

Supporting Information

Atomic-scale understanding of Li storage processes in the Ti_4C_3 and chemically-ordered $\text{Ti}_2\text{Ta}_2\text{C}_3$ MXenes: a theoretical and experimental assessment

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Defect Formation Energy formalism is employed to investigate the thermodynamic stability of the $\text{Ti}_x\text{Ta}_{4-x}\text{C}_3$ MXenes. The 3D plot is shown in **Figure S1**, where each plane represents a different MXene. According to our formalism, the most stable structures exhibit the lowest energy values.

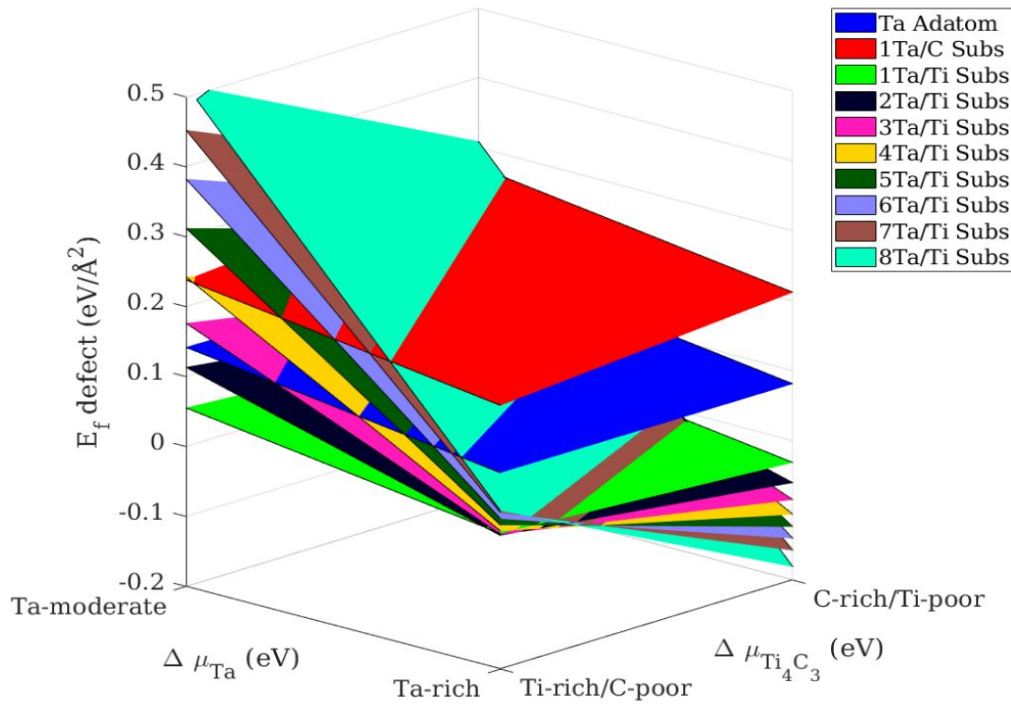


Figure S1. 3D Defect Formation Energy plot.

Same stoichiometry Ta defect analysis

Since Ta defects can be placed in different positions, it is necessary to evaluate which of these sites is more energetically favorable for the MXene. To measure the most stable sites for each defect, we directly compare the DFT total energy, since stoichiometry remains the same

because we are only changing the position and not the number of atoms. In Table S1, we present the relative energies for different Ta-incorporated Ti_4C_3 structures. Each segment of the table represents a different defect, and each column is a different atomic arrangement. For notation purposes, we use “in” to indicate that the defect is located in an inner layer, “out” to indicate that the defect is located in an outer layer. We also use “different layer” or “same layer” when we have more than one defect.

Table S1. Relative energies in Ta-incorporated structures with the same stoichiometry. In each case, the structure with the lowest energy value is the energy reference.

1 Ta Adatom		Bridge	Hollow	T4	Top
Relative energy (eV)		0.00	0.03	0.01	0.63
1 Ta/C Substitution		Out		In	
Relative energy (eV)		0.00		1.82	
1 Ti/Ta Substitution		Out		In	
Relative energy (eV)		0.00		0.54	
2 Ti/Ta	out/out	out/out same	out/in	in/in dif layer	in/in same

Substitution	different layer	layer			layer
Relative					
energy (eV)	0.98	0.99	0.51	0.00	0.05

8Ti/Ta Substitution	mixed	separate	chemically ordered
Relative energy (eV)	0.88	0.83	0.00

The atomistic models of the five most stable systems, according to the DFE formalism are displayed in **Figure S2**. In all cases, the Ta atoms occupies the Ti sites of the middle layers.

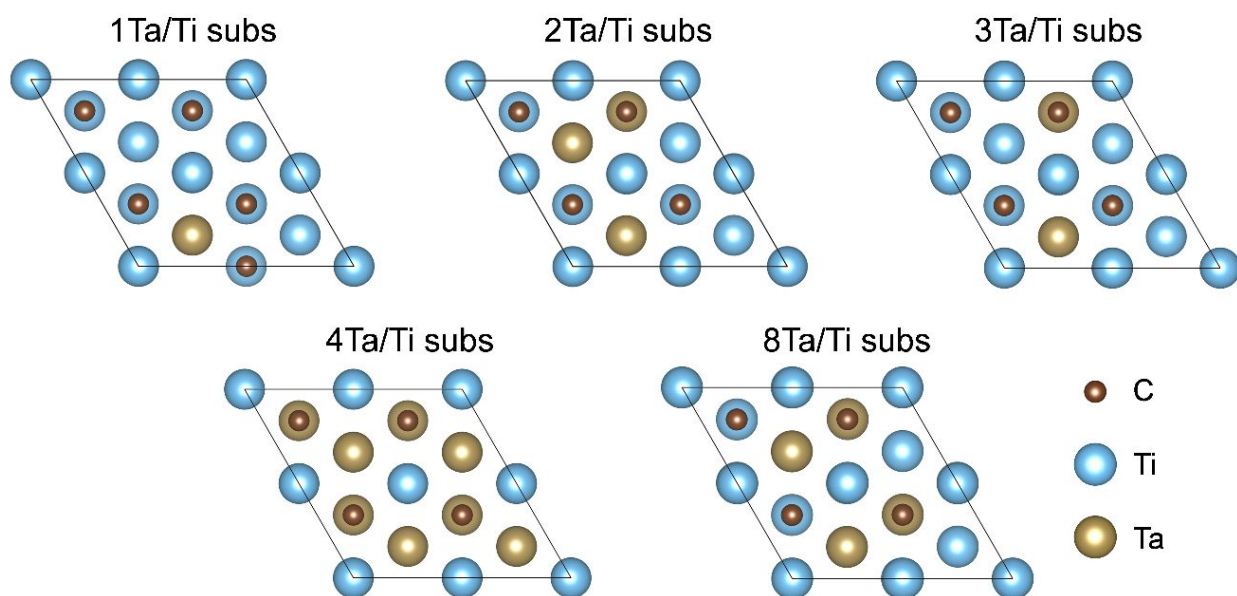


Figure S2. Atomic models for the five most stable MXenes according to the DFE formalism.

The atomic representation of the synthesized $\text{Ti}_2\text{Ta}_2\text{C}_3$ MXenes in their out-of-plane chemically-ordered atomic arrangement, which results to be the most stable configuration is displayed in **Figure S3**.

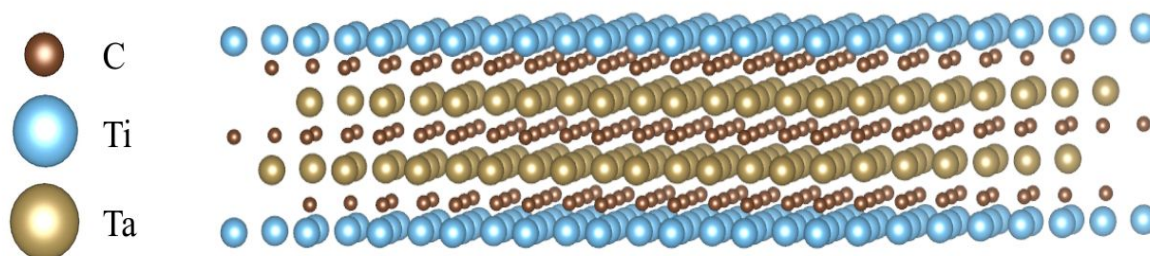


Figure S3. $\text{Ti}_2\text{Ta}_2\text{C}_3$ MXene in its chemically-ordered arrangement.

For clarity, the mixed, separate, and chemically ordered 8Ti/Ta structures are shown in **Figure S4**.

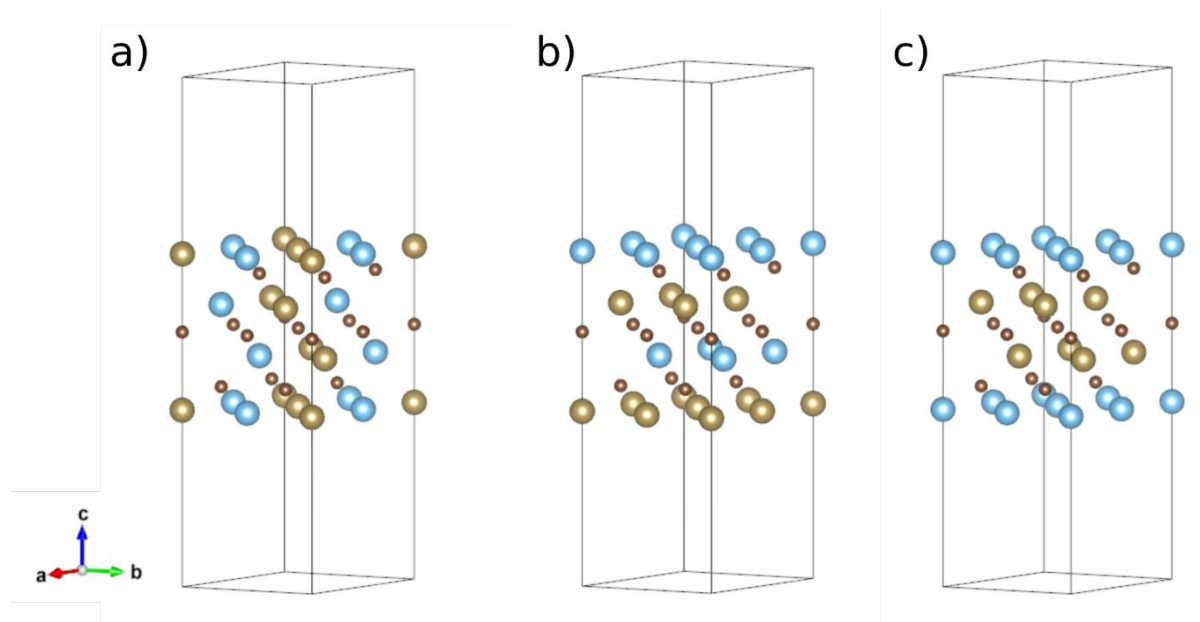


Figure S4. Different structural arrangements for the 8Ti/Ta Ti_4C_3 MXene defect structure. a) mixed, b) separate, c) chemically ordered.

Four different high symmetry sites have been considered to investigate the adsorption of Li on top of the MXene: the T4 configuration occurs when the Li is placed on top of one C atom of the 2nd monolayer; Hollow site is on top of the Ti (Ta) atom of the 3rd monolayer; Bridge site is the middle point between two Ti atoms of the 1st layer, and, Top site is when the Li is on

top of a Ti atom of the 1st monolayer. The atomic representations of the different high symmetry sites are depicted in **Figure S5**.

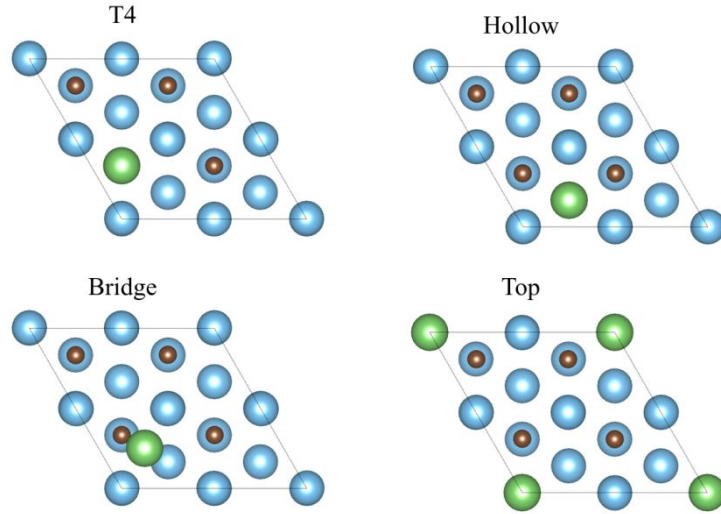


Figure S5. Four high-symmetry Li-atom positions on Ti₄C₃ considered in this work.

The OCV as a function of the Li concentration graph, considering the Li intercalation process in the two sides of the MXene is shown in **figure S6**, we observe a similar behavior in comparison with the one side Li intercalation process, the y_{max} for the pristine and chemical ordered alloy are 2.59 and 2.63, respectively.

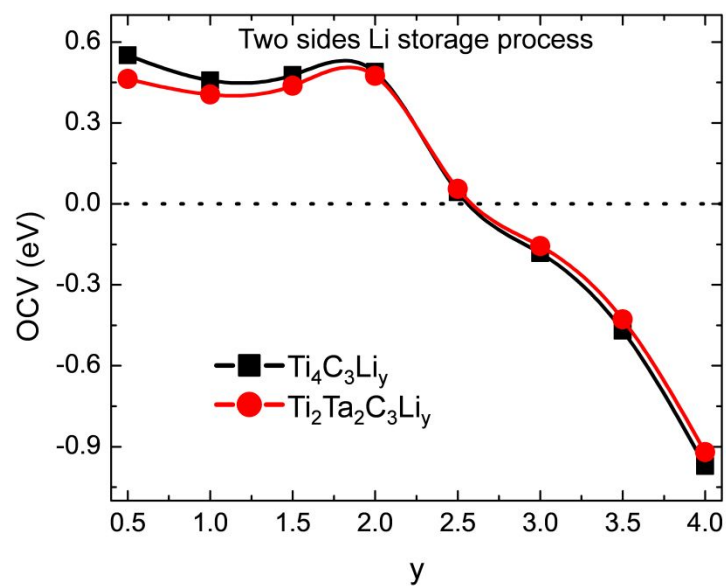


Figure S6. OCV in function of Li content, considering the case when the Li storage occurs in the two sides of the MXene.