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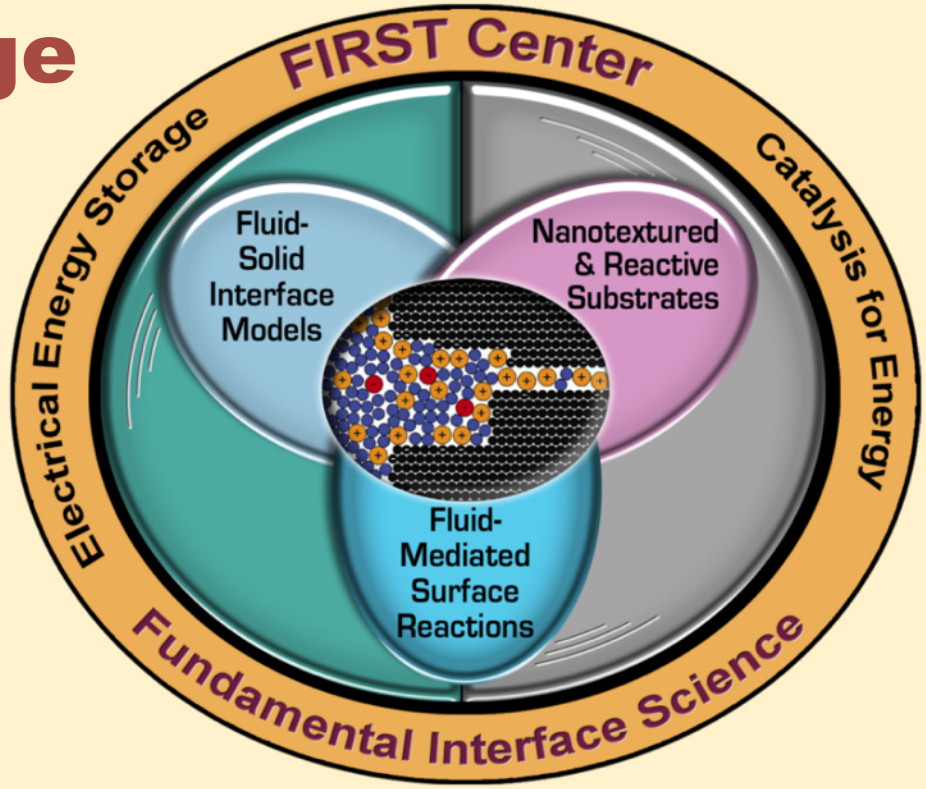
An Energy Frontier Research Center

Fluid Interface Reactions, Structures and Transport Center,
Oak Ridge National Laboratory

Li-ion energy storage of 2D "MXene" transition metal carbides

Paul R. C. Kent
Oak Ridge National Laboratory

http://www.ornl.gov/~pk7



Work supported by the U.S. Department of Energy, Office of Basic Energy Sciences as part of an Energy Frontier Research Center

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Fluid Interface Reactions, Structures and Transport Center,
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Outline

Fluid Interface Reactions, Structures and Transport Center,
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- Background of MAX phases & synthesis of MXenes
- Potential applications
- Key questions
- Methods
- Results
    - Surface structure
    - Surface reactions
    - Li storage capacity
- Conclusions

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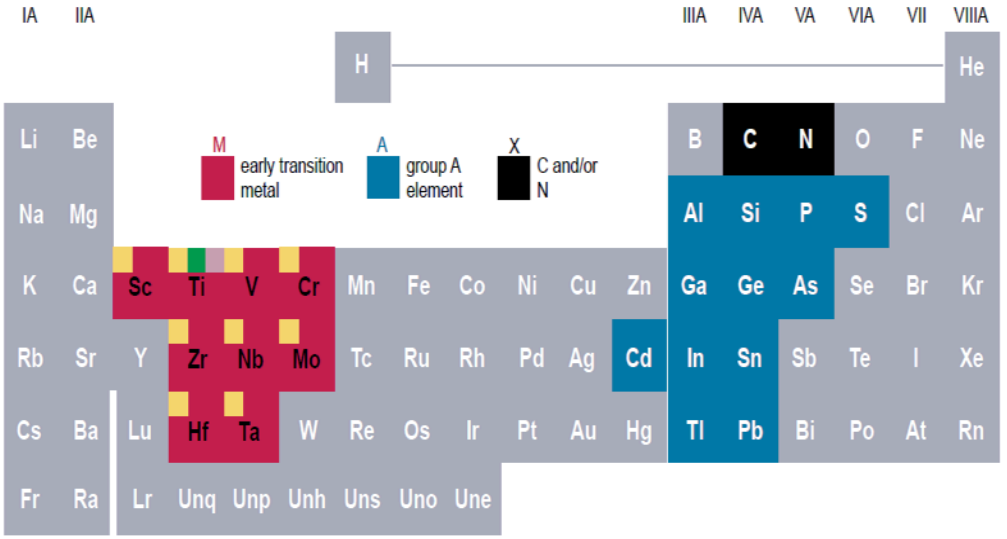
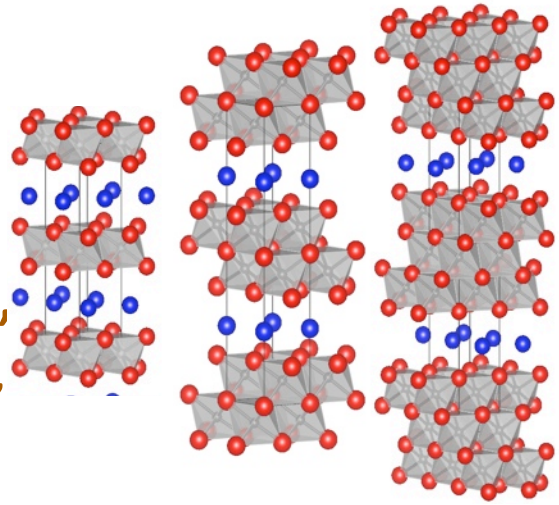
MAX Phases

- MAX Phases are ternary metal carbides and/or nitrides
- Layered hexagonal structure ($P6_3/mmc$)
- Composition of $M_{n+1}AX_n$; with n = 1, 2, 3...



211 Phases	312 Phases	413 Phases
Ti_2CdC, Sc_2InC, Ti_2AlC, Ti_2GaC, Ti_2InC, Ti_2TlC, V_2AlC, V_2GaC, Cr_2GaC, Ti_2AlN, Ti_2GaN, Ti_2InN, V_2GaN, Cr_2GaN, Ti_2GeC, Ti_2SnC, Ti_2PbC, V_2GeC, Cr_2AlC, Cr_2GeC, V_2PC, V_2AsC, Ti_2SC, Zr_2InC, Zr_2TlC, Nb_2AlC, Nb_2GaC, Nb_2InC, Mo_2GaC, Zr_2InN, Zr_2TlN, Zr_2SnC, Zr_2PbC, Nb_2SnC, Nb_2PC, Nb_2AsC, Zr_2SC, Nb_2SC, Hf_2InC, Hf_2TlC, Ta_2AlC, Ta_2GaC, Hf_2SnC, Hf_2PbC, Hf_2SnN, Hf_2SC	Ti_3AlC_2, V_3AlC_2, Ti_3SiC_2, Ti_3GeC_2, Ti_3SnC_2, Ta_3AlC_2,	Ti_4AlN_3, V_4AlC_3, Ti_4GaC_3, Ti_4SiC_3, Ti_4GeC_3, Nb_4AlC_3, Ta_4AlC_3,

- **> 60 phases identified**
- **Considering solid solutions, $(Ti_{0.5}Nb_{0.5})_2AlC$, $Ti_3Al(C_{0.5}N_{0.5})_2$ there will be many more!**



Barsoum, M.W. *Progress in Solid State Chemistry* 28 (2000) 201;
Eklund, P., et al. Thin Solid Films 518(2010) 1851-1878

MAX Phases

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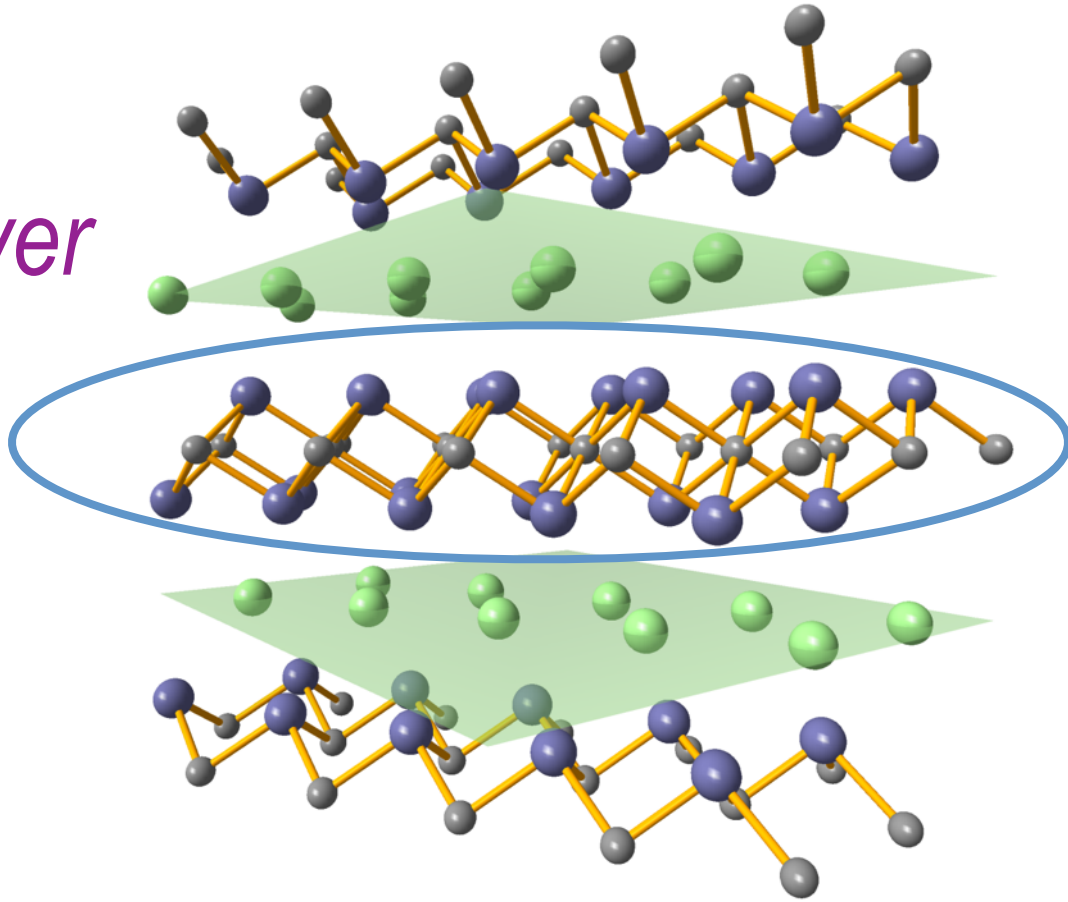
Blocks of "MX" separated by "A" layer



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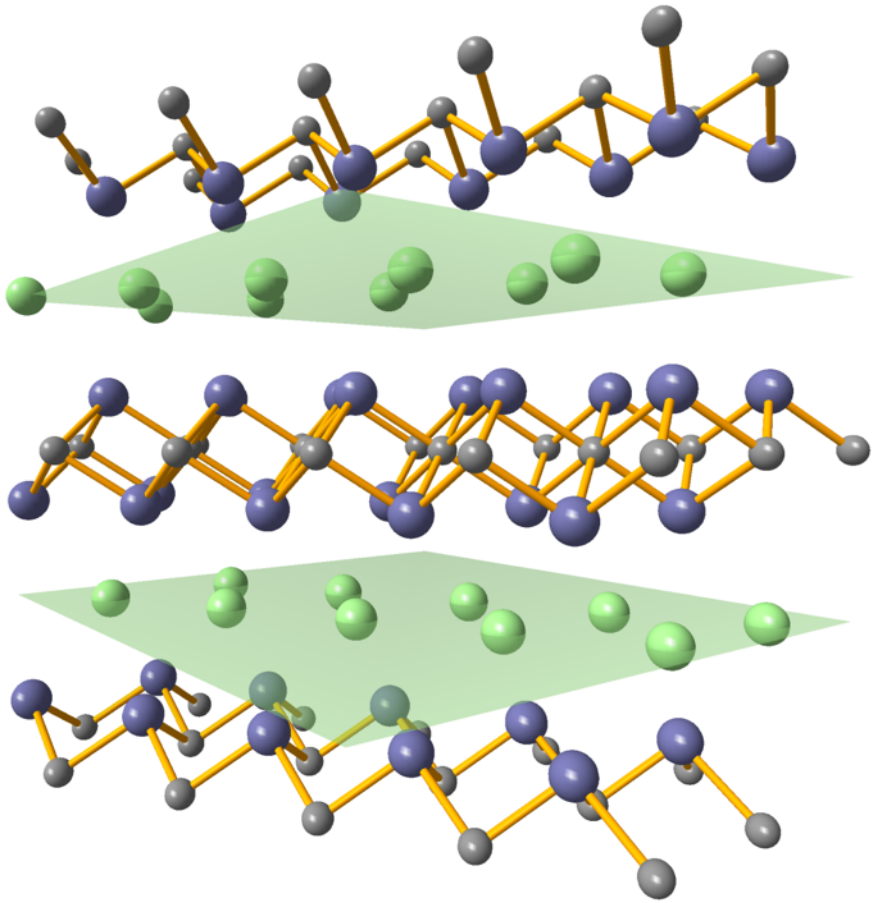
- "A" layer is *relatively* weakly bonded compared to the "MX"



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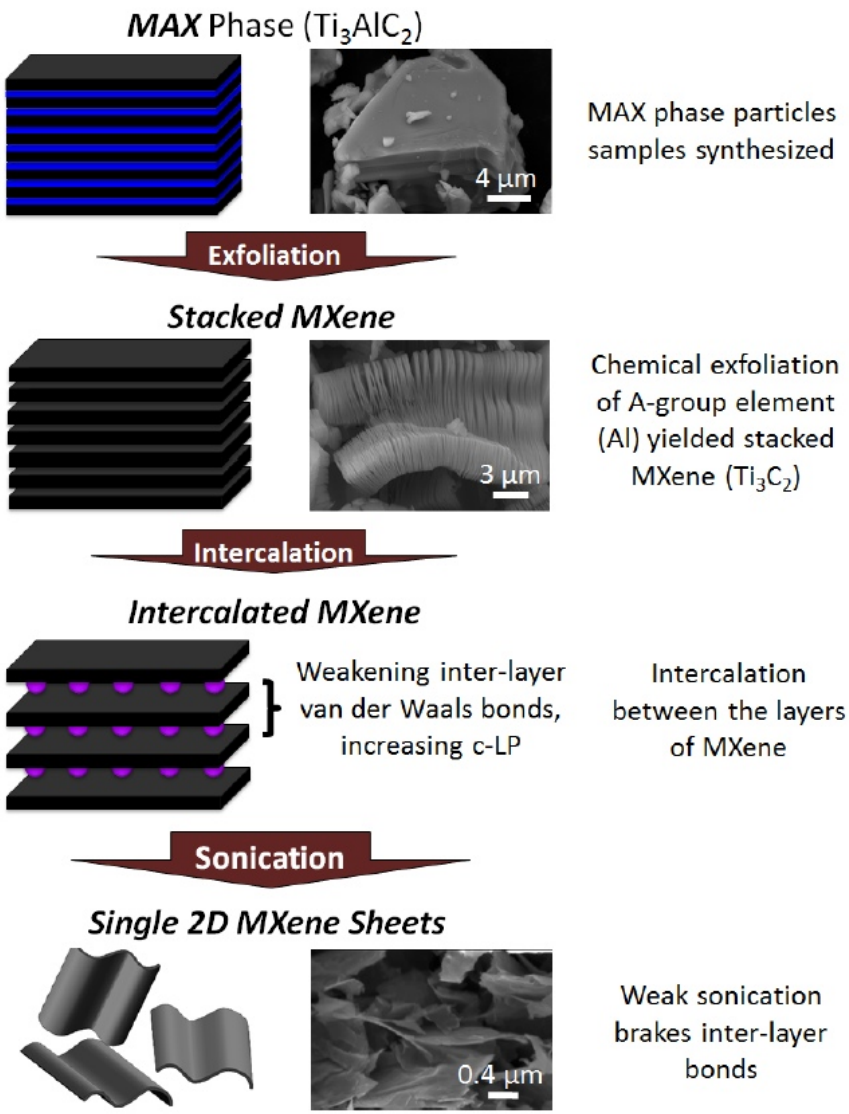
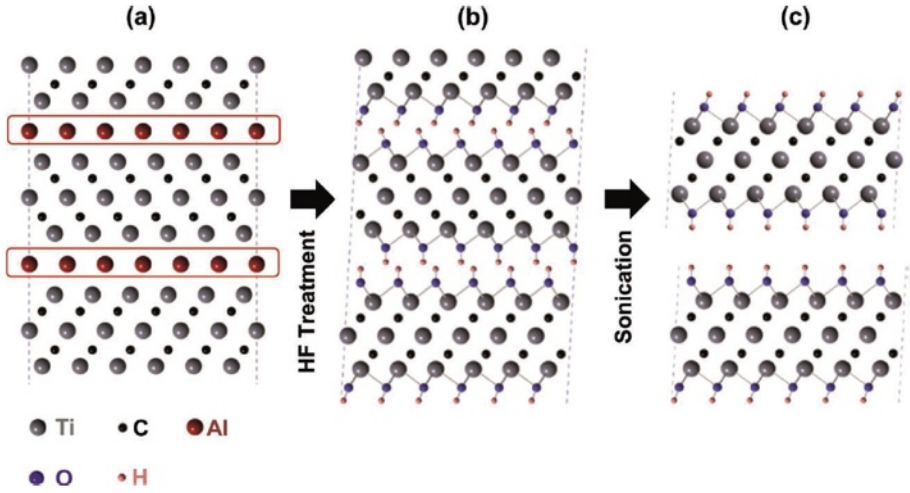
Synthesis of MXenes





- **Synthesized MXene flakes (f-MXene) contain many MXene layers which can be further separated into delaminated MXene (d-MXene) with few MXene layers (<10)**
- **d-MXenes have higher surface areas than f-MXenes**
- **MXene surfaces are terminated by incomplete or mixed F, O/OH functional groups.**

M. Naguib, *et al.* ***Adv. Mater****. 23*, 4248 (2011)

O. Mashtalir, *et al.* ***Nature Comm****. 4*, 1716 (2013)

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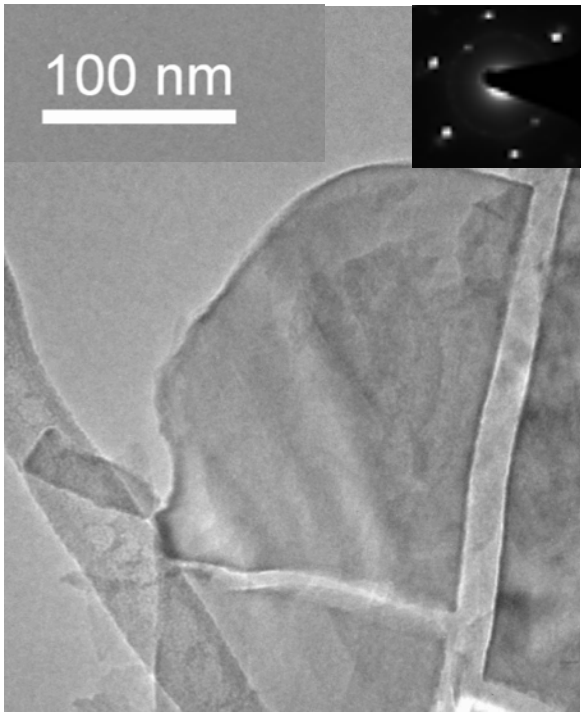
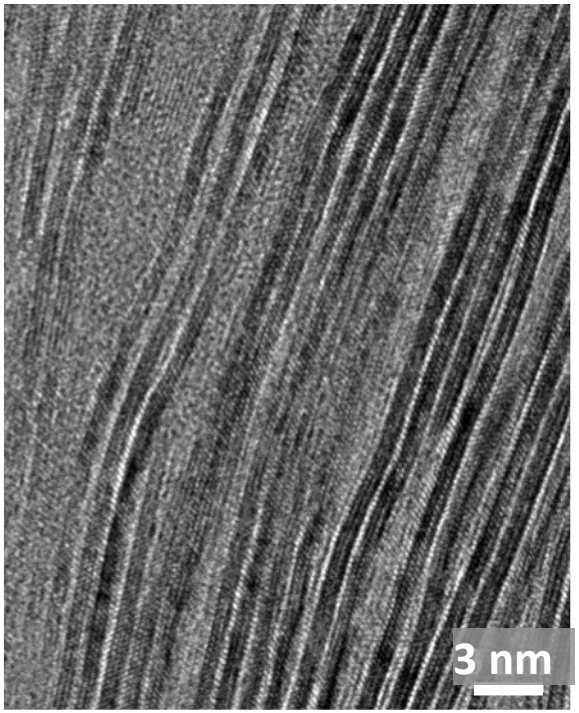
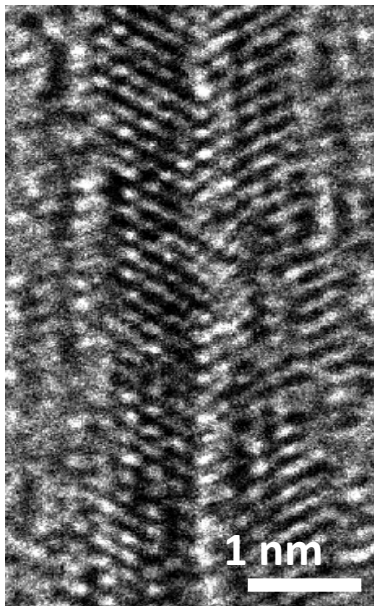
Preparation of MXene sheets

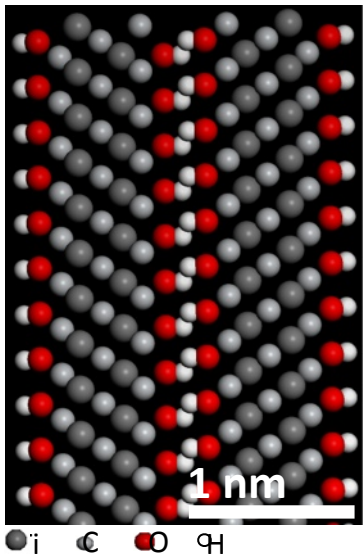
Ti_3AlC_2 + HF 50% for 2 hours at room followed by SONICATION:

TEM shows 2D Sheets





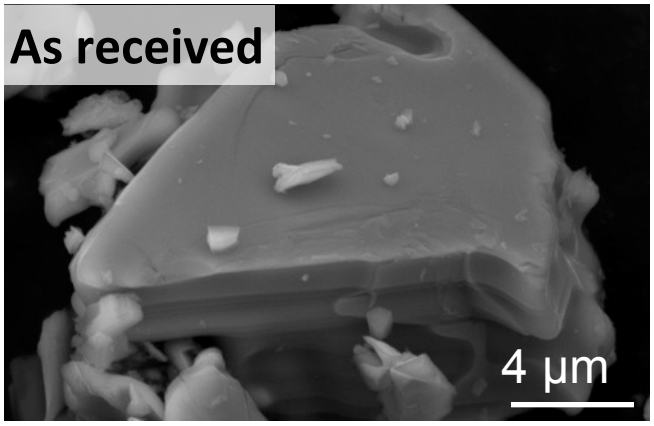




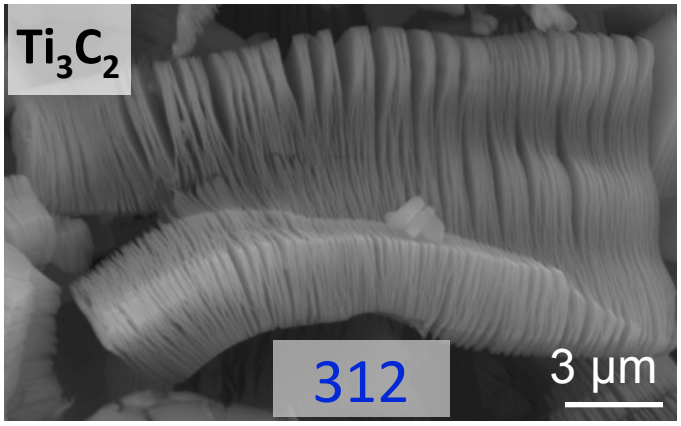
EDS shows: Ti, C, O, F

Michael Naguib, *et al.* Advanced Materials 23 (2011) 4248-4253

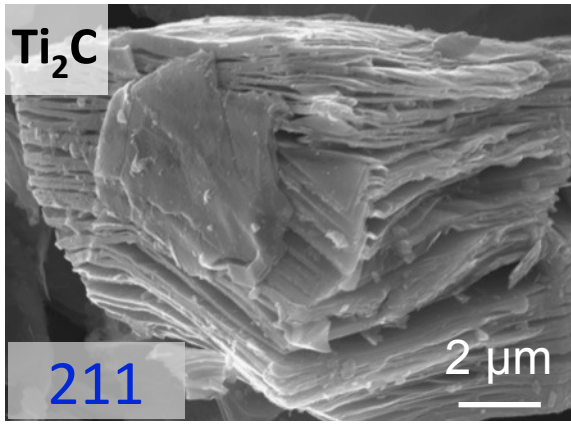
Numerous MAX phases successfully exfoliated to MXenes



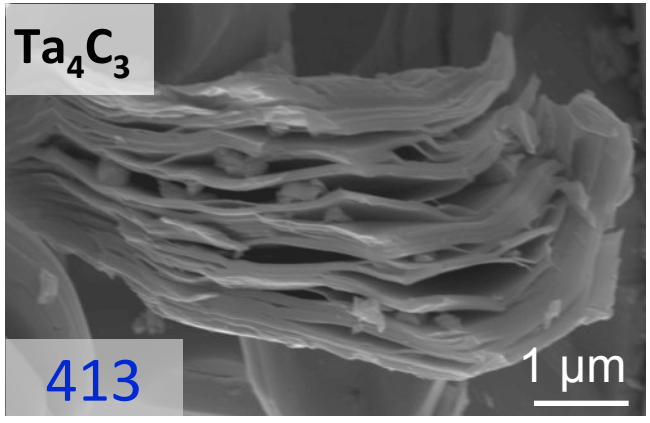
From Ti_3AlC_2



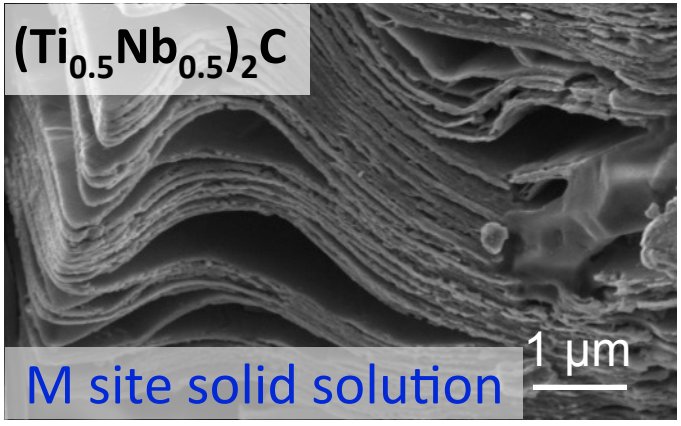
From Ti_2AlC



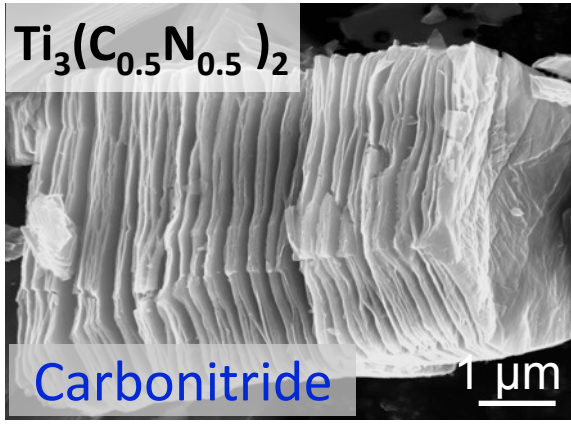
From Ta_4AlC_3



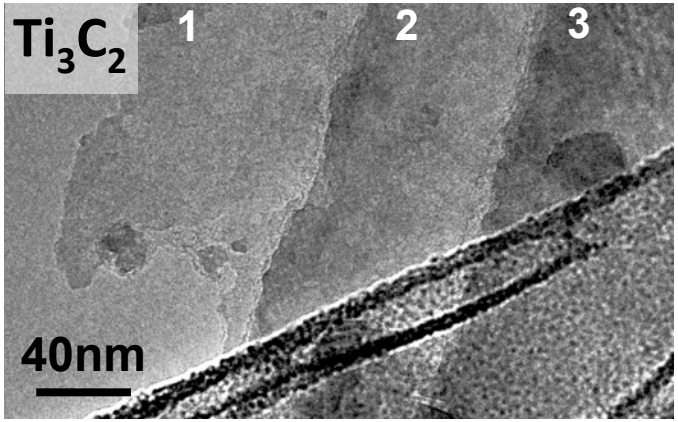
From $(Ti_{0.5}Nb_{0.5})_2AlC$

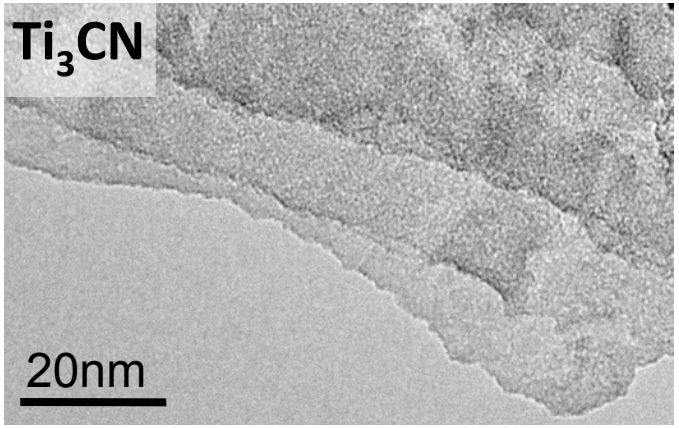


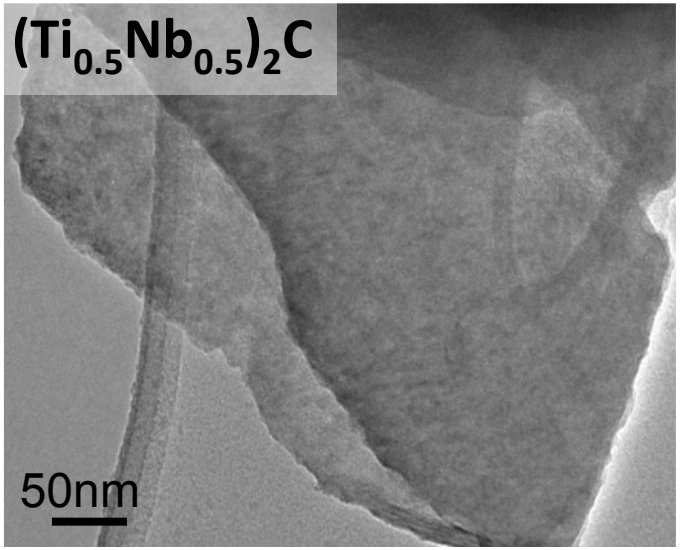
From $Ti_3Al(C_{0.5}N_{0.5})_2$

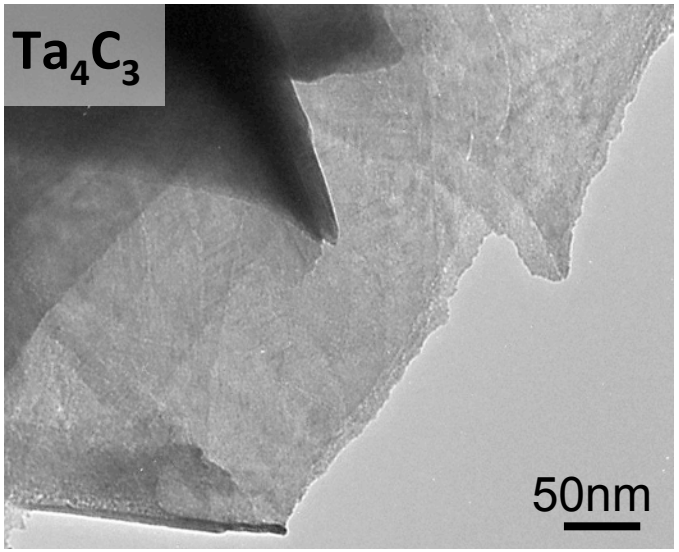


Michael Naguib, et al. *ACS Nano* 6 (2012) 1322-1331

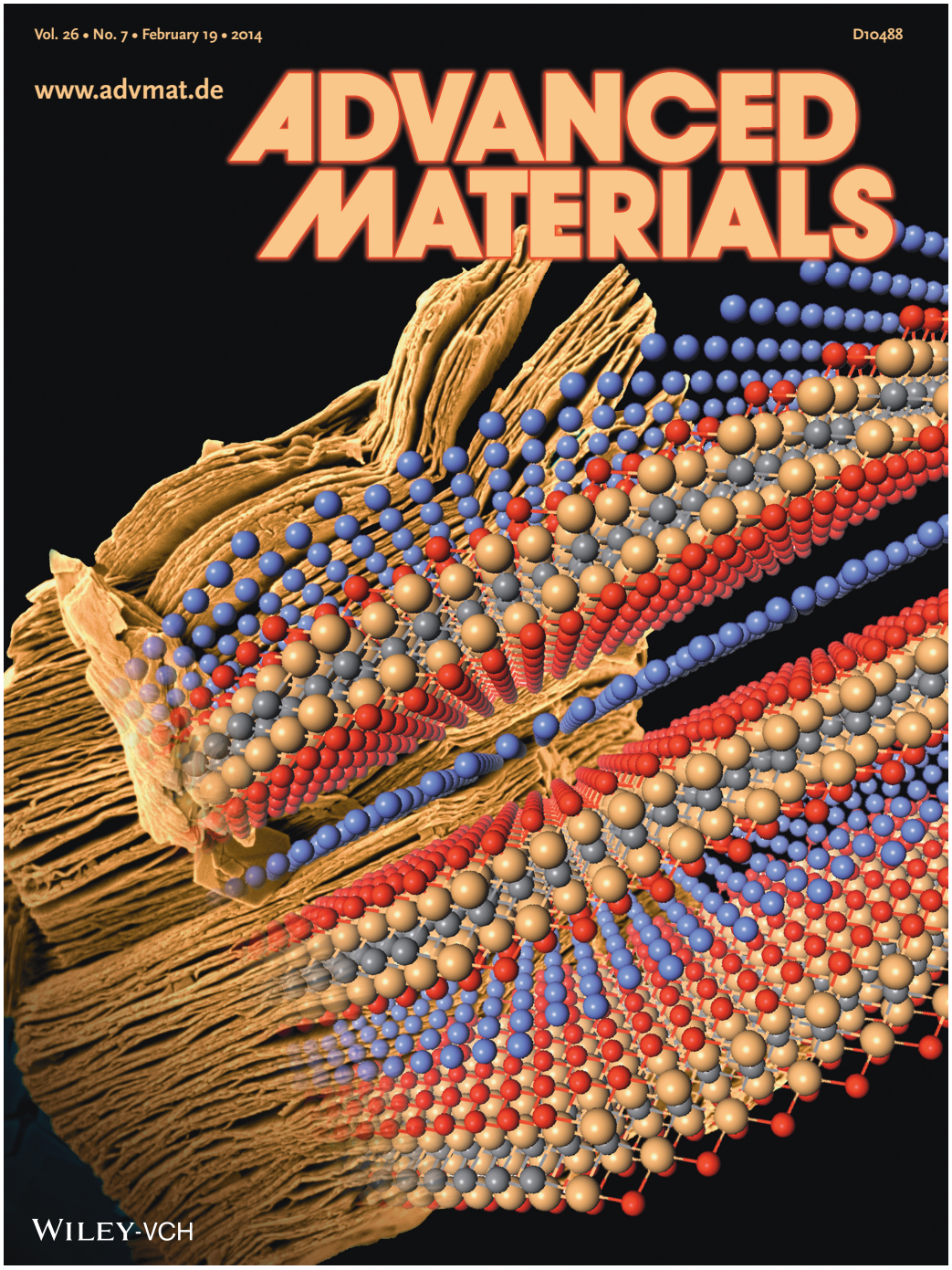








Michael Naguib, *et al.* ACS Nano 6 (2012) 1322-1331



M. Naguib, V.N. Mochalin, M.W. Barsoum, Y. Gogotsi, "MXenes: A New Family of Two-Dimensional Materials", *Advanced Materials*, **26**, 992-1005 (2014)

10.1002/adma.201304138

MXene electronic structure

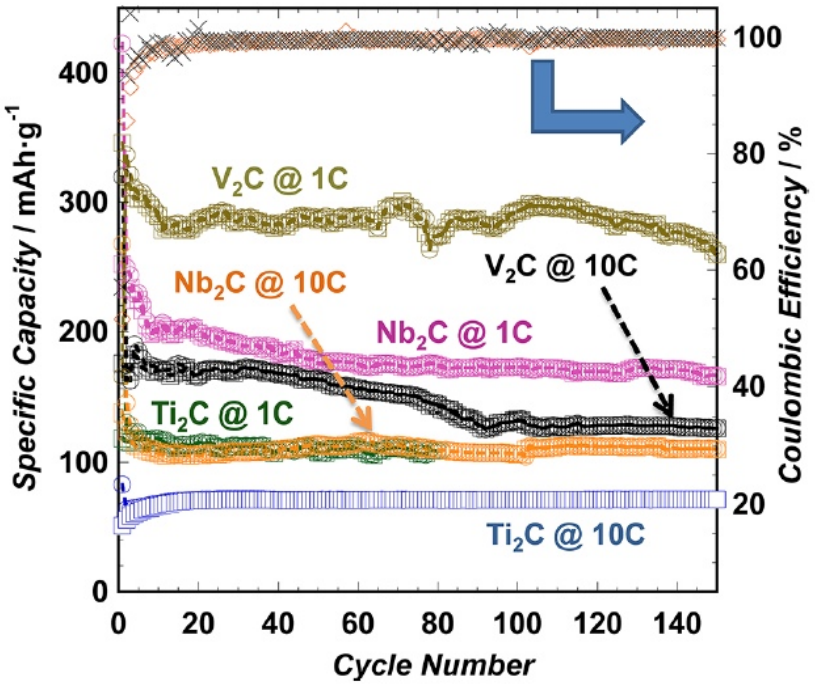
Y. Xie and P. R. C. Kent, "Hybrid density functional study of structural and electronic properties of functionalized Ti*n* +1Xn (*X*=C, N) monolayers"

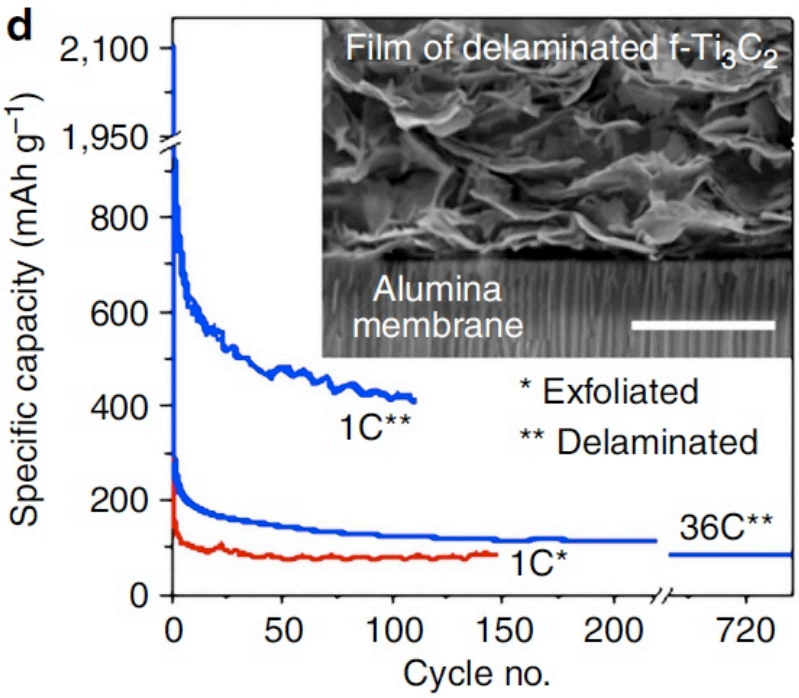
PRB **87** 235441 (2013)

Web of Science search tip

Topic search for MXene*

MXenes as Li-ion battery anodes





Li capacities of currently measured MXenes

f-V_2C	260 mAhg^{-1} at 1 C
f-Nb_2C	170 mAhg^{-1} at 1 C
f-Ti_2C	110 mAhg^{-1} at 1 C
f-Ti_3C_2	100 mAhg^{-1} at 1 C
d-Ti_3C_2	410 mAhg^{-1} at 1 C

Theoretical max Li capacity of graphite is 372 mAhg^{-1} , but graphite is far from ideal.

O. Mashtalir, *et al.* ***Nature Comm****. 4*, 1716 (2013)

M. Naguib, *et al.* ***J. Am. Chem. Soc.*** *135*, 15966 (2013)

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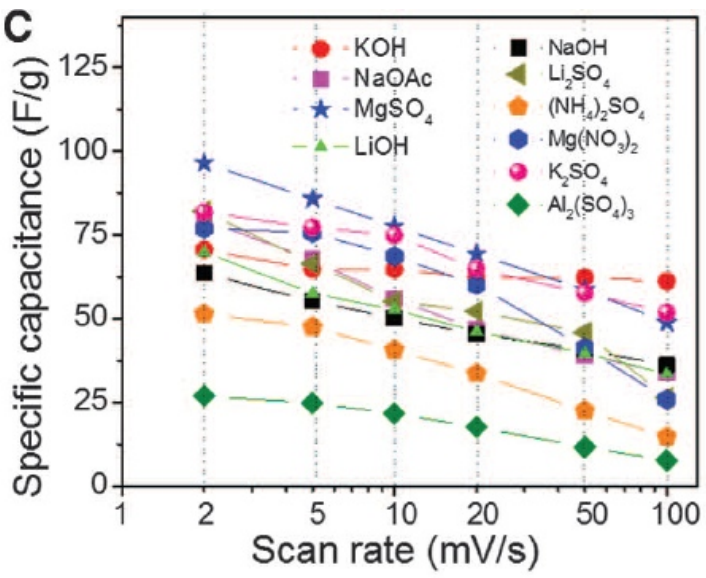
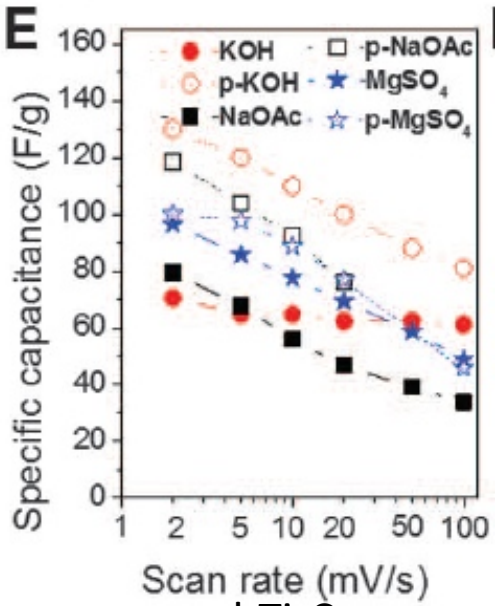
Ti_3C_2 as supercapacitor electrode



f-Ti_3C_2



d-Ti_3C_2

The capacitance is 73 F/g (190 F/cm^3) for KOH.

The capacitance is 130 F/g (340 F/cm^3) for KOH.

M. Lukatskaya, *et al.* ***Science*** *341*, 1502 (2013)

Comparison:

60 - 100 F/cm^3 for active graphene

180 F/cm^3 for micrometer-thin carbide-derived carbon.

MXenes are promising energy storage materials, even at this early stage

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Goals

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1. **Understand the origin of the Li capacity in MXenes**
   To predict the best MXene and processing for specific applications

2. **Explain why Ti-based f-MXenes have lower Li capacity compared to other MXenes? (counterintuitive)**
   e.g. f-Ti2C 110 $mAhg^{-1}$ vs f-Nb2C 170 $mAhg^{-1}$

3. **Explain why d-Ti_3C_2 has a much higher Li capacity than f-Ti_3C_2**

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Methods

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- Computational details
  VASP with PAW potential
  PBE and vDW-DF (optB86) functional
  Packmol for water and HF solution
  AIMD simulations for 15 ps
  Nudged elastic band method for transition state searching

- Experiments
  X-ray diffraction (f-Ti_3C_2, f-Nb_2C)
  High temperature annealing (f-Ti_3C_2, f-Nb_2C)
  Inelastic neutron scattering (f-Nb_2C)
  X-ray adsorption near edge structure (Ti K-edge, f-Ti_3C_2)

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Surface structure of MXenes

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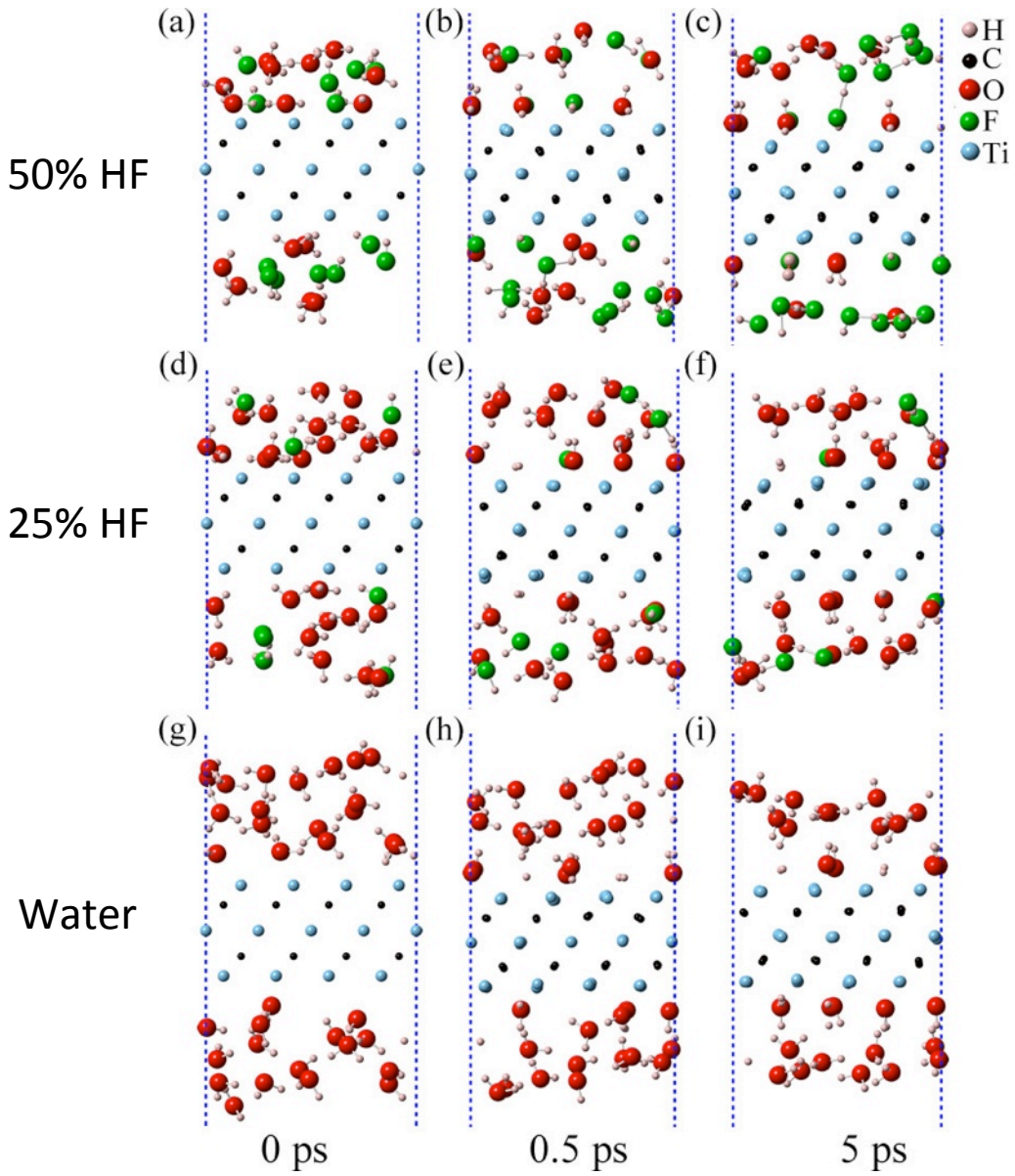

Extensive ab initio molecular dynamics investigations find:

1. Water dissociates on MXene surfaces, leaving OH groups
2. Surface F can easily be replaced by O in water environment.

MXene surfaces should be terminated mainly by OH groups with some F and O present after HF etching.

Snapshots at 0, 0.5, and 5 ps of AIMD simulations of bare Ti_3C_2 monolayer in 50% HF (a-c), 25% HF (d-f), and water (g-i) solution.

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Stacking of multilayer MXene

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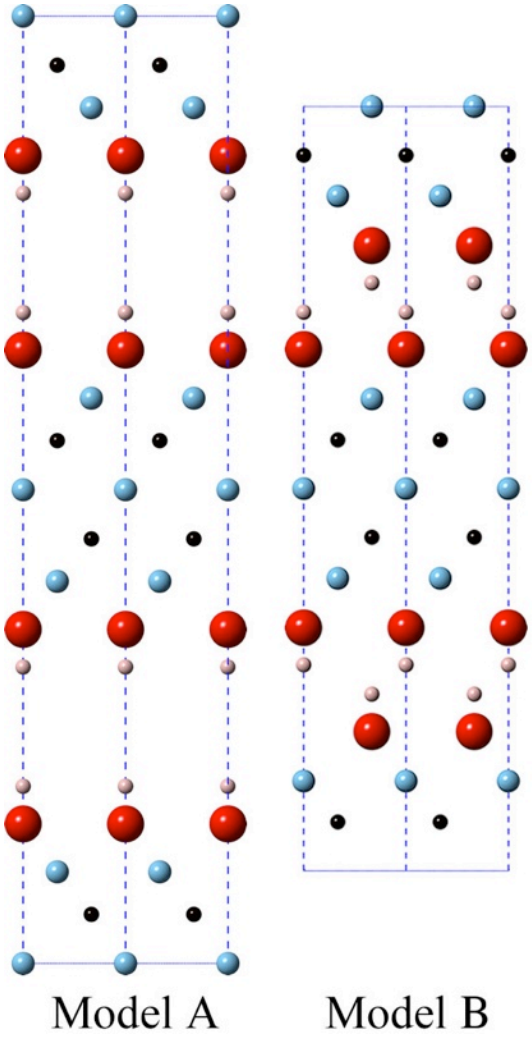
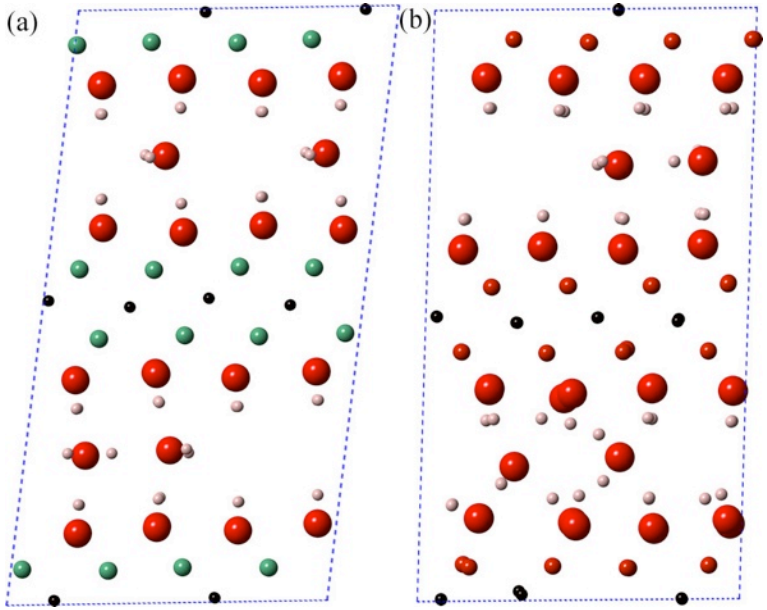
The synthesized MXene flakes contain multiple MXene layers and can contain water. By comparing with XRD we can narrow down our structural models.





- Zig-zag packing (Model B) is the stable multilayer structure
  Stabilized by van der Waals interaction
- We have done extensive comparisons of XRD and predicted lattice constants. Comparison with experimental XRD indicates that water is intercalated into Nb_2C and V_2C but not Ti_2C

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AIMD simulations of annealing

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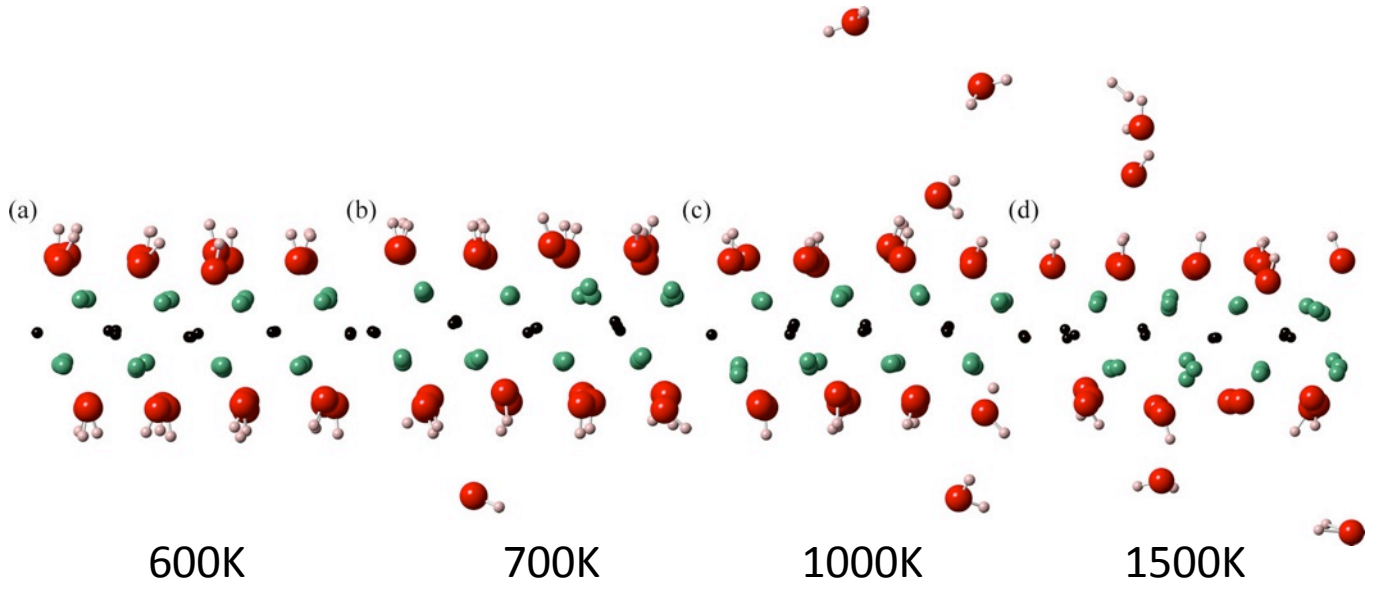
We explored changes in surface structure with annealing



Structures after 10 ps of OH terminated Nb_2C. H_2 is formed at the highest temperature.

- **AIMD fully corroborated by nudged elastic band calculations of reaction barriers**
- **Water formation can happen at lower temperature than H_2 formation**
- **AIMD simulations reveal trends in required annealing temperatures**
- **Ti-based MXenes require higher temperature for water formation than other MXenes (Nb_2C and V_2C)**

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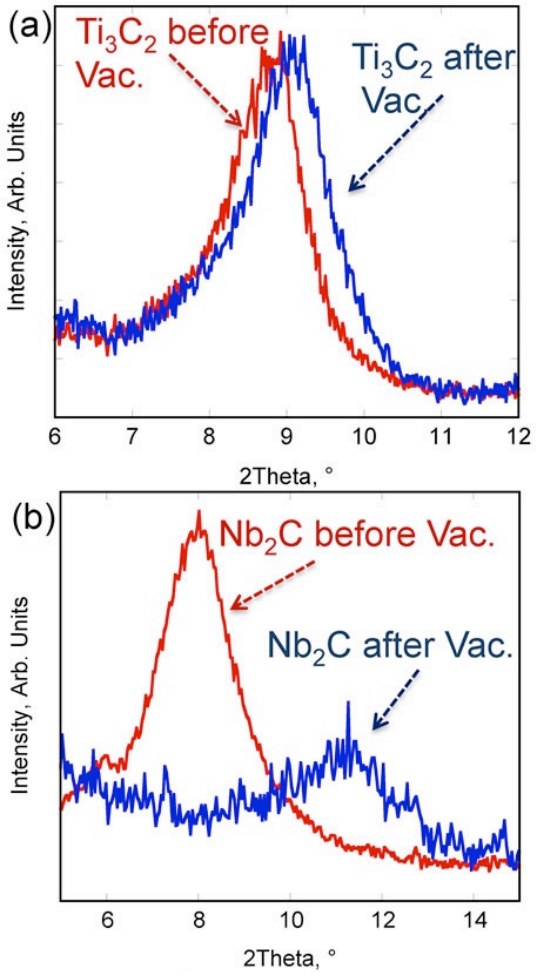
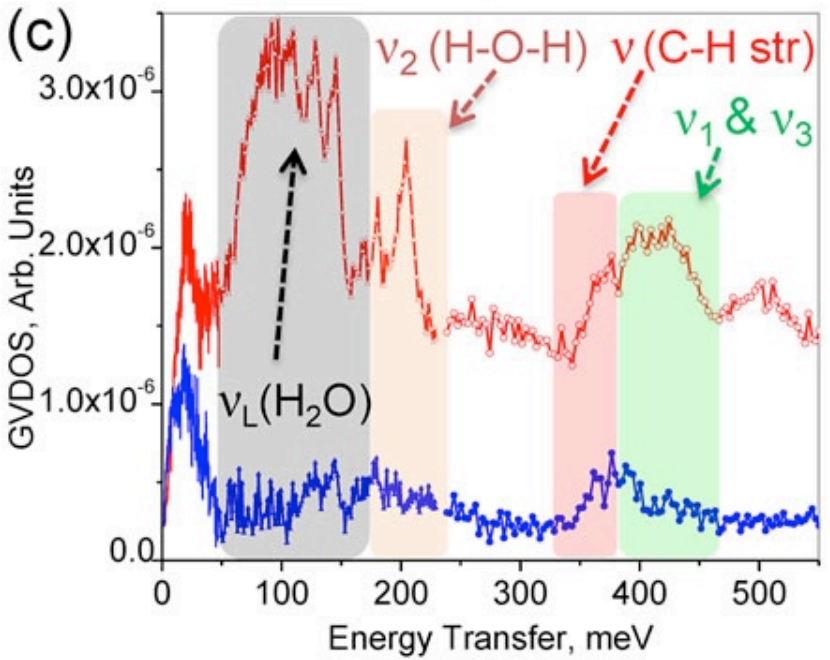
Experimental verification

XRD



INS



Before anneal

Post anneal

- **The *c* lattice paramters of Ti_3C_2 reduced from 19.95 to 19.37 Å after annealing (little water removal), while that of Nb_2C reduced from 22.34 to 15.85 Å (significant water removal)**
- **INS confirms that all of the H_2O/OH are gone**
- **Consistent with predictions of water intercalation**

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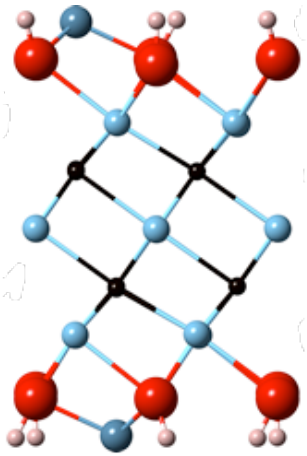
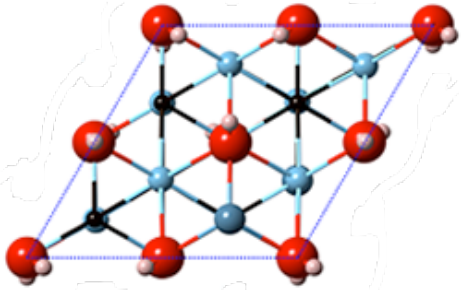
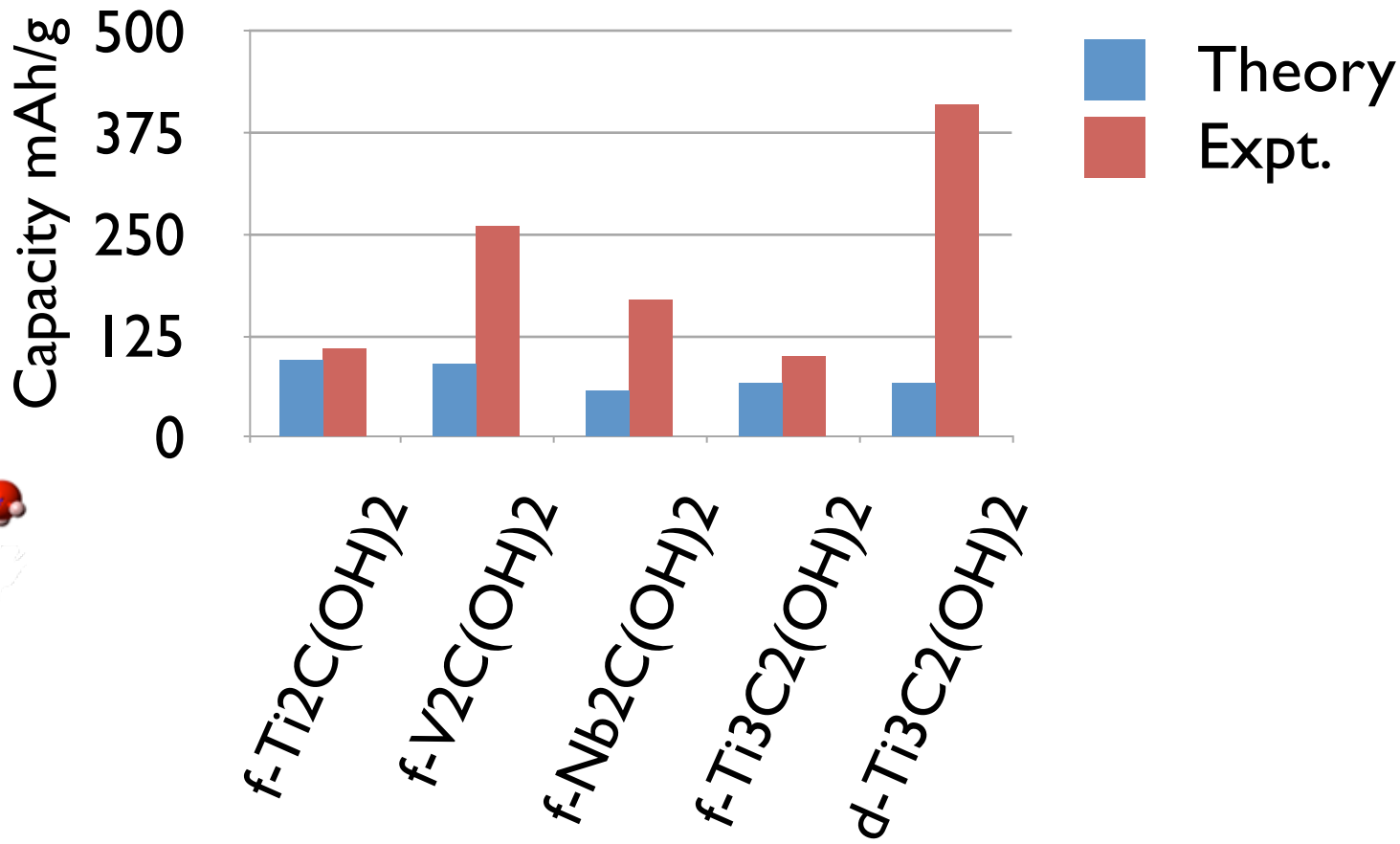
Li adsorption and storage of OH terminated MXenes







Li is weakly adsorbed. Calculated Li capacities are much lower than experimental results. OH termination is not desirable for Li adsorption.

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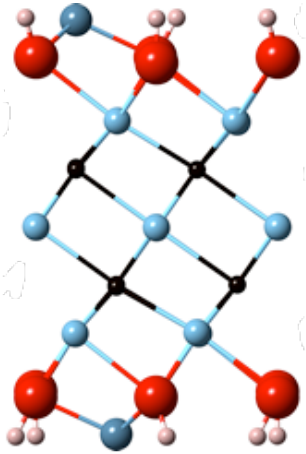
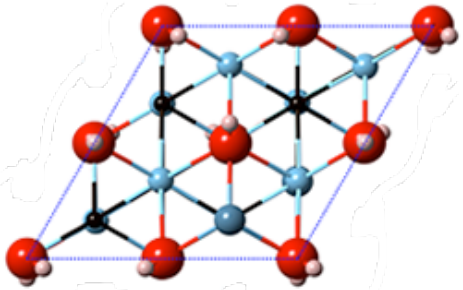
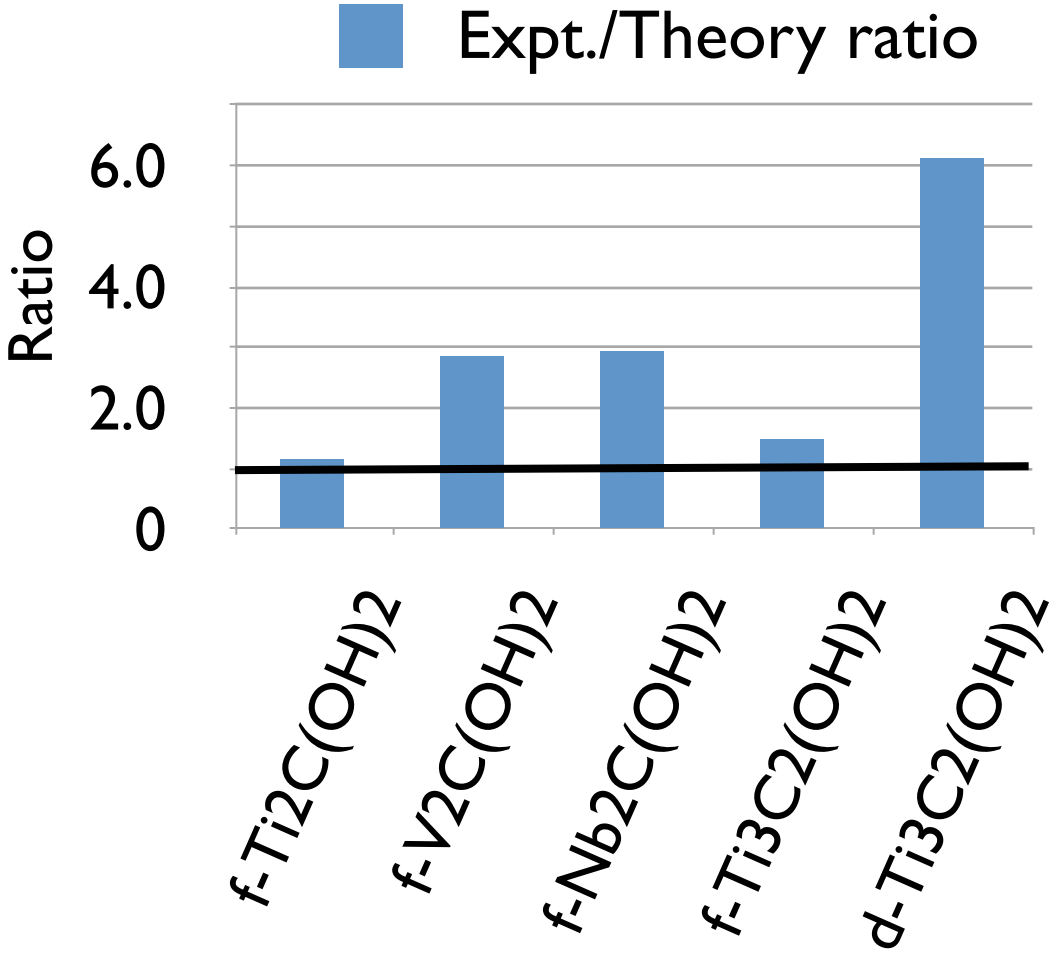
Li adsorption and storage of OH terminated MXenes







Li is weakly adsorbed. Calculated Li capacities are much lower than experimental results. OH termination is not desirable for Li adsorption.

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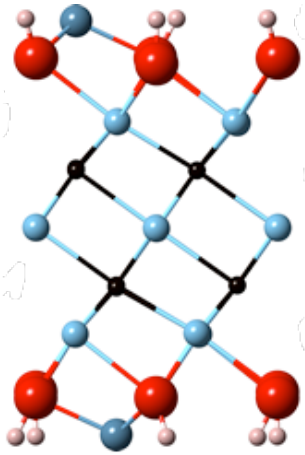
Li adsorption and storage of OH terminated MXenes



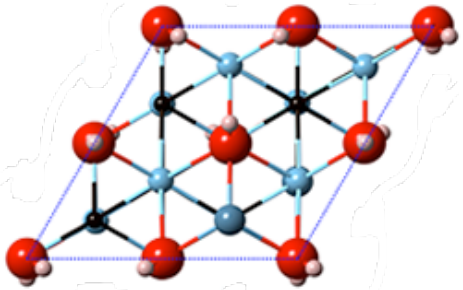


TABLE III. Calculated Li adsorption energy of OH terminated MXenes with vdW–DF methods, and theoretical Li capacities, compared with experimental results.

	E_{ad} (eV)	F (mhA^{-1}/g)		r (Exp./Theo.)
		Theo.	Exp.	
$Ti_2C(OH)_2$	0.065	95	110	1.16
$V_2C(OH)_2$	-0.077	91	260	2.86
$Nb_2C(OH)_2$	0.170	58	170	2.93
$Ti_3C_2(OH)_2$	0.171	67	100 (410)	1.49 (6.12)

Li is weakly adsorbed. Calculated Li capacities are much lower than experimental results. OH termination is not desirable for Li adsorption.

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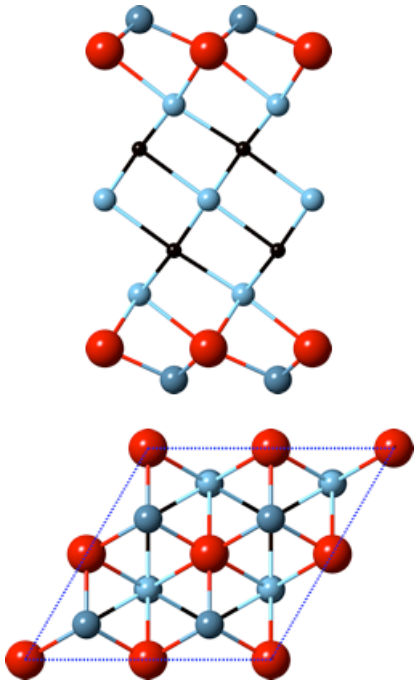
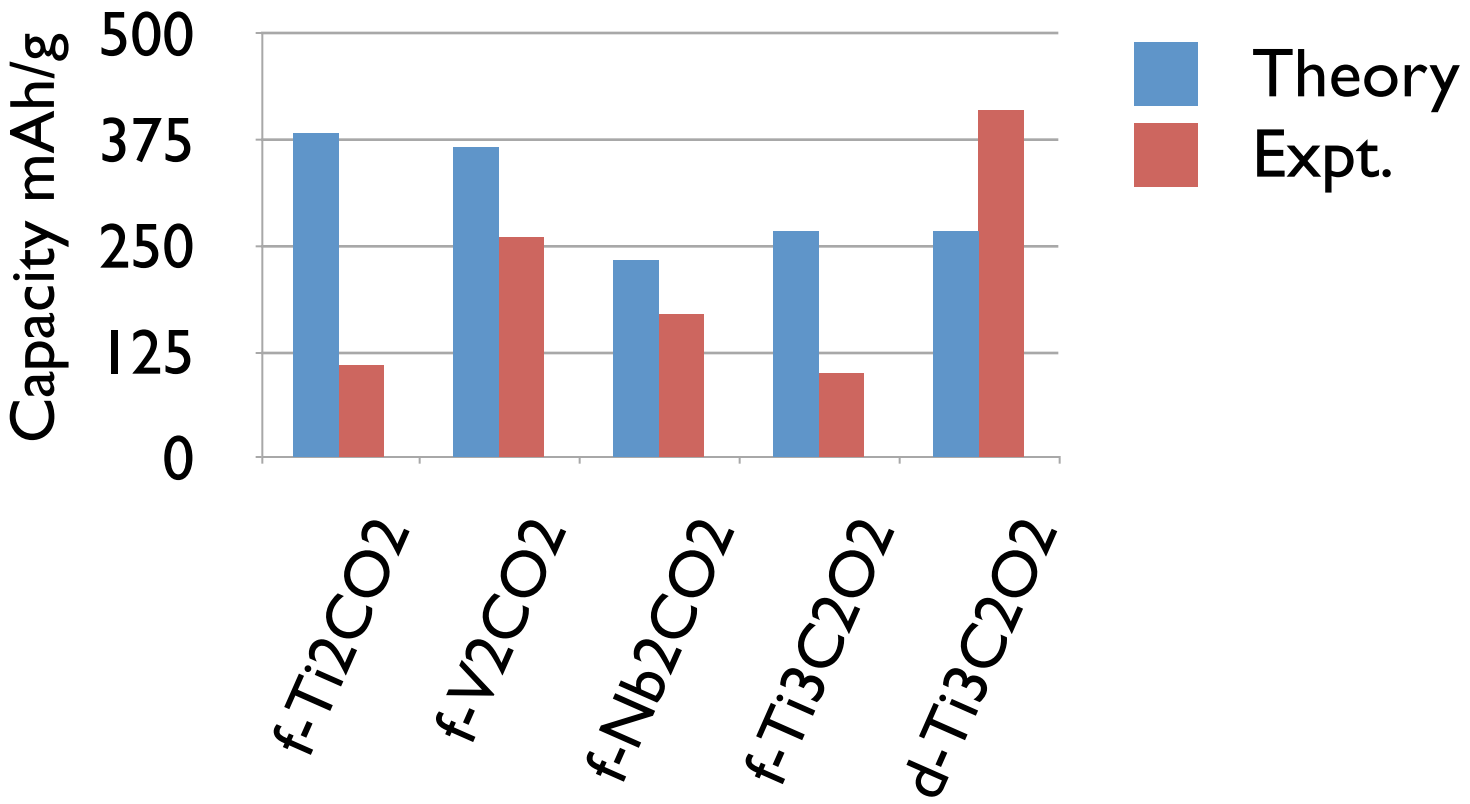
Li adsorption and storage of O terminated MXenes





- **O terminated MXenes can adsorb 2 Li directly per formula unit (same as bare MXenes)**
- **O termination is more preferred for Li storage and gives reasonable capacities**
- **For d-Ti3C2, the Li experimental capacity can't be purely from the single layer of Li (!!)**
- **(Bare MXenes, not shown, display intermediate capacities)**

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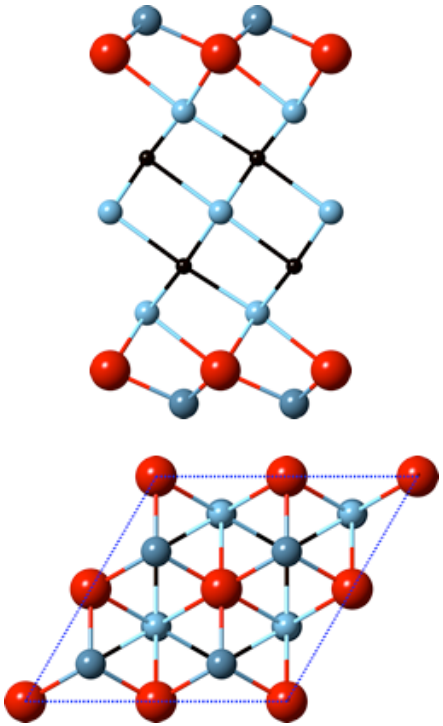
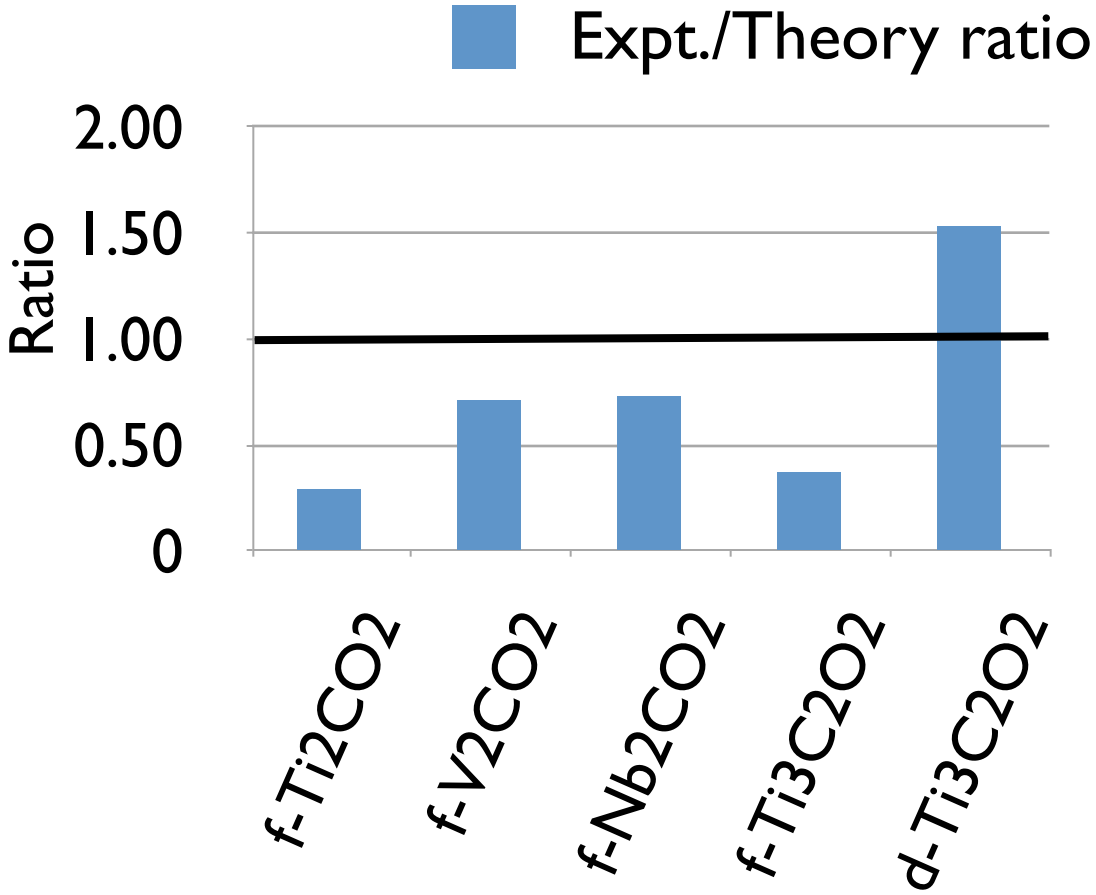
Li adsorption and storage of O terminated MXenes





- **O terminated MXenes can adsorb 2 Li directly per formula unit (same as bare MXenes)**
- **O termination is more preferred for Li storage and gives reasonable capacities**
- **For d-Ti3C2, the Li experimental capacity can't be purely from the single layer of Li (!!)**
  Discrepancy too large to be due to DFT errors

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Li adsorption and storage of MXenes

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Oak Ridge National Laboratory

Li adsorption and storage of O terminated MXenes

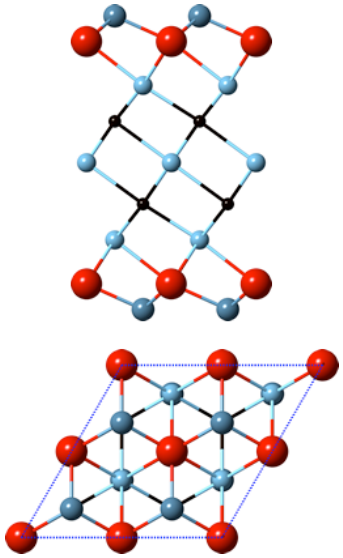

TABLE IV. Calculated vDW–DF Li adsorption energy and Li ion storage capacity of O terminated MXenes.

	E_{ad} (eV)	F (mhA^{-1}/g)		r (Exp./Theo.)	OCV
		Theo.	Exp.		
Ti_2CO_2	-1.364	383	110	0.29	>1
V_2CO_2	-1.539	367	260	0.71	1.5
Nb_2CO_2	-1.019	233	170	0.73	<1
$Ti_3C_2O_2$	-1.404	268	100 (410)	0.37 (1.53)	>1

- **O terminated MXenes can adsorb 2 Li directly per formula unit (same as bare MXenes)**
- **O termination is more preferred for Li storage and gives reasonable capacities**
- **For d-Ti3C2, the Li experimental capacity can't be purely from the single layer of Li (!!)**

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Obtaining O terminations by reaction of OH groups

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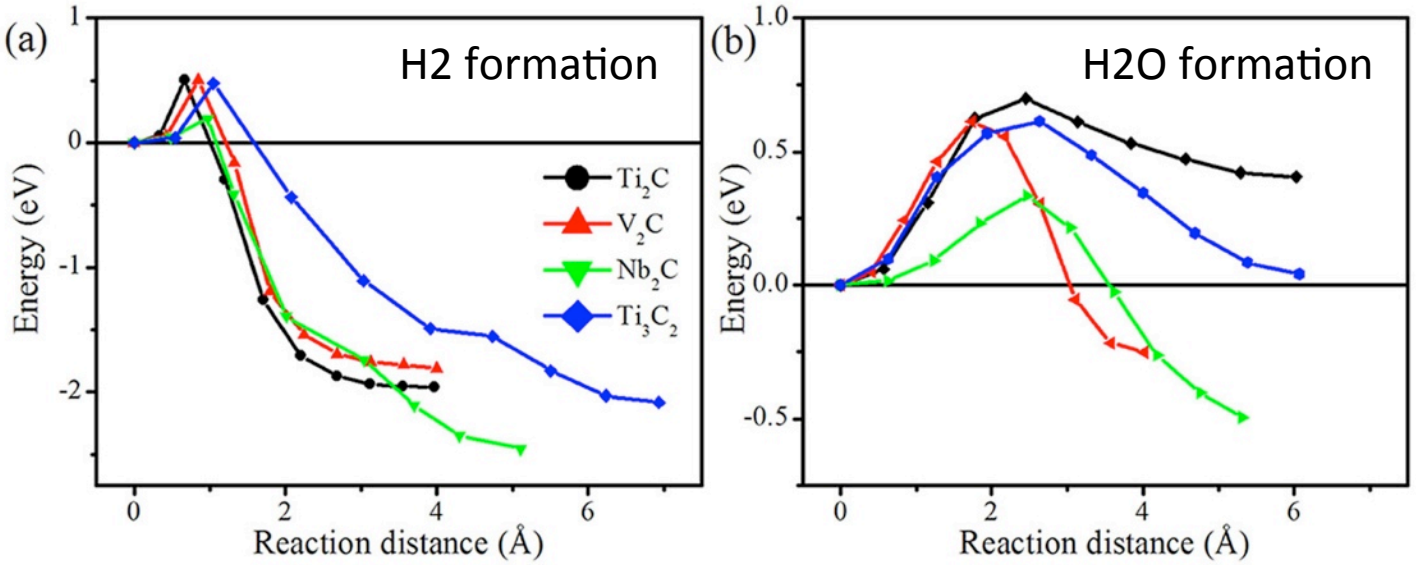
Oak Ridge National Laboratory

Analysis of simple reactions find H2O and H2 formation is feasible. Ti-based materials show the highest reaction barriers... potentially the cause of the lower experimental capacities?

$$M_{n+1}X_n(OH)_2 + 2\,Li \rightarrow M_{n+1}X_nO_2Li_2 + H_2$$

$$M_{n+1}X_n(OH)_2 + 2\,Li \rightarrow M_{n+1}X_nOLi_2 + H_2O$$



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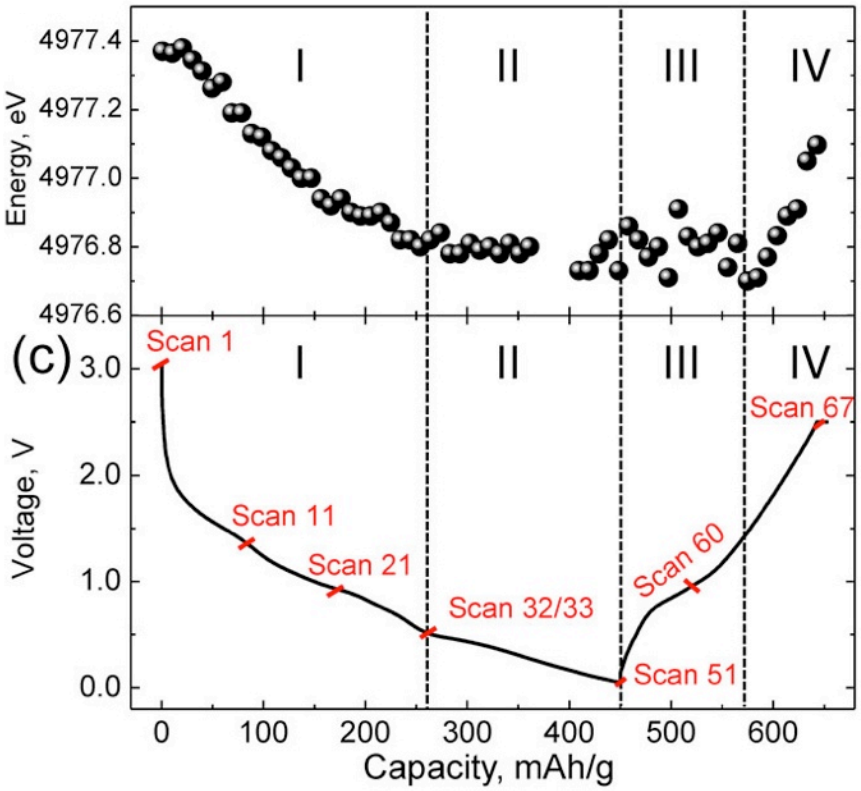
X-ray adsorption spectroscopy measurements of first lithiation/delithiation cycle of f-Ti_3C_2



- Ti^{4+} reduced to Ti^{3+} upon lithiation.
- No additional conversion reactions
- Two distinct region upon lithiation/delithiation.
- Li capacity reaches 262 $mAhg^{-1}$ at the end of region I, which is 1.95 Li adsorbed per $Ti_3C_2O_2$ unit. Gives confidence in DFT predictions.
- 1.4 extra Li need for the capacity from region II.
- The flat XANES of region II and III suggests no direct interaction between Ti and extra Li.
- The irreversible Li capacity may due to the reduced Li diffusion by reaction products (H_2, H_2O, SEI, etc.)

An additional mechanism for Li storage is needed for region II

Our proposal: extra Li may be stored on top of $Ti_3C_2O_2Li_2$

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Adsorption of extra Li layer

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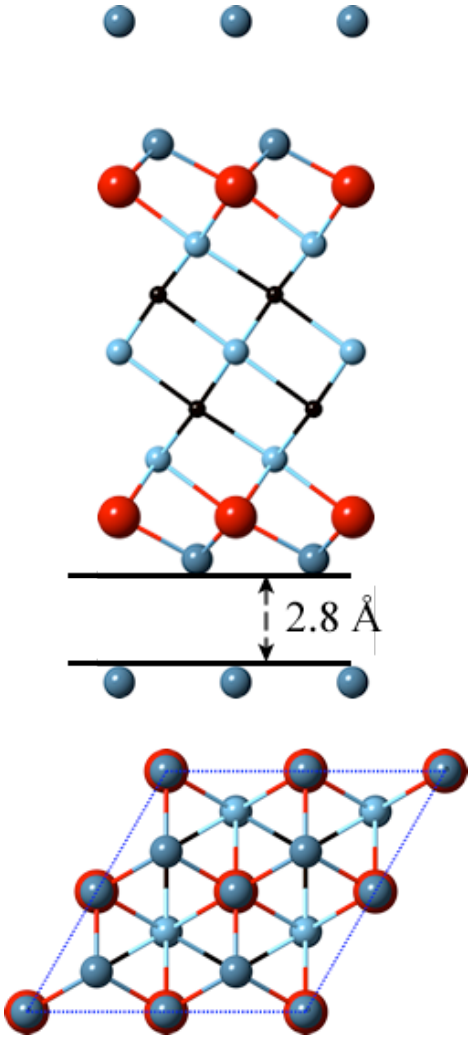
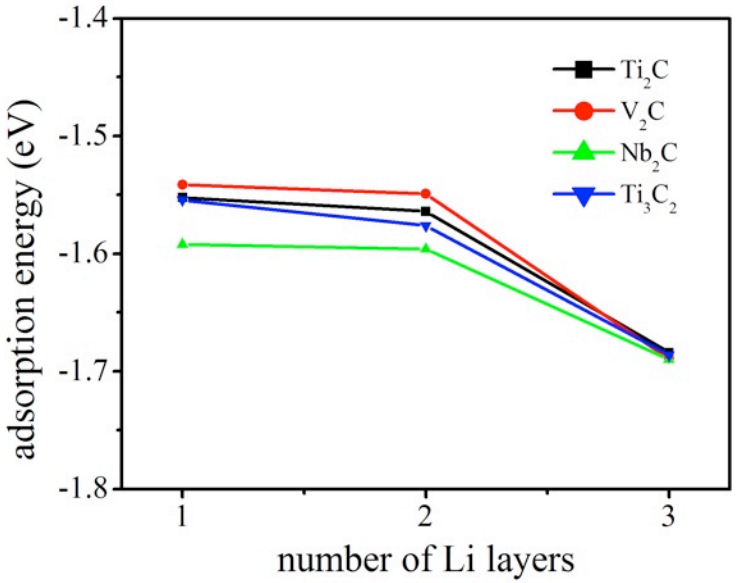
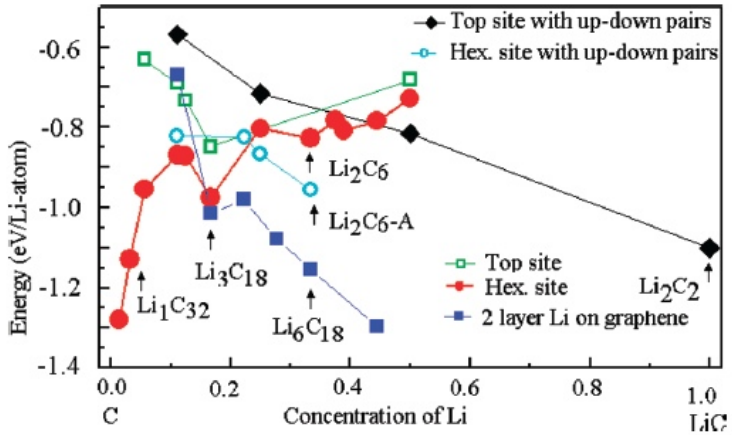




Li adsorption energy as a function of extra Li layers. We used isolated Li atom as the reference. The cohesive energy of bulk Li is -1.65 eV/atom.



Mechanism is similar to what has been suggested for pristine graphene and some related nanomaterials, a tendency to form a 3D structure

A large space is needed for the extra Li layer. F-Ti_3C_2 (20 m^2/g), d-Ti_3C_2 (100 m^2/g).

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Electron localization function of Li layers

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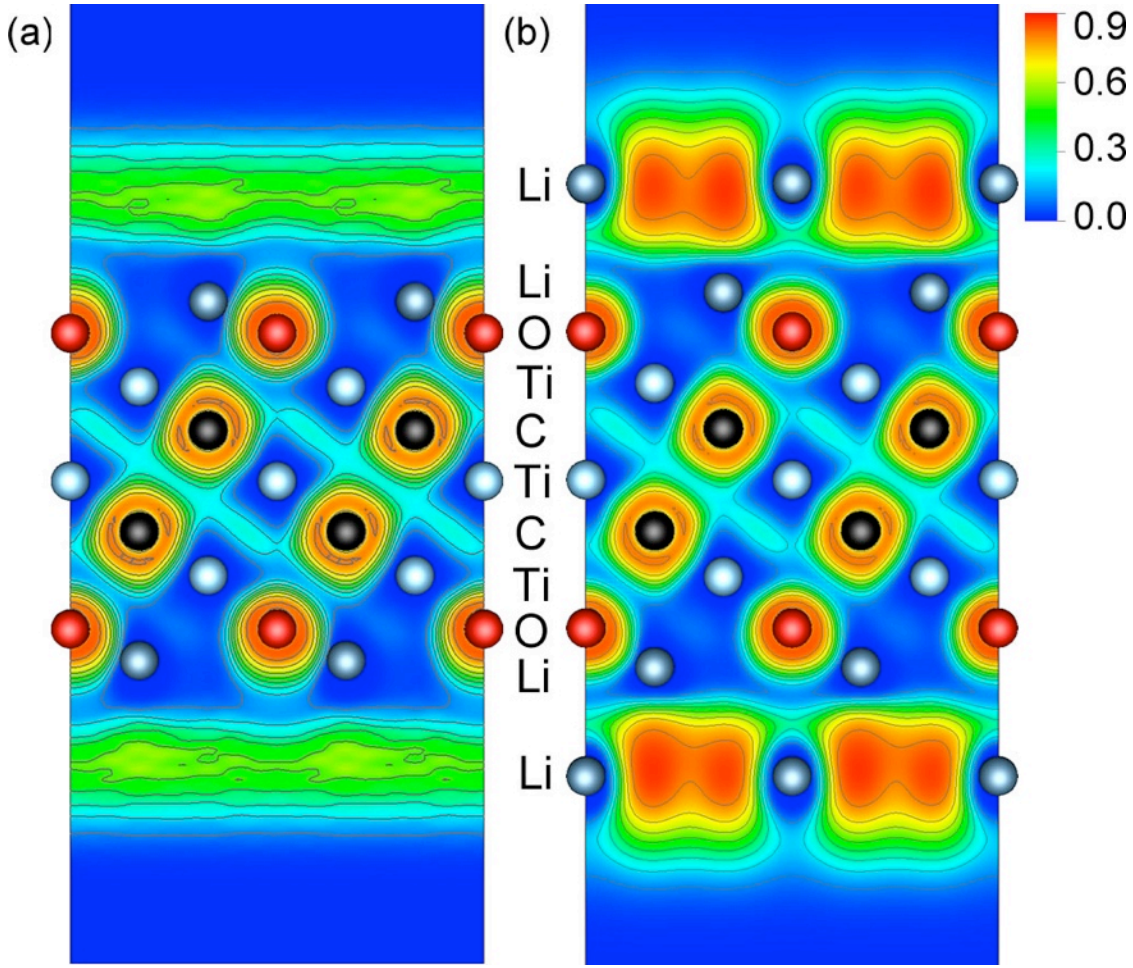

Single Li layer

Two Li layers

- **Additional Li displays distinct bonding to first Li layer**
- **With the additional Li layers, the electrons are localized in the inter layer spaces between Li layers and between outermost Li atoms**
- **Little change around Ti atoms (consistent with XAS)**
- **The negative charged electron pockets may screen the Coulumb repulsion between positive Li ions to stabilize the extra Li layers.**

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Goals

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Oak Ridge National Laboratory

1. **Understand the origin of the Li capacity in MXenes**

   A single adsorbed Li layer explains much of the observed capacity.

   For high capacity, favor oxygen terminated MXenes and reactions/processing that facilitate oxygen termination.

2. **Explain why Ti-based f-MXenes have lower Li capacity compared to other MXenes? (counterintuitive)**

   e.g. f-Ti2C 110 $mAhg^{-1}$ vs f-Nb2C 170 $mAhg^{-1}$

   Ease of surface chemistry varies with MXene. Oxygen termination is preferred.

3. **Explain why d-Ti_3C_2 has a much higher Li capacity than f-Ti_3C_2**

   Additional Li layers

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Prediction of other MXenes

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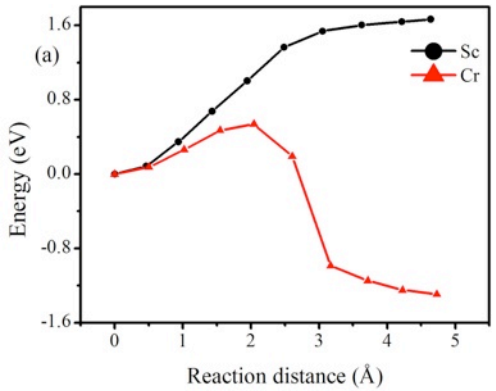
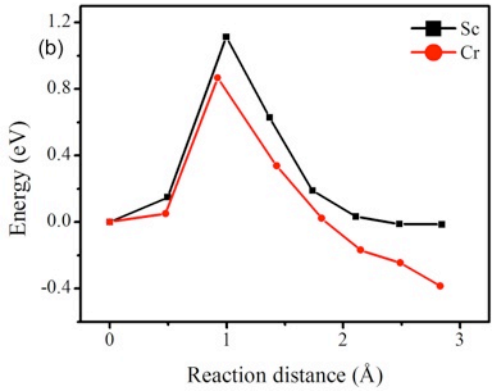
Rules for high capacity:

1. High intrinsic capacity for single layer Li absorbed on oxidized MXene
2. Low energy barriers to react away -OH groups from synthesis
3. Delamination

e.g. We calculate capacities of not-yet synthesized oxidized Sc_2C ~400 $mAhg^{-1}$ and Cr_2C ~360 $mAhg^{-1}$



$$M_{n+1}X_n(OH)_2 \rightarrow M_{n+1}X_nO + H_2O$$



$$M_{n+1}X_n(OH)_2 + 2\,Li \rightarrow M_{n+1}X_nO_2Li_2 + H_2$$

Due to greater reaction barriers, Sc_2C will likely have a lower Li capacity than Cr_2C, while Cr_2C may posses an Li capacity rivaling or exceeding V_2C (~260 $mAhg^{-1}$) Delamination will further increase capacity

Conclusions

- MXenes are a new and extensive family of 2D materials that are promising for applications.
- Sample preparation and surface reactions can significantly influence the energy capacity.
- O termination is preferred for Li storage.
- To explain the high measured capacities of delaminated MXenes, we propose that additional Li capacity may originate from extra Li layers.
- Lots of opportunity to further optimize MXenes.

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