Supporting Information

Molybdenum Boride and Carbide Catalyze Hydrogen Evolution in both Acidic and Basic Solutions**

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Chemicals and Reagents

All manipulations were carried out under an inert N_2 atmosphere using standard Schlenk and/or glovebox techniques unless otherwise mentioned. Mo_2C and MoB (-325 mesh, 99.5%) were purchased from Aldrich and stored under nitrogen. Mo_2C should be stored under N_2. Nickel (99.98%) and platinum (99.95%) wires were purchased from Advent Research Materials. A commercial Pt electrode with a diameter of 2 mm was bought from CH Instruments and polished with alumina powder prior to use. Unless noted, all other reagents were purchased from commercial sources and used without further purification.

Physical methods

GC measurement was conducted on a Perkin-Elmer Clarus 400 GC with a TCD detector and a 5 Å molecular sieves packed column with Ar as a carrier gas. SEM secondary electron (SE) images were taken in a Phillips (FEI) XLF-30 FEG scanning electron microscope. Electrochemical measurements were recorded by an EG&G Princeton Applied Research Potentiostat/Galvanostat model 273 or an IviumStat electrochemical analyzer. A three-electrode configuration was used. For polarization and electrolysis measurements, a platinum wire was used as the auxiliary electrode and an Ag/AgCl (KCl saturated) electrode was used as the reference electrode. Potentials were referenced to a reversible hydrogen electrode (RHE) by adding a value of $(0.197 + 0.059pH)$V. Ohmic drop correction was performed using the current interrupt method. Pressure measurements during electrolysis were performed using a SensorTechnics DSDX0500D4R differential pressure transducer. Pressure data was recorded using an A/D Labjack U12 interface with a sampling interval of 1 point per second. ICP-OES analysis was performed with an Optima 2000 spectrometer (Perkin-Elmer). Molybdenum and Boron contents were determined using the intensity of the following emission lines: Mo - 203.845; B - 208.957. Standards TraceCERT were purchased from Aldrich and were used for calibration. For the determination of the catalyst loading, the surface of the carbon paste electrode was dissolved in hot aqua regia prior to measurement. XRD measurements were carried out on an X'Pert Philips diffractometer in Bragg-Brentano geometry with $CuK_{\alpha 1}$ radiation and a fast Si-PIN multi-strip detector (0.1540 nm).

XPS measurements were performed at SuSoS AG (Surface Solutions – Switzerland) using a PhI5000 VersaProbe spectrometer (ULVAC-PHI, INC.) equipped with a 180° spherical capacitor energy analyzer and a multi-channel detection system with 16 channels. Spectra were acquired at a base pressure of 5 x 10-8 Pa using a focused scanning monochromatic Al-Ka source (1486.6 eV) with a spot size of 200 μm. The instrument was run in the FAT analyzer mode with electrons emitted at 45° to the surface normal. Pass energy used for survey scans was 187.85 eV and 46.95 for detail spectra. Charge neutralisation utilizing both a cool cathode electron flood source (1.2 eV) and very low energy Ar+–ions (10 eV) was applied throughout the analysis.

The carbon paste pellets analyzed by XPS were prepared inside of a Glove Box filled with pure nitrogen and activated in galvanostatic mode with a current density of 10 mA/cm^2 for 15 minutes. After activation, the pellets were washed with pure bidistilled water and let dry inside of the Glove Box for 30 minutes. The pellets were transferred to a small desiccator inside the box and transported under nitrogen for analysis. The samples were exposed briefly to air (≈1 minute) during the transfer to the XPS antechamber.

Fabrication of electrodes

(a) Preparation of carbon paste electrode

8 g of powdered synthetic graphite (<20 μm) and 2 g of white paraffin wax were placed in a round-bottom flask. 40 mL of hot toluene was added to the flask. The mixture was sonicated in an ultrasonic bath for 5 minutes. The solvent of the resulting solution was removed under vacuum to yield a conductive graphite powder. The powder was pressed to fill the empty body of a home-made electrode, to give the carbon paste electrode. The homemade electrode consists of a PEEK tube with a back contact made of brass. The back contact can be screwed to allow the removal of the carbon paste pellet for surface analysis. The active area of the electrode is 0.1964 cm^2 (5 mm diameter).

(b) Preparation of MoB and Mo$_2$C-modified electrodes

The surface of the carbon paste electrode was cleaned using a weighing paper. Powdered Mo$_2$C and MoB were pressed against the soft surface of the carbon paste electrode and were spread evenly on the surface using a weighing paper.

(c) Preparation of disk electrodes

0.450 g of powdered Mo_2C and MoB were mixed with 0.050 g of Teflon powder (1μm). The mixture was pressed in a conventional KBr pelletizer under 10 Tons to produce a 13mm diameter pellet. A copper wire contact was glued to one side of the pellet using silver conductive epoxy glue (CircuitWorks CW2400 - Chemtronics). A 5mm hole mask was glued to the other side of the electrode to limit the surface area. With the exception of the active area, the whole body of the electrode was insulated with molten polypropylene.

Pure Molybdenum rod (99.95% / 4mm diameter) was acquired from Advent Research Materials and used to fabricate a 0.1257 cm^2 electrode.

Preparation of the electrolytes:

1M H_2SO_4 was used as electrolyte for measurements at pH = 0. A phosphate buffer (metrohm standard) was used for the experiments at pH = 7. 1M KOH was used as electrolyte for the measurements conducted at pH = 14.

Polarization measurements

Polarization curves were measured in a T-shape cell under nitrogen. The Pt counter electrode was separated from the main compartment by a porous glass frit (porosity 3). The Ag/AgCl reference electrode was kept as close as possible from the working electrode. The scan rate was 1 mV s^{-1}. Ohmic drop was corrected by the potentiostate or manually using the current interrupt method or corrected mathematically as follows:

The overpotential η (V) observed during an experiment is given by equation (1):

$$\eta = a + b\ln j + jR \text{ (1)}$$

where a (V) is the Tafel constant, b (V dec^{-1}) is the Tafel slope, j (A cm^{-2}) is the current density and R (Ω cm^2) is the total area-specific uncompensated resistance of the system, which is assumed to be constant. The derivative of Eq. (1) with respect to current density gives Eq. (2) from which b and R can be easily obtained by plotting $d\eta/dj$ as a function of $1/j$.

$$d\eta/dj = b/j + R \text{ (2)}$$

The estimation of *R* allows correcting the experimental overpotential by subtracting the ohmic drop *jR* according to equation (3):

$$\eta_{corr} = \eta - jR \quad (3)$$

During the calculations, the derivative $d\eta/dj$ was replaced by their finite elements $\Delta\eta/\Delta j$ estimated from each pair of consecutive experimental points.

The overpotential was calculated as the difference of the operating potential and the thermodynamic potential (RHE = -0.059 x pH V vs. NHE). Ag/AgCl = 0.197 V vs. NHE. The current-potential curves for Pt were corrected against the real surface area of Pt electrode, determined by the hydrogen adsorption peaks between -100 and -150 mV *vs* Ag/AgCl (J. M. D. Rodríguez, J. A. H. Melían, J. P. Peña, *J. Chem. Ed.* **2000**, 77, 1195-1197.)

Galvanostatic Electrolysis

Electrolysis experiments were performed in an H shape cell. A total liquid volume of 30 mL was used to fill the cell. The headspace is 8.2 mL. The platinum counter electrode was separated from the solution through a porous glass frit (porosity 3) and this whole assembly inserted into one side of the H cell. The modified working electrode was inserted in the other side of the cell, together with a magnetic stirring bar and a Luggin capillary. Solution resistance was not corrected.

Two small inlets were present in the cell allowing the connection to the pressure monitoring device and the other kept closed by a septum for sampling of the gas phase. The whole cell apparatus is gas-tight and the pressure increase is proportional to the gases generated ($H_2 + O_2$). Prior to each experiment, the assembled cell was calibrated by injecting known amounts of air into the closed system and recording the pressure change. After the calibration, the cell was purged with nitrogen for 20 minutes and the measurements were performed. Control experiments were performed using platinum as a working electrode and a quantitative Faradaic yield was obtained by measuring the pressure (97-102 %) and confirmed by GC analysis of the gas in the headspace (92-96 %) at the end of the electrolysis.

The Faradaic yield was calculated as follow:

The total amount of charge (Q) passed through the cell was obtained from the current-potential curve. The total amount of hydrogen produced (x) was measured using the pressure sensor. Assuming 2 electrons are needed to make one H2 from two protons.
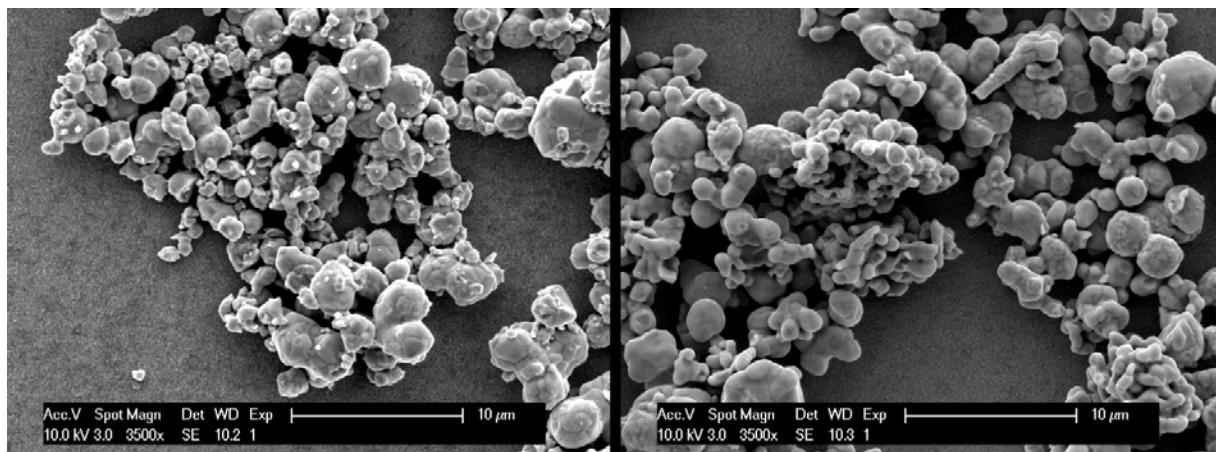
Faradaic yield for $H_2 = Q/2xF$

Potentiostatic Electrolysis

The setup was similar to that of Galvanostatic electrolysis except that the electrolysis was conducted at a fixed potential.
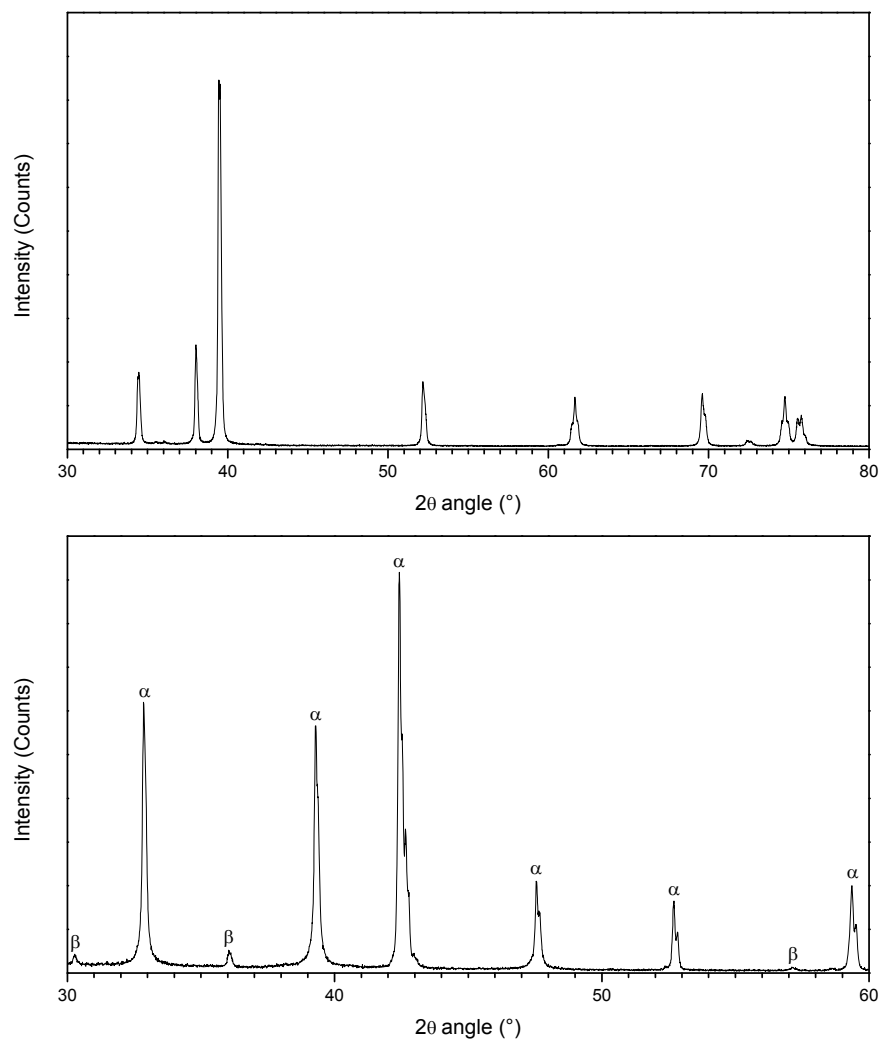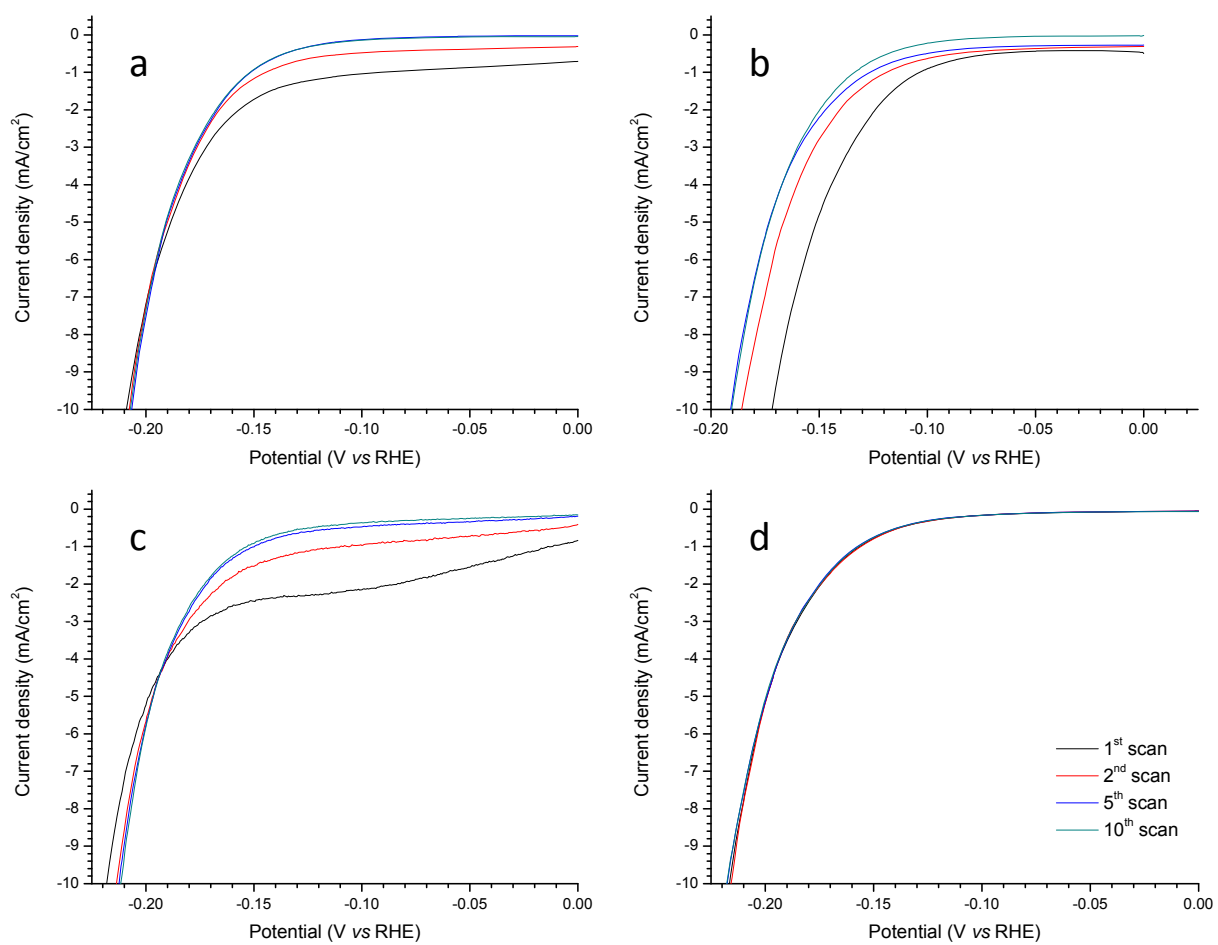
Figure S1. XRD patterns of Mo$_2$C (top) and MoB (bottom). For MoB, the assignments of the alpha (α) and beta (β) phases are shown.

Figure S2. SEM images for Mo_2C (left) and MoB (right) particles.

Figure S3. Consecutive polarization curves for Mo₂C at pH = 0 (**a**) and pH = 14 (**b**) and MoB at pH = 0 (**c**) and pH = 14 (**d**). A pre-activation process is evident in (**a**)-(**c**).
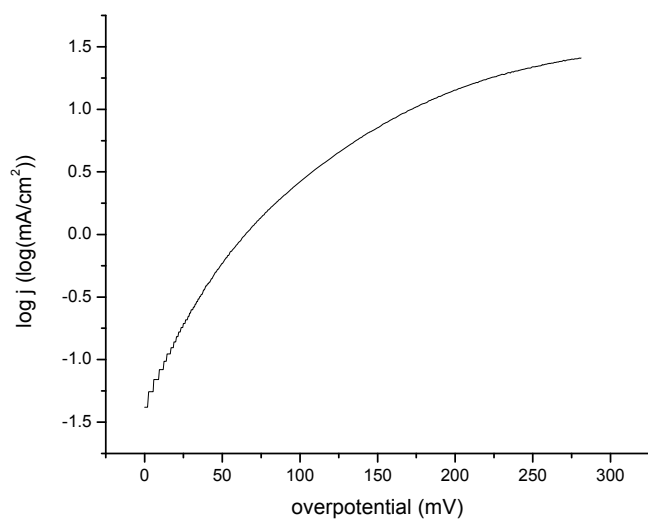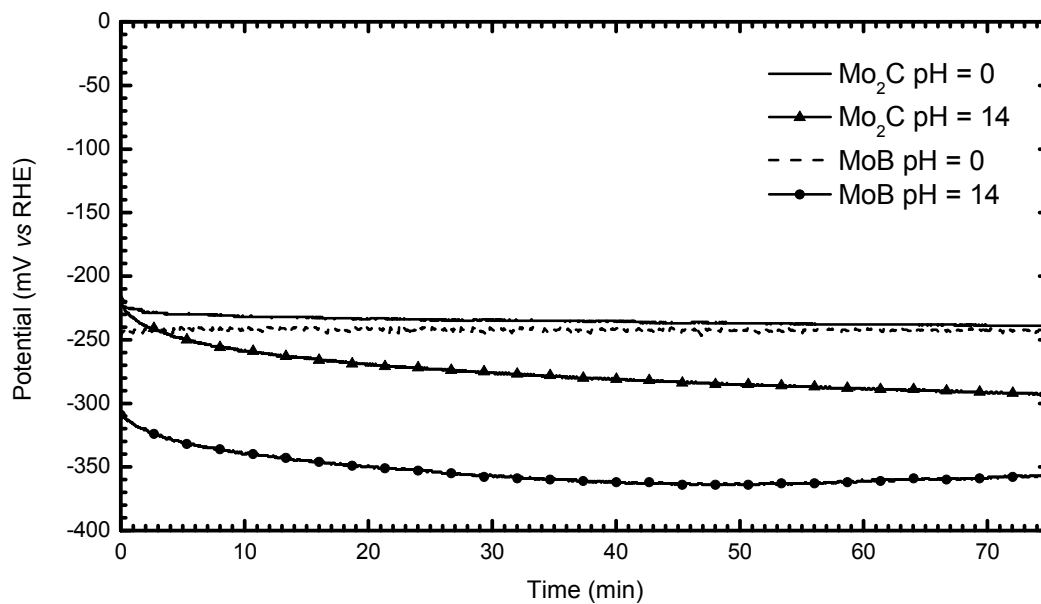
Figure S4. Tafel plot for Pt at pH = 14, Scan rate 1mV/s. Ir-drop was corrected. It appears that at overpotential > 100 mV, the current is mass-transport-controlled.
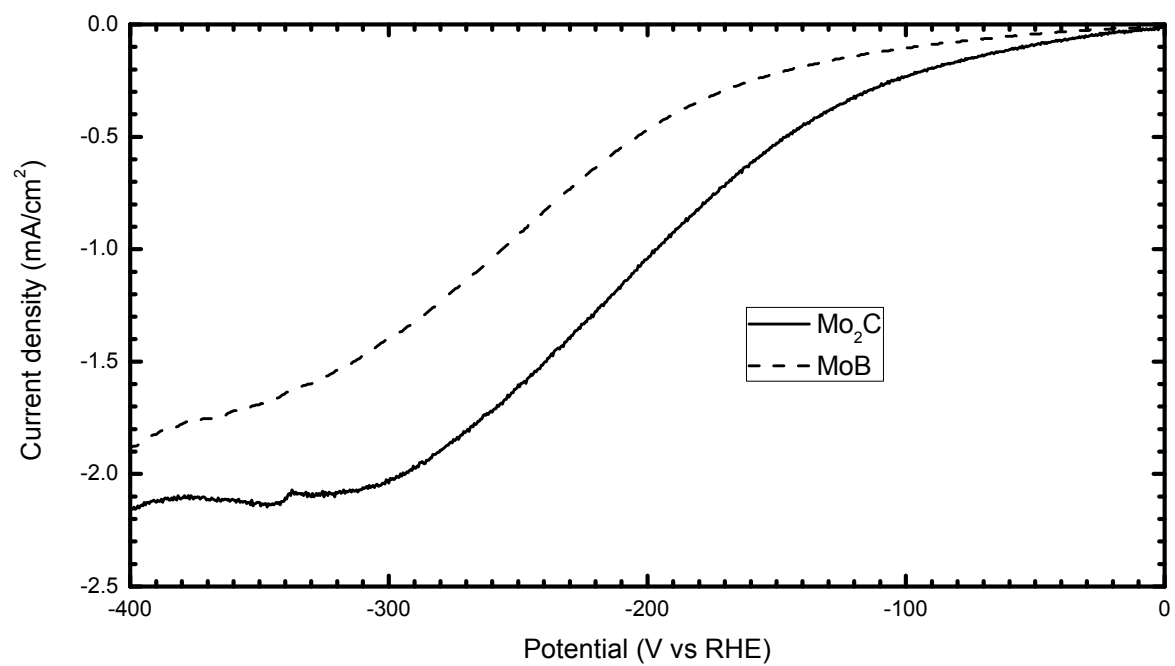
Figure S5. Polarization curves (10th) of MoB and Mo$_2$C at pH = 7 (phosphate buffer). Scan rate: 5 mV/s.
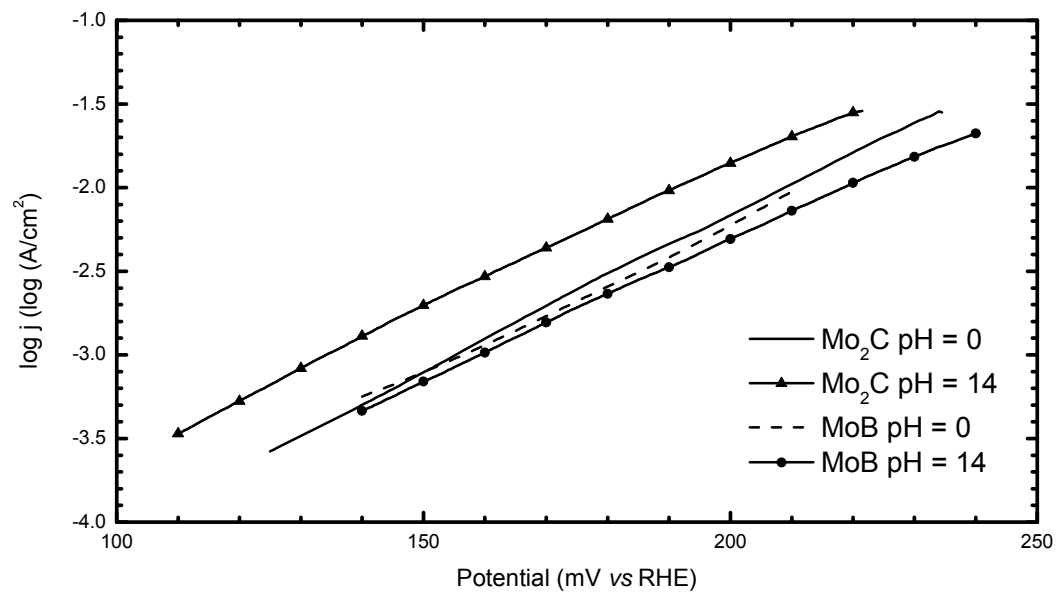
Figure S6. Tafel plots of the polarization curves of MoB and Mo₂C at pH = 0 and 14.

Figure S7. The time dependence of potential under Galvanostatic electrolysis at J = 20.4 mA/cm^2 for MoB and Mo$_2$C catalysts. The loadings are: 2 mg/cm^2 (MoB, pH = 0); 3.3 mg/cm^2 (Mo$_2$C, pH = 0); 0.9 mg/cm^2 (MoB, pH = 14); 1.1 mg/cm^2 (Mo$_2$C, pH = 14). For simplicity, solution resistance was not corrected. To reach the same current density, a larger overpotential is required in Galvanostatic electrolysis than in polarization measurements. This is mainly due to substantial Ohmic resistance drop in the former experiment where the resistance is not corrected. The resistance is about 1.7 Ohm at pH = 0, and 4 Ohm at pH = 14.
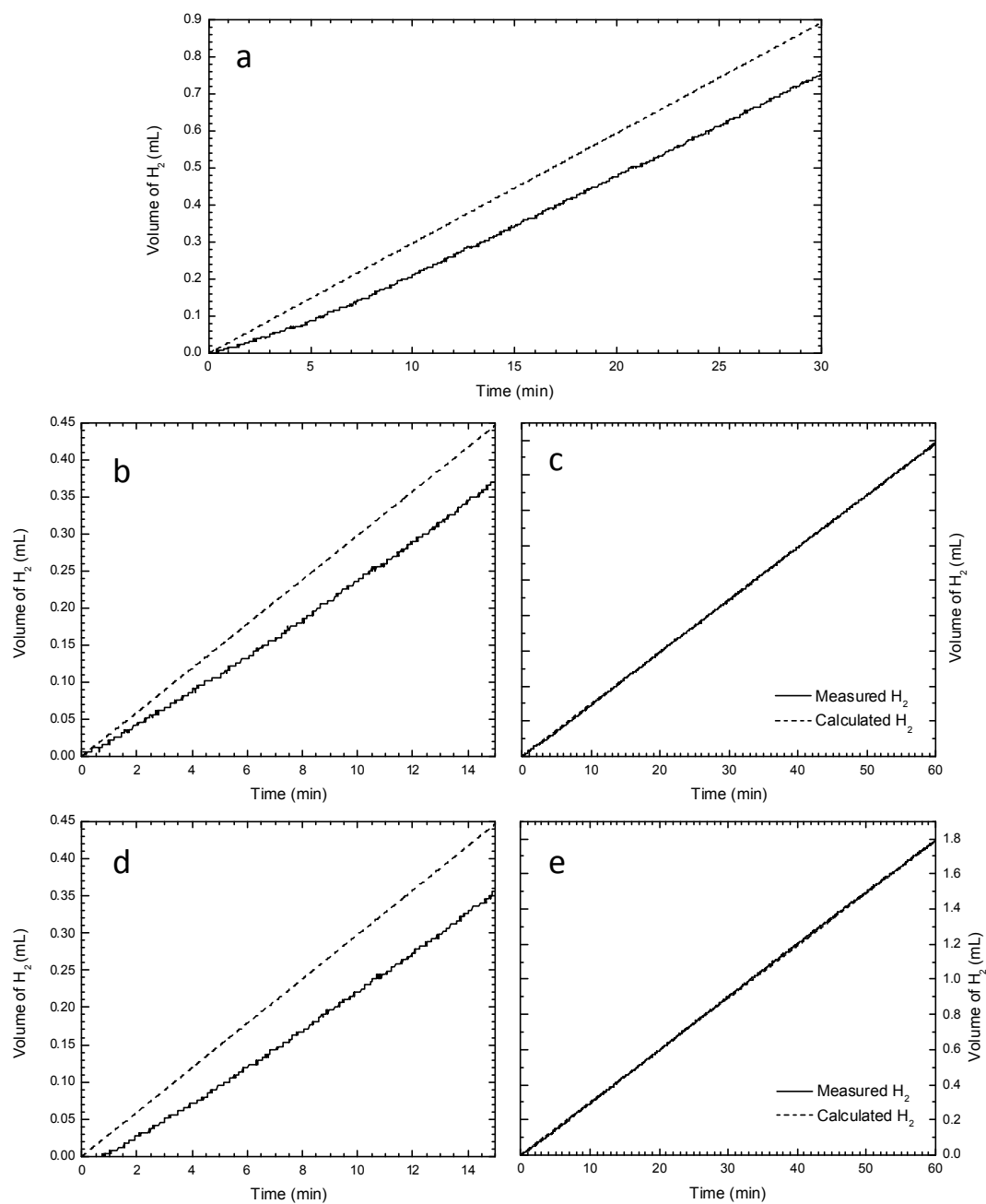
Figure S8. Hydrogen production efficiency for HER under Galvanostatic electrolysis. The calculated H_2 lines represent the expected amount of H_2 assuming a quantitative Faradaic yield. The measured H_2 lines represent the experimentally detected H_2. Faradaic yields for Mo_2C during the activation time (**a**) at pH = 14; Mo_2C at pH = 0 during activation (**b**) and after activation (**c**); MoB at pH = 0 during activation (**d**) and after activation (**e**).
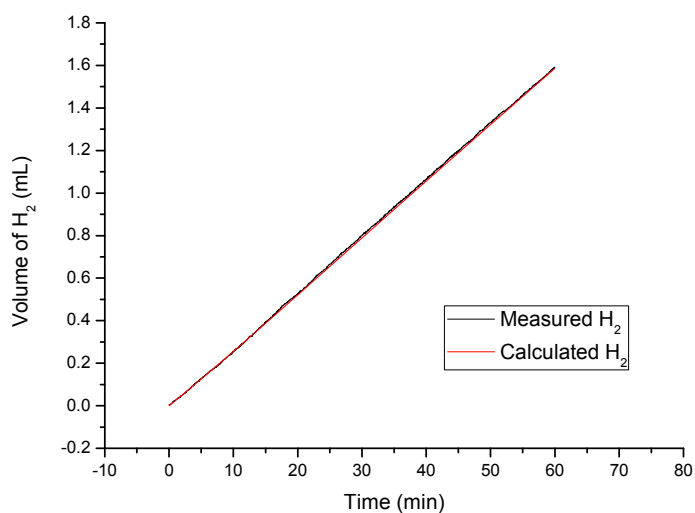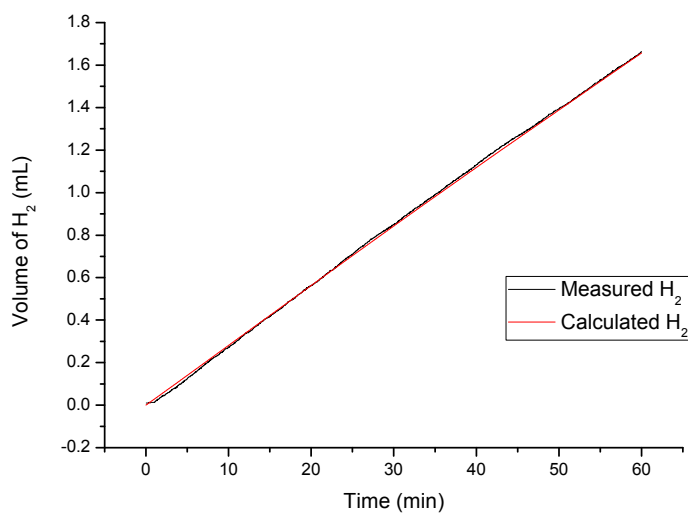
Figure S9. Hydrogen production efficiency for HER under potentiostatic electrolysis. The calculated H_2 lines represent the expected amount of H_2 assuming a quantitative Faradaic yield. The measured H_2 lines represent the experimentally detected H_2. (Top) Faradaic yields for Mo_2C at pH = 0 and η = 250 mV after activation. (Bottom) Faradaic yields for MoB at pH = 0 and η = 250 mV after activation. The activation process was a Galvanostatic electrolysis at 20 mA/cm^2 (reduction) for 15 minutes.
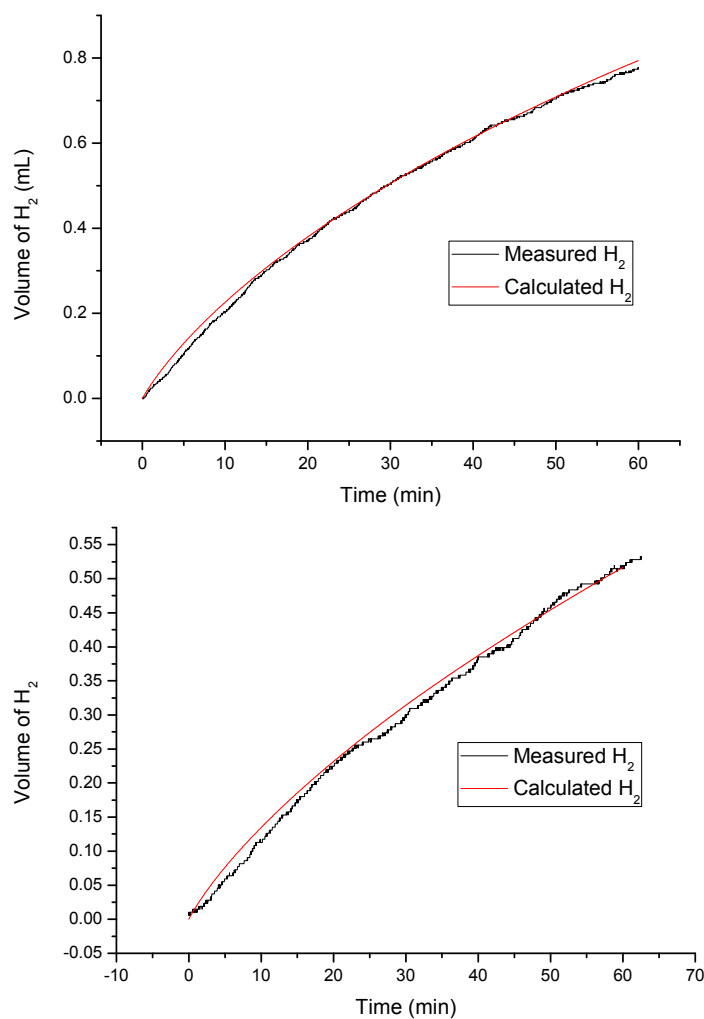
Figure S10. Hydrogen production efficiency for HER under potentiostatic electrolysis. The calculated H_2 lines represent the expected amount of H_2 assuming a quantitative Faradaic yield. The measured H_2 lines represent the experimentally detected H_2. (Top) Faradaic yields for Mo_2C at pH = 14 and η = 250 mV after activation. (Bottom) Faradaic yields for MoB at pH = 14 and η = 250 mV after activation. The activation process was a Galvanostatic electrolysis at 20 mA/cm^2 (reduction) for 15 minutes.
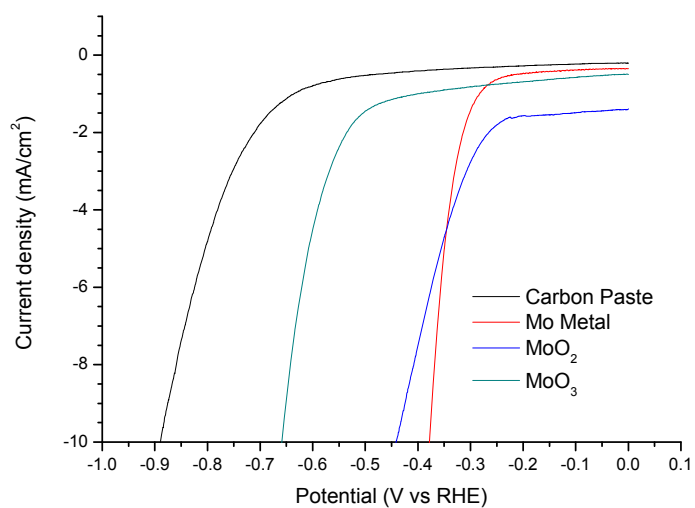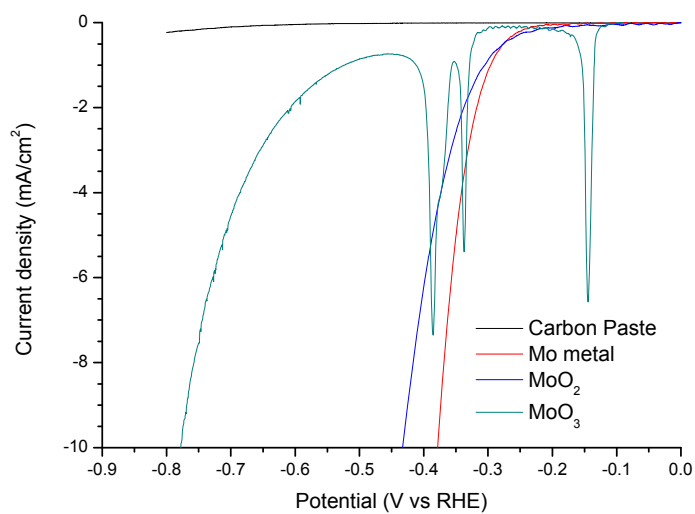
Figure S11. Polarization curves of MoO_2, MoO_3, Mo, and carbon paste electrodes. (Top) Polarization curves at pH = 0. (Bottom) Polarization curves at pH = 14.

Scan rate: 5 mV/s. These curves show that MoO_2, MoO_3, or Mo is not responsible for the HER activity observed with Mo_2C and MoB.