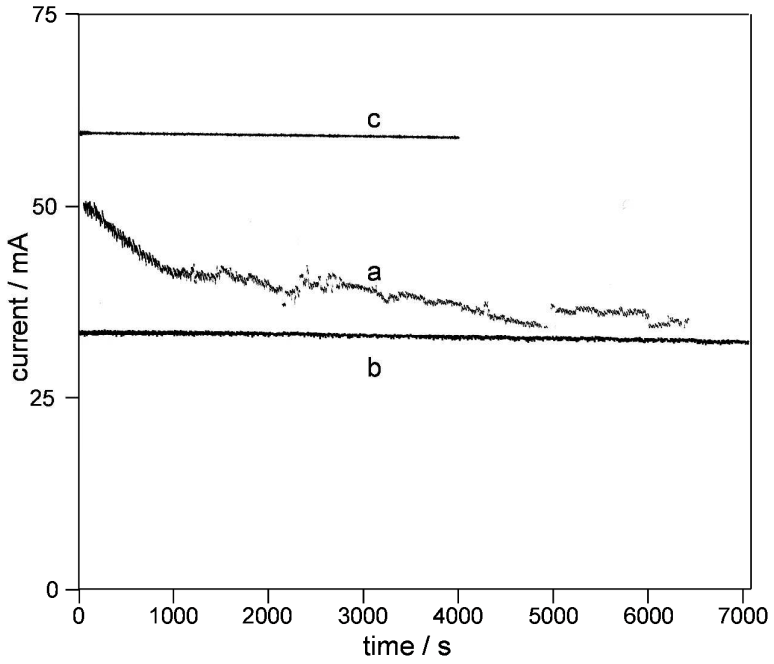

Figure S5. Current-time curves for protons reduction and HER at –0.3 V *vs.* RHE, using poly**1**-MoS_x modified carbon foam (0.8 cm^3) electrodes modified with different poly**1**-MoS_x materials (see Table 2); in every case the charge passed was 250 C. Curve a (corresponding to Entry 2 in Table 2): C|poly**1** electrode soaked in 2 mM $(Et_4N)_2MoS_4$ in CH_3CN, then repetitively cycled in 0.1 M $NaClO_4$, pH 6 (8 μmol of poly**1** + 5.4 μmol of MoS_x). Curve b (corresponding to Entry 3 in Table 2): C|poly**1** electrode soaked in 10 mM aqueous $(NH_4)_2MoS_4$, then repetitively cycled in 0.1 M $NaClO_4$, pH 6 (5.5 μmol of poly**1** + 3.3 μmol of MoS_x). Curve c (corresponding to Entry 4 in Table 2): C|poly**1**-MoS_x electrode prepared in the same conditions as electrode for curve b (9.4 μmol of poly**1** + 5.6 μmol of MoS_x).