

Supporting Information

MoTe₂ rendered into an efficient and stable electrocatalyst for the hydrogen evolution reaction by polymorphic control

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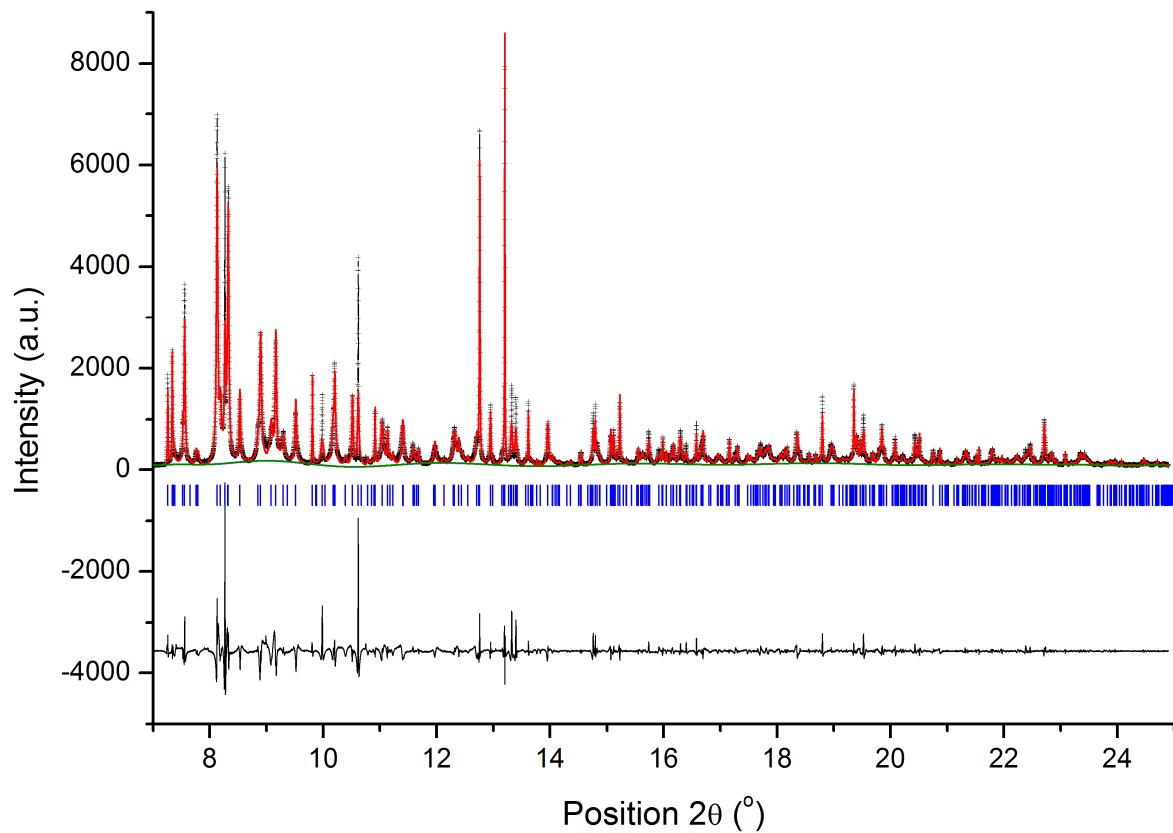


Fig. S1 Ambient temperature SXRD data from 1T'-MoTe₂ with observed (black), calculated (red), peak position (blue) and difference (grey) plots from Le Bail fit in $P2_1/m$. The unit cell parameters ($a = 6.32985(6)$ Å; $b = 3.47827(2)$ Å; $c = 13.8178(2)$ Å, $\beta = 93.838(1)^{\circ}$) are in close agreement with the literature ($a = 6.33$ Å; $b = 3.469$ Å; $c = 13.86$ Å, $\beta = 93.55$ $^{\circ}$). The poorly fitted peaks consistently originated from 01/ and 00/ reflections.

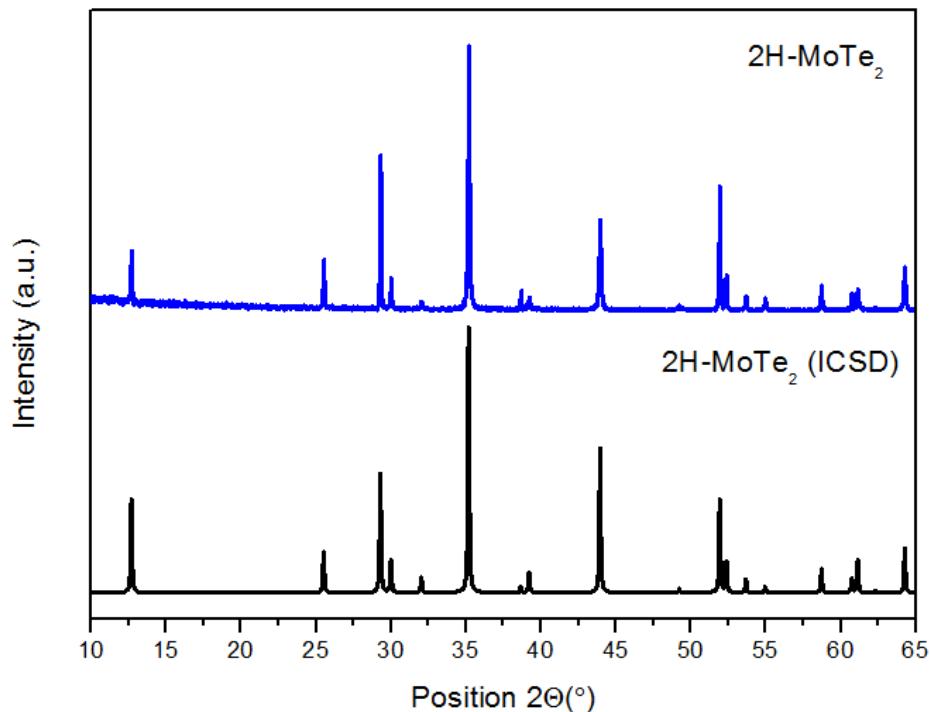


Figure S2. XRD analysis of as synthesised 2H-MoTe₂ and calculated pattern from the ICSD database, card number 15431.

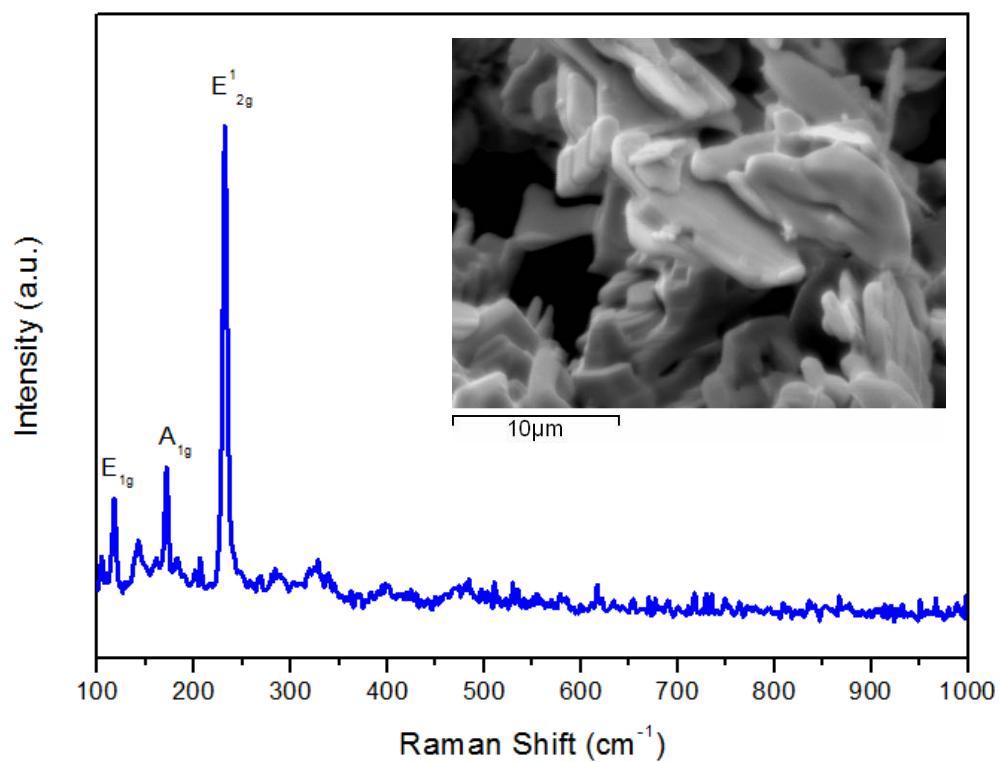


Figure S3. Raman spectrum of 2H-MoTe₂, indicating the absence of impurity phases. The inset shows particle morphology from SEM images.

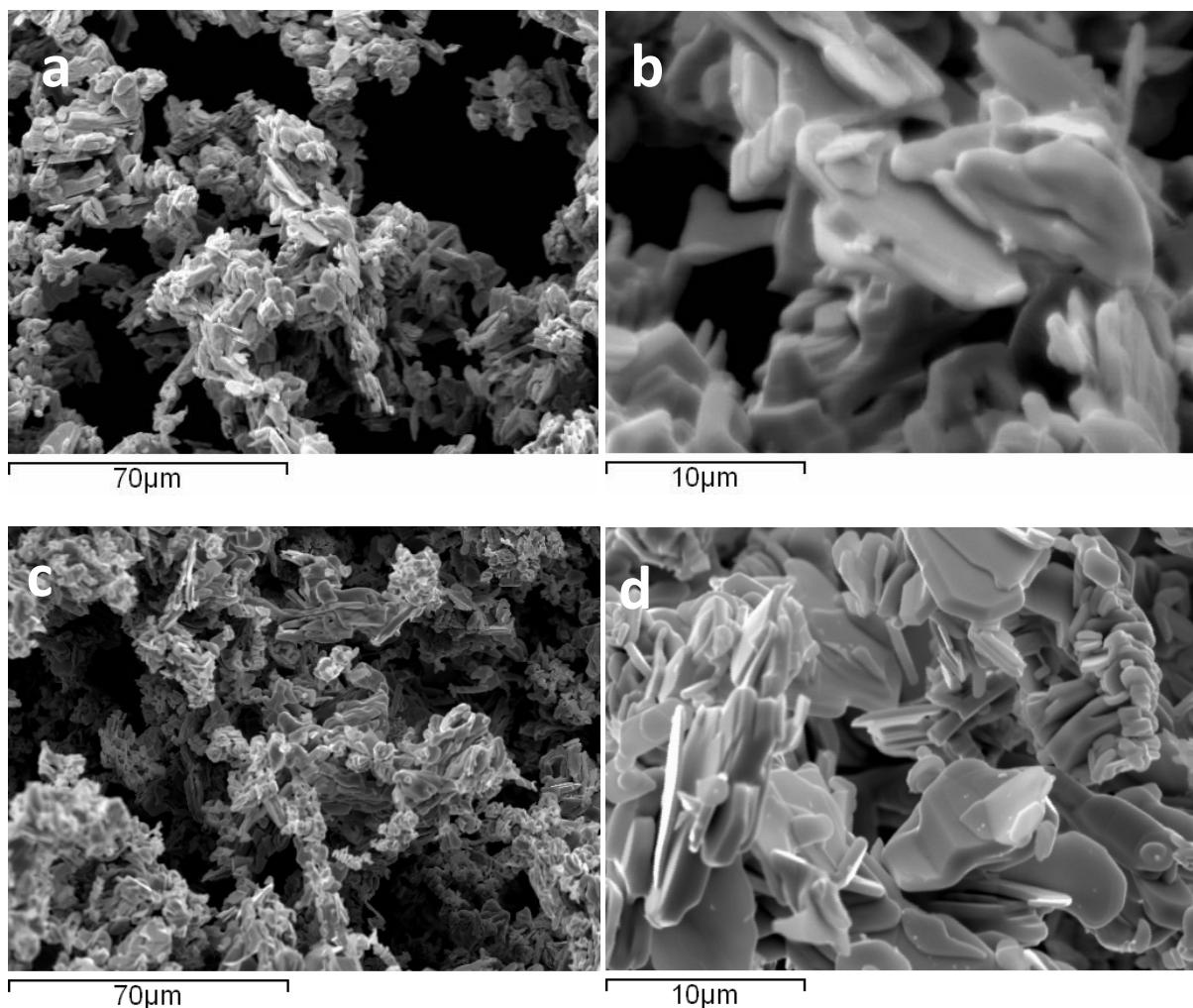


Figure S4. SEM images of 2H-MoTe₂ (a,b) and 1T'-MoTe₂ (c,d) showing particles in the micrometre range under various magnifications in line with the bulk character of the sample.

Table S1: Summary of overpotentials required by each catalyst for $j = 10 \text{ mA cm}^{-2}$ and their corresponding Tafel slopes.

| Catalyst | Overpotential for $j = 10 \text{ mA cm}^{-2}$ | Tafel slope |
|-----------------------|---|--------------------------|
| 2H-MoTe ₂ | - 0.65 V | 159 mV dec ⁻¹ |
| 1T'-MoTe ₂ | - 0.34 V | 78 mV dec ⁻¹ |

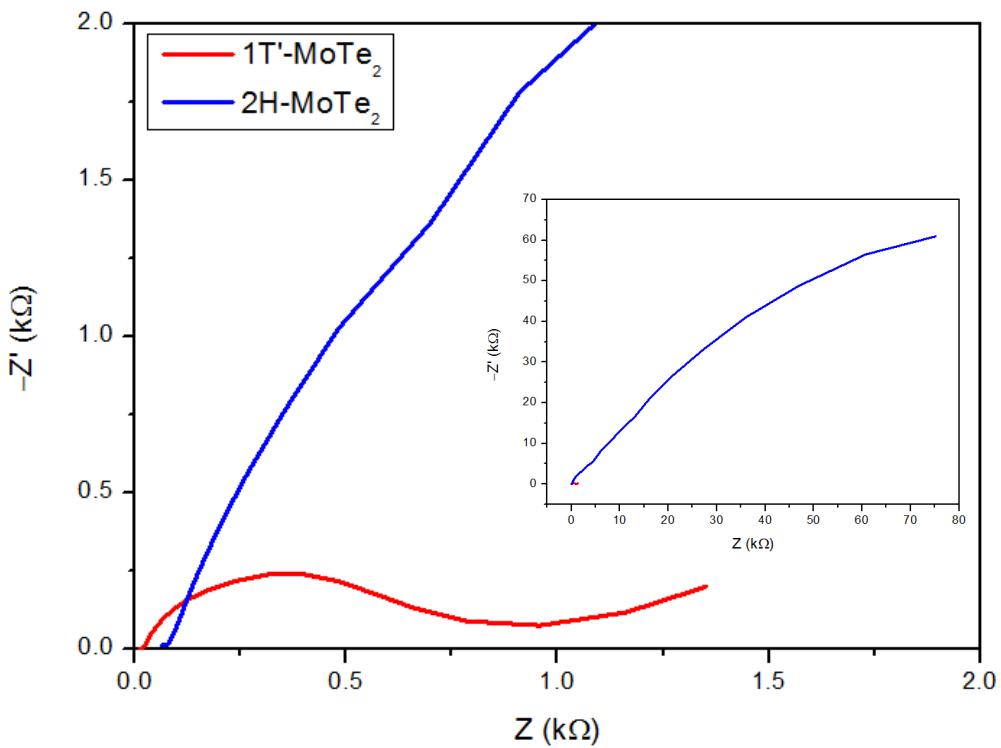


Figure S5: Nyquist plot showing electrochemical impedance spectroscopy on $2H\text{-MoTe}_2$ and $1T'\text{-MoTe}_2$ catalysts in 1 M H_2SO_4 electrolyte at a potential of -0.2 V (vs. NHE). The inset shows $2H\text{-MoTe}_2$ over the full range. Uncompensated resistances were calculated as $R_u = 63.7 \Omega$ and $R_u = 12.3 \Omega$ for $2H\text{-MoTe}_2$ and $1T'\text{-MoTe}_2$, respectively. These values are in close agreement with the iR compensation function on the potentiostat, which gave values of 67.9Ω and 12.7Ω .

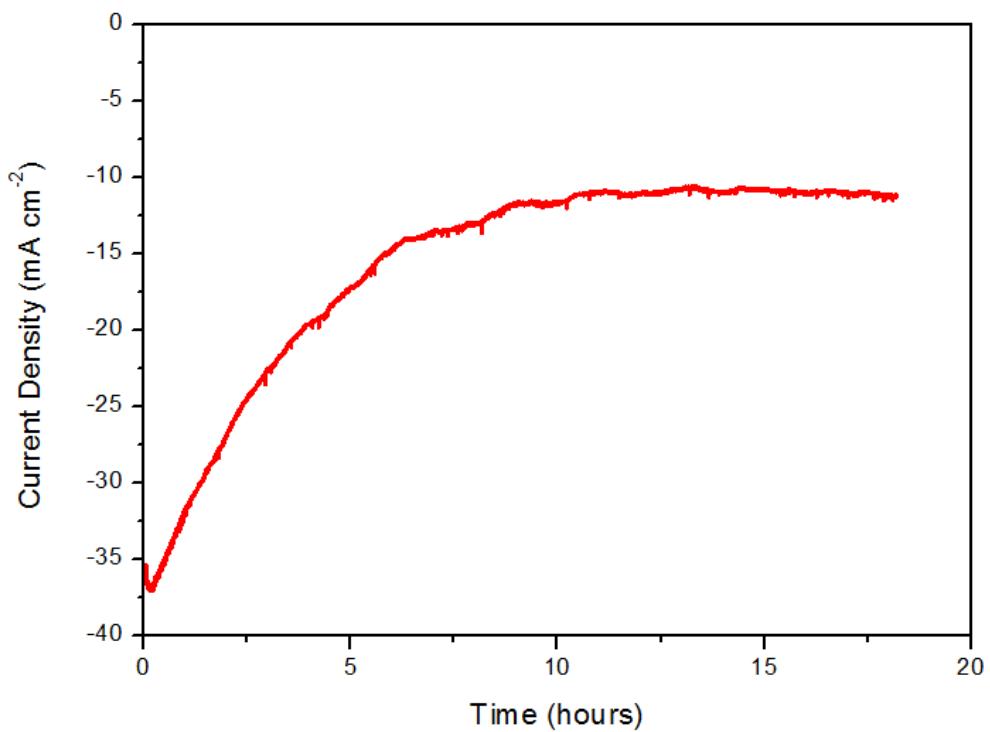


Figure S6: Bulk electrolysis of $1T'\text{-MoTe}_2$ on a glassy carbon working electrode in 1 M H_2SO_4 . A constant overpotential of -0.34 V was applied corresponding to an expected current density of 10 mA cm^{-2} (see Figures 3 and 4 in the main text).

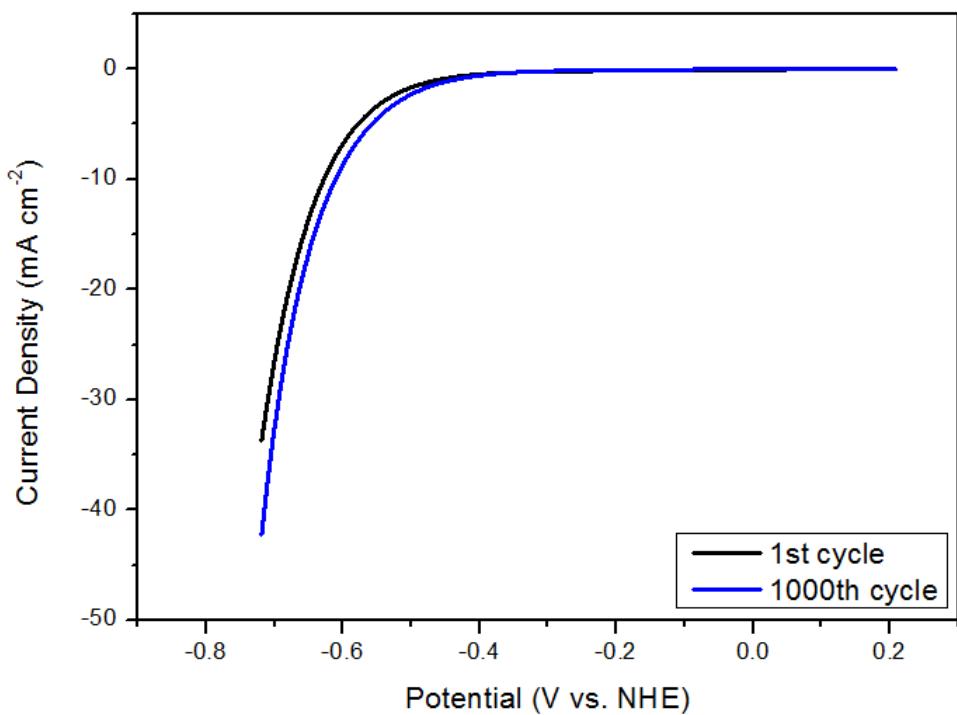


Figure S7: Stability test of 2H-MoTe₂ performed by continuous cyclic voltammetry measurements. The potential was swept between 0.2 and −0.74 V (vs. NHE) for 1000 cycles at a scan rate of 0.1 V s^{-1} in 1 M H₂SO₄ electrolyte.

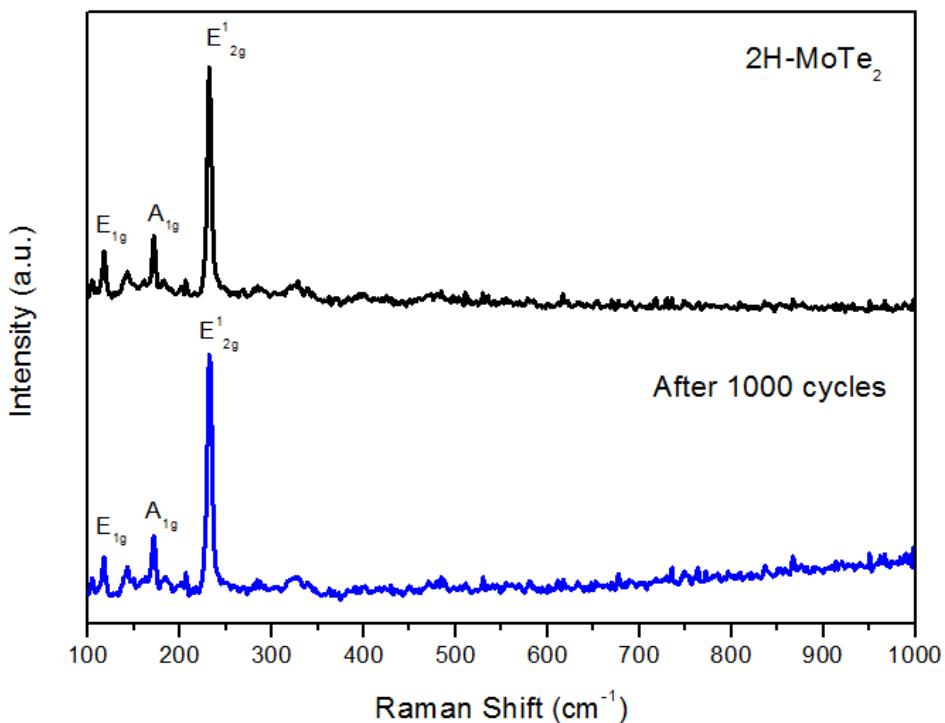


Figure S8: Comparison of the Raman spectra of 2H-MoTe₂ obtained before and after stability tests. The increased background after 1000 cycles is most likely due to the presence of Nafion within the sample after electrochemical tests.

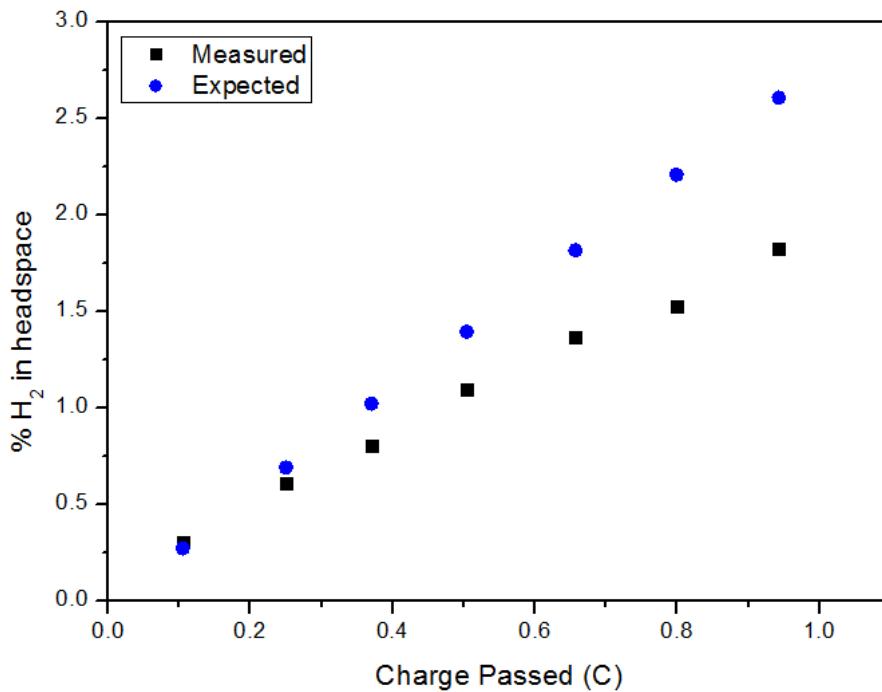


Figure S9: Gas chromatographic analysis of the single cell headspace during electrolysis of 2H-MoTe₂ where a constant current of -0.24 mA was applied in 1 M H₂SO₄. The expected % of hydrogen in the headspace was calculated based on the charge passed, while the experimentally measured % of hydrogen was determined by gas chromatography.

Estimation of turnover frequencies:

The surface area of MoTe₂ was calculated from BET measurements. Since the number of hydrogen binding sites on MoTe₂ is not known, the turnover frequencies were estimated per surface atom of both Mo and Te.^[1]

Turnover Frequency Calculation:

Molar mass: 351.14 g/mol

Density: 7.7 g/cm³

Molar volume: 45.60 mL/mol

Current density at 340 mV overpotential: 0.010 A cm⁻² (1T'-MoTe₂); 0.001 A cm⁻² (2H-MoTe₂)

BET Surface Area: 24.31 cm²/mg

Average surface atoms per 1 cm²:

$$\left(\frac{3 \times 6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{45.60 \text{ cm}^3} \right)^{\frac{2}{3}} = 1.16 \times 10^{15} \frac{\text{atoms}}{\text{cm}^2}$$

Surface atoms per testing area (Glassy carbon electrode: 0.071 cm²):

$$\frac{1 \text{ mg}}{0.071 \text{ cm}^2} \times \frac{24.31 \text{ cm}^2(\text{particle})}{1 \text{ mg}} \times \frac{1.16 \times 10^{15} \text{ atoms}}{1 \text{ cm}^2(\text{particle})} = 3.07 \times 10^{17} \frac{\text{atoms}}{\text{test}}$$

Turnover frequency (per surface atom) at η = 340 mV:

$$\begin{aligned} \frac{1 \text{ turnover}}{2 e^-} \times \frac{0.01 \text{ A}}{1 \text{ cm}^2} \times \frac{1 \text{ mol}}{96485 \text{ C}} \times \frac{6.022 \times 10^{23} \text{ e}^-}{1 \text{ mol}} \times \frac{1 \text{ test}}{3.07 \times 10^{17} \text{ atoms}} \\ = 0.102 \text{ s}^{-1} \text{ atoms}^{-1} \end{aligned}$$

Table 2: Summary of the turnover frequencies calculated at an overpotential of 340 mV.

| Sample | TOF at 340 mV overpotential |
|-----------------------|---|
| 1T'-MoTe ₂ | 0.102 s ⁻¹ atoms ⁻¹ |
| 2H-MoTe ₂ | 0.010 s ⁻¹ atoms ⁻¹ |

- [1] E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrot, N. S. Lewis and R. E. Schaak, *J. Am. Chem. Soc.* **2013**, 135, 9267-9270.