Supporting information

Electrocatalytic CO₂ reduction on earth abundant 2D Mo₂C and Ti₃C₂ MXenes

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Table of contentsMaterials and methods	Page 3
Synthesis of Ti ₃ C ₂	3
Synthesis of Mo ₂ C	4
Electrochemical Characterization	4
Product analysis	5
Computational details	6

List of Figures

Figure S1: Gas chromatogram with and without CO ₂ for d-Mo ₂ C	8
Figure S2: Tafel plots	9
Figure S3: ¹ H-NMR spectra of the electrolytes	10
Figure S4: Chronopotentiometry curve for d-Ti ₃ C ₂	11
Figure S5: Gas chromatogram for the headspace of d-Mo ₂ C in aqueous IL	12
Figure S6: XPS spectra of Mo-3d and Ti-2p regions	13
Figure S7: XPS spectra of Mo_2C and Ti_3C_2 surfaces after electrolysis	14
Figure S8: CV curves and Δj vs scan rate plots for ECSA estimation	15
Figure S9: Reaction free energy diagram for bare d-Mo ₂ C	16
Figure S10: The relaxed structures of CO and CO ₂ on oxygenated Mo_2C and Ti_3C_2 surface	17
Figure S11: CV curve obtained for ferrocene/ferrocenium (Fc/Fc ⁺) couple in acetonitrile	18
Figure S12: The free energy diagram calculated using the PBE+U functional	19

References

20

Materials and Methods. Chemicals

All chemicals were analytical grade or technical grade and were used as received from the supplier (Fischer, Alfa Aesar and Sigma Aldrich) without further purification. 1-ethyl-3methylimidazolium tetrafluoroborate ([EMIM]BF₄) was purchased from Alfa Aesar. High purity carbon dioxide, ultra-high purity helium and ultra-high purity argon were purchased from Air Gas Company. Tetraethylammonium perchlorate (TEAP) electrochemical grade (>99.0%), acetronitrile (ACN) HPLC grade (99.9%), and silver nitrate (AgNO₃) were purchased from Fischer scientific. Silver nano powder (<100 nm, 99.5%) was purchased from Sigma Aldrich.

Synthesis of Ti₃C₂

Synthesis of the Ti₃AlC₂ MAX phase and its associated Ti₃C₂ MXene have been described previously.¹ Briefly, one gram of Ti₃AlC₂ powder was slowly added into a solution composed of 1 g lithium fluoride (LiF, Alfa Aesar, 98+ %) in 20 ml 9 M hydrochloric acid (HCl, Fisher, technical grade, 35-38%). This addition was followed by stirring at 35 °C for 24 h. The acidic suspension was washed with 100 ml of deionized (DI) water and centrifuged until a pH \ge 6 was reached and a stable dark green supernatant of Ti₃C₂ was collected after 30 min centrifugation at 3500 rpm. The resulting Ti₃C₂ supernatant solution was filtered using vacuum-assisted filtration through a polypropylene filter (3501 Coated PP, Celgard LLC, Charlotte, NC), followed by drying at room temperature under vacuum.

Synthesis of Mo₂C

The synthesis of Mo₂Ga₂C has been described previously.² The Mo₂Ga₂C powder was sieved to achieve a particle size of < 37 μ m. To prepare delaminated Mo₂CT_x (*d*-Mo₂C), 2 g of Mo₂Ga₂C powder was added to a mixture of 20 mL of 9 M hydrochloric acid (HCl; Fisher Scientific) and 4 g of lithium fluoride (LiF; Alfa Aesar) for ~ 2 min and held for 72 h at 35°C while stirring with a Teflon coated bar.³ The mixture was washed at least 5 times by adding deionized (DI) water, shaking for 1 min and centrifuging for 2 min at 3500 rpm for each of 5 cycles until a pH of > 6 was obtained. Finally the supernatant was decanted and the sediment was kept. After decantation of the last centrifuge supernatant, 40 mL of DI water was added to the residue and was sonicated for 45 min, before centrifuging for 1 h at 3500 rpm. Lastly, the supernatant was collected. The concentration of the resulting d-Mo₂CT_x colloidal solution was ~1 mg mL⁻¹.

Electrochemical Characterization

Electrochemistry was performed using a CHI660E potentiostat/galvanostat. Cyclic and linear sweep voltammetry experiments were performed using a standard three-electrode configuration. The working electrode was a homemade bare glassy carbon electrode (GCE, 5.0 mmx 5.0 mm). The catalyst ink was prepared by dispersing 5 mg of the catalyst in 1 mL of deionized water and sonicating the mixture for 1 hour. 10 uL of the catalyst was deposited on the GCE. Coiled platinum wire was used as used as the auxiliary electrode. All potentials were measured against a Ag/Ag+ reference electrode (ANE) (0.1 M AgNO3, 0.1 M TEAP, CH₃CN) and converted to the SCE reference scale using the $E_{SCE} = E_{Ag/Ag^+} + 0.430 \text{ V}$.⁴ The reference electrode was calibrated against Fc/Fc+ in acetonitrile (Figure S9). Cyclic and linear sweep voltammograms were recorded at 10

mV/s with iR drop compensation. The glassy carbon electrode was polished with a slurry of 0.05micron alumina powder in deionized (DI) water. Residual alumina was rinsed from the GCE surface with DI water, and the electrode was then sonicated in DI water for 15 minutes followed by acetone for 10 min. Cyclic voltametry and Linear Sweep voltametry (LSV) curves were obtained in CO₂ saturated acetonitrile/EMIMBF₄ (ACN/IL) media. Prior to obtaining CV or LSV curves the electrolyte was vigorously bubbled with high purity CO₂ gas for 30 min. All electrochemical experiments were carried out in a two-compartment cell separated by a cation exchange nation membrane. 10 mL of the electrolyte was filled into the cathode compartment and 6 mL onto the anode compartment. The solution was continuously stirred with a stir bar magnet at a speed 200 rpm. The headspace of the cell was purged with high purity CO₂ gas prior to any electrochemical measurements to ensure that there was a blanket of CO₂ above the electrolyte. At the end of chronoamperometric measurements the headspace was analyzed by GC. ECSA estimations were carried out in 0.1 M H₂SO₄ with 10 uL of the catalysts (Mo₂C and Ti₃C₂) deposited on 3 mm glassy carbon electrode at scan rates 20,40, 60, 80, 100 and 120 mV/s in the potential range -0.16 and -0.26 V vs SCE (Figure S6).

Product analysis

A 500 uL sample from the headspace after electrolysis was injected into a GC (Hewlett Packard series ii 5890) equipped with a ShinCarbon ST Packed Column (Restek) and a thermal conductivity detector (TCD). For analysis of CO, ultra-high purity helium (purchased from Air gas) was used as the carrier gas and for H₂ ultra-high purity Ar (purchased from Air gas) served as the carrier gas. The GC was calibrated for CO and H₂ by injecting specific volumes of the gases

into the electrochemical cell with the electrolyte saturated with CO₂ gas. The system was then allowed to equilibrate for 1hr. Thereafter, 500 uL of the headspace was injected into the GC using a gas tight syringe equipped with a sample lock. The GC oven was run at isothermal conditions (temperature 40 0 C) for 6 min followed by a temperature ramp to 100 0 C which was then held at 100 0 C for 14 min. A peak corresponding to CO appeared at 4.54 min and H₂ at 0.80 min with He carrier gas while H₂ appeared at 1.25 min with Ar carrier gas. The corresponding peaks were integrated to obtain a calibration curve. The faradaic efficiency (FE) was obtained by injecting 500 uL of the dead volume of the cathode compartment under similar conditions to the calibration. The FE was calculated using equation 1. The electrolyte was analyzed by 1H-NMR with dimethylsulfoxide (DMSO) as an internal standard.

FE %= amount of product/amount of charge passed*100

 $FE\% = \frac{(anF)}{o} x100$ (Equation 1)

where *a* is the stoichiometric amount of the specific product from the reduction of CO_2 , *n* is the number of moles of product, F is Faraday's constant (96485 Cmol⁻¹) and Q is the total charge passed during electrolysis.

Computational Details

First-principles calculations were performed using density functional theory (DFT) as implemented in the Vienna ab Initio Simulation Package (VASP)⁵. The projected-augmentedwave (PAW) potentials were used to describe ion-electron interactions.⁶ Within the framework of generalized gradient approximation, the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional⁷ were used to treat the electron exchange correlation energy. A 4x4x1 Γ-centered kpoint mesh and a plane wave basis set with an energy cut-off of 500 eV is applied for the calculations. To minimize the effect of adsorbate–adsorbate interaction, all of the surface absorption calculations were performed on a $3x_3x_1$ supercells. A vacuum distance of 20 Å was imposed to avoid the interlayer interactions. Atomic structures were relaxed until the final force exerted on each atom was less than 0.02 eV/Å and the change in total energy between the two steps was less than 10^{-5} eV. Adsorption energies were computed as $E_{ads} = E_{adsorbate + surface} - E_{adsorbate} - E_{slab}$, where $E_{adsorbate + surface}$, $E_{adsorbate}$, and $E_{surface}$ are the total energies of the adsorbed system, the gas phase species, and the surface, respectively. To take into account the strong on-site Coulomb interactions of the localized d electrons in Ti₃C₂ and Mo₂C, we include the additional Hubbard-like parameters by using the DFT+U method⁸, with a U value of 3 eV applied on both surfaces. Figure S10 shows the free energy diagrams for the electrochemical reduction of CO₂ to CO using the DFT+U method. We did not observe any significant difference in the trend for the electrochemical reduction of CO₂ to CO and the main conclusion obtained from the standard DFT calculations holds true.



Figure S1: Gas chromatograms of headspace of the cell after electrolysis with CO_2 saturated electrolyte and N_2 saturated electrolytes with *d*-Mo₂C as the catalyst. Ar carrier gas is used to identify H_2 gas and He in order to identify CO. H_2 gas has a thermal conductivity this is similar to He and Ar has a thermal conductivity similar to CO, thus different carrier gases was used for CO and H_2 analysis.



Figure S2: Tafel plots of d-Mo₂C, d-Ti₃C₂ and silver nanoparticles.



Figure S3: H-NMR spectra for the electrolyte before chronopotentiometry measurements (black) and after 30 min of electrolysis obtained from the anode (blue) and cathode (red) compartments under CO₂ saturated electrolyte conditions.



Figure S4: Chronopotentiometry curve for Ti_3C_2 . Potentials applied are recorded with respect to the SCE. At higher potentials the Ti_3C_2 shows lower current stability duruing CO_2RR .



Figure S5: Gas chromatogram from the analysis of headspace with aqueous EMIMBF₄ (96%) as the electrolyte. Electrolysis was carried out at -1.0 V vs RHE with Mo₂C as the electrode material. Large amounts of H₂ are generated with no detectable amounts of CO under aqueous conditions.



Figure S6: XPS spectra of the a) Mo_2C Mo 3d region and b) Ti_3C_2 Ti 2p region. The Mo 3d region and Ti 2p regions were fitted to emphasize the presence of different functionalities and bonds on the MXenes.



Figure S7: XPS spectra of the a) Mo_2C Mo 3d region and b) Ti_3C_2 Ti 2p region after electrolysis for 30 min at -2.4 V and -2.6 V vs SCE, repectivley. The Mo 3d region does not show noticeable changes for the Mo_2C MXene, whereas the and Ti 2p regions show a decrease in the Ti-O and Ti-F surface functional groups.



Figure S8: Cyclic voltammetry curves used to estimate the double layer capacitance for a) Mo_2C and b) Ti_3C_2 MXenes respectively. c) Plot of $\Delta j=j_a-j_c$ vs scan rate for the MXene samples. The double layer capacitance values obtained for each sample are indicated on the plot.



Figure S9: Reaction free energy diagram for CO_2 reduction to CO by using bare Mo_2C and Ti_3C_2 as a catalyst. Species attached with * represent the chemisorption.



Figure S10: The relaxed structures of (a) CO and (b) CO_2 on oxygenated Mo_2C surface. CO and CO₂ adsorption energy is ~0.02 eV. The relaxed structures of (c) CO and (d) CO₂ on oxygenated Ti₃C₂ surface. CO adsorption energy -0.05 and CO₂ -0.04 eV. The optimized distance between the surface and the adsorbent is large >3 Angstrom, and this indicates that there is no activity of the adsorbate with the surface.



Figure S11: CV obtained for ferrocene/ferrocenium (Fc/Fc⁺) couple in acetonitrile, TEAP used for the calibration of the reference electrode Ag/Ag^+ . $E_{1/2}$ for the Fc/Fc⁺ is 50 mV. The potential vs SCE is +430 mV.



Figure S12: The free energy diagram for CO_2 reduction reaction at the oxygen vacancy on Ti_3C_2 (in black) and Mo_2C (in red) calculated using the PBE+U functional with U = 3 eV.

DFT calculations with Grimme's DFT-D3

Our calculations with the dispersion corrections of Grimme's DFT-D3 and the zero-point energy and entropy corrections applied show that the activation of $*CO_2$ to *COOH in the first hydrogenation step demands free energy input of 0.97 eV and 0.65 eV in Ti₃C₂ and Mo₂C, respectively. Hence, the free energy input for Mo₂C is 0.32 eV less than that for Ti₃C₂ in the ratelimiting step.

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