

Layered MAX phase electrocatalyst activity is driven by only a few hot spots

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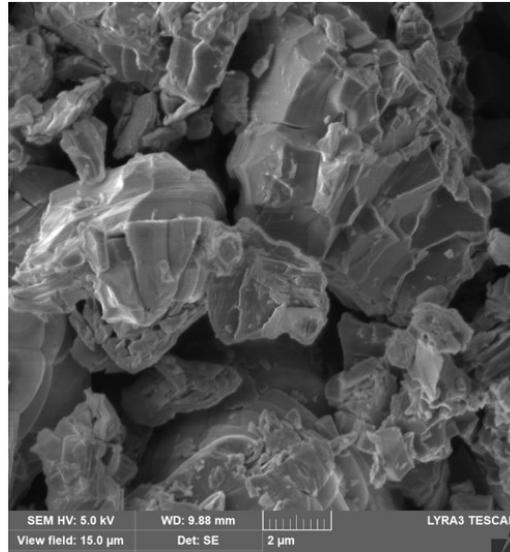


Figure S1. SEM micrograph of the $\text{Mo}_2\text{TiAlC}_2$ microparticles

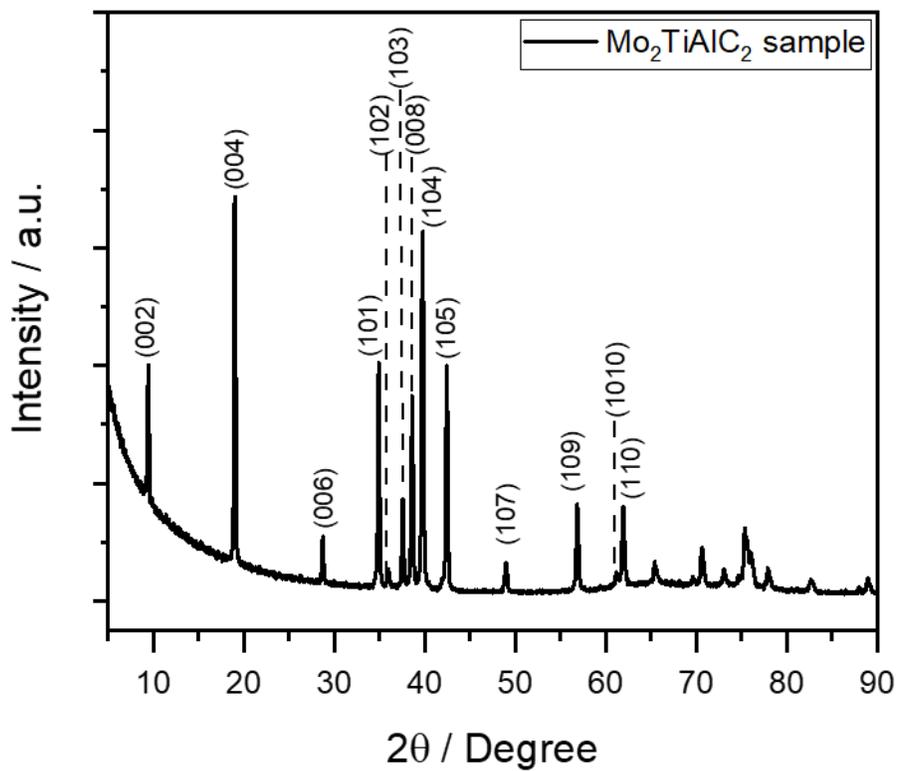


Figure S2. X-ray diffraction pattern of the $\text{Mo}_2\text{TiAlC}_2$ sample without Nafion with indicated crystal phases.

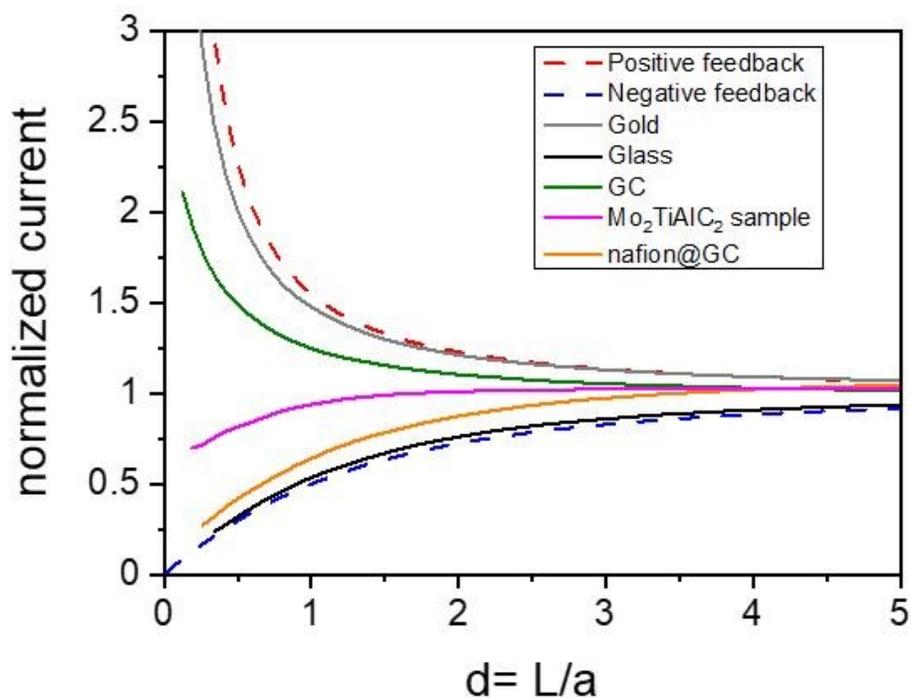


Figure S3. Probe approach curves (PACs) for the theoretically calculated positive and negative feedback (dash lines) with the measured curves for glass (black), gold (gray), glassy carbon (GC) (green), glassy carbon covered with Nafion (nafion@GC) (yellow) and $\text{Mo}_2\text{TiAlC}_2$ film (magenta). The PACs measurements were performed with 25 μm diameter Pt UME in FcMeOH mediator solution with UME tip potential of 0.64 V (vs RHE). A max. approach speed of 1 $\mu\text{m s}^{-1}$, step width of 1 μm and waiting time of 0 ms was used.

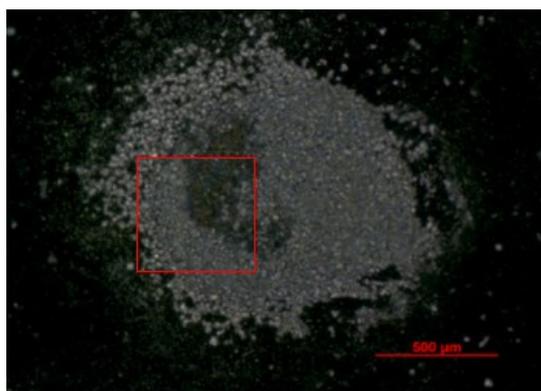


Figure S4. Optical image of the $\text{Mo}_2\text{TiAlC}_2$ film with marked scanning area (red).

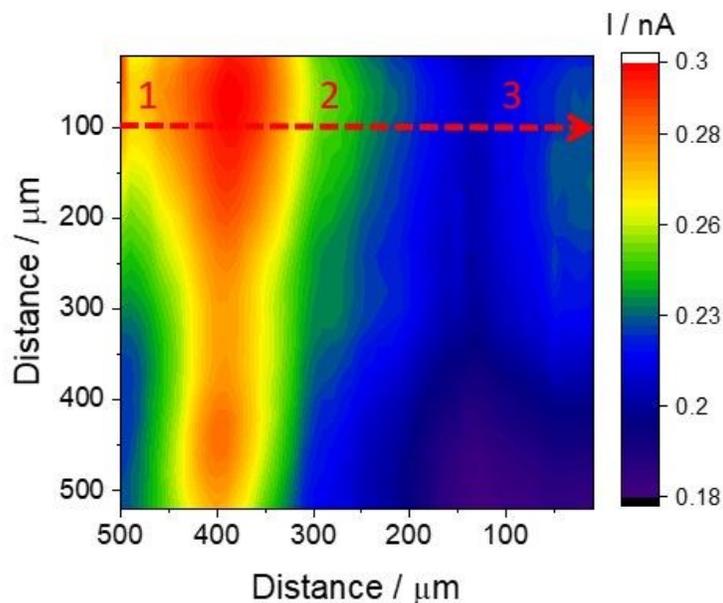


Figure S5. Scanning electrochemical image of the $\text{Mo}_2\text{TiAlC}_2$ film recorded in substrate generation/tip collection mode in 0.5 M H_2SO_4 solution with the tip potential of 0.1 V and generation hydrogen potential of -0.55 V, with labeled high (1), medium (2) and low (3) HER active points. For imaging a maximum scan rate of $300 \mu\text{m s}^{-1}$, pixel size of $10 \times 10 \mu\text{m}$ and waiting time of 4 ms was used. The SECM image was recorded with $25 \mu\text{m}$ diameter Pt disc UME.

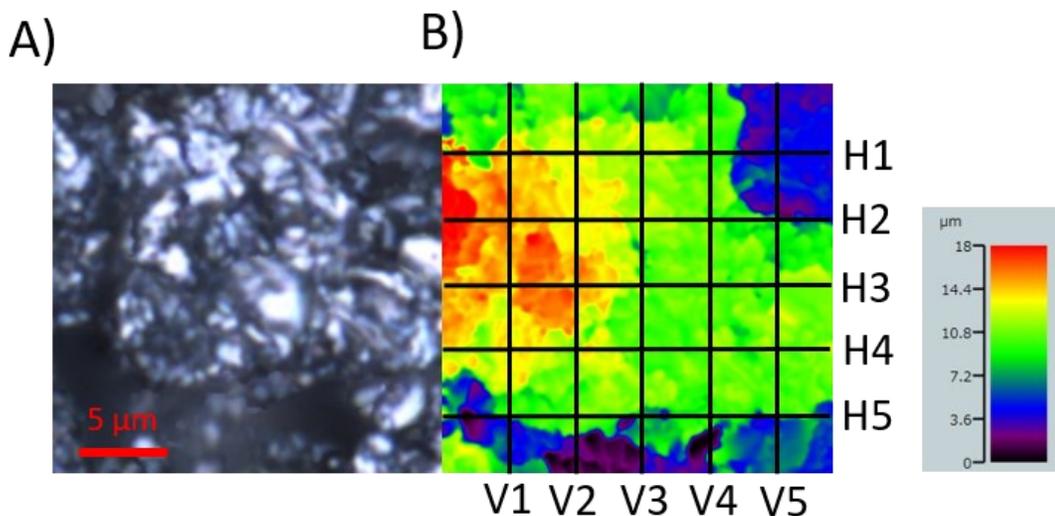


Figure S6. Optical microscopic characterization of the $\text{Mo}_2\text{TiAlC}_2$ films performed by confocal laser scanning microscopy (CLSM) with 100x lenses. (A) Color CLSM image of the $22 \times 22 \mu\text{m}^2$ surface area, (B) corresponding false-color image with indicated line roughness measurements (black lines), V-vertical line and H-horizontal line.

Table S1. R_q values of the line roughness measurements of the $\text{Mo}_2\text{TiAlC}_2$ film.

Line	$R_q / \mu\text{m}$
Vertical 1 (V1)	0.152
Vertical 2 (V2)	0.127
Vertical 3 (V3)	0.145
Vertical 4 (V4)	0.142
Vertical 5 (V5)	0.160
Horizontal 1 (H1)	0.154
Horizontal 2 (H2)	0.139
Horizontal 3 (H3)	0.151
Horizontal 4 (H4)	0.112
Horizontal 5 (H5)	0.167

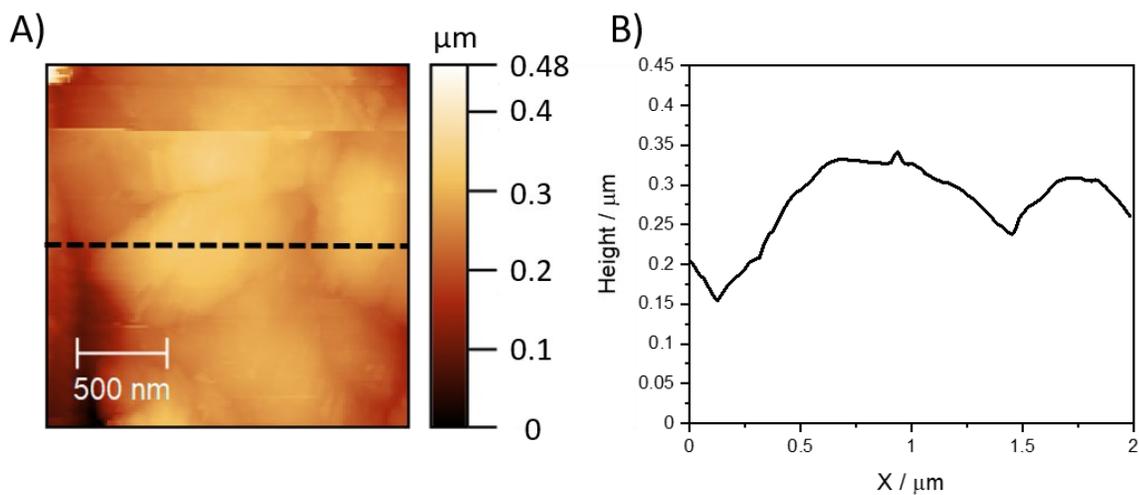
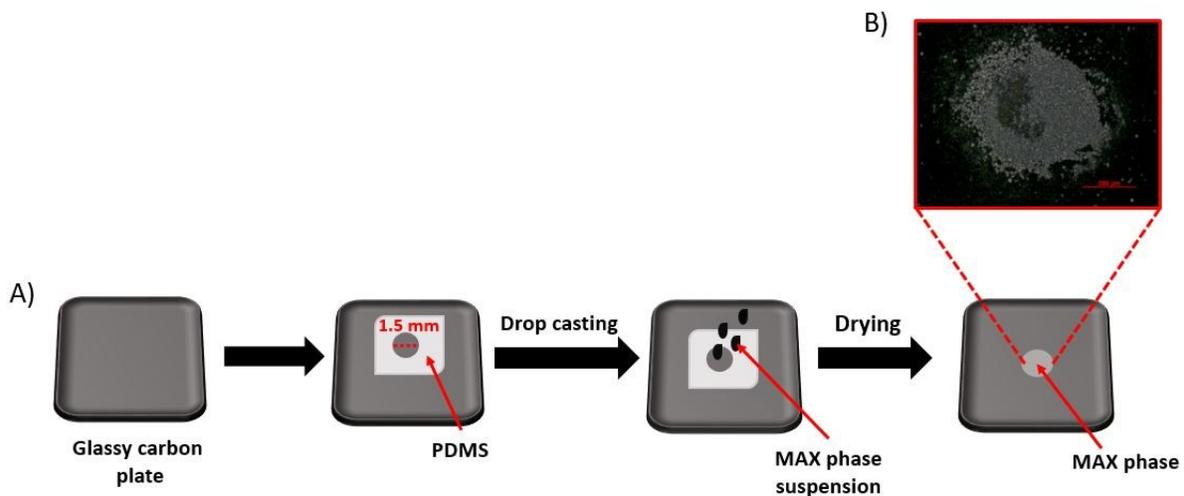


Figure S7. Atomic force microscopy (AFM) analysis of the $\text{Mo}_2\text{TiAlC}_2$ films. (A) AFM image of the $\text{Mo}_2\text{TiAlC}_2$ particle, (B) extracted line scan profile corresponding to the dashed line in (A).



Scheme S1. (A) Schematic illustration of the $\text{Mo}_2\text{TiAlC}_2$ sample preparation with (B) the optical image of the prepared $\text{Mo}_2\text{TiAlC}_2$ film.

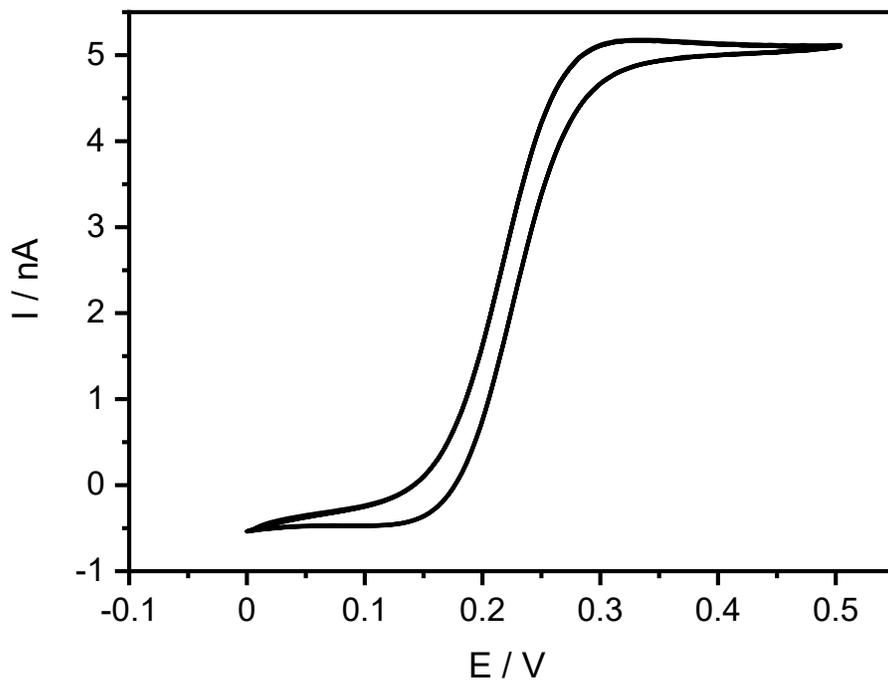


Figure S8. Cyclic voltammogram of 25 μm diameter Pt UME tip probe. Measurement was done in 1.5 mM FcMeOH and 0.2 M KNO_3 mediator solution with a scan rate of 50 mV s^{-1} .