Supporting Information

MoTe$_2$ 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’-MoTe$_2$ 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 01l and 00l reflections.
Figure S2. XRD analysis of as synthesised 2H-MoTe$_2$ and calculated pattern from the ICSD database, card number 15431.

Figure S3. Raman spectrum of 2H-MoTe$_2$, indicating the absence of impurity phases. The inset shows particle morphology from SEM images.
Figure S4. SEM images of 2H-MoTe$_2$ (a,b) and 1T'-MoTe$_2$ (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 $j = 10$ mA cm$^{-2}$ and their corresponding Tafel slopes.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Overpotential for $j = 10$ mA cm$^{-2}$</th>
<th>Tafel slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H-MoTe$_2$</td>
<td>$-0.65$ V</td>
<td>$159$ mV dec$^{-1}$</td>
</tr>
<tr>
<td>1T'-MoTe$_2$</td>
<td>$-0.34$ V</td>
<td>$78$ mV dec$^{-1}$</td>
</tr>
</tbody>
</table>
Figure S5: Nyquist plot showing electrochemical impedance spectroscopy on 2H-MoTe₂ and 1T'-MoTe₂ catalysts in 1 M H₂SO₄ electrolyte at a potential of −0.2 V (vs. NHE). The inset shows 2H-MoTe₂ over the full range. Uncompensated resistances were calculated as $R_u = 63.7 \, \Omega$ and $R_u = 12.3 \, \Omega$ for 2H-MoTe₂ and 1T'-MoTe₂, respectively. These values are in close agreement with the iR compensation function on the potentiostat, which gave values of 67.9 Ω and 12.7 Ω.

Figure S6: Bulk electrolysis of 1T'-MoTe₂ on a glassy carbon working electrode in 1 M H₂SO₄. 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 H$_2$SO$_4$. 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 MoTe$_2$ was calculated from BET measurements. Since the number of hydrogen binding sites on MoTe$_2$ is not known, the turnover frequencies were estimated per surface atom of both Mo and Te.$^{11}$

**Turnover Frequency Calculation:**

Molar mass: 351.14 g/mol

Density: 7.7 g/cm$^3$

Molar volume: 45.60 mL/mol

Current density at 340 mV overpotential: 0.010 A cm$^{-2}$ (1T’-MoTe$_2$); 0.001 A cm$^{-2}$ (2H-MoTe$_2$)

BET Surface Area: 24.31 cm$^2$/mg

Average surface atoms per 1 cm$^2$:

$$
\left( \frac{3 \times 6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{45.60 \text{ cm}^3} \right)^{\frac{2}{3}} = 1.16 \times 10^{15} \frac{\text{atoms}}{\text{cm}^2}
$$
Surface atoms per testing area (Glassy carbon electrode: 0.071 cm$^2$):

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

Turnover frequency (per surface atom) at $\eta = 340$ mV:

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

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>TOF at 340 mV overpotential</th>
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<tbody>
<tr>
<td>1T'-MoTe$_2$</td>
<td>0.102 s$^{-1}$ atoms$^{-1}$</td>
</tr>
<tr>
<td>2H-MoTe$_2$</td>
<td>0.010 s$^{-1}$ atoms$^{-1}$</td>
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