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Intikhab, S., Natsu, V., Li, J., Li, Y., Tao, Q., Rosén, J., Barsoum, M. W., Snyder, J., (2019), Stoichiometry and surface structure dependence of hydrogen evolution reaction activity and stability of MoxC MXenes, *Journal of Catalysis*, 371, 325-332. <https://doi.org/10.1016/j.jcat.2019.01.037>

Original publication available at:

<https://doi.org/10.1016/j.jcat.2019.01.037>

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Stoichiometry and Surface Structure Dependence of HER Activity and Stability of Mo_xC MXenes

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Abstract

The exploration of non-precious catalysts for the hydrogen evolution reaction (HER) remains critical in the commercialization of electrochemical energy storage and conversion technologies. Two-dimensional transitional metal carbides called MXenes have been found to have great potential as electrocatalysts for HER. In this work, we synthesize two Mo based MXenes: Mo_{1.33}CT_z and Mo₂CT_z and measure their HER activity and operational durability. The ordered divacancies on the basal planes of Mo_{1.33}CT_z cause a marked decrease in HER activity compared to Mo₂CT_z. The stoichiometry and atomic surface structure of MXenes is found to be critically important for catalytic activity while having less of an impact on operational durability. This work provides insight for the development active 2D materials for HER and other technologically relevant electrochemical reactions.

1. Introduction

Advances in electrochemical energy storage and conversion are required to drive commercialization of renewable energy technologies, i.e. solar and wind, bridging the gap between peak power production and peak energy demand. Hydrogen sourced from water, with its high energy density and single intermediate electrochemical oxidation/reduction reactions, is an ideal carbon neutral electrochemical fuel, storing intermittent renewable energy in the form of chemical bonds¹. The cathodic production of hydrogen gas through water electrolysis, H₂-evolution reaction

(HER), is traditionally driven with nanostructured Pt or other platinum group metals (PGM)^{2,3}. However, commercialization of electrochemical energy storage and conversion technologies, specifically fuel cells and electrolyzers, is reliant upon the development of new electrocatalytic materials that reduce operational overpotentials and lower, or eliminate, PGM loadings. Significant effort has centered on the development of non-PGM HER electrocatalysts including sulfides^{2,4-6}, nitrides⁷, carbides^{8,9}, phosphides^{10,11}, etc., possessing a range of stoichiometries and morphologies. To this point, however, limitations associated with activity and operational durability of these materials remain³.

Molybdenum carbide is one of the most widely studied transition metal carbide based catalysts for HER^{9,12-15}. Vrubel et al. showed that the activity of bulk Mo₂C is relatively independent of pH, with overpotentials at 10 mA/cm², η , at pH 0 and 14 of 209 mV and 191 mV⁹, respectively. Since then, many different phases of Mo_xC such as α -Mo₂C, β -Mo₂C, η -MoC, and γ -MoC, among others, have been assessed for their HER activity^{9,13-15}. Furthermore, various strategies including nano-structuring, N/S doping, etc. have also been used to further improve the performance of the Mo_xC catalysts^{8,13-16}. Significant reduction in HER η for Mo_xC materials has been achieved through N/S doping of either the supporting material¹⁵ or the Mo_xC materials themselves¹⁶. The effect of covalent interaction between the active Mo sites in the material and dopants induces a redistribution of charge, optimizing the adsorption free energy of the H intermediate.^{15,16}

MXenes, an exfoliated material possessing the general formula M_{n+1}X_nT_z (n = 1-3) where M is a transition metal, X is carbon and/or nitrogen, and T_z represents surface functional groups including -O, -OH, and -F, are derived from the selective etching of the A-layers from MAX phases^{17,18}. MAX phases are ternary layered hexagonal machinable carbides and nitrides where M is an early transition metal, A is an A group element and X is either C and/or N. MXenes possess a broad range of properties that make them attractive materials for electrocatalysis^{8,19}. Recent computational and experimental analysis of Mo based MXenes have demonstrated their potential as an effective HER catalyst^{8,20,21}. DFT analysis of HER reactive intermediate adsorption on M₂CT_z (M = transition metal) single layer materials predicted a near thermoneutral free energy of adsorption for H ($\Delta G_{H_{ad}}$) over a wide range of H surface coverages, with Mo₂CT_z sitting close to the peak of the reactivity volcano²⁰. Seh et al.⁸ measured the HER activity of Mo₂CT_z experimentally and found it to be a promising HER catalyst, reporting an overpotential of 283 mV

at 10 mA/cm². Respectable HER activity has also been demonstrated for Mo-based 2D borides following etching of Al from the MoAlB MAB phase, exposing the catalytically active basal planes²¹. Even though both the β -Mo₂C¹⁶ nanosheets and Mo₂C MXene⁸ have similar nanostructures, the overpotentials (320 mV and 283 mV respectively, in 0.5 M H₂SO₄) are significantly different indicating a role of crystal structure and surface terminations on the catalyst activity. Atomic scale defects/vacancies can have significant effects on electrocatalytic activity as demonstrated for Mo₂C where surfaces possessing an off-stoichiometry and Mo³⁺ defects are found to have enhanced HER activity²². For oxidative reactions, lower coordinated defects can promote the formation of participatory hydroxyl species^{23–30}. For reductive reactions, surface defects in the form of vacancies can potentially increase the active site density (higher population of reactive, dangling bonds), change the intrinsic conductivity of the catalyst³¹, or manipulate the electronic properties of the surface. All of these effects have the potential to impact catalyst activity.

Typical methodologies for introducing defects, however, lack control over the defect type, extent and density of defect distribution throughout the material, and are typically limited to macroscale defects. A new type of chemically ordered quaternary MAX phase, *i*-MAX, of the general formula $(M_{2/3}^1 M_{1/3}^2)_2 AlC$ ^{32,33}, evolves into a MXene, upon etching, possessing ordered divacancies present in a chain-like sinusoidal pattern^{31,32,34}. A Mo-carbide MXene with ordered divacancies, possessing the stoichiometry Mo_{1.33}CT_z, can be formed through the etching of Al and Sc/Y from $(Mo_{2/3}Sc_{1/3})_2 AlC$ or $(Mo_{2/3}Y_{1/3})_2 AlC$, respectively^{31,35}. The result is a Mo_{1.33}CT_z 2D MXene with ordered divacancies, imparting both an enhanced conductivity and electrochemical capacitance to the material³¹.

In this work, we assess and compare the stoichiometry and surface structure dependency of HER activity and operational durability for Mo based MXenes; Mo_{1.33}CT_z vs. Mo₂CT_z. Comparison of the HER activities indicates a marked decrease in activity for the Mo_{1.33}CT_z, containing ordered divacancies^{31,36}, with respect to Mo₂CT_z. We hypothesize that the presence of the vacancy defects on Mo_{1.33}CT_z basal surfaces changes the average coordination of carbon and -O terminated Mo sites, resulting in a detrimental effect to the adsorption of the reactive H intermediate. Further, the activity of both MXenes, as with other Mo carbide electrocatalysts, was found to be independent of pH. This is in contrast to Pt, and other PGM materials, in which the

HER activity at alkaline pH is found to be orders of magnitude lower³⁷. Operational durability testing through load cycling indicates acceptable stability of both Mo₂CT_z and Mo_{1.33}CT_z.

2. Experimental Details

2.1 Mo₂Ga₂C Synthesis

The Mo₂Ga₂C MAX phase, used as a precursor for making Mo₂CT_z MXene, was synthesized according to a process reported previously by Halim et al.³⁸ Briefly, α -Mo₂C, (~99.5% purity, Alfa Aesar, USA) powder was mixed with gallium, Ga, metal in a 1:8 molar ratio, respectively. To ensure a homogeneous mixture, Ga shot, with a melting point close to room temperature, was added to the α -Mo₂C powder in a mortar and mixed thoroughly using a pestle until a homogenous slurry was obtained. This mixture was then transferred to a quartz tube, which was evacuated using a mechanical vacuum pump. The vacuum (~ 90 kPa) was pulled for 1 h and then the tube was purged with argon, Ar. This step was repeated 3 times to ensure all residual air was displaced. Vacuum was pulled overnight, and the quartz tube was sealed off while under vacuum. The tube was then placed vertically in a box furnace and heated in air to 850°C at a heating rate of 5°C/min, and held at that temperature for 168 h and then cooled to room temperature (RT). To dissolve excess Ga, the resulting powders were removed from the tube and soaked in 12 M hydrochloric acid, HCl, under 500 rpm stirring at RT for 12 h. After HCl treatment the powders were washed to neutral pH using DI water and air dried before further use.

2.2 Mo₂CT_z MXene Synthesis

One gram of Mo₂Ga₂C powder was slowly added to 40 mL of 14 M solution of hydrofluoric acid, HF, and stirred at 500 rpm at 55°C for 168 h. After etching, the acidic slurry was carefully added to a centrifuge tube and DI water was added to the solution which was subsequently centrifuged at 3500 rpm for 2 mins. After centrifugation, the clear supernatant was discarded, and DI water was added again and the tube was thoroughly shaken. This process was repeated several times until the pH of the supernatant was > 6. The thick slurry obtained after the last wash was added to 2 ml of 1.5 M tetrabutylammonium hydroxide, TBAOH, solution. The mixture was then shaken using a vortex mixer for 0.5 h to promote TBA⁺ ion intercalation. Then 40 ml of 200 proof ethanol, EtOH, was added, and the solution was further shaken for 2 mins and centrifuged at 3500 rpm for 2 mins. The EtOH supernatant was then discarded and the process was repeated 3 more

times. The ethanol step was carried out to wash off any excess TBAOH, since it is known to be a good solvent for TBAOH. It also prevents MXene from deflocculating. After the final wash, 30 ml of DI water was added to the MXene slurry which was subsequently shaken for 0.5 h to form a Mo_2CT_z colloidal suspension. To separate the non-delaminated MXene particles, the colloidal solution was centrifuged at 3500 rpm for 0.5 h and the supernatant was stored for further use. To measure the MXene concentration, a known volume of colloid suspension was vacuum filtered through a Celgard membrane. The vacuum filtered films were then peeled off and dried in vacuum at 100 °C for 12 h before weighing. This free standing MXene paper was used for XRD analysis.

2.3 $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ Synthesis

To synthesize the $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ MAX phase, graphite (99.999%), Mo (99.99% Sigma-Aldrich), Al (99.8% Alfa Aesar), and Sc (99.99% Stanford Advanced Material) powders were mixed in an agate mortar in the $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ stoichiometric ratio and heated to 1500°C in an alumina crucible under flowing Ar for 20 h. After cooling down to RT in the furnace, a loosely packed powder was obtained. The powder was crushed and passed through a 200 mesh sieve (particle size <74 μm).

2.4 $\text{Mo}_{1.33}\text{CT}_z$ MXene Synthesis

One gram of $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ powder was added to 20 mL of 28 M HF solution and stirred at RT and 500 rpm for 24 h. After etching, the washing and delamination procedures were similar to those described above for Mo_2CT_z . Briefly, the etched $\text{Mo}_{1.33}\text{CT}_z$ powders were washed with DI water until the pH of the supernatant was ~7. This was followed by TBA^+ ion intercalation. The excess TBAOH was removed with EtOH followed by formation of a colloidal suspension with DI water. The colloidal suspension was centrifuged at 3500 rpm for 0.5 h to separate out any non-delaminated particles.

2.5 Electrochemical Measurements

The electrochemical experiments were conducted in a three electrode FEP electrochemical cell with an Autolab (PGSTAT302N) potentiostat. HER activity was measured using a rotating disk electrode (RDE) setup at a rotation rate of 1600 rpm. MXenes were used to prepare catalytic inks by diluting with ultrapure DI water. A known volume of ink was drop-cast onto a glassy carbon (GC) disk (5 mm diameter) and dried under Ar (Research grade, Airgas) flow. The disk

was mounted in a hanging meniscus holder and transferred into the electrochemical cell with H₂ purged electrolyte under potential control. The electrolytes were prepared with high purity HClO₄ (70 wt%, Suprapur, Merck) or KOH pellets (99.99% [metal basis], Sigma) and 18.2 MΩ cm Milli-Q water. GDL carbon paper was used as the counter electrode and a Ag/AgCl reference (BASi) electrode was used for all measurements. All potentials, reported in the manuscript, have been converted to the reversible hydrogen electrode (RHE) scale. All voltages were corrected for iR drop.

2.6 Material Characterization

A VersaProbe 5000 spectrometer (Physical Electronics, Chanhassen, Minnesota, USA) was used for X-ray photoelectron spectroscopy (XPS) surface analysis. The glassy carbon disks unto which the MXene was drop cast, were directly mounted on the sample holder in the XPS. A pass energy of 23.5 eV was used for all scans. The step size and step times were set to 0.050 eV and 100 ms, respectively. No Ar⁺ sputtering was used during this analysis. The number of repeat scans was set to 25. CasaXPS Version 2.3.19PR1.0 software was used for peak fitting using the similar procedure outlined in Refs.^{31,38}. The XPS spectra was calibrated by setting the valence edge to zero. Because MXenes are conductive, asymmetric peaks were used to fit the Mo-C regions. The separation between the 3d_{5/2} and 3d_{3/2} peaks of Mo was constrained to 3.2 eV for the Mo-C peaks and 3 eV for the oxide peaks. The area ratio of the 3d_{5/2} to 3d_{3/2} peaks was constrained to 3:2.

X-ray diffraction (XRD) patterns were recorded using a diffractometer (Rigaku Smart Lab, Tokyo, Japan) with Cu K_α radiation (40 KV and 30 mA), a step size of 0.05°, and dwell time of 1.5 s, in the 2θ range of 3-65°.

Transmission electron microscopy (TEM) were performed at 120 keV on a JEOL JEM-2100 microscope.

3. Results and Discussion

XRD patterns of the parent MAX phases and their corresponding MXenes shown in Figure 1a confirm that the vacuum filtered MXene paper does not contain any residual MAX phase or other salt impurities. We can therefore attribute the electrochemical performance solely to the MXene. Further, the absence of any peak around 61°, which is attributed to the <110> family of planes, indicates that the vast majority of the flakes are parallel to the substrate. In our previous

work it has been shown that drop cast MXene sheets lie parallel to the substrate³⁹. This orientation with respect to the substrate ensures that the majority of the catalytic activity can be attributed to the basal plane of the MXene. TEM images of typical Mo₂CT_z and Mo_{1.33}CT_z colloidal solids (Figs. 1b and c) confirm that they are indeed delaminated few or single layers. Analysis of the XPS spectra, Figure 2, of the drop cast films gives calculated Mo:C ratios of 1.30 ± 0.1 for Mo_{1.33}CT_z and 2 ± 0.15 for Mo₂CT_z which is in agreement with the expected stoichiometry of the MXenes.

Figure 3a plots the anodic sweep of the HER polarization curves of Mo_{1.33}CT_z, Mo₂CT_z, and commercial Pt/C catalyst. The HER activity of Mo_{1.33}CT_z is lower than Mo₂CT_z, with overpotentials at 10 mA/cm² of 422 and 239 mV, respectively. The intrinsic per-site activity of Mo₂CT_z at low, and high, pH as a function of loading is reported as a turn over frequency (TOF) in Figure S4. To obtain these values we used the calculation procedure outlined by Seh et al.⁸, assuming all -O terminated Mo atoms to be active sites. At an overpotential of 200 mV and loading of 0.1 mg/cm², the TOF of Mo₂CT_z was found to be approximately ~ 0.03 H₂ s⁻¹ which is in line with previous results for Mo₂CT_z⁸. In order to reach a similar TOF, Mo_{1.33}CT_z requires ~ 392 mV of overpotential.

General intuition would suggest an opposing trend to that observed for HER activity as a function of surface stoichiometry for the two different Mo-carbide MXenes. Intuitively, the addition of atomic scale vacancy defects, as highlighted in the high resolution transmission electron micrographs (HRTEM) in previous characterizations of Mo_{1.33}CT_z³¹, would be expected to increase the activity due to a higher density of lower coordinated, more reactive sites and the intrinsic increase in conductivity and capacity that is observed for Mo_{1.33}CT_z³¹. Previous DFT analysis of Mo₂CT_z MXenes indicates that the lowest free energy of adsorption for H is on the -O termination of the surface, converting it to -OH⁸. This ostensibly makes the -O terminations on the surface the active sites. The -O terminated active sites can be further categorized by their particular geometry: bridge, on top, fcc, and hcp. H adsorption on -O terminated hcp sites is found to have the lowest free energy of adsorption⁸. This is an indication that hcp coordination is the desired active site geometry. Figure 4 displays the atomic geometry and coordination of both Mo₂CT_z and Mo_{1.33}CT_z from a top and in-plane view. Central to the hcp site in Mo₂CT_z is a six-fold coordinated C atom, Figure 4b. The introduction of divacancies in Mo_{1.33}CT_z changes the distribution of coordination geometries on the surface. From the structural models in Figure 4c and d, it is clear that there are no longer any hcp sites with a central 6-fold coordinated C atom. In fact, there are

no six-fold coordinated C atoms in the entire structure. We argue that it is this loss in the optimal H-adsorption site coordination and geometry that defines the observed lower activity on $\text{Mo}_{1.33}\text{CT}_z$. The cathodic shift in the onset potential for the reaction, when comparing Mo_2CT_z to $\text{Mo}_{1.33}\text{CT}_z$, points to a weakening of H adsorption, which would put $\text{Mo}_{1.33}\text{CT}_z$ lower on the right leg of the activity volcano⁸. These combined effects provide an explanation for the observed dependence of HER activity on MXene stoichiometry and surface atomic structure.

The operational stabilities of the $\text{Mo}_{1.33}\text{CT}_z$ and Mo_2CT_z electrodes are assessed through an accelerated durability testing (ADT) load cycling protocol (H_2 saturated 0.1 M HClO_4 , 1600 rpm, 50 mV/s, -0.6 to 0.1 V vs. RHE). Figure 3b shows the anodic sweep of the HER polarization curves pre- and post-ADT for both electrodes. Both Mo_2CT_z and $\text{Mo}_{1.33}\text{CT}_z$ are found to decrease in activity after 1000 ADT cycles (~ 60 mV increase in overpotential at 10 mA/cm^2 after 1000 ADT cycles). While the stoichiometry and surface coordinations are different for the two MXenes tested, the observed degree of activity decay appears to be comparable.

XPS both pre- and post-ADT is used to assess the change in surface chemistry with potential cycling. Spectra are recorded for as-made, after 3 reductive cycles, and after 1000 ADT cycles in 0.1 M HClO_4 . Figures 2a to c show the high-resolution XPS spectra of the Mo 3d region for the Mo_2CT_z electrodes and Figures 2d to f plot the same for the $\text{Mo}_{1.33}\text{CT}_z$ electrodes. In both cases, the fitting was based on the assignment of the peak at 228.5 eV to the Mo-C moiety in the MXene. The peak at ~232 eV is due to both Mo-C and Mo^{6+} , and that at ~235 eV is due to Mo^{6+} only^{31,34,38,40}. In both cases, the relative area of the latter peak increases with cycling, indicating a slow oxidation of the MXenes during HER ADT cycling. This conclusion is consistent with that of Kang et al. who also observed oxidation of commercial Mo_2C powders during HER⁴¹. Table 1 summarizes the XPS peak fitting results. A general increase in the proportion of higher valent Mo species is observed for both Mo_2CT_z and $\text{Mo}_{1.33}\text{CT}_z$ after 1000 ADT cycles. This is a direct indication of the oxidation of the MXene during HER and the argued source of activity loss during ADT. Both the increase in overpotential, Figure 3b, and the increase in higher valent Mo^{6+} species are similar for the two stoichiometries tested. This is an indication that both the degree and mechanism of degradation is the same and independent of initial surface structure. These results are in seeming contradiction to what would be expected for catalyst operation at reductive conditions. For PGM materials, a relative pH insensitive operational stability is assumed when the upper potential limit is kept below the potential for the initiation of anodic dissolution. This

inherent stability at cathodic electrolysis conditions is often assumed to translate to non-PGM materials, especially if the operational potentials remain below those that would initiate anodic corrosion of the parent metal of the non-PGM catalyst. The results presented here highlight the need to more carefully assess the operational stability of any newly developed, non-PGM catalysts even for operation under reductive conditions as they may still be susceptible to oxidation and/or hydrolysis.

The strong pH dependence of the reversible hydrogen reaction is well established for Pt and other transition metal catalysts^{1,37,42–46}. The exchange current density, a measure of the intrinsic reaction rate, for the reversible H₂ reaction on Pt is several orders of magnitude lower at pH 13 compared to pH 1^{1,37,42–46}. In Figure 5, we observe a pH independence of the HER activity on both Mo₂CT_z and Mo_{1.33}CT_z, when normalized to the reversible hydrogen electrode. This pH universal HER activity has been demonstrated for other non-PGM materials^{47,48}. However, its origin is not fully understood. Current controversy surrounding the pH dependent activity and mechanism of the H reactions³⁷ complicates any true assessment of the source of this pH universal behavior. In Figure 5, while the HER activity is essentially identical at both pH 1 and pH 13, a slight difference is observed where both stoichiometries are found to be more active at pH 13.

Previous work on Mo₂CT_z and Ti₂CT_z has demonstrated the impact of surface F passivation on HER activity. For Ti₂CT_z, the initial HER activity, at pH 1, has an overpotential of ~900 mV at 10 mA/cm²¹⁹. The observed overpotential at pH 13, however, is significantly lower at ~675 mV. Following potential cycling in a pH 13 electrolyte, the HER overpotential dramatically decreases at pH 1, matching that observed at pH 13. Post-mortem XPS analysis indicates that the as-synthesized Ti₂CT_z has a high -F termination content while that after potential cycling at pH 13 is significantly lower. It was thus concluded that cycling in pH 13 electrolyte effectively removes surface -F species, freeing active sites and resulting in the dramatic decrease in overpotential¹⁹. Figure 6 shows the F 1s XPS spectra for Mo₂CT_z and Mo_{1.33}CT_z as-synthesized, after 3 cycles, and after 1000 ADT cycles in 0.1 M HClO₄. Following similar synthesis procedures, Mo₂CT_z is found to have a F/Mo ratio of 0.13, while that for Mo_{1.33}CT_z is considerably larger at 0.92. Following three quick cycles in 0.1 M HClO₄, the Mo₂CT_z and Mo_{1.33}CT_z F/Mo ratios drastically decrease to 0.03 and 0.38, respectively. After ADT testing, no measurable -F terminations are remaining. We observe no increase, or change, in HER activity for Mo_{1.33}CT_z during the early ADT cycles while the XPS indicates a significant decrease in the -F surface coverage. This demonstrates that while

the initial F/Mo ratio is significantly higher for Mo_{1.33}CT_z, removal of that -F does not result in any increase in activity. Thus, we conclude that the difference in initial and final HER activity between Mo₂CT_z and Mo_{1.33}T_z is not due to the difference in F/Mo ratio, but rather some intrinsic property of the material surface.

4. Conclusions

In summary, we have shown that Mo based MXenes show promise as HER catalytic materials with a pH universal activity and sufficient operational durability. MXene stoichiometry and atomic surface structure is found to be critically important for catalytic activity, however, it is found to have less of an impact on operational durability. Mo_{1.33}CT_z possessing ordered surface divacancies, is less active for the HER than Mo₂CT_z which is attributed to changes in both the electronic properties of the surface, as well as a decrease in the proportion of the optimal -O terminated, hcp sites with a central six-fold coordinated C atom. This work provides important insight for the design and development of Mo-based 2D materials as effective catalysts for HER with potential application to other technologically relevant electrochemical reactions including oxygen evolution, oxygen reduction, and carbon dioxide reduction.

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6. Acknowledgements

J.S. and S.I. acknowledge support from NSF CBET-Catalysis under grant 1602886. J.R. acknowledge the Swedish Research Council for funding under grant no. 642-2013-8020, and the Knut and Alice Wallenberg (KAW) Foundation for a Fellowship grant. J.R. and M.B. also acknowledge the Swedish Foundation for Strategic Research (SSF) through project funding (EM16-0004).

7. Figures

Figure 1: (a) XRD patterns of $\text{Mo}_2\text{Ga}_2\text{C}$ MAX phase (blue), Mo_2CT_z paper (red), $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ MAX phase (green) and $\text{Mo}_{1.33}\text{CT}_z$ paper (black). TEM images of (b) Mo_2CT_z MXene flake and (c) $\text{Mo}_{1.33}\text{CT}_z$ MXene flake.

Figure 2: XPS of Mo 3d region for Mo_2CT_z , (a) as-received prior to cycling, (b) after 3 and, (c) after 1000 ADT cycles and for $\text{Mo}_{1.33}\text{CT}_z$, (d) as-received prior to cycling, (e) after 3 and, (f) after 1000 ADT cycles. All cycling was completed in H_2 saturated 0.1 M HClO_4 .

Figure 3: (a) HER activity of MXene: Polarization curves for Mo_{1.33}CT_z (red), Mo₂CT_z (blue) (mass loading: 0.1 mg/cm²), and Pt/C (black) (Pt loading: 15 μg/cm²) in H₂ saturated 0.1 M HClO₄ measured at a scan rate of 50 mV/s and rotation rate of 1600 rpm. (b) Polarization curves for Mo_{1.33}CT_z (red), Mo₂CT_z (blue) (mass loading: 0.1 mg/cm²) before (solid) and after (dashed) 1000 ADT cycles (H₂ saturated 0.1 M HClO₄, 1600 rpm, 50 mV/s, -0.6 to 0.1 V vs. RHE).

Mo₂C MXene

Mo_{1.33}C MXene

Figure 4: Mo₂C MXene: (a) top view (along c-direction) and (b) side view (along b-direction); Mo_{1.33}C MXene: (c) top view (along c-direction) and (d) side view (along b-direction). The insets in (b) and (d) show the bonding and coordination of carbon to Mo for the different MXene stoichiometries. The Mo atoms in the top (red) and bottom (blue) layer with respect to carbon are color coded for differentiation in the top view, (a) and (c).

Figure 5: pH universal HER activity of MXenes: Polarization curves for $\text{Mo}_{1.33}\text{CT}_z$ (red) and Mo_2CT_z (blue) (mass loading: $0.1 \text{ mg}/\text{cm}^2$) in H_2 saturated 0.1 M HClO_4 (solid line) and 0.1 M KOH (dashed line) measured at a scan rate of $50 \text{ mV}/\text{s}$ and rotation rate of 1600 rpm .

Figure 6: XPS spectra of F 1s spectra of, a) Mo_2CT_z and b) $\text{Mo}_{1.33}\text{CT}_z$. Black (bottom) line is F spectra of as-received samples, red (middle) is after 3 cycles, blue (top) is after 1000 cycles.

Table 1: Summary of XPS peak fittings shown in Figure 3 for Mo₂CT_z and Mo_{1.33}CT_z. The numbers in brackets in column 2 are peak locations for Mo 3d_{3/2} and full width at half maximum (FWHM) values for Mo 3d_{3/2} peaks are in brackets in column 3. The binding energy (BE) and the FWHM values for the Mo 3d_{5/2} peaks are in column 2 and 3 respectively but outside of the brackets.

Sample	BE (eV)	FWHM(eV)	Fraction	Assigned To	References
Mo ₂ CT _z (as-received)	228.3 (231.5)	0.7 (0.9)	0.85	C-Mo-T _x	38
	231.4 (234.4)	1.4(2.0)	0.15	Mo ⁺⁶	
Mo ₂ CT _z (3 cycles)	228.6 (231.8)	0.6 (0.8)	0.65	C-Mo-T _x	38
	231.8 (234.8)	1.3 (1.7)	0.35	Mo ⁺⁶	
Mo ₂ CT _z (1000 cycles)	228.4 (231.6)	0.7 (0.9)	0.57	C-Mo-T _x	38
	231.7 (234.7)	1.4 (1.6)	0.43	Mo ⁺⁶	
Mo _{1.33} CT _z (as-received)	228.5 (231.7)	0.6 (0.7)	0.83	C-Mo-T _x	31
	231.4 (234.4)	1.7 (2.0)	0.17	Mo ⁺⁶	
Mo _{1.33} CT _z (3 cycles)	228.5 (231.7)	0.6(0.7)	0.71	C-Mo-T _x	31
	231.5 (234.5)	1.6 (1.9)	0.29	Mo ⁺⁶	
Mo _{1.33} CT _z (1000 cycles)	228.0(231.2)	0.7 (0.8)	0.68	C-Mo-T _x	31
	231.0 (234.0)	1.6 (1.9)	0.32	Mo ⁺⁶	

Stoichiometry and Surface Structure Dependence of HER Activity and Stability of Mo_xC MXenes

Supporting Information

a.

b.

Figure S1: Overpotential at a current density of 10 mA/cm² as a function of loading in 0.1 M HClO_4 (red) and 0.1 M KOH (blue) for Mo_2C (a) and $\text{Mo}_{1.33}\text{C}$ (b).

a.

b.

Figure S2: Mass activity, HER current normalized by catalyst mass, as a function of loading in 0.1 M HClO₄ (red) and 0.1 M KOH (blue) for Mo₂C at an overpotential of 250 mV (a) and Mo_{1.33}C at an overpotential of 400 mV (b).

Roughness Factor Calculation

Hydrogen evolution reaction (HER) currents on PGM free catalysts are usually normalized by a capacitively measured roughness factor^{1,2}. Capacitance of Mo₂C and Mo_{1.33}C (mass loading: 0.1 mg/cm²) was calculated from double layer charging by cycling potential between 0.05 - 0.4 V (vs RHE) at different scan rates (50, 100, 150, 200, 250, 300 mV/s) as shown in Fig. S3a and Fig. S3b. The measured capacitive currents at 0.2 V (vs RHE) are plotted as a function of scan rate in Fig. S3c and the slope of the linear fit gives the specific capacitance of Mo₂C and Mo_{1.33}C. We observe a slightly higher specific capacitance for Mo_{1.33}C (24.3 mF/cm²) compared to the specific capacitance of Mo₂C (15.3 mF/cm²). Roughness factor (RF) is obtained by taking the ratio of the specific capacitance of MXenes to that of bare glassy carbon electrodes (0.0153 mF/cm²) giving values of 1000 and 1588 for Mo₂C and Mo_{1.33}C respectively. This indicates that Mo_{1.33}C has a much larger active surface area compared to Mo₂C.

Figure S3: Electrochemical capacitance measurement in 0.1 M HClO_4 at a loading of 0.1 mg/cm^2 for Mo_2C (a) and $\text{Mo}_{1.33}\text{C}$ (b). Measured capacitive currents vs. scan rate for Mo_2C and $\text{Mo}_{1.33}\text{C}$ (c). Capacitance and roughness factor (RF) are calculated from the slope.

Turnover frequency (TOF)

TOF has been calculated for Mo₂C through the following formula:

$$TOF_{avg} = \frac{\text{Number of hydrogen turnovers per geometric area}}{\text{Number of sites per geometric area}}$$

Geometric current density gives the number of hydrogen turnovers and are obtained at 200 mV overpotential. The number of sites per geometric area can be estimated from the mass loading and the DFT calculated surface coverage of Seh et al. taking all O atoms as the active sites³.

Figure S4: Turn Over Frequency (TOF) as a function of loading for Mo₂CT_x at an overpotential of 200 mV in 0.1 M HClO₄ (red) and 0.1 M KOH (blue).

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