Imidazolium Cation Intercalation for $Ti_3C_2T_x$ MXene: Insights into Electrochemical Properties via First-Principles Calculations and Machine Learning Interatomic Potentials

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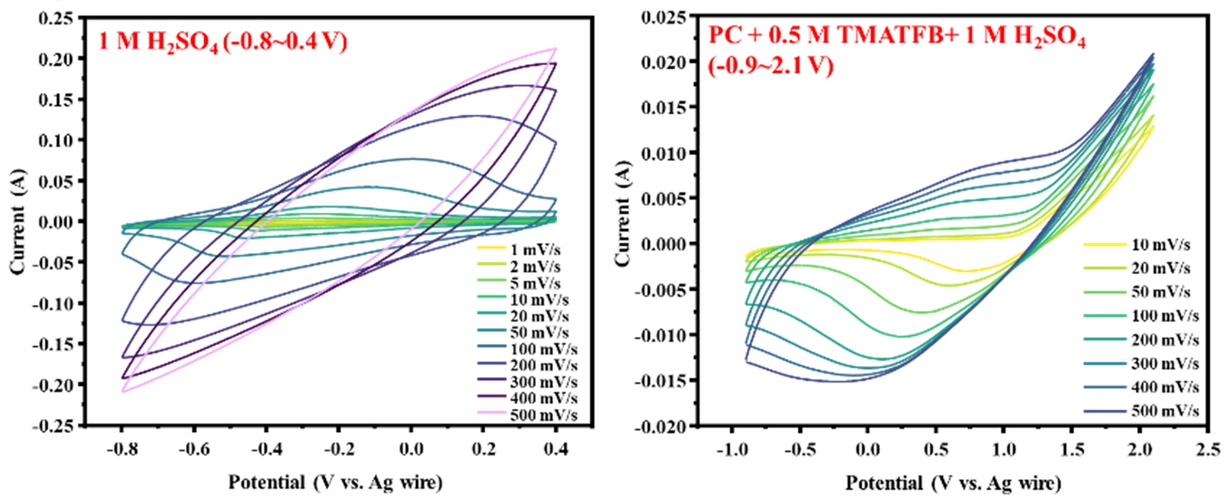
Introduction

MXene is a two-dimensional layered material derived from MAX phases through selective etching. It features high electrical conductivity, tunable surface terminations, and excellent electrochemical properties, making it highly promising for supercapacitor applications. However, van der Waals interactions cause the layers to easily restack, which limits ion transport and reduces electrochemical performance. To overcome this issue, intercalation strategies have been employed to enlarge the interlayer spacing and facilitate ion accessibility. Imidazolium-based ionic liquids are particularly attractive, as their cations can insert between MXene layers and effectively tune the spacing. Since interlayer spacing directly influences ion pathways and thereby governs proton diffusion and overall electrochemical activity, this study employs computational simulations to investigate the effects of different imidazolium cations on spacing and proton transport.

Why Do Ionic Liquids Matter in Supercapacitors?

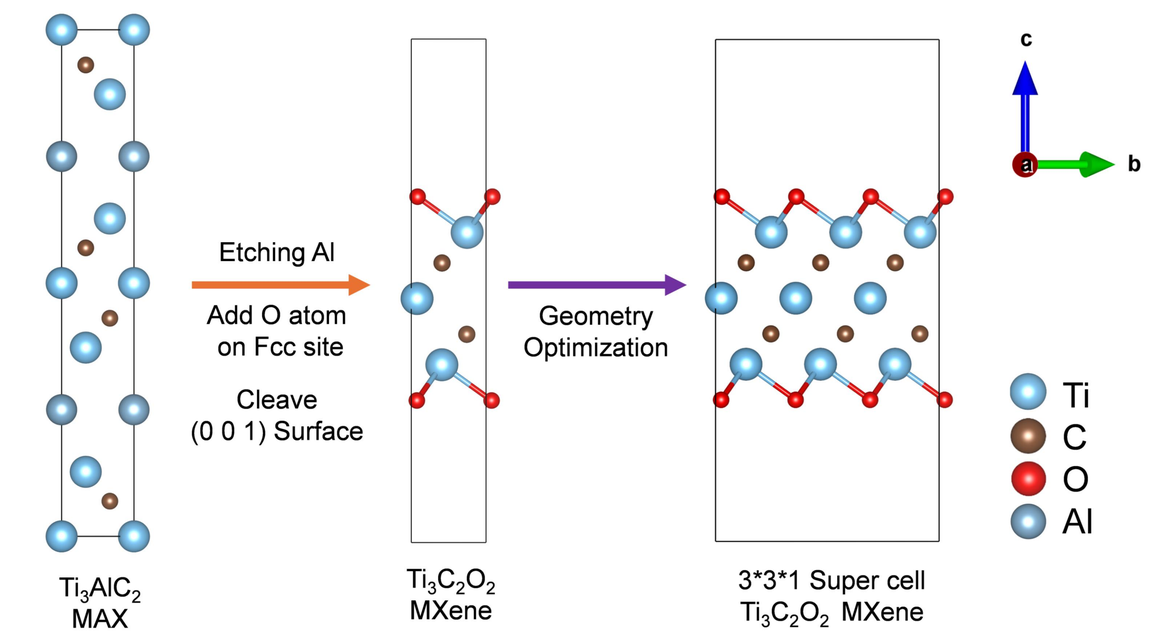
[1]



Can we identify how ionic liquids influence capacitance?

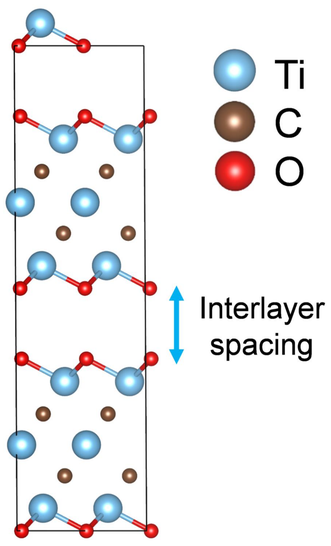
Build MXene structure

Simulate the etching process to build the $Ti_3C_2O_2$ MXene structure.



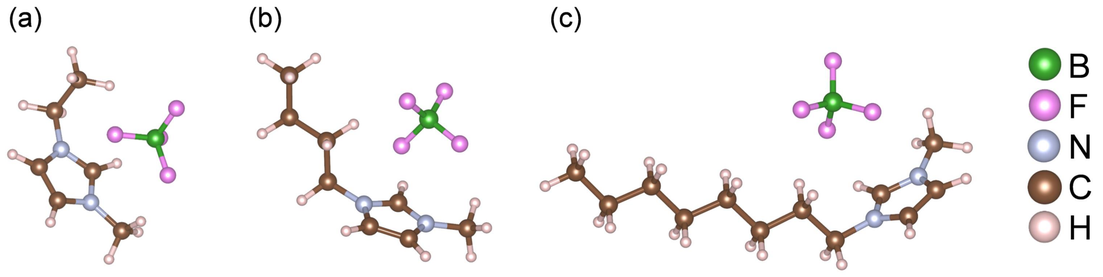
Determine the initial interlayer spacing

Using the optimized monolayer MXene to construct a multilayer structure.



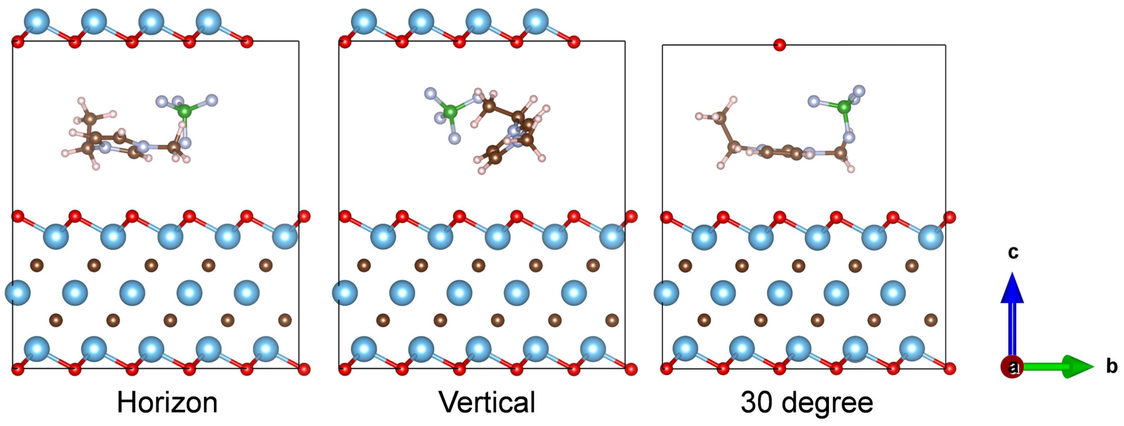
Properties	Exp.[2][3]	DFT results
a	6.04	6.03
b	6.04	6.03
c	19.56	19.56
Ti-C (long)	2.180	2.179
Ti-C (short)	2.140	2.143
Ti-O	1.970	1.968
thickness	6.945	6.941
interlayer spacing	2.835	2.840

Intercalation of Ionic Liquids into MXene



(a) **$EMIMBF_4$** (1-Ethyl-3-methylimidazolium Tetrafluoroborate)
(b) **$BMIMBF_4$** (1-Butyl-3-methylimidazolium Tetrafluoroborate)
(c) **$OMIMBF_4$** (1-Methyl-3-octylimidazolium Tetrafluoroborate)

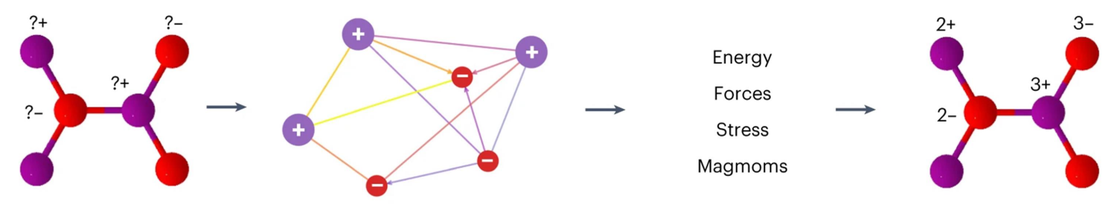
Testing **different orientations** of $EMIMBF_4$ to determine the configuration for subsequent simulations.



Orientation	c[Å]	interlayer spacing[Å]	E[eV]	Thickness[Å]
Horizon	14.9166	7.95360	-1779.3	6.963
Vertical	14.92108	7.96908	-1779.0	6.952
30 degree	14.92163	7.94763	-1779.1	6.974

$BMIMBF_4$ and $OMIMBF_4$ require excessive time and computational resources

[4]



	Pristine MXene	$EMIMBF_4$ Intercalation
Total Energy(eV) (DFT)	-525.7478	-1779.2585
Total Energy(eV) (CHGNet, no fine-tuned)	-519.5475	-1764.4239
Total Energy(eV) (CHGNet, fine-tuned with DFT data)	-524.4156	-1782.3915

Reference

[1] Huang, Jeremiah Hao Ran, Shih-Wen Tseng, and I-Wen Peter Chen. "In-situ electrochemical XRD and raman probing of ion transport dynamics in ionic liquid-etched Ti3C2Tx MXene for energy storage applications." Chemical Engineering Journal 503 (2025)
[2] Komen, P., Ngamwongwan, L., Jungthawan, S., Junkaew, A., & Suthirakun, S. (2021). Promoting Electrochemical Performance of Ti3C2O2MXene-Based Electrodes of Alkali-Ion Batteries via S Doping: Theoretical Insight. ACS Applied Materials and Interfaces
[3] Mu, Xinpeng, et al. "Revealing the pseudo-intercalation charge storage mechanism of MXenes in acidic electrolyte." Advanced Functional Materials 29.29 (2019)
[4] Deng, B. et al. CHGNet as a pretrained universal neural network potential for charge-informed atomistic modelling. Nat Mach Intell 5, 1031–1041 (2023).