MXenes - A New Family of 2-D Transition Metal Carbides for Li-ion Battery Anodes


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MAX Phases

- Ternary metals carbides and/or nitrides
- Layered hexagonal structure (P6₃/mmc)
- Composition of $M_{n+1}AX_n$; with $n = 1, 2, 3$
- Examples: Ti₂AlC, Ti₂AlN, Ti₃AlC₂, Ti₄AlN₃, Ta₂AlC, Ta₄AlC₃, Cr₂AlC, Cr₃AlC₂, V₂AlC, V₃AlC₂, Nb₂AlC, Nb₄AlC₃ (>60 phase), $\text{(Ti}_{0.5}\text{Nb}_{0.5})_2\text{AlC}$, $\text{Ti}_3\text{Al(C}_{0.5}\text{N}_{0.5})_2$
  (considering solid solution, there will be more)

Can we exfoliate MAX Phases; to produce 2-D transition metal carbides and/or nitrides?!
**MAX** phases are layered ternary carbides, nitrides, and carbonitrides consisting of “M“, “A“, and “X“ layers.

- **MAX** phase

- *“A” layer etching*

- **Sonaicaiton**

- Selective etching only of the “A” layers from the **MAX** phase

- Physically separated 2-D **MXene** sheets after sonication

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 Patent pending – US and international patents filed
Etched Ti₃AlC₂

Ti₃AlC₂ in HF 50% for 2 hours at room temperature:

Ti₃AlC₂ after HF treatment

Exfoliated Graphite

TEM Analysis of Ti$_3$C$_2$

2-D Sheets

Ti$_3$AlC$_2$ treated in HF 50% for 2 hours at room temperature, then sonication

Other MAX phases have been successfully exfoliated producing MXenes.

As received

From Ti$_3$AlC$_2$

From Ti$_2$AlC

From Ta$_4$AlC$_3$

From (Ti$_{0.5}$Nb$_{0.5}$)$_2$AlC

From Ti$_3$Al(C$_{0.5}$N$_{0.5}$)$_2$

413

312 3 μm

211 2 μm

Ta$_4$C$_3$

(Ti$_{0.5}$Nb$_{0.5}$)$_2$C

M site solid solution

Ti$_3$(C$_{0.5}$N$_{0.5}$)$_2$

Carbonitride

MXenes Electronic Performance

- $\text{Ti}_3\text{C}_2(\text{OH})_2$: OH terminated $\text{Ti}_3\text{C}_2$ nanosheets
- $\text{Ti}_3\text{C}_2$: Bare layers, no terminations
- $\text{Ti}_3\text{C}_2\text{F}_2$: F-terminated $\text{Ti}_3\text{C}_2$ nanosheets

Ti₂C in Lithium Ion Batteries

- Ti₂C powder
- Li foil
- Half cell

Ti₂C (<30 microns) was mixed with carbon black and PVDF binder in a 80:10:10 weight ratio. The slurry was cast onto a copper foil.

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

**Ti$_2$C based anode**

\[ \text{Ti}_2\text{CO}_x + y\text{Li}^+ + ye^- \leftrightarrow \text{Li}_y\text{Ti}_2\text{CO}_x \]

- Number of Inserted Li in the Structure (y)
- Specific Capacity (mAh·g$^{-1}$)
- Potential (V vs. Li/Li$^+$)

Michael Naguib, *et al.* *Electrochemistry Communications* 16 (2012) 61-64
MXenes as Anodes in LIBs

In-situ XRD for Ti$_2$C anode

No new peaks, the charge storage is due to the intercalation of Li$^+$ ions not due a conversion reaction.

• Selective etching of “A” layer from “MAX” phases results in the formation of a new family of 2-D transition metals carbides and/or nitrides called “MXenes” (7 so far, 3 lattice structures, dozens of new materials expected).

• Band gap of MXene is predicted to change with the surface chemistry; experiments show metallic character of conductivity – unique property for an O/OH-terminated layered material.

• Sufficiently ductile for cold pressing. Binder-free paper can be produced.

• Additive-free delaminated Ti$_3$C$_2$ anodes showed high Li$^+$ uptake at high rates: 410 mA.h.g$^{-1}$ at 1 C, and 110 mA.h.g$^{-1}$ at 36 C (200 cycles).

• MXenes show promising performance in anodes of Li-ion batteries.

• Further improvements in anode performance to be achieved by tuning surface chemistry, accessible surface area and insertion potential.