FIRST Center Research Perspective:

Interfacial Properties of Two-Dimensional Carbides and Carbonitrides, MXenes

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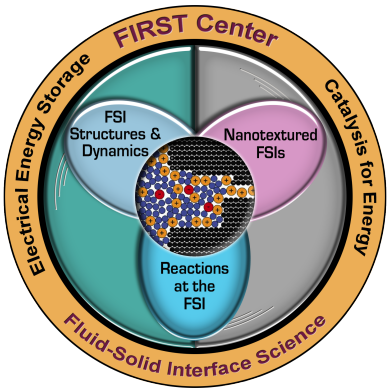

Research Summary:

The family of two-dimensional (2D) materials has been recently augmented by a group of early transition metal carbides and carbonitrides – *MXenes,* discovered and developed at Drexel University. One of the very promising applications of MXenes that has been explored experimentally is using them as electrode materials for electrochemical energy storage systems. With the excellent computational facilities at ORNL, we were able to answer questions raised from the experimental findings, such as: (1) how could we control the surface chemistry, (2) why does V_2C have better performance than Ti_2C or Nb_2C MXenes, and (3) can we calculate the maximum theoretical capacity of MXenes?

Technical Details:

MXenes were produced by selective etching A atoms from MAX phases (**Figure 1**). The latter have composition of $M_{n+1}AX_n$; where M is early transition metal (Ti, Mo, V, etc.), A is a group A element (e.g. Al, Si), X is carbon and/or nitrogen and n = 1, 2, or 3. So far, the following MXenes have been produced experimentally Ti_3C_2, Ti_2C, V_2C, Nb_2C, $(Ti_{0.5}Nb_{0.5})_2C$, Ta_4C_3, $(V_{0.5}Cr_{0.5})_3C_2$, Ti_3CN, and many more are expected to be stable. The as-synthesized MXene surfaces are terminated with O, OH, and F. According to DFT calculations, the terminations are expected to modify the electronic structure of MXenes, for example bare MXenes are expected to be metallic conductors, while OH terminated MXenes are predicted to be semiconductors with relatively small band gaps.

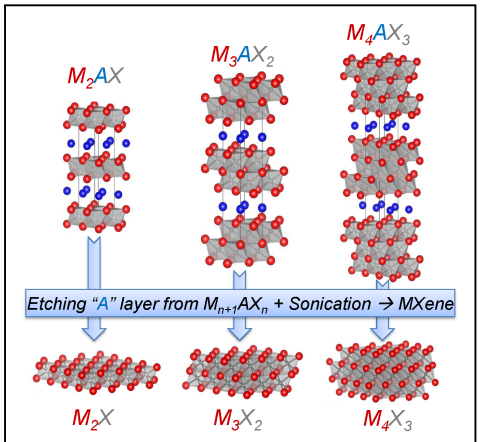

Figure 1. Schematic for MXenes structures with different number of atomic layers and their MAX phases counterpart. (Naguib, 2014)

The modeling studies reported thus far on MXenes have been primarily focused on properties in vacuum. DFT-based modeling has been performed for the structure of bare MXenes and, in order of stability H, O, OH, and F terminations (Xie, 2013). However, previous calculations were almost all performed for single MXene sheets, and do not reflect the experimental reality of stacked MXene "flakes" consisting of multiple MXene sheets. Our own *ab initio* calculations for pure MXenes (Xie, 2013) showed good agreement with the available X-ray diffraction data. However, our DFT-MD simulations indicate that bare MXenes in contact with water become terminated by hydroxyl groups or

oxygen atoms, influencing their structure, reactivity, and ability to adsorb and transport ions (**Figure 2**). The interaction dynamics of molecules and ions with MXenes, and their capacitive, intercalation and ion exchange properties, can only be addressed by CMD simulations. Accordingly, we are developing ReaxFF force fields for MXenes, validating them against *ab initio* calculations, which in turn will be validated against thermochemical measurements

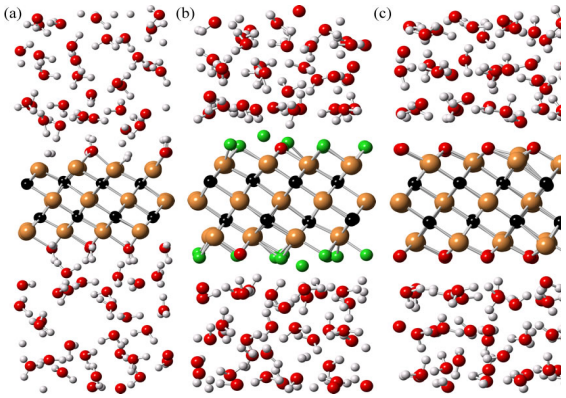

Figure 2. Structure of (a) bare Ti_3C_2, (b) F and (c) O terminated Ti_3C_2 MXenes in water, from van der Waals DFT-MD simulations (Xie, 2014)

Our calculations predict that oxygen terminated MXenes have the highest Li uptake capacity among terminated MXenes. Also, the calculations predicted that OH termination can be turned into O by heating to high temperatures. Using this approach, we managed, experimentally, to get rid of the OH groups by annealing Nb_2C at 400 °C. The absence of OH groups after annealing was confirmed by inelastic neutron scattering at ORNL. In agreement with experimental data, the calculations showed that oxygen terminated V_2C has the lowest Li diffusion barrier (0.17 eV) compared to other MXenes.

Significant Impacts on Science and Technology: The development of reliable force fields for MXenes (e.g. ReaxFF) will open new possibilities for studying fluid-solid interface (FSI) phenomena that are prohibitively large/complex for DFT, and will guide synthesis and characterization of functional FSIs. The excellent agreement between theoretical calculations and experimental work on MXenes, in addition to tunability of thickness (3, 5 or 7 atomic layers for M_2X, M_3X_2 or M_4X_3, respectively), composition (Ti, Nb, V, Ta, etc. on the M site and N or C on the X site) and slit width (intercalation of different molecules) makes this group of materials an excellent model system for understanding ion behavior of ions in slit pores, as well as at interfaces with electrolytes.

Publications and Manuscripts:

1. Xie, Y.; Kent, P. R. C. Hybrid Density Functional Study of Structural and Electronic Properties of Functionalized $Ti_{n+1}X_n$ (X = C, N) Monolayers, *Phys. Rev. B* **2013**, *87*, 235441. [10.1103/PhysRevB.87.235441]
2. Naguib, M.; Mochalin, V.N.; Barsoum, M.W.; Gogotsi, Y., 25th Anniversary Article: *MXenes*: A New Family of Two-Dimensional Materials, *Advanced Materials* **2014**, DOI: 10.1002/adma.201304138.
3. Shi, C.; Beidaghi, M.; Naguib, M.; Mashtalir, O.; Gogotsi, Y.; Billinge, S.J.L. Structure of Nanocrystalline Ti_3C_2 MXene Using Atomic Pair Distribution Function, *Phys. Rev. Lett., Under Review* **2014**.
4. Xie, Y.; Naguib, M.; *et al.*, Role of Surface Structure on Li-ion Energy Storage Capacity of Two-dimensional Transition Metal Carbides, *In preparation* **2014**.