

# Electronic Supporting Information

## Parameter optimization for electrochemically activated MoTe<sub>2</sub>

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### **Catalyst synthesis and characterisation:**

1T'-MoTe<sub>2</sub> was prepared using a stoichiometric mixture of elemental molybdenum (Sigma Aldrich, 99.95%) and tellurium (Alfa Aesar, 99.999%) unless otherwise stated. The powders were sealed under a vacuum pressure of  $4.5 \times 10^{-2}$  mbar in a quartz ampoule which was carefully shaken in order to homogenise the mixture. All MoTe<sub>2</sub> materials were prepared using a stoichiometric mixture of elemental molybdenum (Sigma Aldrich, 99.95%) and tellurium (Alfa Aesar, 99.999%) unless otherwise stated. The powders were sealed under a vacuum pressure of  $4.5 \times 10^{-2}$  mbar in a quartz ampoule which was carefully shaken in order to homogenise the mixture. The materials were then reacted at temperature of 400 °C (heating rate of 5 °C min<sup>-1</sup>) for 16 hours. The materials were then reground and reannealed under identical conditions. Additionally, ICP-OES measurements confirmed the elemental composition to be MoTe<sub>1.97(5)</sub> and MoTe<sub>1.98(2)</sub> before and after cycling, respectively. In the case of 1T'-MoTe<sub>1.8</sub>, the molar equivalent of tellurium was lowered by 10%, and reacted in an identical manner as described above. In the case of 1T'-MoTe<sub>2.2</sub>, the molar equivalent of tellurium was taken in excess of 10%, and reacted in an identical manner as described above.

Materials were identified as being phase pure by Powder X-Ray Diffraction (PXRD) performed on a Panalytical Xpert-pro diffractometer with Cu K $\alpha$  ( $\lambda = 1.54178$  Å) operating in Bragg Brentano geometry. Raman spectroscopy was also employed using a Horiba Jobin-Yvon LabRam Raman HR800 operating with a 532 nm laser. An aperture size of 100  $\mu$ m and a 1% filter was used in order to prevent sample degradation. XPS spectra were acquired with a K-Alpha instrument (Thermo Scientific, East Grinstead, UK) under inert atmosphere on the EPSRC National Facility for XPS ("Harwell XPS") using a micro-focused monochromatic AlK $\alpha$  source (X-ray energy 1486.6 eV, spot size 400  $\times$  800 microns). The emission angle was zero degrees and the pass energy was 200 eV for surveys and 40 eV for high resolution. Charge neutralization was enabled. The resulting spectra were referenced to the adventitious C 1s peak

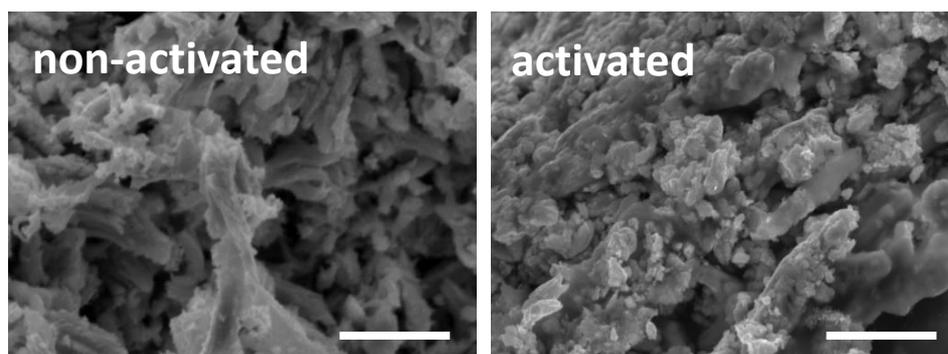
(285.0 eV). Scanning Electron Microscopy (SEM) images were obtained using a Phillips XL30 ESEM instrument coupled with an Oxford Instruments X-act spectrometer for EDX measurements. The EDX was calibrated using the INCA EDX software with Cu as the calibration standard.

### **Electrochemical characterisation:**

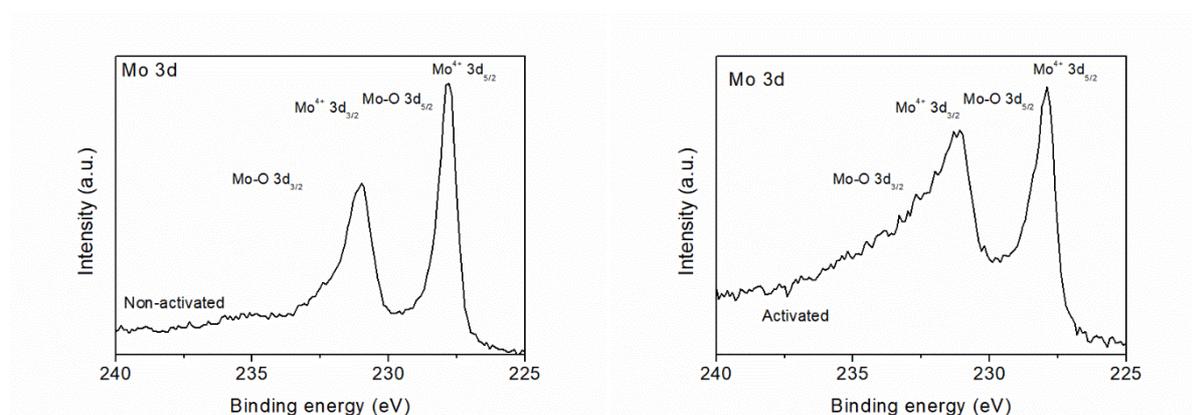
All electrochemical measurements were performed using a Biologic SP-150 potentiostat with a single cell, three-electrode setup in 1 M H<sub>2</sub>SO<sub>4</sub>, unless otherwise stated. This involved a three-necked flask containing 1 M H<sub>2</sub>SO<sub>4</sub> as the electrolyte, the catalyst-deposited glassy carbon as the working electrode, carbon felt as the counter electrode and Ag/AgCl in 3 M NaCl as the reference electrode (IJ Cambria). The electrode potentials were converted to NHE scale using  $E(\text{NHE}) = E(\text{Ag}/\text{AgCl}) + 0.209 \text{ V}$ .

Catalysts were depositing on the glassy carbon working electrode by preparing the catalyst as an ink. This involved sonicating 10 mg of catalyst in 1 ml water:ethanol (3:1) and 80  $\mu\text{L}$  Nafion. 30  $\mu\text{L}$  of this ink was then deposited on to the surface of glassy carbon, yielding a catalyst loading of 3.94 mg cm<sup>-2</sup>.

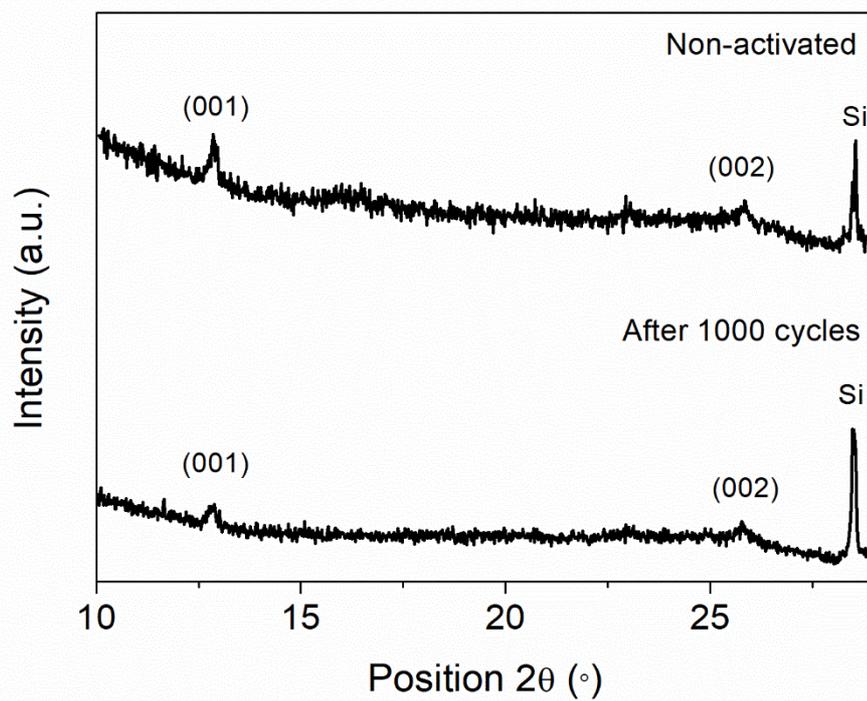
Cyclic voltammetry (CV) was performed with a scan rate of 100 mV s<sup>-1</sup>, while linear sweep voltammograms (LSV) were collected with a scan rate of 2 mV s<sup>-1</sup>. Tafel slopes were then extrapolated using data collected by LSV. Chronoamperometry was performed using an identical three-electrode set up, with a constant potential of -400 mV (vs. NHE) being applied.



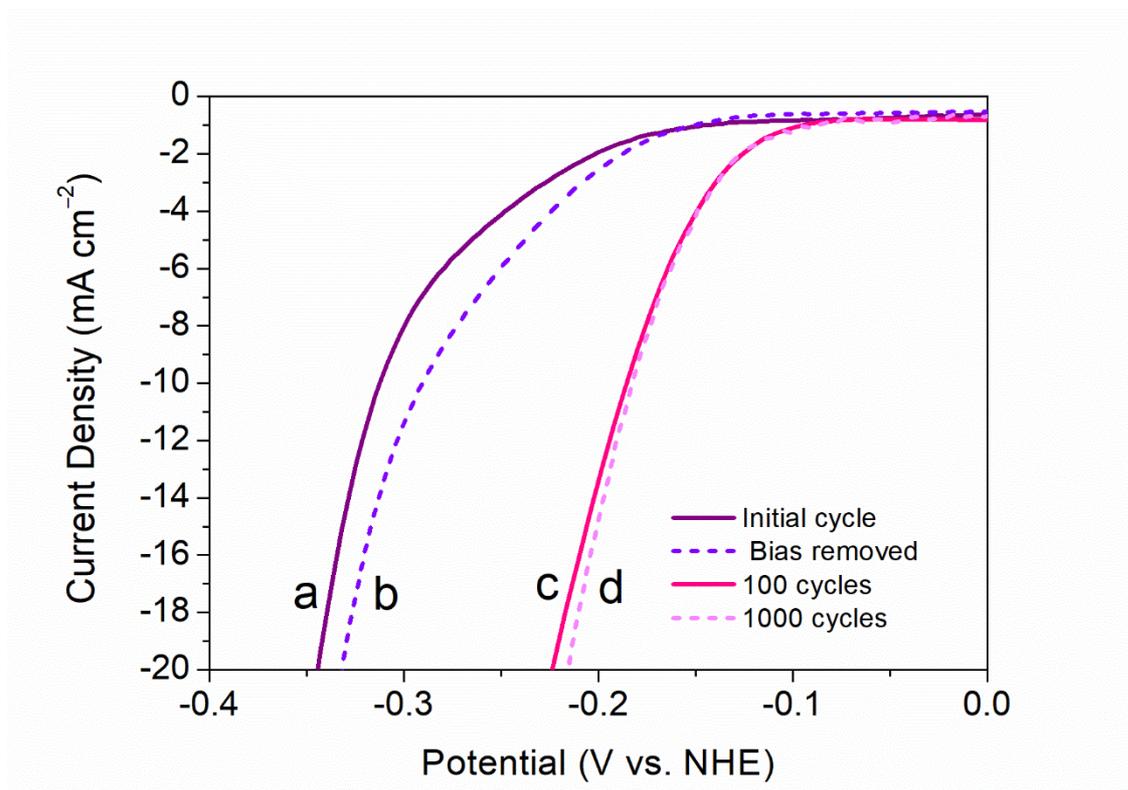
**Figure S1:** SEM images of nanocrystalline 1T'-MoTe<sub>2</sub> before and after activation by cycling 100 times. The cycling CV scans were carried out in 1 M H<sub>2</sub>SO<sub>4</sub> between the potential range of +0.2 V and -0.5 V (vs. NHE). The scale bar is 10 nm.



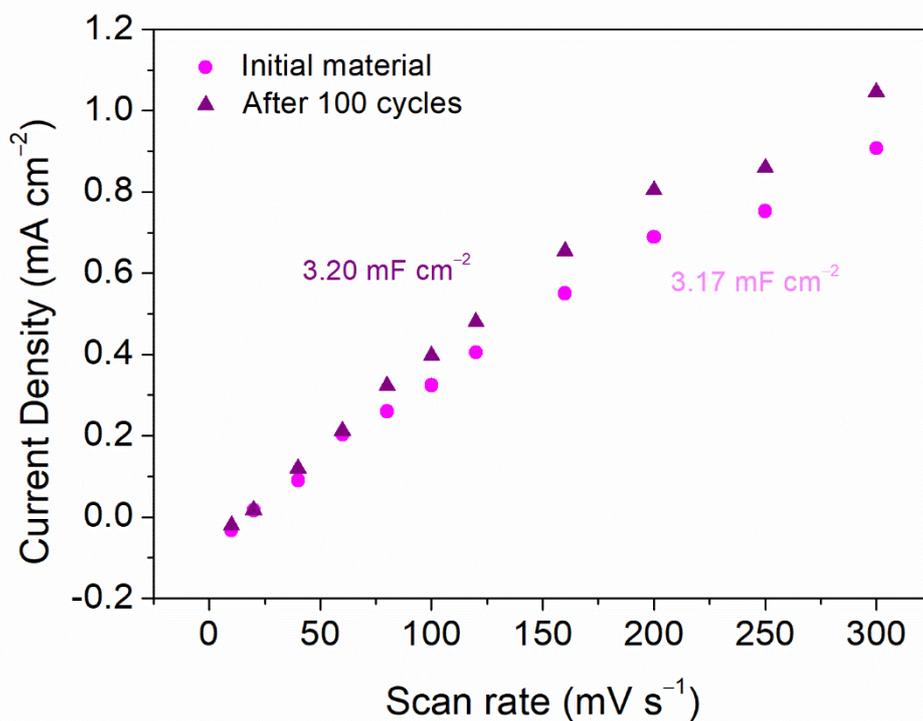
**Figure S2:** XPS of 3d Mo spectra. (left) After 1 cycle and (right) after 100 cycles. Electrochemical activation was carried out by sweeping the applied potential between +0.2 V and -0.5 V (vs. NHE) under inert gas conditions. The measurements were carried *ex situ* on the materials kept under inert atmosphere.



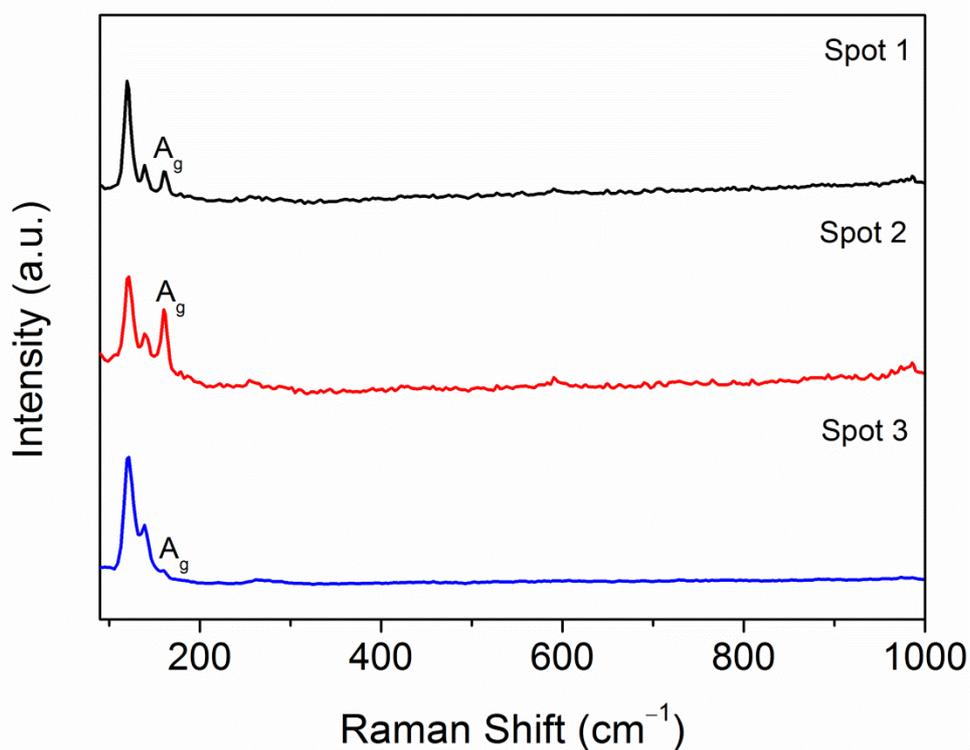
**Figure S3:** PXRD patterns of the initial nanocrystalline 1T'-MoTe<sub>2</sub> material before activation (top) and after 1000 CV cycles (bottom). Patterns were obtained directly on the glassy carbon electrode surface on which the catalyst ink was deposited. Si powder was used as an internal standard.



**Figure S4:** Comparison of the current densities achieved by nanocrystalline 1T'-MoTe<sub>2</sub> (a) after 1 cycle; (b) the polarisation curve obtained when the cathodic bias is removed after activation; (c) after 100 cycles and (d) after 1000 cycles in 1 M H<sub>2</sub>SO<sub>4</sub> between the potential range of +0.2 V and -0.5 V (vs. NHE).



**Figure S5:** Current density differences of nanocrystalline 1T'-MoTe<sub>2</sub> before and after 100 cycles plotted against scan rates. The capacitance currents were measured at 150 mV (vs. NHE).



**Figure S6:** Wide-range Raman spectra of nanocrystalline 1T'-MoTe<sub>2</sub> measured after 50 cycles ranging between +0.2 V and -0.6 V. The A<sub>g</sub> band of 1T'-MoTe<sub>2</sub> is highlighted for clarity. Bands observed at 123 cm<sup>-1</sup> and 142 cm<sup>-1</sup> are attributed to elemental tellurium.

**Table S1:** Electrochemical processes during the H evolution reaction in acidic electrolyte

Volmer step	$\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$	Discharge step
Heyrovsky step	$\text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$	Electrochemical desorption step
Tafel step	$\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$	Recombination step