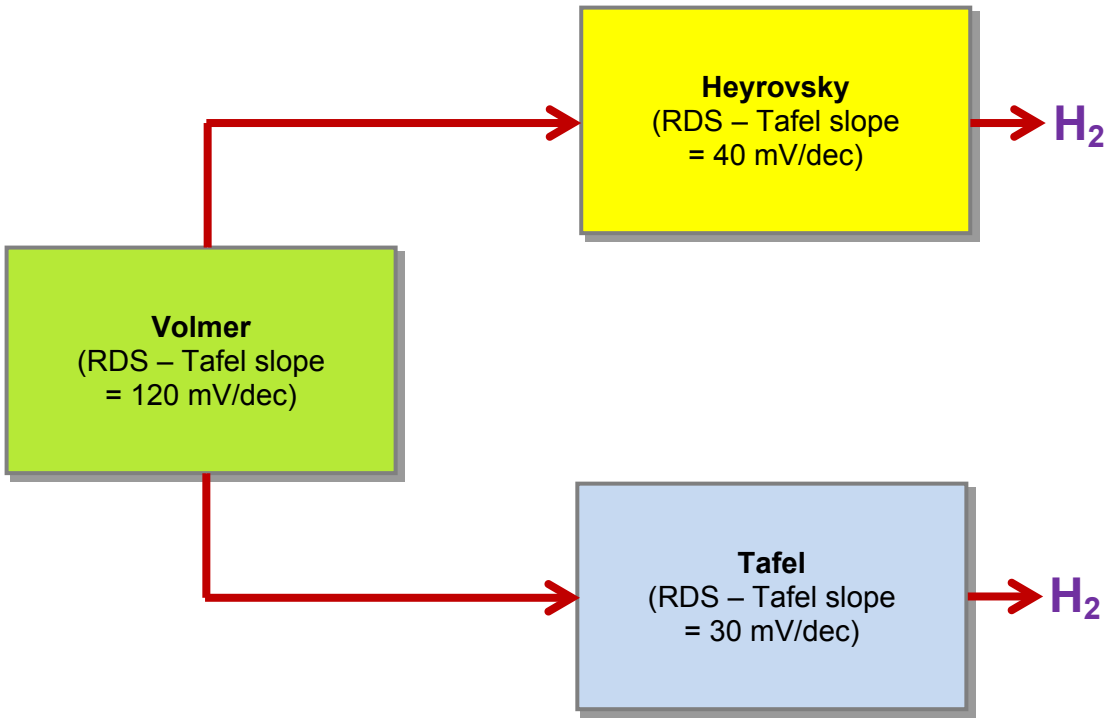
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.



Scheme 1. A schematic diagram showing production of hydrogen either through Volmer + Heyrovsky or Volmer + Tafel steps with distinctive rate determining steps.

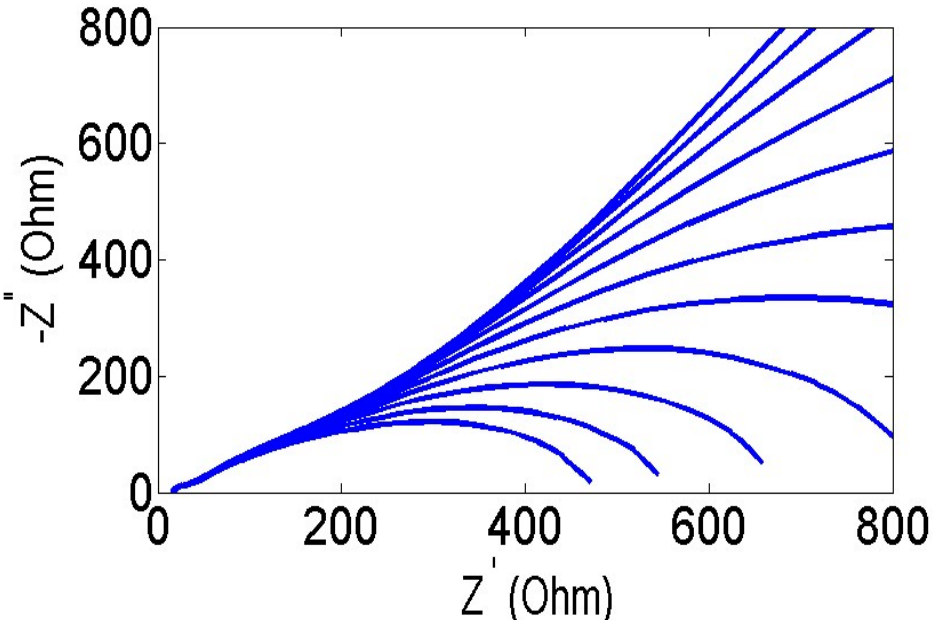


Figure S1. Expanded complex plane impedance plots of MoS_2 near high frequency region showing minor semicircle and small 45º line feature.

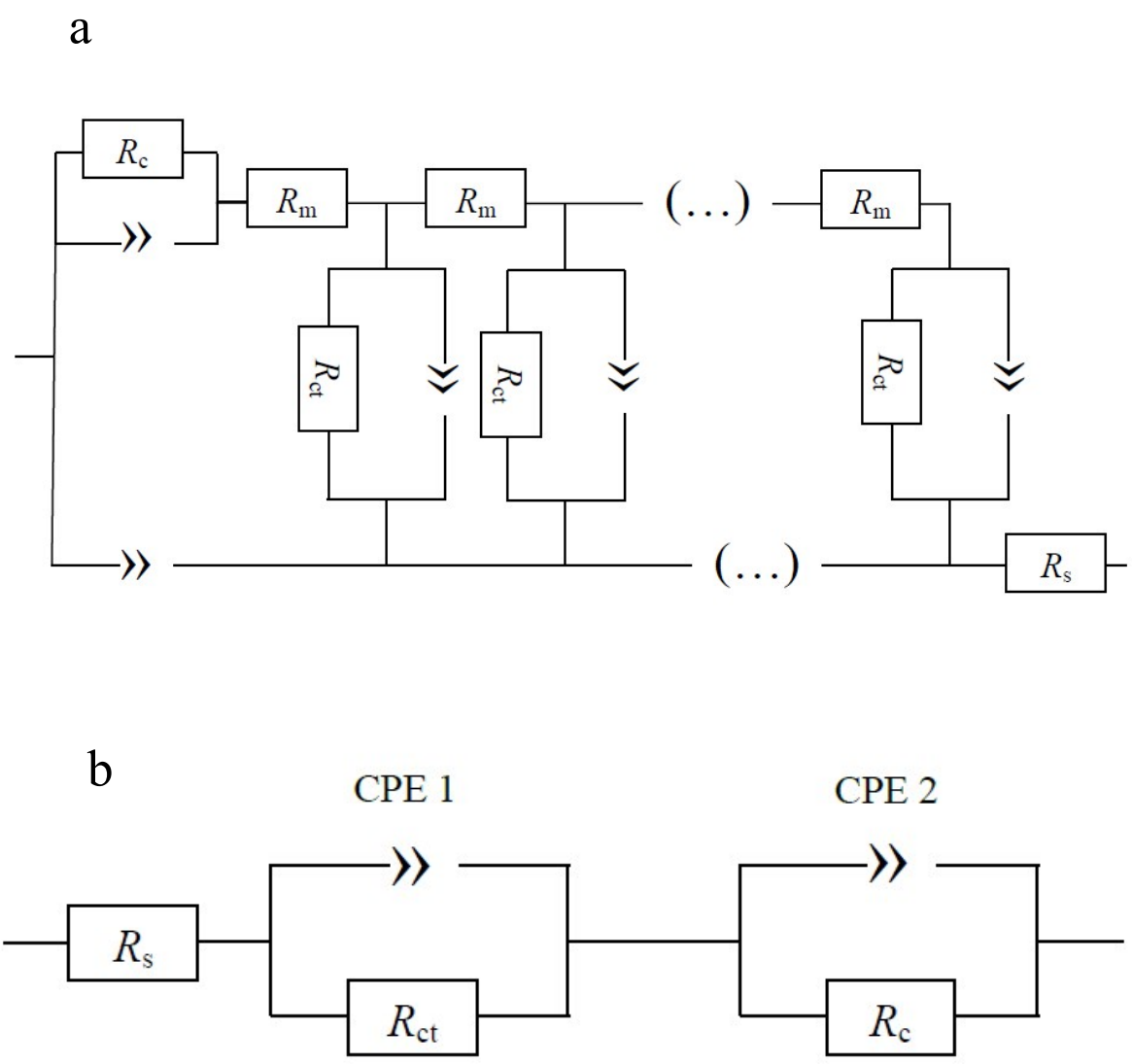


Figure S2 . a) A transmission line equivalent circuit and b) a 2 CPE equivalent circuit.

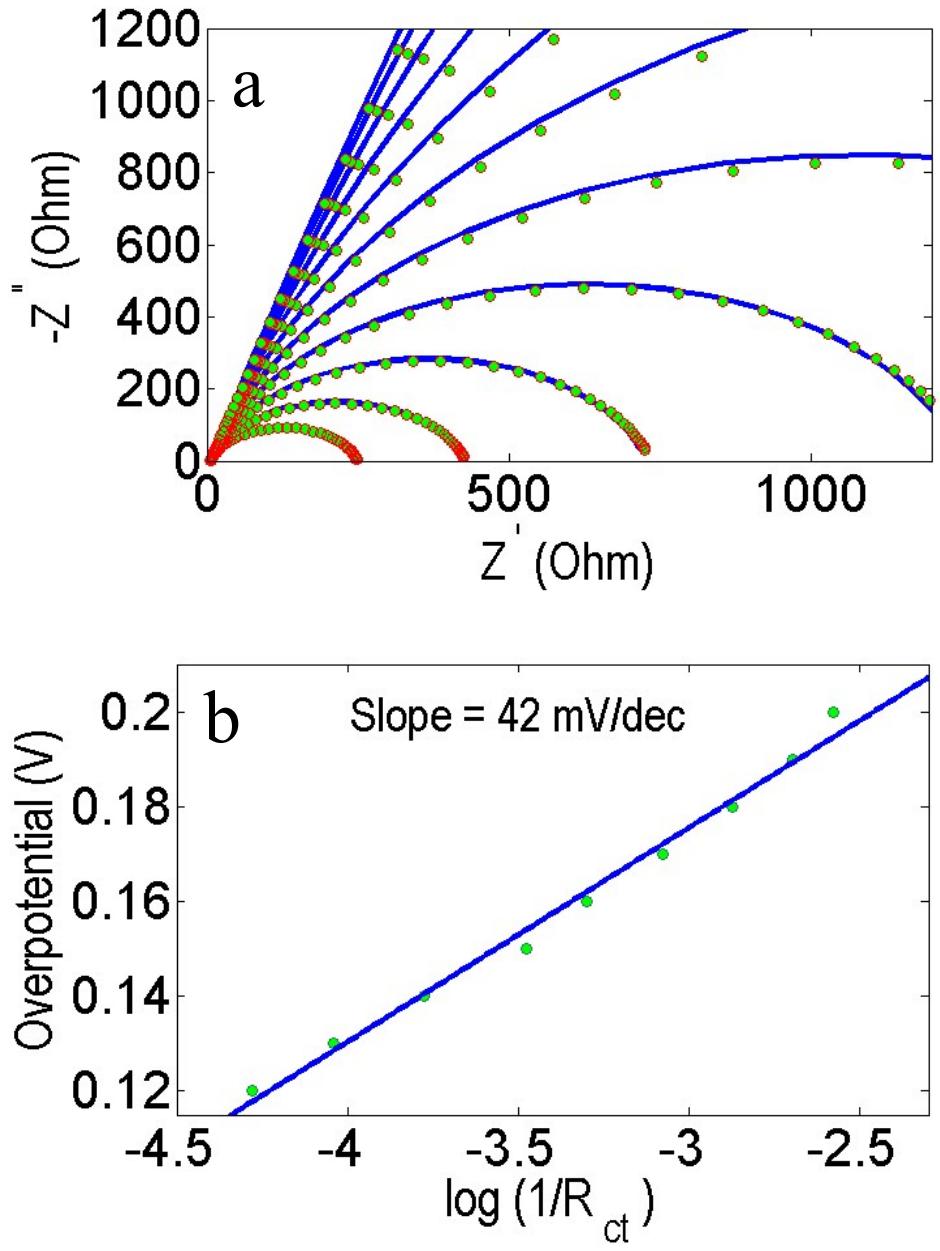


Figure S3. a) Complex plane impedance plots of MoS_2/CNT as a function of overpotential from 0.2 V (smallest semi-circle) to 0.1 V (largest semi-circle) in increments of 0.01 V. Solid lines are experimental data while circles denote fitting. b) Tafel plot of MoS_2/CNT obtained using R_{ct} data from impedance analysis.

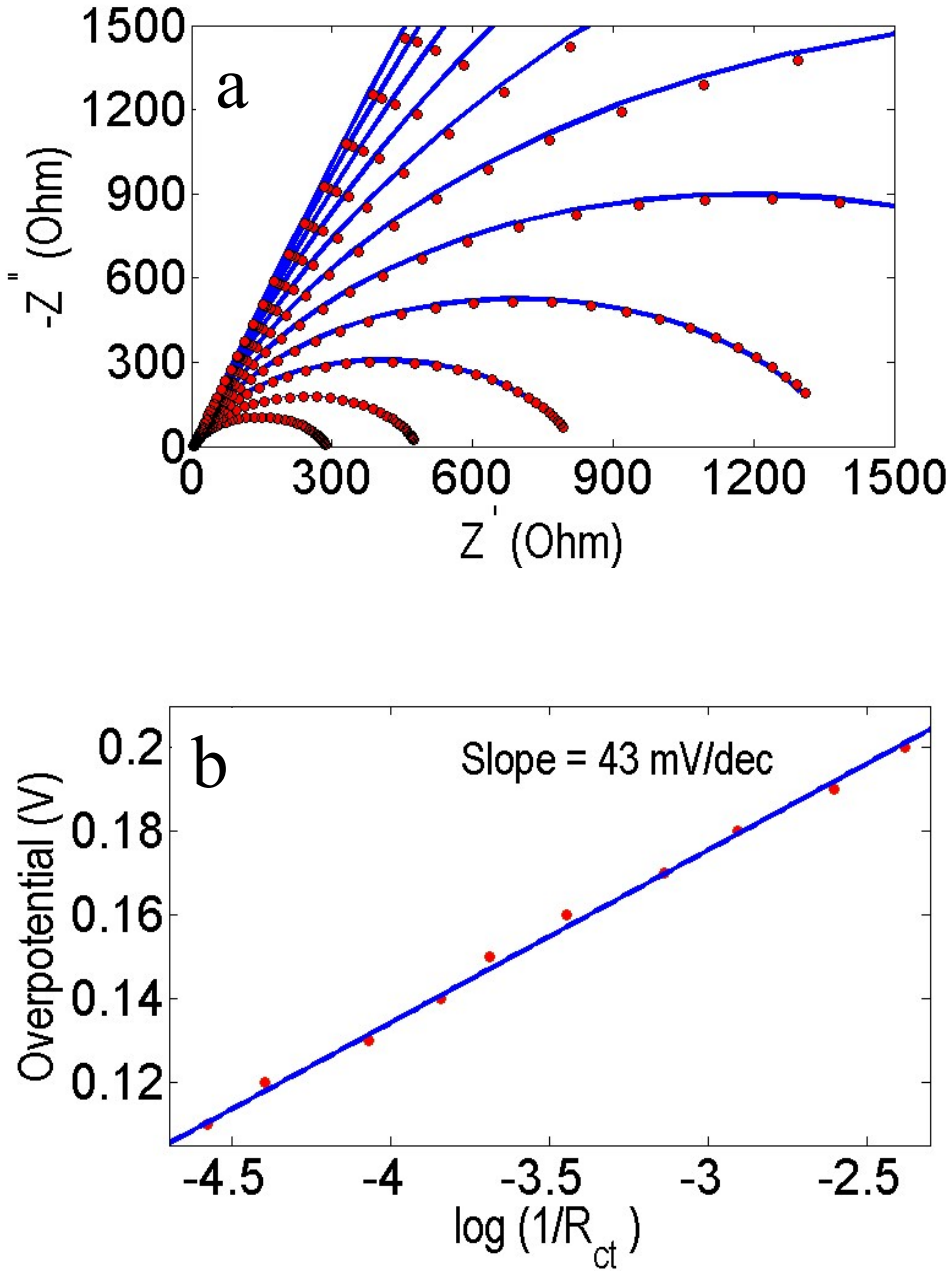


Figure S4. a) Complex plane impedance plots of MoS_2/AB as a function of overpotential from 0.2 V (smallest semi-circle) to 0.1 V (largest semi-circle) in increments of 0.01 V. Solid lines represent experimental data and circles denote fitting. b) Tafel plot of MoS_2/AB obtained using R_{ct} data from impedance analysis.

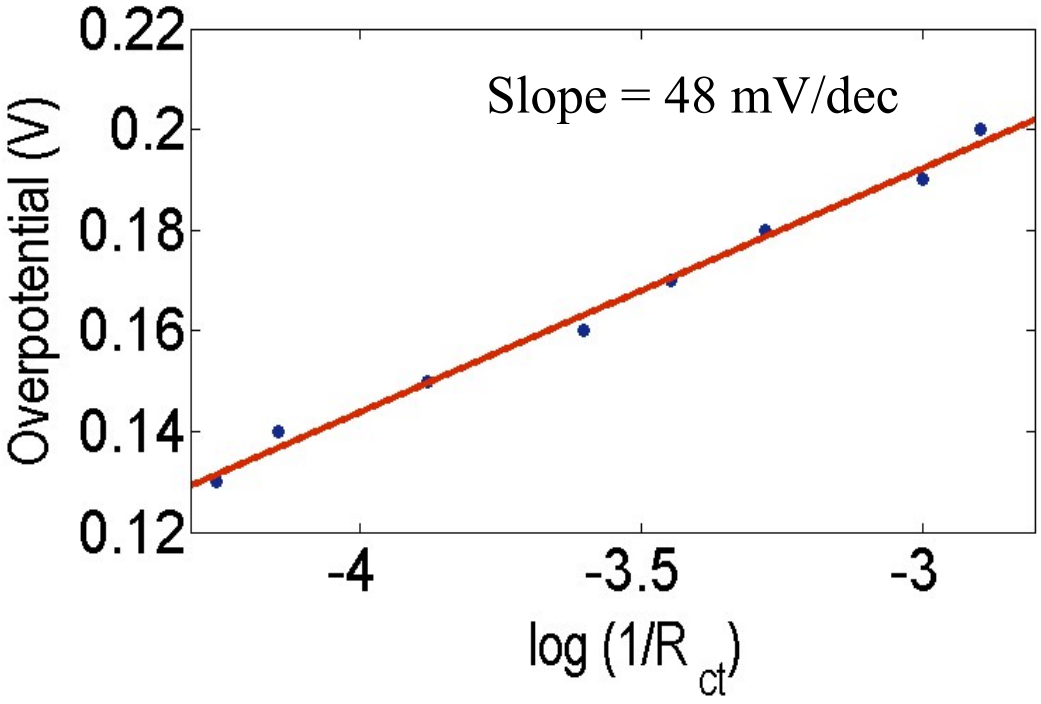


Figure S5. Tafel plot of MoS_2/VC-100 obtained using R_{ct} data from impedance analysis (Figure 5a).

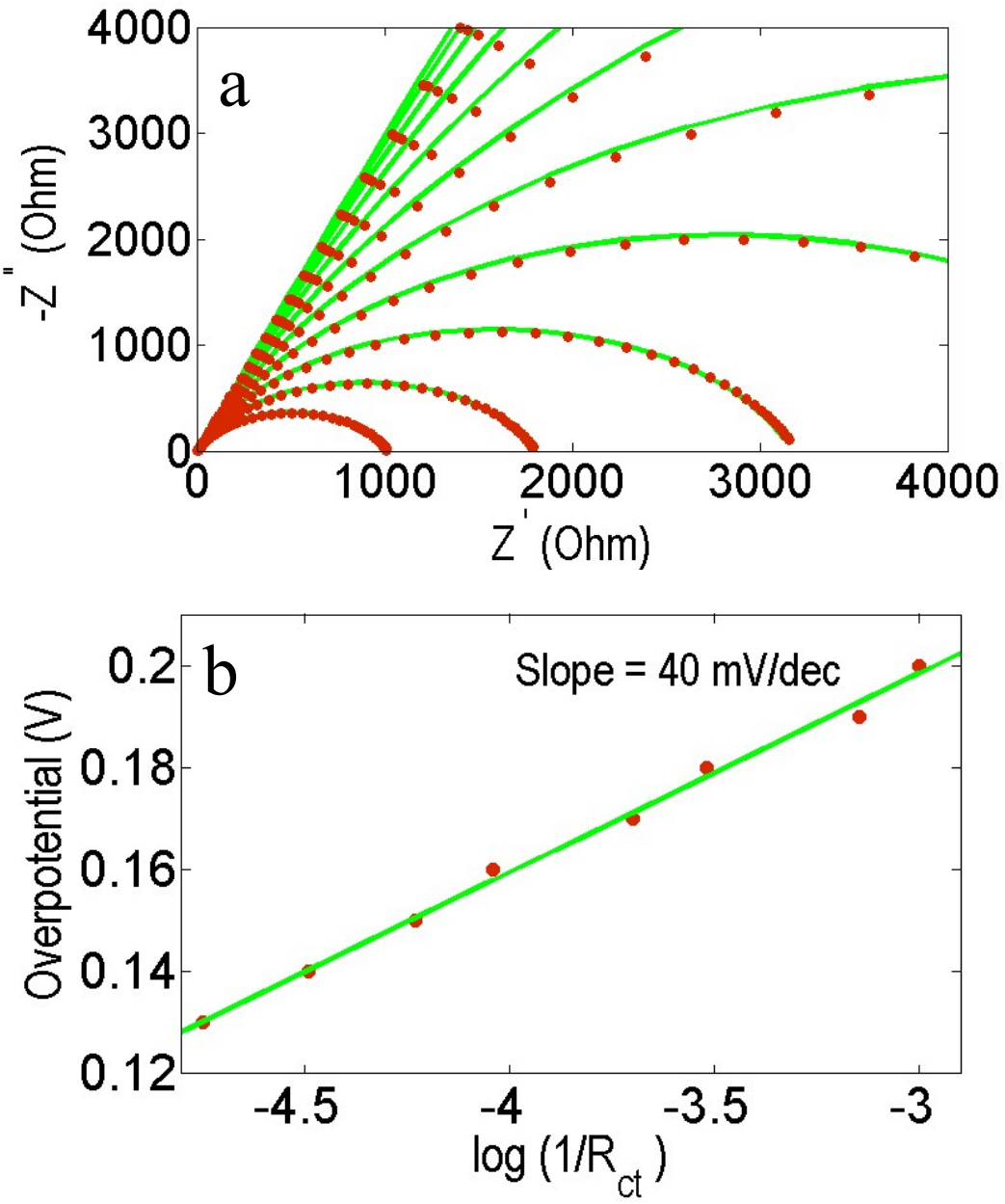


Figure S6. a) Complex plane impedance plots of MoS_2/VC-25 as a function of overpotential from 0.2 V (smallest semi-circle) to 0.1 V (largest semi-circle) in increments of 0.01 V. Solid lines are experimental data while circles denote fitting. b) Tafel plot of MoS_2/VC-25 obtained using R_{ct} data from impedance analysis.

Table S1. Crystalline size, micro-strain and dislocation density data of MoS_2 and MoS_2/C electrocatalysts.

Electrocatalyst	Crystalline size (nm)	Micro-strain	Dislocation density
MoS_2	6.89	2.367	0.021
MoS_2/AB	6.74	2.419	0.022
MoS_2/VC	6.78	2.399	0.021
MoS_2/CNT	6.28	2.594	0.025
MoS_2/CNF	4.02	3.968	0.061