

Supporting Information for:

## **New Two-Dimensional Niobium and Vanadium Carbides as Promising Materials for Li-ion Batteries**

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*Synthesis of  $M_{n+1}AX_n$  phases:* Nb<sub>2</sub>AlC powders were synthesized by mixing powders of niobium, Nb (Atlantic Equipment Engineers, Bergenfield, USA, 99.8 wt. % purity; - 325 mesh), aluminum, Al (Alfa Aesar, Ward Hill, USA, 99.5 wt.% purity; -325 mesh), and graphite, C (Alfa Aesar, Ward Hill, USA, 99 wt.% purity; - 300 mesh) in an atomic ratio of 2.0:1.1:1.0, respectively, for 18 h in a ball mill. The mixture was then heated in a tube furnace to 1600 °C at a heating rate of 5 °C/min under a flow of argon, Ar. The powder was then soaked at that temperature for 4 h, before furnace cooling to RT. Powders from the resulting lightly sintered blocks were obtained by milling using a titanium-nitride-coated milling bit. The powders were then sieved and only - 400 mesh powders were used for further experiments.

The V<sub>2</sub>AlC powders were synthesized by mixing powders of vanadium, V (Alfa Aesar, Ward Hill, USA, 99 wt% purity; -325 mesh), Al (Alfa Aesar, Ward Hill, USA, 99.5 wt% purity; -325 mesh), and C (Alfa Aesar, Ward Hill, USA, 99 wt% purity; - 300 mesh) in an atomic ratio of 2.0:1.3:1.0, respectively, for 18 h in a ball mill. The mixture was then heated in a tube furnace to 1500 °C at a heating rate of 5 °C/min under a flow of Ar. The powder was then soaked at that temperature for 4 h, before furnace cooling to RT. After cooling to RT, powders were obtained and sieved as described above for Nb<sub>2</sub>AlC. Some V<sub>2</sub>AlC powders were also attrition milled at 700 rpm for 4 h using stainless steel balls in an ethanol medium prior to their exfoliation.

*Etching of Al:* The - 400 mesh, Nb<sub>2</sub>AlC or V<sub>2</sub>AlC powders were immersed in a 50 % concentrated HF (Fisher Scientific, Fair Lawn, NJ) solution and stirred for 90 h at RT. Complete etching of Al from Nb<sub>2</sub>AlC could also be achieved by immersing the powders in a 55 °C HF solution for 40 h instead of 90 h. The attrition-milled powders were submerged in the same solution for 8 h. In all cases, after the HF treatment, the resulting suspensions were washed several times using deionized water and centrifuged to separate the settled powders from the supernatants. The settled powders were removed from vials using ethanol, and dried at RT.

*Characterization:* A XRD machine (Rigaku SmartLab, Tokyo, Japan) was used to identify the phase composition and measure the lattice parameters using a scan step of 0.02° 2 $\theta$  and 1 s per step. Silicon, Si, powder was added to some samples as an internal standard to calibrate the diffraction angles and the instrumental peak broadening. In order to obtain highly oriented samples for XRD along {000 $l$ } planes; powders were cold pressed at 450 MPa into thin discs. A SEM (Supra 50VP, Zeiss, Oberkochen, Germany) equipped with EDS (Oxford Inca X-Sight, Oxfordshire, UK) was used to investigate the chemical composition and the morphology of the particles after etching.

A TEM, FEI Tecnai G2 TF20 UT with a field emission gun operated at 200 kV and a point resolution of 0.19 nm was used for high-resolution imaging and SAED. Elemental analysis by X-ray energy dispersive spectroscopy (EDX) in the TEM was carried out using a FEI image/probe double C<sub>s</sub> corrected HRTEM (Titan3 G2 60-300 at Linköping). The instrument was operated at 300 kV with an ultra-thin window X-ray energy dispersive spectrometer and a monochromator. Plan-view TEM specimens was prepared by sonicating the MXenes powders in ethanol for 10 minutes. Then droplets from the solution were left to dry on a lacey-carbon coated copper grid (200 mesh). Cross-sectional specimens of the cold-pressed MXenes powder samples was prepared by embedding them in a Ti grid, mechanically polishing down to 50  $\mu$ m and finally ion milling to electron transparency.

*XPS Analysis:* X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical state of the particles after treatment. For the Nb<sub>2</sub>C sample, a Kratos AXIS Ultra DLD instrument was used employing a 800  $\mu$ m monochromatic Al-K $\alpha$  X-ray to irradiate the surface of the sample. Photoelectrons were collected by a 180° hemispherical electron energy analyzer.

Samples were analyzed at a 90° takeoff angle between the sample surface and the path to the analyzer. High-resolution spectra were taken at a pass energy of 20.00 eV, with a step size of 0.1 eV. For the V<sub>2</sub>C sample, a Physical Electronics VersaProbe 5000 instrument was used employing a 100 μm monochromatic Al-Kα X-ray to irradiate the sample surface. Photoelectrons were collected by a 180° hemispherical electron energy analyzer. Samples were analyzed at a 45° takeoff angle between the sample surface and the path to the analyzer. High-resolution spectra were taken at a pass energy of 11.75 eV, with a step size of 0.05 eV. The spectra of Nb<sub>2</sub>C were taken after the sample was sputtered with an Ar beam operating at 3.8 kV and 150 μA for 10 min, while the spectra of the V<sub>2</sub>C sample were taken without Ar sputtering. All binding energies were referenced to that of free carbon at 284.5 eV.

A high-resolution spectrum of the Nb<sub>2</sub>CT<sub>x</sub> layers in the Nb 3d region (Figure S1a) revealed the presence of photoemission which could be best fit with components corresponding to:

- i) MXene, Nb<sub>2</sub>C, (33.3% of Nb 3d photoemission; 202.8 eV, FWHM 1.2 eV, Nb 3d<sub>5/2</sub>; 205.5 eV, FWHM 1.2 eV, Nb 3d<sub>3/2</sub>),<sup>1-3</sup>
- ii) functionalized Nb<sub>2</sub>C and mixed oxide, NbC<sub>x</sub>O<sub>y</sub>F<sub>z</sub>, species (35.5% of Nb 3d photoemission; 203.9 eV, FWHM 2.0 eV, Nb 3d<sub>5/2</sub>; 206.7 eV, FWHM 2.0 eV, Nb 3d<sub>3/2</sub>)<sup>2,4</sup> and,
- iii) oxidized Nb (31.2% of Nb 3d photoemission; 206.7 eV, FWHM 2.5 eV, Nb 3d<sub>5/2</sub>; 209.7 eV, FWHM 2.5 eV, Nb 3d<sub>3/2</sub>).<sup>2,4,5</sup>

The oxidized Nb is likely Nb<sub>2</sub>O<sub>5</sub> forming a separate phase on the MXene's surfaces. The large FWHM of the peaks corresponding to NbC<sub>x</sub>O<sub>y</sub>F<sub>z</sub> and the oxidized Nb is likely due to the fact that a mixture of functional groups (O, OH, and F) are also present on the surface, while ~ 33.3% of the photoemission comes from Nb<sub>2</sub>C. The ratio of mixed oxide/fluoride surface groups to highly-oxidized Nb is ~ 1:1.

A high-resolution spectrum in the O 1s region (Fig. S1b) could be fit by broad peaks (FWHM 1.6 eV) at 530.0, 531.8 and 532.4 eV. The component centered at 530.0 eV (72.6% of O 1s photoemission) is consistent with oxygen in Nb<sub>2</sub>O<sub>5</sub>.<sup>3</sup> The component centered at 531.8 eV (18.6% of O 1s photoemission) likely arises from O or OH groups bound to the surface of the MXene layers.<sup>3</sup> The peak centered at 532.8 eV (8.8% of O 1s photoemission) can be attributed to adsorbed water and most likely arises from water trapped between the MXene layers.<sup>6,7</sup>

A high-resolution spectrum in the C 1s region (Figure S1c) was best fit by three components, the first being a low-binding energy peak corresponding to carbon in Nb<sub>2</sub>C (37.2% of C 1s photoemission, 281.8 eV, FWHM 0.71 eV),<sup>8</sup> non-stoichiometric C (e.g. near a defect) in Nb<sub>2</sub>C (24.9% of C 1s photoemission, 282.0 eV, FWHM 1.1 eV) and a broad peak corresponding to adventitious contamination (37.4% of C 1s photoemission, 283.6 eV, FWHM 2.4 eV). Excluding the photoemission from the Nb<sub>2</sub>O<sub>5</sub> and adventitious components, the ratio of Nb to C was 2.00:0.68. The excess of Nb signal is likely due to the added contribution of the mixed Nb-oxide species to the photoemission in this region. The presence of Nb<sub>4</sub>C<sub>3</sub> was indicated by XRD (see text), but not by the high-resolution XPS spectrum in the Nb 3d and C 1s regions. This may be due to the overlap of these photoemission peaks with that of Nb<sub>2</sub>C or NbC<sub>x</sub>O<sub>y</sub>F<sub>z</sub> and or due to its small weight fraction. More work is needed to sort some of these issues.

The V<sub>2</sub>CT<sub>x</sub> layers were also analyzed by XPS. A high-resolution spectrum of the V 2p region (Figure S2a) revealed the presence of photoemission which could be best fit with components corresponding to:

- i) unreacted MAX phase V<sub>2</sub>AlC (13.6% of V 2p photoemission; 513.4 eV, FWHM 1.5 eV, V 2p<sub>3/2</sub>; 521.0 eV, FWHM 1.5 eV, Nb 2p<sub>1/2</sub>)<sup>7</sup> and,
- ii) oxidized vanadium (86.4% of V 2p photoemission; 516.4 eV, FWHM 2.4 eV, V 2p<sub>3/2</sub>; 523.8 eV, FWHM 2.4 eV, Nb 2p<sub>1/2</sub>).<sup>7,9</sup>

The slight overestimation of the V 2p<sub>1/2</sub> peak centered at 523.8 eV is due to overlap with the O 1s region resulting in increased background emission. It is clear though, that these data are consistent with a sample that contains both V<sub>2</sub>C MXene layers that are partially terminated in an oxide monolayer, and some mixed vanadium oxide.<sup>7</sup>

A high-resolution spectrum in the O 1s region (Figure S2b) could be fit by broad peaks (FWHM 1.9 eV) at 529.9, 531.3 and 532.9 eV. The components centered at 529.9 eV (26.3% of O 1s photoemission) and 531.3 eV (57.5% of O 1s photoemission) are consistent with mixed vanadium oxide (VO<sub>x</sub>) and surface oxide groups,<sup>7</sup> while the peak centered at 532.9 eV (16.2% of O 1s photoemission) is again consistent with intercalated water.<sup>6,7</sup>

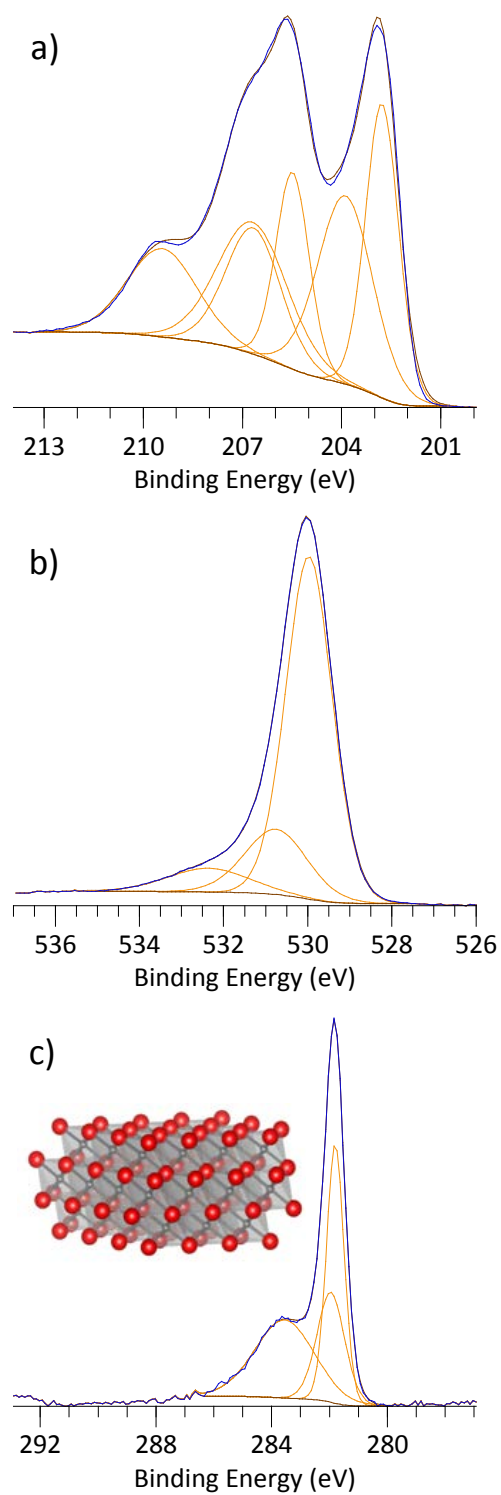
A high-resolution spectrum in the C 1s region (Figure S2, c) was best fit by four components with the first two corresponding to adventitious contamination (19.5% of C 1s photoemission, 286.1 eV, FWHM 1.5 eV; and, 61.7% of C 1s photoemission, 284.5 eV, FWHM 1.5 eV), a high-binding energy peak similar to a peak attributed to adsorbed methanol (10.1% of

C 1s photoemission, 288.3 eV, FWHM 1.5 eV),<sup>9</sup> and – similar to Nb<sub>2</sub>C – a low-binding energy peak (8.7% of C 1s photoemission, 281.8 eV, FWHM 1.5 eV) that corresponds to C in V<sub>2</sub>C.<sup>8</sup> The large amount of contamination and low intensity of the Nb<sub>2</sub>C signal is due to the lack of Ar sputtering. The source of the contaminant found at 287.2 eV is likely the ethanol used during the ball milling of the samples. The ratio of total V photoemission to the V<sub>2</sub>C carbon component was again 2.00:0.68, which is off from the expected 2:1 ratio. This is likely due to the overestimation of the V signal due to the presence of vanadium oxide, and well as the overlap of the V 2p signal with that of the O 1s signal.

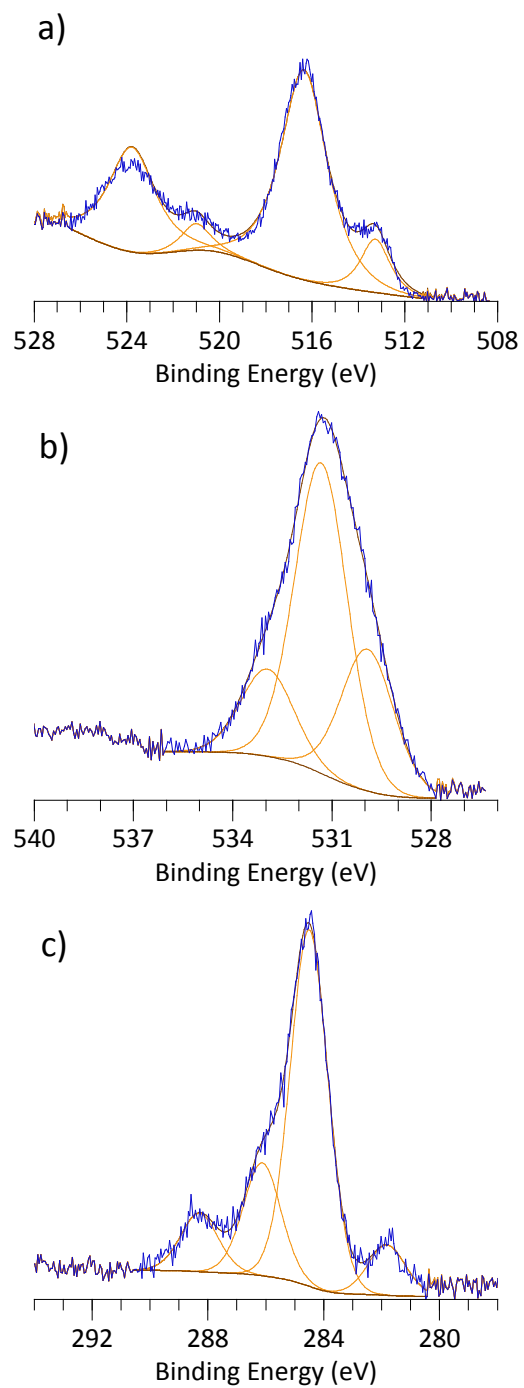
*Preparation of lithium coin cells:* Electrodes were formed by mixing the MXene powders, acetylene carbon black (Alfa Aesar, Ward Hill, USA) and 10 wt.% polyvinylidene fluoride (Alfa Aesar, Ward Hill, USA) that was dissolved in 1-methyl-2-pyrrolidinone (Alfa Aesar, Ward Hill, USA), respectively, in a 80:10:10 ratio by weight. The mixture was then coated onto copper foil using a doctor blade and dried under vacuum at 140°C for 12 h, producing an electrode that was ~60 μm thick.

CR-2016 stainless steel coin cells were assembled using a crimping machine (MTI EQ-MSK-110, Richmond, CA, USA) in an Ar filled glove box with H<sub>2</sub>O and O<sub>2</sub> contents < 1 ppm. The cells consisted of a MXene electrode and a Li (Alfa Aesar, Ward Hill, USA) foil counter electrode separated from each other by a sheet of borosilicate glass fiber (Whatman GF/A, Buckinghamshire, UK). The electrolyte was 1 M LiPF<sub>6</sub> solution in a mixture of ethylene carbonate, EC, and diethyl carbonate, DEC in a 1:1 by weight ratio.

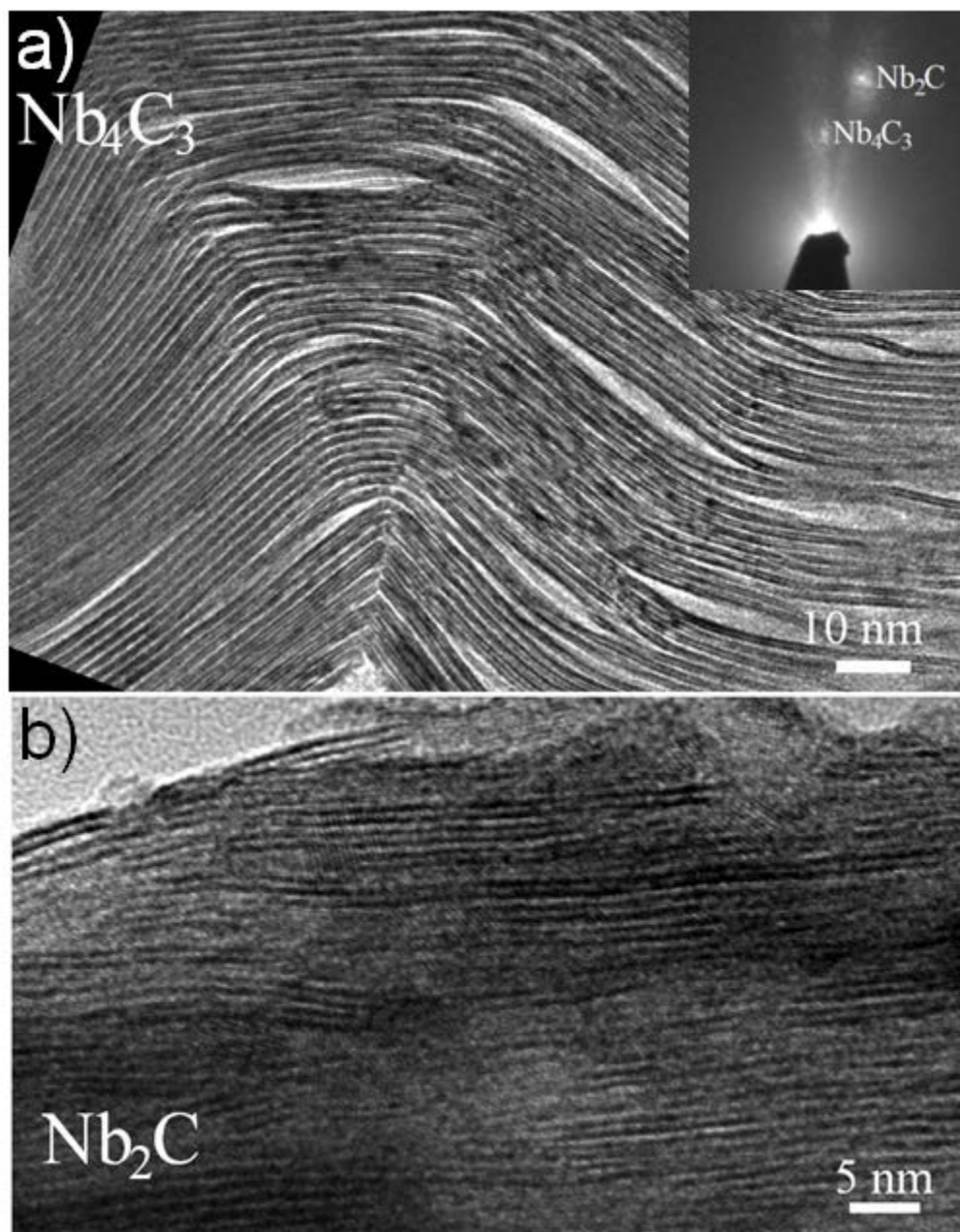
*Electrochemical testing:* Coin cells were tested using two different techniques: GV and CV. The GV was carried out using a battery cycler (Arbin BT-2143- 11U, College Station, TX, USA). For the CV measurements, a potentiostat (VMP3, Biologic, Knoxville, TN, USA) was used.



**Figure S1.** High-resolution XPS spectra of Nb<sub>2</sub>C MXene films in the, (a) Nb 3d region, (b) O 1s region, and (c) C 1s region. Inset in (c) is a structural representation of one Nb<sub>4</sub>C<sub>3</sub> layer. The C atoms are located in the octahedral sites of the Nb atoms, that are in a near close-packed arrangement.

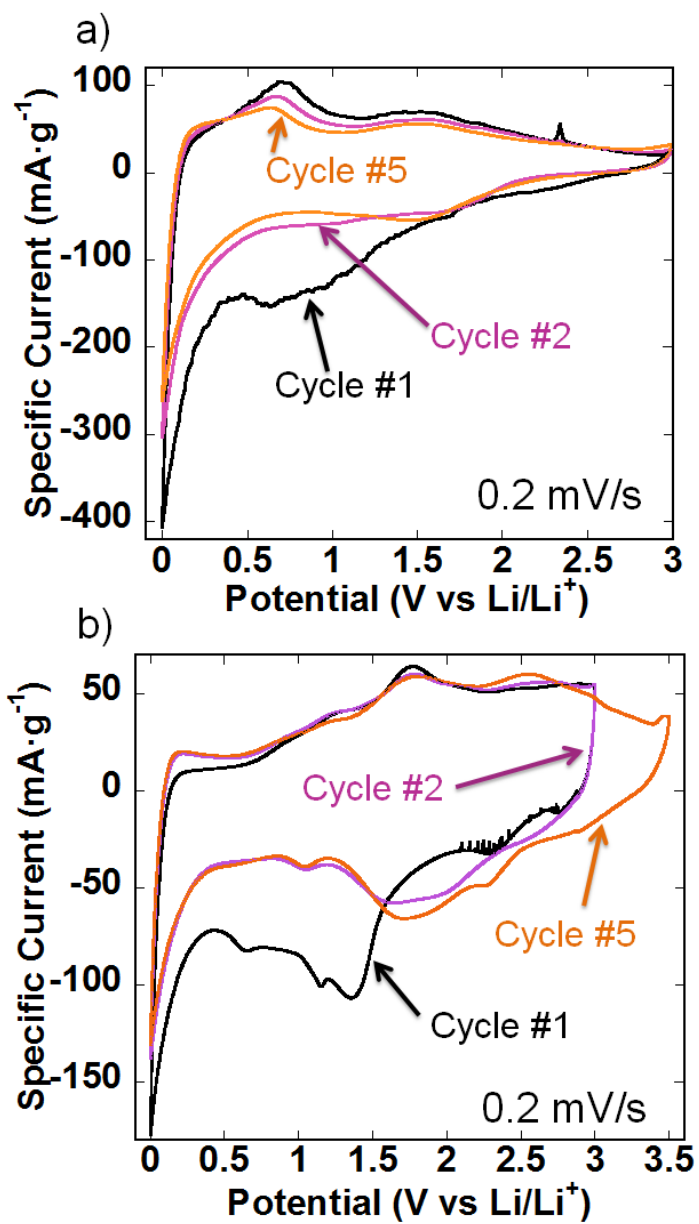


**Figure S2.** High-resolution XPS spectra of V<sub>2</sub>C MXene films in the (a) V 2p region, (b) O 1s region, and (c) C 1s region.



**Figure S3.** Cross-section TEM images of (a) Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> and (b) Nb<sub>2</sub>CT<sub>x</sub> layers. Inset in (a) shows the SAED pattern.





**Figure S4.** Cyclic voltammograms recorded at 0.2 mV/s (vs. Li) for, (a) Nb<sub>2</sub>CT<sub>x</sub> and (b) V<sub>2</sub>CT<sub>x</sub>. The latter was synthesized by immersion in 50% HF for 90 h at RT.

## References:

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