New Layered Nanolaminates for Use in Lithium Battery Anodes

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Project ID # ES146

Overview

Timeline

- Project start date: Jan. 2011
- Project end date: Dec. 2014
- Percent complete: 25%

Budget

- Total project funding
  - $1M
- Funding received in FY11: $245K
- Funding for FY12: $245K

Barriers

- Barriers addressed
  A. Short life-span of modern batteries,
  B. Low charge density, and
  C. Compromised safety.

Partners

Externally supported collaborations

- Paul Sabatier University, Toulouse, France, Prof. P. Simon
- Linkoping University, Sweden Prof. L. Hultman

Technical Objectives and Technical Approach

- **Objectives of this Study:**

Replace graphite with a new material. Layered ternary carbides and nitrides known as MAX phases - may offer combined advantages of graphite and Si anodes with a higher capacity than graphite, lesser expansion, longer cycle life and, potentially, a lower cost that Si nanoparticles.

Milestones for FY11

Month/Year	Milestone
June-11	Produce porous anodes of MAX phase that require neither binder nor carbon black additives **Complete**
June-11	Demonstrate by modeling that MAX phases have a potential to surpass conventional carbon anodes **Abandoned due to change in research direction to concentrate on MXenes (exfoliated MAX phases) instead of pristine MAX phases.**
September- 11	Achieve particle size reduction and exfoliation of MAX phases into graphene-like 2-D structure "MXene" **Complete**
December-11	Conduct a complete electrochemical characterization of MAX phases and demonstrate the effect of vacancies in the metal sublattice on lithium uptake by the anode.

Milestones for FY12

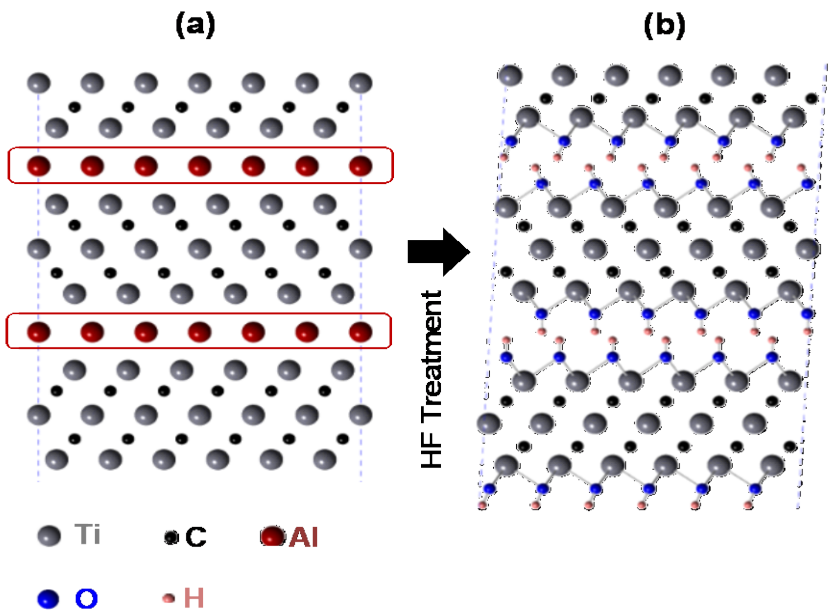
Month/Year	Milestone
March-12	Reduce the particle size of MAX phase to submicrometer level and demonstrate a correlation between the particle size and the Li uptake capacity.
September-12	**Partially/and or fully remove the A-group layer from the MAX phase (fully removing "A" layer resulted in exfoliation of MAX phases into graphene-like 2-D structure which were labeled "MXene") and study its effect on electrochemical behavior as anodes Li-ion batteries.**
December- 12	**Produce anodes from MAX and/or MXene with the capacity of about 80% of the commercial graphite anodes.**

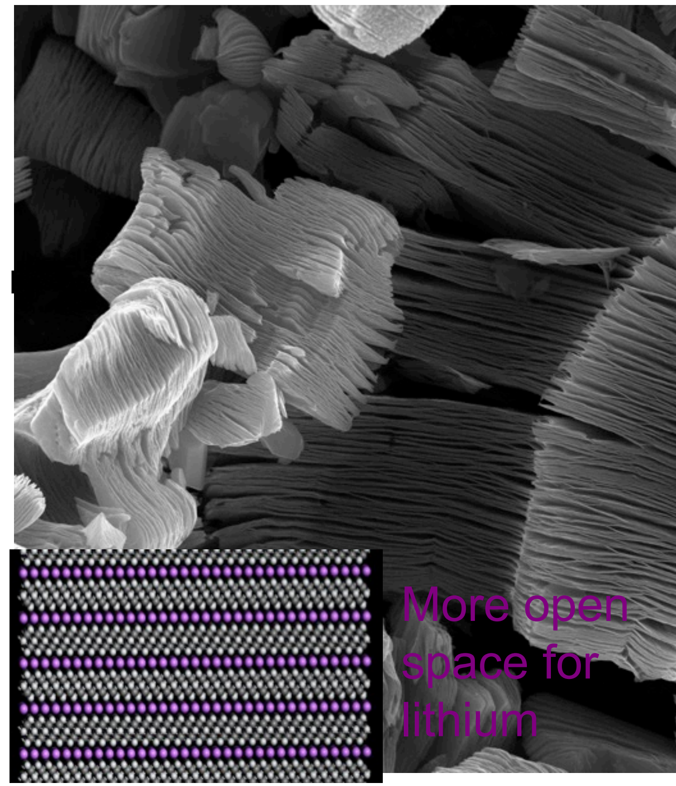
Approach/Strategy

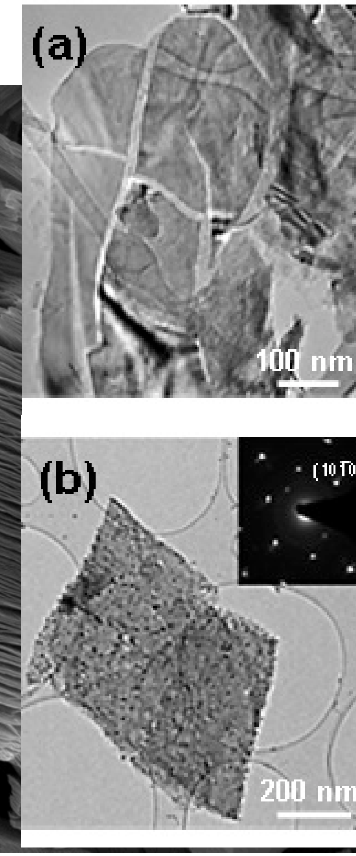
- Rapid screening of as many MAX phases as possible shall be carried out to find out the most promising chemistry, by testing their performance in LIB.
- *ab initio* calculations to guide the selection of best MAX phase.
- Reducing particle size, selective etching of an A element from the MAX structure, and exfoliation of these layered structure also will be investigated to increase the Li uptake of these structures and increase the charge density.

Technical Accomplishments

Previous Presented







Immersing Ti_3AlC_2 in hydrofluoric acid (50% conc.) at room temperature for 2h resulted in selective etching of Al out from the structure and exfoliation of 2-D layers of Ti_3C_2 we called “MXene”. MXenes should have much higher lithium uptake than MAX phases due to the more open structure of former than the latter.

Naguib, M.; Kurtoglu, M.; Presser, V.; Lu, J.; Niu, J.; Heon, M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W., Two Dimensional Nanocrystals Produced by Exfoliation of Ti_3AlC_2. Advanced Materials 23 (2011) 4248-4253

Technical Accomplishments

MXene (family not just a phase)

Compound	HF Conc. %	Time (h)	*c* lattice parameter (nm)		Yield (wt. %)
			Before HF	After HF	
Ti_2AlC (211)	10	10	1.36	1.504	60 %
Ta_4AlC_3 (413)	50	72	2.408	3.034 2.843	90%
TiNbAlC Solid solution 211	50	28	1.379	1.488	80%
$(V_{0.5}Cr_{0.5})_3AlC_2$ Solid solution 312	50	69	1.773	2.426	NA
Ti_3AlCN Carbonitrides	30	18	1.841	2.228	80%
Ti_3AlC_2 (312)	50	2	1.842	2.051	100%

Since MAX phases has different sub-classes (M_2AX, M_3AX_2, M_4AX_3, solid solutions at M sites, and carbonitrides) we selected MAX phases, other than Ti_3AlC_2, represent the different classes of MAX and investigated the possibility of exfoliation. We found that all of them can be exfoliated by controlling the concentration and time for the HF treatment. Which turns in a new family of 2-D transition metals carbides and carbonitrides

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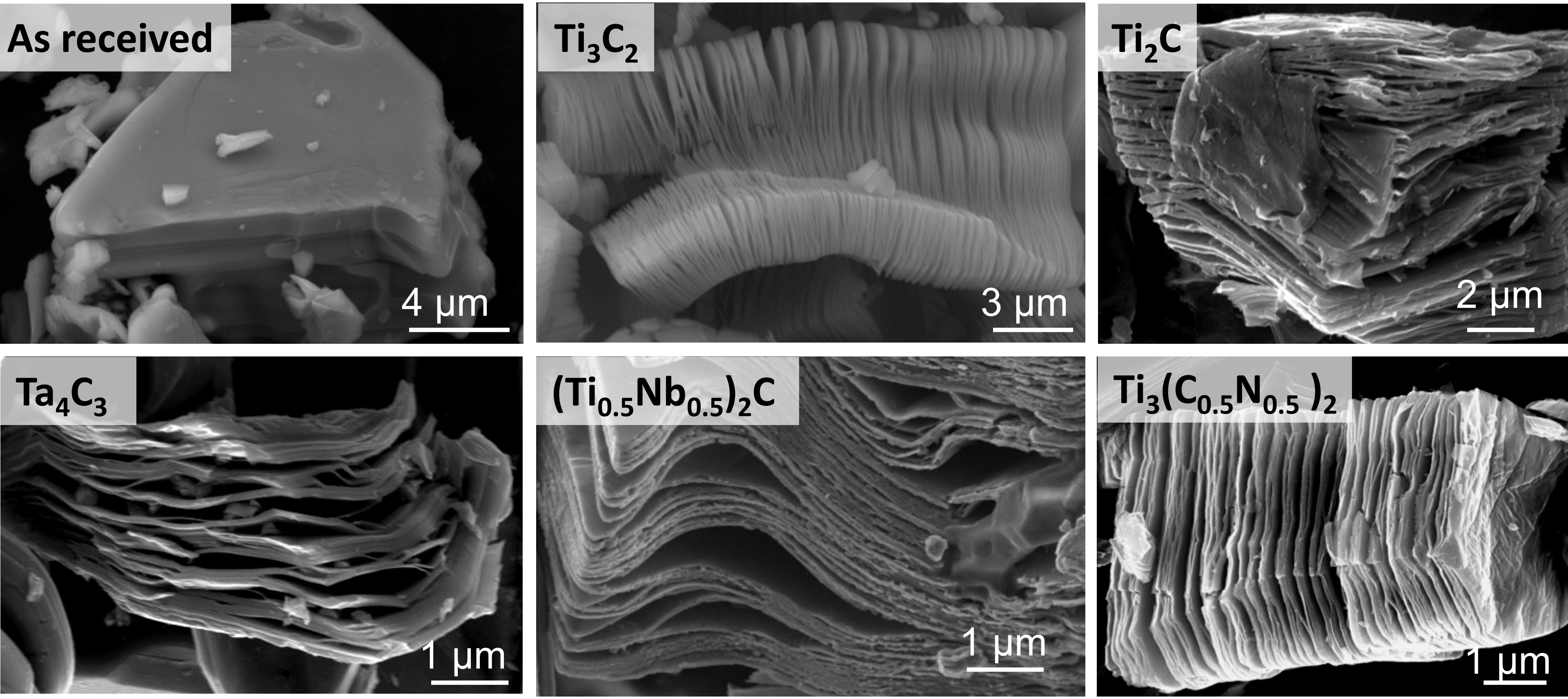
Technical Accomplishments

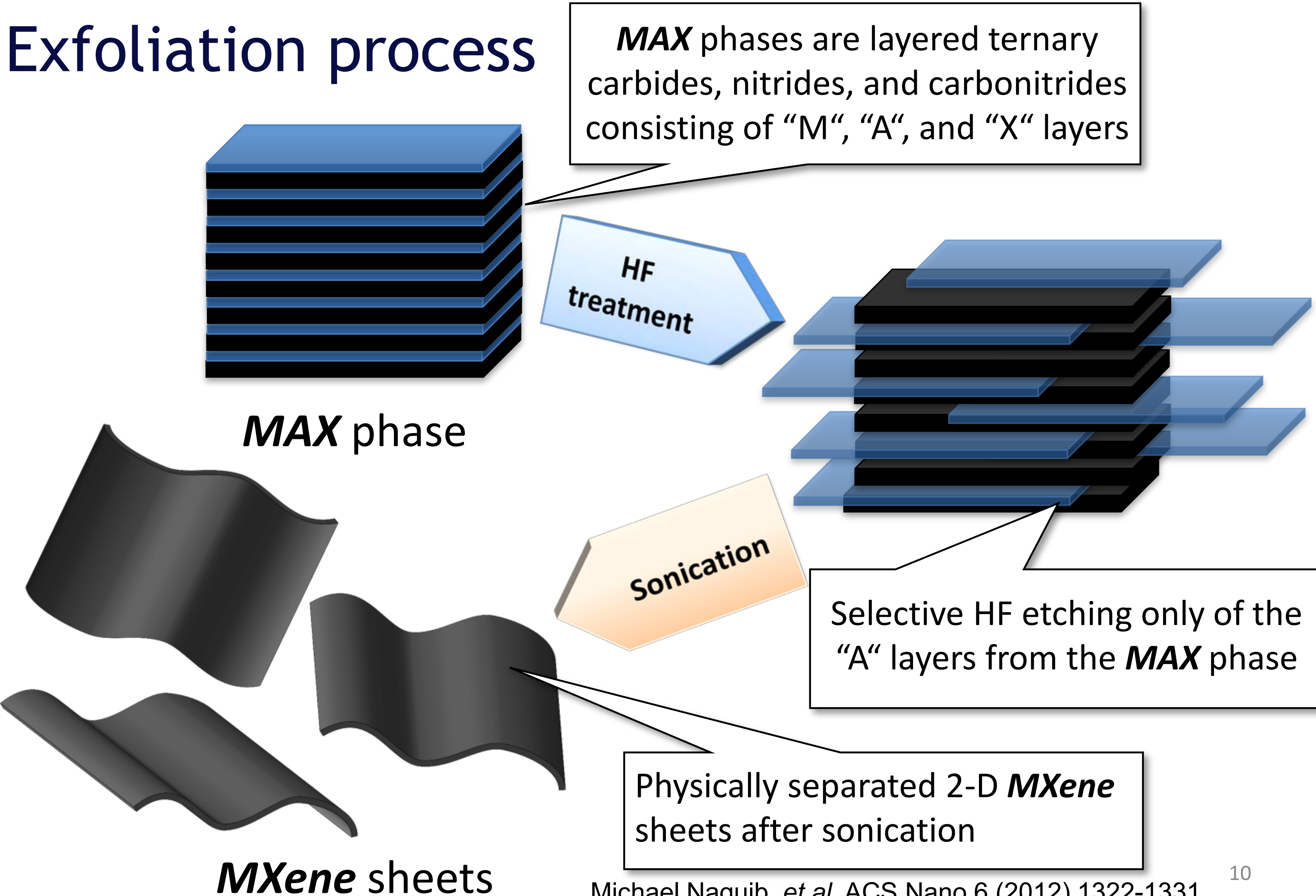
MXene (family not just a phase)



SEM images confirm the exfoliation of different MAX phases

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

Exfoliation process



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

Technical Accomplishments
Resistivity and Contact Angle of MXene

- MXene can be cold pressed in the form of thin (300μm) free standing discs.
- Resistivity is comparable to multi layer graphene.
- Contact angle measurements of water showed **hydrophilic** behavior.

	Ti_2C	Ta_4C_3	$(Ti_{0.5}Nb_{0.5})_2C$	$Ti_3(C_{0.5}N_{0.5})_2$
R:	***330*** Ω/□	***104*** Ω/□	***171*** Ω/□	***125*** Ω/□
CA:	***32°***	***41°***	***31°***	***27°***

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

Technical Accomplishments

MXene in Lithium Ion Batteries (LIB)

- Gas (N_2) sorption analysis

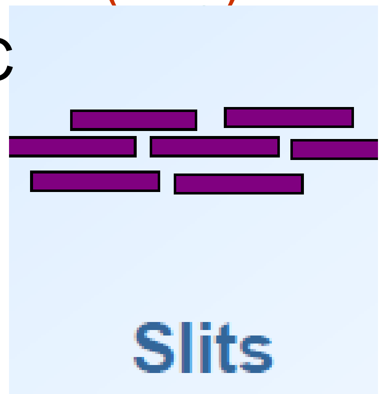
HF treated Ti_2AlC (Ti_2C)

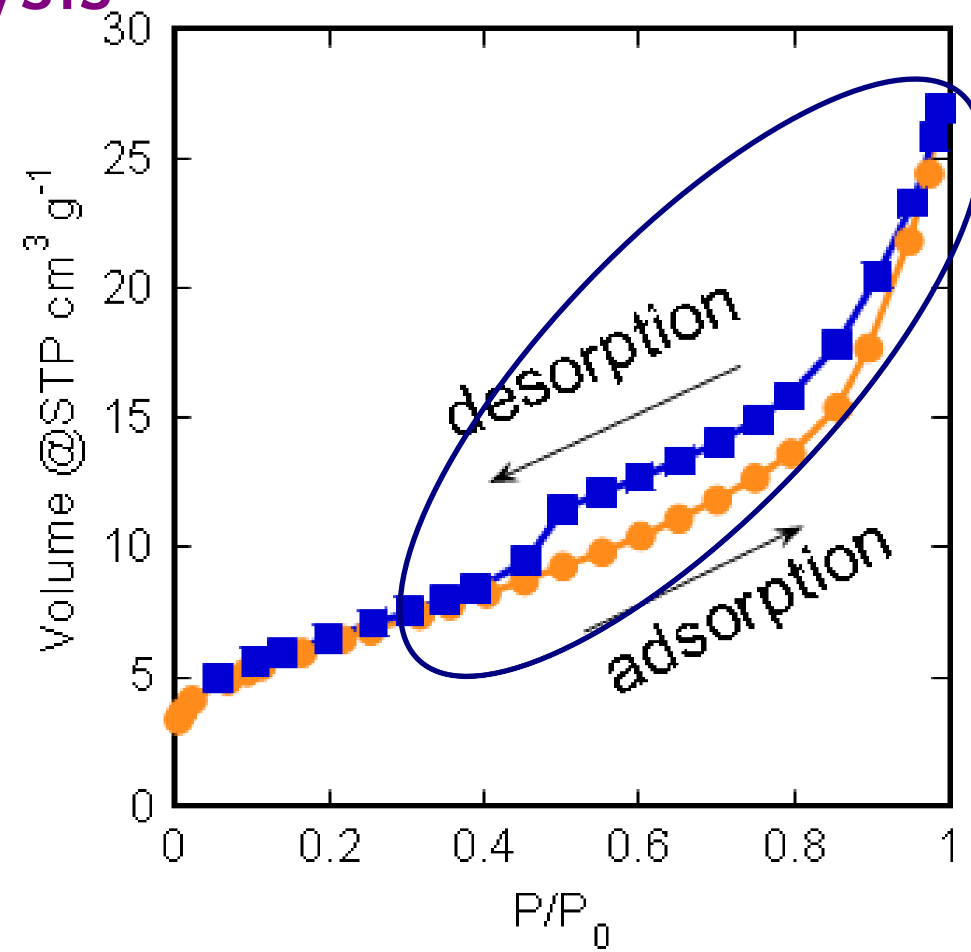
BET SSA before HF~ 22.9 m^2/g

>10 times

Type B (Slits)

Ti_2AlC





Michael Naguib, *et al.* Electrochemistry Communications 16 (2012) 61-64

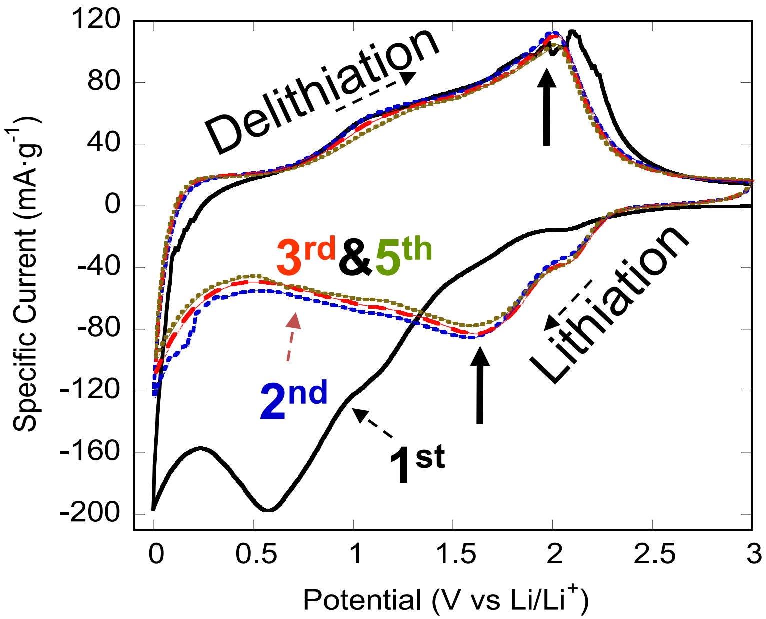
Lowell, S.; Shields, J. E., *Powder Surface Area and Porosity*. 3rd ed.; Chapman & Hall: New Yourk, 1991

Technical Accomplishments

MXene in Lithium Ion Batteries (LIB)

Ti_2C based anode

- The lithiation peak around potentials 1.6V.
- The delithiation peak around potentials 2.0V.
- Those potentials are close to titania based anodes.



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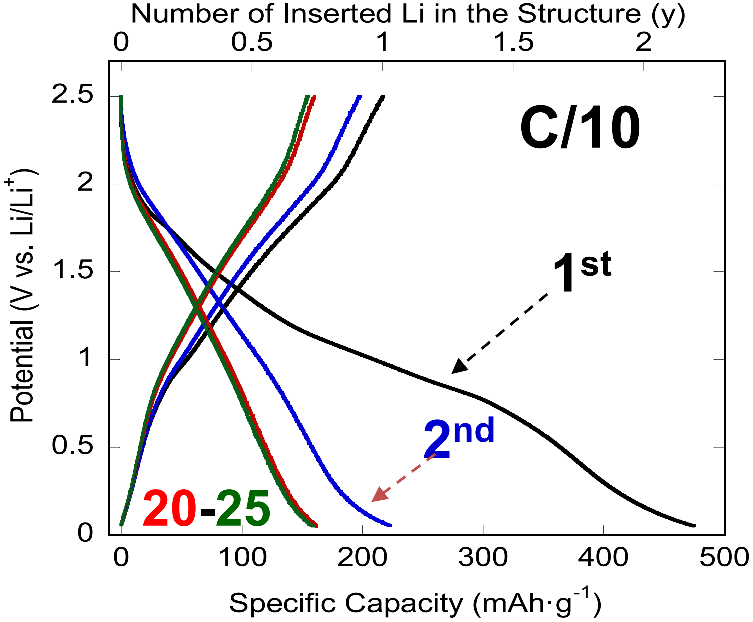
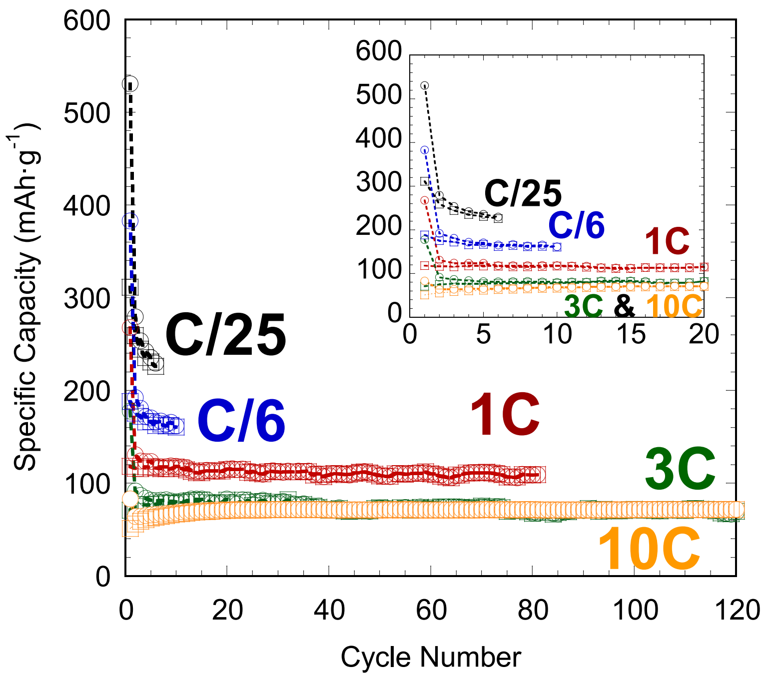
Technical Accomplishments

MXene in Lithium Ion Batteries (LIB)

Ti_2C based anode





- Stable capacity of 170 mAh/g at C/10 , also Ti_2C can be cycled at fast cycling rate
- Large 1st cycle irreversibility, can be due to SEI, or trapped Li between Ti_2C layers

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Activities for the Next Fiscal Year

- Investigate different MXenes as anodes in LIBs
  - Ti_2C, Ti_3C_2, Ti_3CN, TiNbC, Nb_2C, Ta_4C_3
- Work on reducing the 1st cycle irreversibility and increase the stable capacity:
  - Study the lithiation and delithiation mechanisms in different MXenes
  - Study the effect of different carbon additives on the performance of MXene anodes

Summary

- Selective etching of A out from MAX phases results in exfoliation of MX layers forming new family of 2-D transition metals carbides and carbonitrides we call "MXene"
- Li intercalates reversibly between the MXene sheets (MXene anodes in LIB)
- The potential and reversible capacity are comparable to titania-based anodes in LIB
- Large 1st cycle irreversible capacity