Electronic Supplementary Information:

Revealing and Accelerating Slow Electron Transport in Amorphous Molybdenum Sulphide Particles for Hydrogen Evolution Reaction

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Experimental Section

Physical measurements

Electrochemical measurements were recorded on an EG&G Princeton Applied Research Potentiostat/Galvanostat model 273. A three-electrode configuration was used. For polarization and electrolysis measurements, a platinum wire was used as the counter electrode and a home-made Ag/AgCl (KCl saturated) electrode was used as the reference electrode. The reference electrode was placed in a position very close to the working electrode, often with the aid of a Luggin tube. Potentials were referenced to a standard hydrogen electrode (SHE) or reversible hydrogen electrode (RHE), respectively, by adding a value of $(0.197+0.059 \cdot pH)$ V. Gas chromatography measurements were conducted on a home-made gas analyzer equipped with a Valco microvolume dual filament TCD detector and a HayeSep DB 100/120 mesh, 30 ft. long, 2 mm internal diameter, stainless steel packed column (part number G3591-80088 – Agilent Technologies). X-ray photoelectron spectroscopy (XPS) data were collected by an Axis Ultra (Kratos Analytical, Manchester, UK) under ultra-high vacuum condition ($>10^{-8}$ Torr), using a monochromatic Al K_α X-ray source (1486.6 eV), in the Surface Analysis Laboratory of CIME at EPFL. The source power was maintained at 150 W (10 mA, 15 kV) Gold (Au $4f_{7/2}$) and copper (Cu $2p_{3/2}$) lines at 84.0 and 932.6 eV, respectively, were used for calibration, and the adventitious carbon 1s peak at 285 eV as an internal standard to compensate for any charging effects. For quantification, relative sensitivity factors from the supplier were used. Ohmic drop was corrected by current interrupt technique on the PAR 273 equipment. Impedance data was recorded with an IviumStat Electrochemical Interface. The parameters of the EIS experiments were fixed for all measurements: 100 points were recorded in the frequency range between 0.1 and 10^6 Hz (14 points per decade) with the amplitude of the sinusoidal perturbation fixed at 15 mV. Potentials from 100 to 200 mV *vs*. RHE were applied with steps of 10 mV. A pre-treatment was performed at the desired potential for 10 s before each experiment. The modified electrodes were pre-activated prior to EIS measurements by galvanostatic electrolysis at 10 mA·cm^2 for 10 mim. Experimental data was analyzed and fitted using ZView software (Scribner Associates). For Tafel analysis, polarization curves were recorded with a scan rate of 1 mV·s^{-1} and ohmic drop was corrected by the potentiostat using the current interrupt technique.

Electrodes fabrication

For the preparation of the reference electrodes, porous Vycor® was initially used as a bridge for the fabrication of the reference electrodes. Since its shortage on the market, it was successfully replaced by porous silica gel spheres, typically used for desiccation. Type II silica gel of 3.5 mm bead size (Aldrich, catalog n. S7500-1KG) was first soaked in pure acetone for an hour. Acetone was removed and replaced by water. After 24 hours the water solution was replaced by saturated KCl solution and the solution renewed each day for 3 consecutive days. The spheres can be stored under saturated KCl solution for months and are ready to use. Direct addition of water to the dry spheres will cause them to break.

Ag/AgCl reference electrodes were built using a 4 mm external diameter glass tube with an inner diameter of 3 mm. The desired length was cut and the tips heated briefly with an Oxygen / Propane burner. A pure silver wire (0.5 mm diameter, 99.9 %, Aldrich) was wound around a 0.5 mm supporting copper wire to yield a silver coil. The silver coil was transferred to a branch of a U-shape glass tube filled with 6.0 M HCl. The silver wire was connected to the positive pole of a laboratory power supply and the negative pole was connected to a small platinum wire on the other branch of the U-tube. A constant current of 3 mA was applied during 30 minutes to oxidize the surface of the silver to silver chloride. A previously prepared silica gel sphere filled with saturated KCl solution was fixed to the tip of the glass tube using a transparent heat-shrink polyolefin tube by heating it inside a boiling solution of saturated aqueous KCl. The tube was filled with saturated KCl/AgCl mixture and the coiled silver wire added. The top of the tube was sealed with hot glue to ensure no leaks or evaporation of the filling solution. The electrode was kept immersed in saturated aqueous KCl when not in use. The potential of the reference electrodes was periodically checked using a standard reference electrode from Metrohm. To verify the potential of the electrode, both electrodes were dipped into concentrated KCl solution, and the potential difference between them measured using a high precision digital voltmeter (Fluke 87V). If the difference between the electrodes was bigger than 5 mV the home-made electrode was discarded and a new electrode was built.

Synthesis of MoS$_3$ particles

Two methodologies were developed for the synthesis of MoS$_3$, the latter being improved for the preparation of colloidal dispersions.

Method I:

In a typical procedure, molybdenum trioxide (1.0 g, 6.95 mmol) was added to an aqueous solution of sodium sulfide (8.34g, 34.74 mmol of $Na_2S \cdot 9H_2O$ in 250 mL of water) to form a light yellow solution. This solution was kept under vigorous stirring while 6.0 M aqueous HCl was added slowly (~ 10 minutes) until the solution reached the pH of 4. At first darkening of the solution was observed; close to the end of the addition, a large amount of gaseous H_2S was produced. After addition of acid, the solution was boiled for 30 minutes to remove the H_2S present in solution and to improve the filtration step. After being cooled to ambient temperature, the solution was filtered under vacuum and washed with a copious amount of water and then ethanol. The dark paste obtained was oven dried for 12 hours at 80 ºC to yield a black vitreous solid that could be powdered with the aid of a mortar.

Method II:

Since this method is more adapted for the preparation of MoS_3 sols, the quantities used for the synthesis were reduced. In a typical procedure, MoO_3 (250 mg, 1.74 mmol) was added to a hot solution of sodium sulfide (2.09g, 8.68 mmol of $Na_2S \cdot 9H_2O$ in 25 mL of water) to form a light yellow solution. This solution was kept under vigorous stirring while acetic acid (1.10 g, 18.32 mmol dissolved in 10mL of water) was added dropwise. The color of the solution intensifies passing from bright yellow to deep orange. At the end of the addition of acetic acid, the dark solution was left stirring for 5 minutes. Aqueous HCl (15 mL, 2.5 M) was added at once causing evolution of H_2S and formation of a brown solid. The solution was left stirring for further 10 minutes and centrifuged at 5500 rpm for 5 minutes. The pellet was washed 2 times with pure deionized water being centrifuged at 5500 rpm for 5 minutes after each washing step, and another 2 times being centrifuged at 5500 rpm for 20 minutes. The solid suspends easily in neutral water, which is the reason for the longer centrifugation times in the last washing steps.

The wet pellet was suspended in isopropanol by sonication and transferred to a volumetric flask with a total volume of 250 mL. The concentration of this stock solution of MoS_3 was determined by ICP-OES to be 1.31 g·L^{-1} (0.666 g·L^{-1} on Mo). This concentration corresponds to a yield of 98.5 %.

Synthesis of MoS₃ dispersed in Vulcan®

In a typical procedure, MoO_3 (55 mg, 0.38 mmol) was added to a hot solution of sodium sulfide (460 mg, 1.91 mmol of $Na_2S \cdot 9H_2O$ in 5 mL of water) to form a bright yellow solution. This solution was kept under vigorous stirring while acetic acid (240 mg, 4.0 mmol dissolved in 1.0 mL of water) was added dropwise. The color of the solution intensifies passing from bright yellow to deep orange. This orange solution was added to a slurry of Vulcan® XC-72R (100 mg in 2 mL of isopropanol) under constant stirring. Aqueous HCl (3 mL, 2.5 M) was added at once and the suspension left stirring for 10 minutes. The suspension was centrifuged at 5500 rpm for 5 minutes. The pellet was washed 4 times with pure deionized water being centrifuged at 5500 rpm for 10 minutes after each washing step. The wet pellet was suspended in isopropanol by sonication and transferred to a volumetric flask with a total volume of 100 mL. The concentration of this stock solution of MoS_3/Vulcan® was determined by ICP-OES to be 0.3435 $g \cdot L^{-1}$. This concentration corresponds to a yield of 93.7 %. The solid residue after evaporation was determined gravimetrically as 1.32 $g \cdot L^{-1}$, which corresponds to a molybdenum loading of 26 % in weight related to the total mass of solid (MoS_3+carbon).

Synthesis of MoS_x species by reduction with $NaBH_4$

A solution of $(NH_4)_2MoS_4$ (250 mg, 0.96 mmol dissolved in 50 mL of water) was freshly prepared and filtered through a Nylon membrane filter (0.22 μm) to remove the insoluble MoS_3 particles present in the solution. The clear red solution was left stirring while $NaBH_4$ (100 mg, 2.64 mmol dissolved in 3 mL of water) was added at once. The solution becomes immediately dark with slow evolution of gas. The mixture was left stirring for 10 minutes and brought to boil. A large amount of black precipitate was formed and then, 1.0 mL of acetic acid was added to quench the excess of $NaBH_4$. The solution was centrifuged at 5500 rpm for 5 minutes and washed 4 times with water following the same centrifugation method. After washing the wet pellet was suspended in isopropanol by sonication and transferred to a volumetric flask with a total volume of 100 mL. The concentration of this stock solution of MoS_x was determined by ICP-OES to be 0.7118 $g \cdot L^{-1}$ (in Mo). This concentration corresponds to a yield of 77 % based on Mo. The relative low yield is explained by the appreciable amount of solution lost during the filtration step to remove MoS_3 particles present in the commercial starting material.

Synthesis of MoS_x dispersed in Vulcan® by reduction with $NaBH_4$

A solution of $(NH_4)_2MoS_4$ (100 mg, 0.384 mmol dissolved in 20 mL of water) was filtered through a Nylon membrane filter (0.2 µm) to remove insoluble MoS_3 particles. The red solution was added to a slurry of Vulcan® (100 mg in 5mL of isopropanol) that was previously sonicated to disperse the carbon black particles. The suspension was left stirring while a solution of $NaBH_4$ in water (100 mg, 2.64 mmol dissolved in 3mL of water) was added at once. The suspension was left stirring for 10 minutes and heated until boil. Acetic acid (1.0 mL) was added drop wise to quench the excess of $NaBH_4$. The suspension was centrifuged at 5500 rpm for 5 minutes and then washed 4 times with water centrifuging for 10 minutes. The wet pellet at the bottom of the tube was suspended in 30 mL of isopropanol by sonication and transferred to a 100 mL volumetric flask, which was put to the final volume with isopropanol. The concentration of Mo in this solution was determined by ICP-OES to be 0.2907 $g \cdot L^{-1}$, corresponding to a yield of 79 %. The solid residue after evaporation was determined gravimetrically as being approximately 1.4 $g \cdot L^{-1}$ which corresponds to a Mo loading of 21 % in weight related to the total mass of solid (MoS_x + carbon).

Preparation of MoS$_3$ modified glassy carbon electrodes by spray casting

The glassy carbon electrodes were cleaned and polished as described above. 10 µL of MoS_3 sol in EtOH (various concentrations), were spray cast on a glassy carbon electrode with an airbrush. Previous to spray cast, the suspensions were sonicated for several minutes to ensure a homogeneous deposition.

ICP-OES measurements

The molybdenum content of colloidal dispersions was determined by ICP-OES. In a typical procedure, 1.000 mL of the colloidal dispersion was taken using a micropipette (air displacement pipette) and transferred to a 30 mL vial. Since the colloidal dispersions are in isopropanol, the reverse pipette method was used. Samples were analyzed in triplicate.

The isopropanol was removed by placing the vials on top of a plate heated to 50 ºC. A small flow of nitrogen was blow on top of the vials to accelerate the evaporation of the solvent. Once dry, 1.0 mL of hot aqua regia was added to the vials and the solid dissolved. For samples containing Vulcan®, the carbon component was not soluble and was removed by filtering through a 0.22 µm Nylon membrane prior to ICP analysis.

EIS data processing

EIS data was fitted using ZView software with the equivalent circuits shown in Figure 4. For the transmission line model (Figure 3), the extended element "Bisquert#2" was used. The transmission line model consists of three impedances representing the electronic transport in the solid phase, the ionic transport in the electrolyte and the electrochemical recombination. Each impedance consists on a parallel combination of a resistance and a CPE. For our systems, the impedance due to ionic transport was approximated to zero since the low frequency domain of the Nyquist plots are dominated by the recombination. R_{sol} and R_{ct} represent respectively the solution and recombination resistances. R_2 and CPE_2 represent an additional impedance necessary for a proper fitting which originates from the contact impedance between the electrocatalyst and the glassy carbon electrode.

Table S1: Fit parameters for MoS_x modified electrode 25.2 $\mu g \cdot cm^{-2}$

η (mV)	R_{sol} (Ω)	R_c (Ω)	CPE_c ($F^{-1} \cdot s^{1-n}$)	R_m (Ω)	R_{ct} (Ω)	CPE_{ct} ($F^{-1} \cdot s^{1-n}$)	n CPE_{ct}
100	5.378	0.86314	0.001724	5.414	48248	0.000144	0.91016
110	5.405	0.86314	0.00174	5.477	25383	0.000145	0.91065
120	5.439	0.86314	0.002012	5.84	13081	0.000142	0.91538
130	5.461	0.86314	0.002203	6.034	6381	0.000144	0.91695
140	5.484	0.86314	0.002309	6.154	3244	0.000148	0.91739
150	5.532	0.86314	0.002528	6.448	1626	0.000147	0.92126
160	5.717	0.86314	0.002662	6.647	821.2	0.000149	0.92288
170	5.991	0.86314	0.002773	7.03	426.7	0.000153	0.92282
180	6.203	0.86314	0.002794	7.203	226.3	0.000158	0.92498
190	6.552	0.86314	0.002559	7.152	128.8	0.00016	0.91932
200	6.477	0.86314	0.003177	8.543	72.49	0.000157	0.93413

Constant parameters:

n CPE_c: 0.8

Table S.2: Fit parameters for MoS_x modified electrode 252 $\mu g \cdot cm^{-2}$.

η (mV)	CPE_c $(F^{-1} \cdot s^{1-n})$	R_m (Ω)	R_{ct} (Ω)	CPE_{ct} $(F^{-1} \cdot s^{1-n})$	n CPE_{ct}
100	0.000886	12.67	5408	0.000979	0.93083
110	0.000836	14.03	2665	0.000984	0.92908
120	0.000729	14.62	1796	0.000984	0.92991
130	0.000725	15.41	871.2	0.000988	0.93175
140	0.000676	16.04	430.9	0.001003	0.93111
150	0.00065	16.57	219.5	0.001022	0.93008
160	0.000605	17.03	116.9	0.00106	0.92685
170	0.000527	17.62	65.95	0.001103	0.92293
180	0.00051	17.91	39.04	0.001147	0.91778
190	0.000459	18.54	24.04	0.001194	0.91833
200	0.00038	18.61	15.57	0.001288	0.90994

Constant Parameters:

R_{sol}: 4.8 Ω

R_c: 0.64 Ω

n CPE_c: 0.8

Table S.3: Fit parameters for MoS$_3$ modified electrode 28.2 μg·cm^{-2}.

η (mV)	CPE$_c$ (x10^{-5} F^{-1}·s^{1-n})	R$_m$ (Ω)	R$_{ct}$ (Ω)	CPE$_{ct}$ (F^{-1}·s^{1-n})	n CPE$_{ct}$
100	1.38	90.48	28224	0.000143	0.87206
110	1.46	90.6	14874	0.000147	0.86394
120	1.48	92.38	7641	0.000145	0.86932
130	1.49	90.34	3960	0.000152	0.86506
140	1.46	91.35	2061	0.000152	0.87147
150	1.44	88.82	1122	0.000158	0.87013
160	1.49	82.3	640.8	0.000165	0.86316
170	1.45	77.16	379.7	0.000172	0.85758
180	1.42	71.29	237.2	0.000179	0.84948
190	1.46	67.31	154	0.000184	0.8453
200	1.46	63.52	103.6	0.000186	0.84522

Constant Parameters:

R$_{sol}$: 5.8 Ω

R$_c$: 6.4 Ω

n CPE$_c$: 0.8

Table S.4: Fit parameters for MoS$_3$ modified electrode 282 µg·cm^{-2}.

η (mV)	CPE$_c$ (x10^{-5} F^{-1}·s^{1-n})	R$_m$ (Ω)	R$_{ct}$ (Ω)	CPE$_{ct}$ (F^{-1}·s^{1-n})	n CPE$_{ct}$
100	5.89	306.8	4946	0.000817	0.92767
110	5.88	298.3	2739	0.000795	0.90174
120	5.66	290	1401	0.000771	0.88523
130	5.76	288	714.8	0.000763	0.9024
140	5.90	302	381.4	0.000784	0.93789
150	6.52	332	212.1	0.000891	0.96265
160	6.56	389.2	112.3	0.001255	0.93612
170	5.80	402.7	59.06	0.001621	0.89892
180	5.63	414.5	31.05	0.001982	0.88053
190	5.38	442.1	16.32	0.002481	0.86235
200	5.34	481.4	8.58	0.003142	0.8511

Constant Parameters:

R$_s$: 4.82 Ω

R$_c$: 3.45 Ω

n CPE$_c$: 0.8

Table S.5: Fit parameters for MoS_3-Vulcan modified electrode 145 µg·cm^{-2}; 2 CPE model.

η (mV)	R_{sol} (Ω)	R_2 (Ω)	C_2 (x 10^{-4} F)	R_{ct} (Ω)	C_{ct} (x 10^{-4} F)
100	4.478	0.58518	1.688	7180	4.71265
110	4.484	0.60977	1.653	3998	4.34444
120	4.488	0.63157	1.6745	2088	4.16234
130	4.492	0.65096	1.6985	1083	4.0644
140	4.5	0.66537	1.7694	567.1	4.02815
150	4.503	0.66822	1.7993	300.8	4.0752
160	4.509	0.66732	1.859	163.3	4.14883
170	4.517	0.65229	1.9039	91.24	4.24962
180	4.539	0.63649	1.9462	52.58	4.35718
190	4.53	0.60216	1.9365	31.74	4.46152
200	4.543	0.56882	1.9	19.97	4.55479
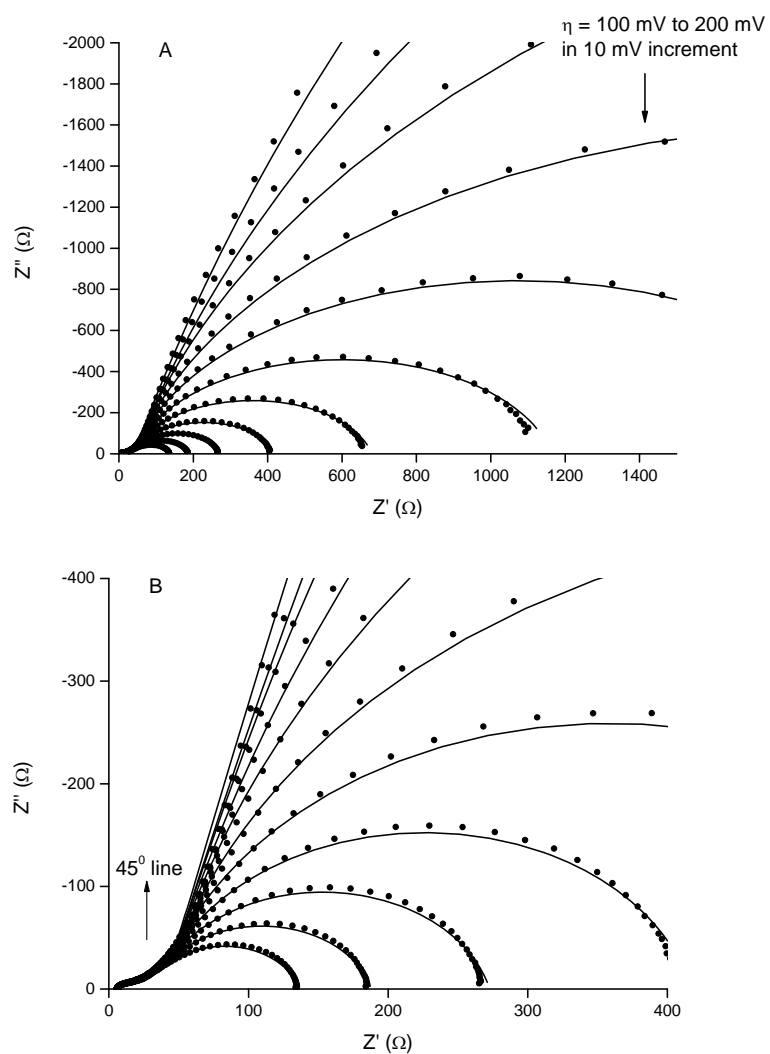
Fig. S1. The Nyquist plot and fitting for the impedance response of MoS_3-modified electrodes at a loading of 28.2 µg•cm-2. Full plot (A) and zoom-in plot showing the 45° line (B).
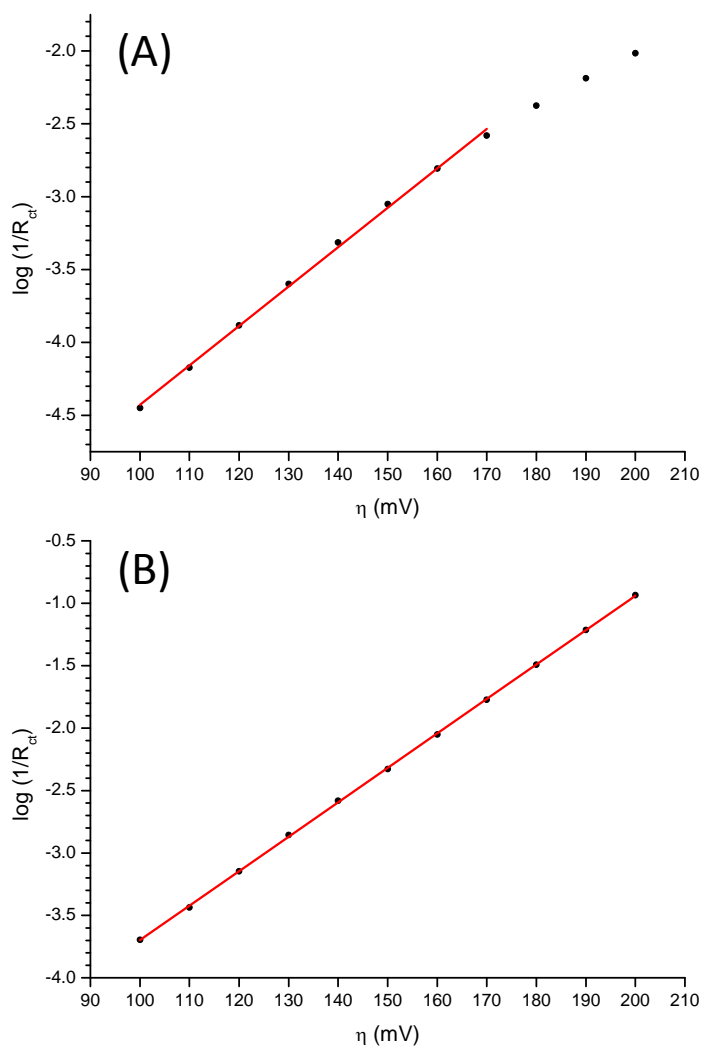
Figure S2. Plots of log (R_{ct}^{-1}) *vs.* η for (A) MoS_3, 28.2 $\mu g \cdot cm^{-2}$ and (B) MoS_3, 282 $\mu g \cdot cm^{-2}$.

(A)

(B)

Binding energy (eV)

Binding energy (eV)
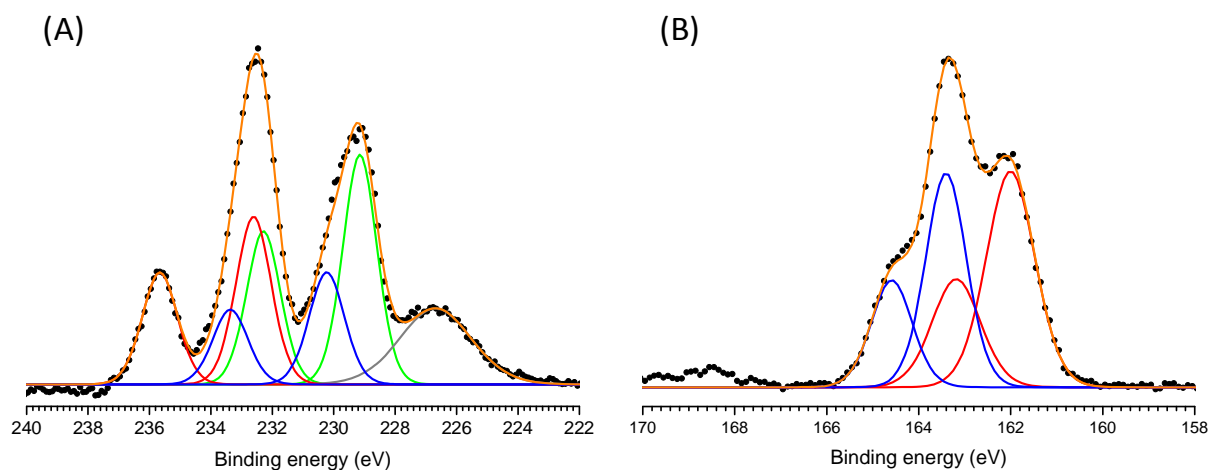
Figure S3. XPS spectra for MoS$_x$-CR produced by reduction with NaBH$_4$. (A) Mo 3d region: experimental data ($\cdots$), fitting envelope (—), Mo^{A}S$_3$ (—), Mo^{B}S$_3$ (—), MoO$_3$ (—) S 2s (—); S 2p region: experimental data ($\cdots$), fitting envelope (—), doublet I (—), doublet II (—).

η = 100 mV to 200 mV in 10 mV increment

Z'' (Ω)

Z' (Ω)
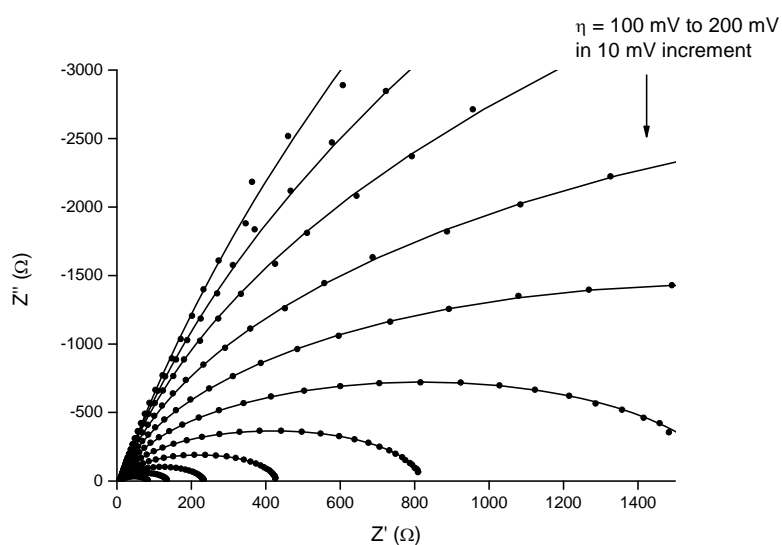
Fig. S4. The Nyquist plot and fitting for the impedance response of a MoS$_x$-CR-modified electrode; loading: 25.2 µg·cm^{-2}.
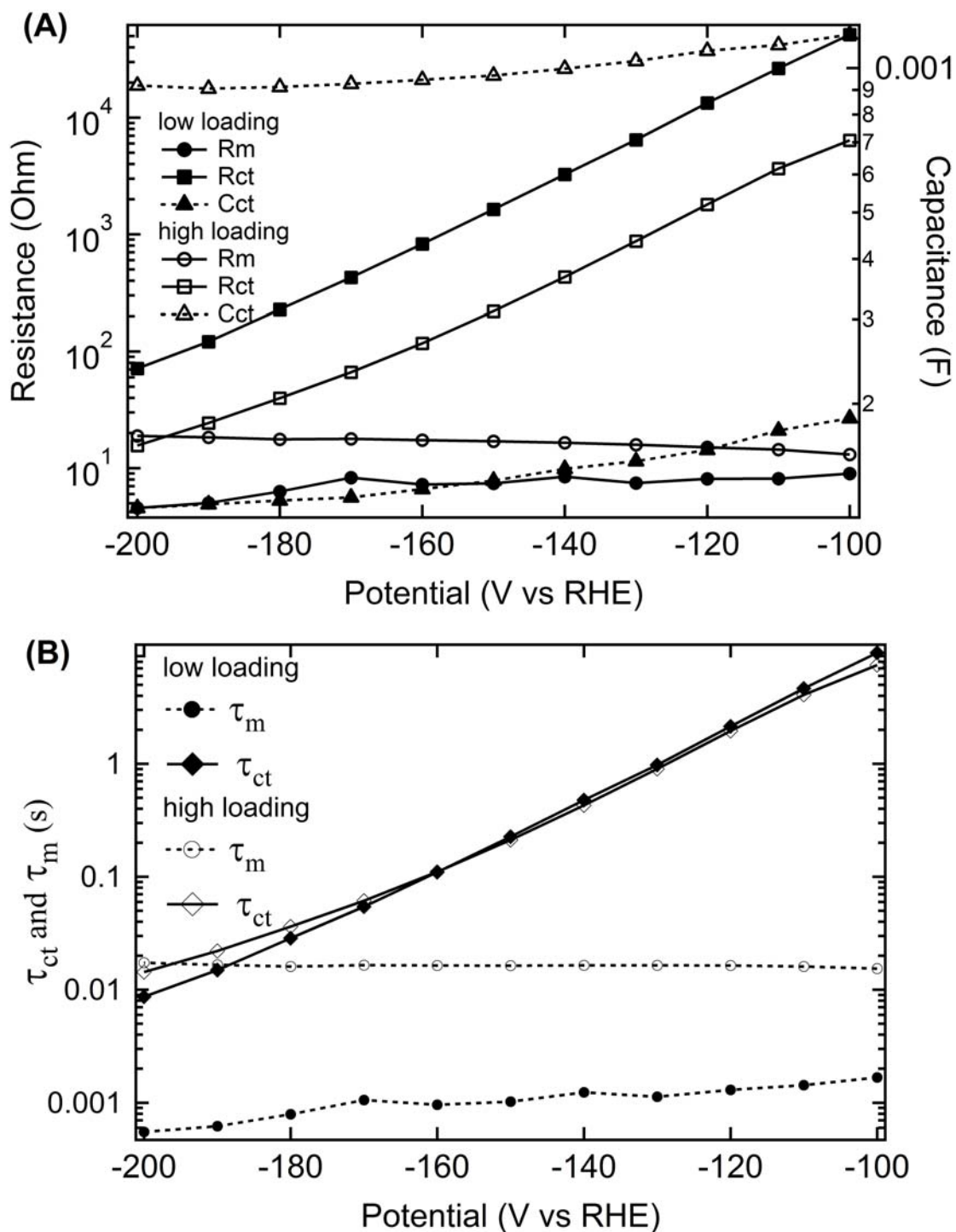
Fig. S5. The characteristic parameters of recombination and transport in MoS_x-CR-modified electrodes (top) and the associated time constants for the recombination and transport processes (bottom).
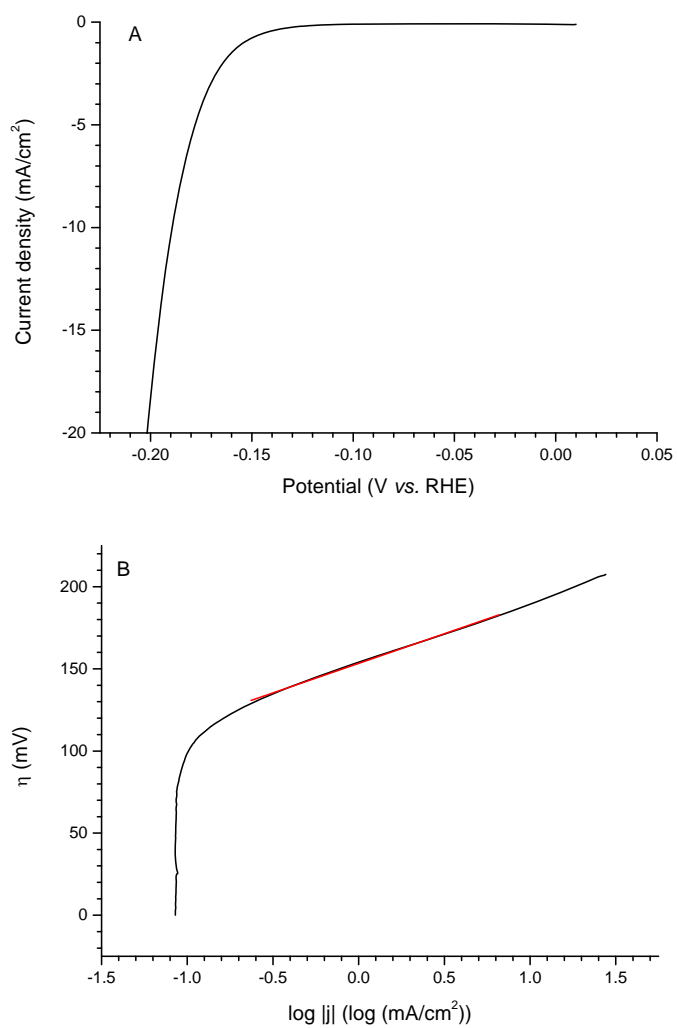
Figure S6. (A) Stable polarization curves (10th) of glassy carbon electrodes modified with MoS$_3$-V. Loading: 145 µg/cm^2; scan rate = 1 mV·s^{-1}; 1 M H$_2$SO$_4$. (B) Corresponding Tafel plot.
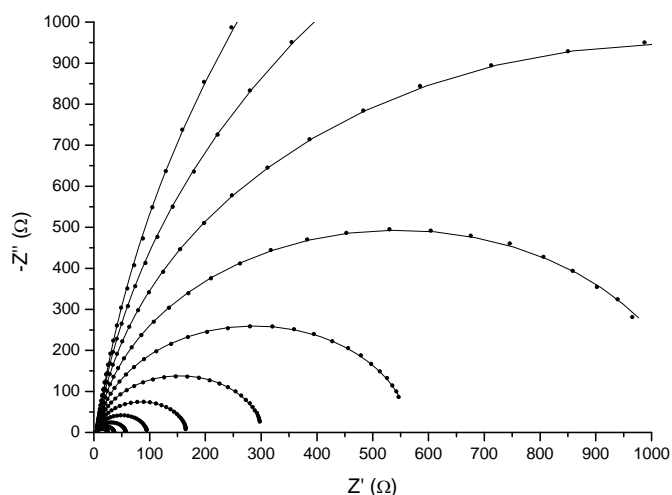
Figure S7. The Nyquist plot and fitting for the impedance response of a MoS_3-V-modified electrode; loading: 145 µg/cm^2. Even through Figure S7 appears similar to Figure 5 at a first glance, there is a difference in that the 45° line at the high frequency is absent in Figure S7 whereas it is present, albeit very small, in Figure 5. Therefore, a 2CPE instead of transmission line model is used to fit the impedance data.
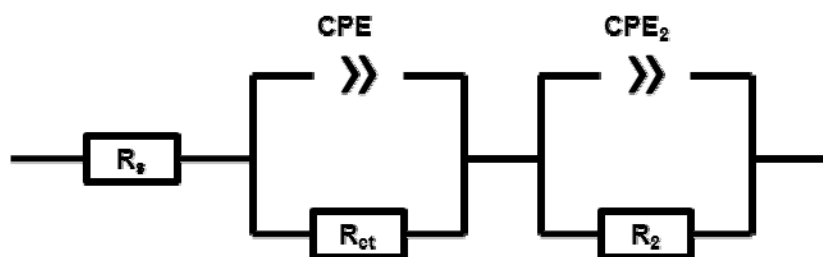

Figure S8. A 2CPE equivalent circuit. CPE and R_{ct} represent the charge transfer reaction; R_2 and CPE_2 represent the contact between the electrode and the catalyst layer.