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Atomic Scale Simulations for Pseudocapacitive MXene electrode

25th SANKEN International Symposium
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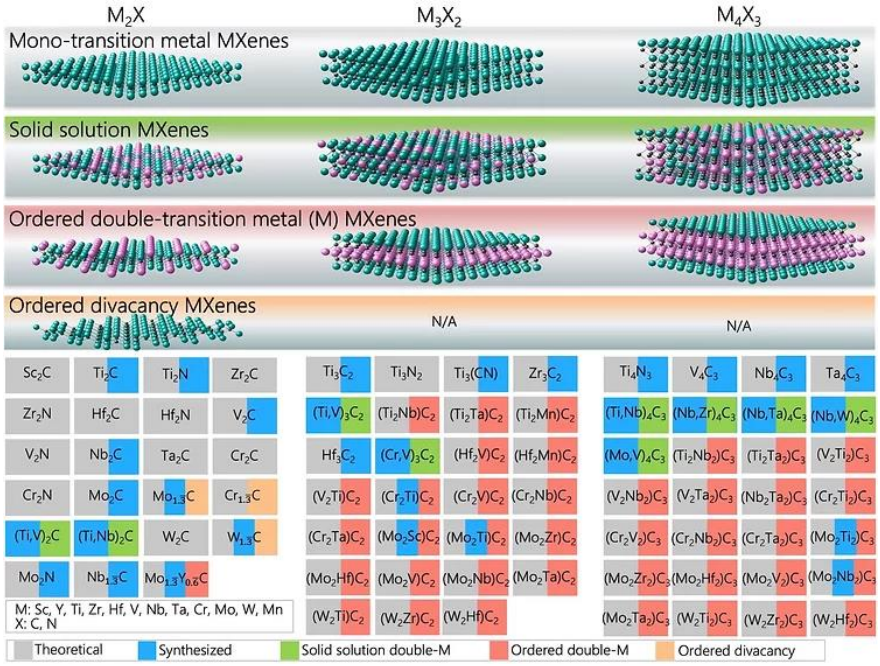
MXene (2011 ~) : 2-D Materials

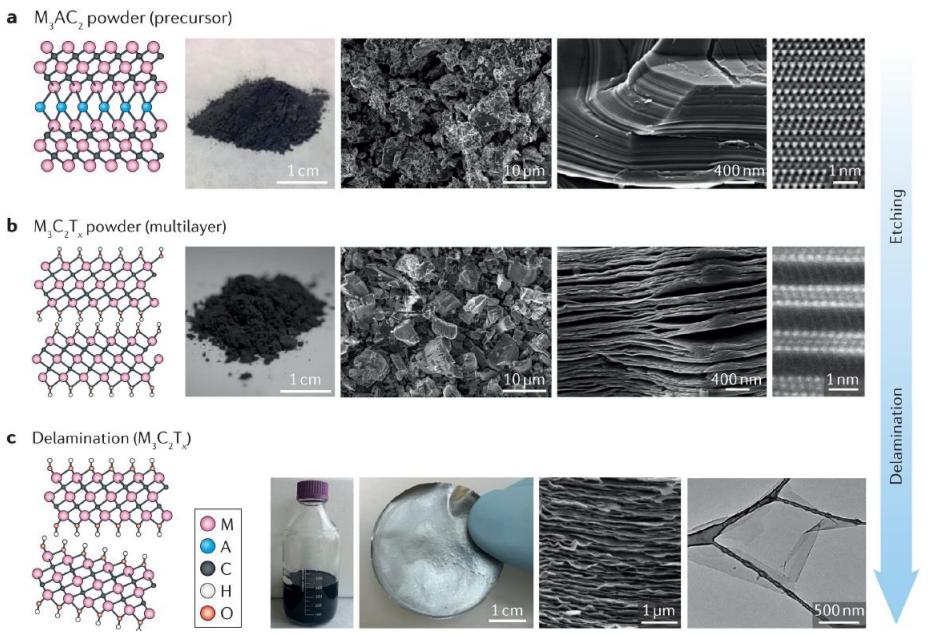
New family of 2-D materials

Properties are tunable by composition and surface modification



https://www.babakanasori.com

Hong, W., Wyatt, B.C., Nemani, S.K. et al., MRS Bulletin **45,** 850–861 (2020).



NATURE REVIEWS MATERIALS **2**, 16098 (2017)

MXene (2011 ~) : 2-D Materials

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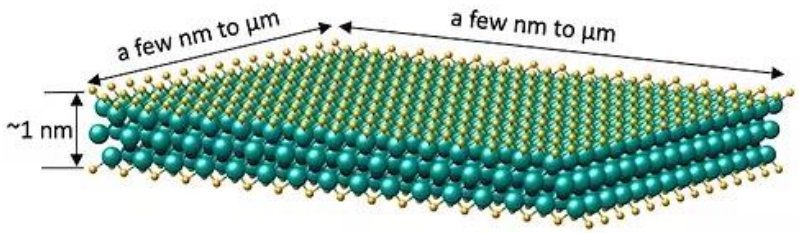
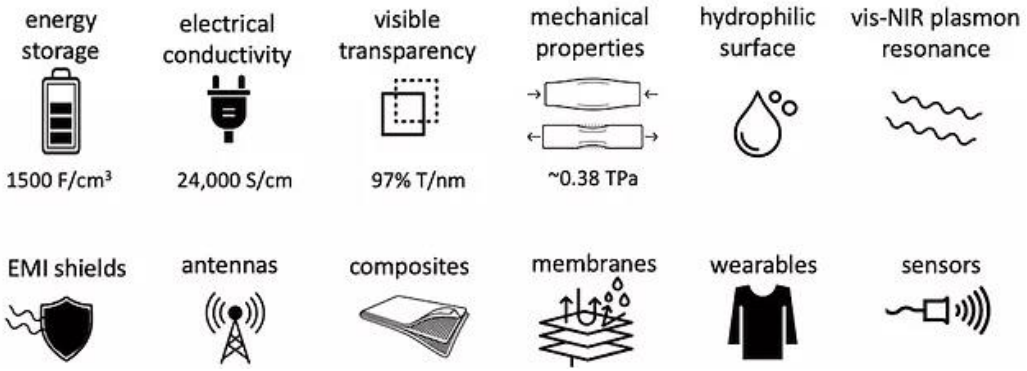
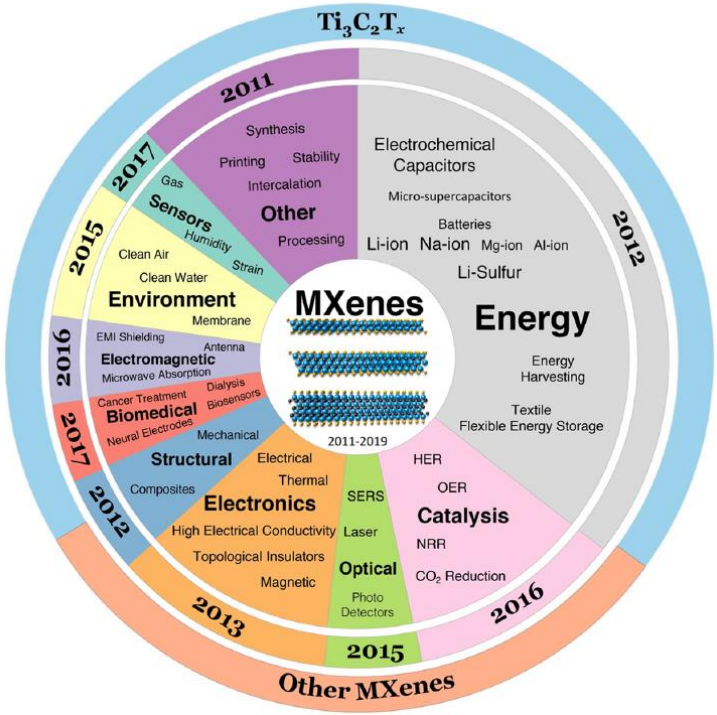


A MXene flake schematic & MXenes applications and properties

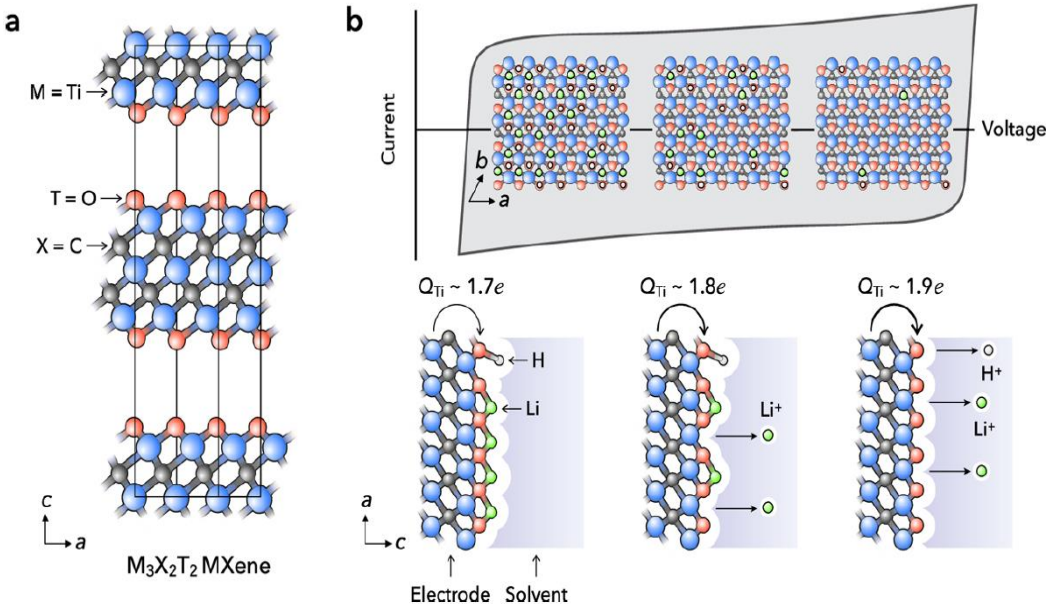




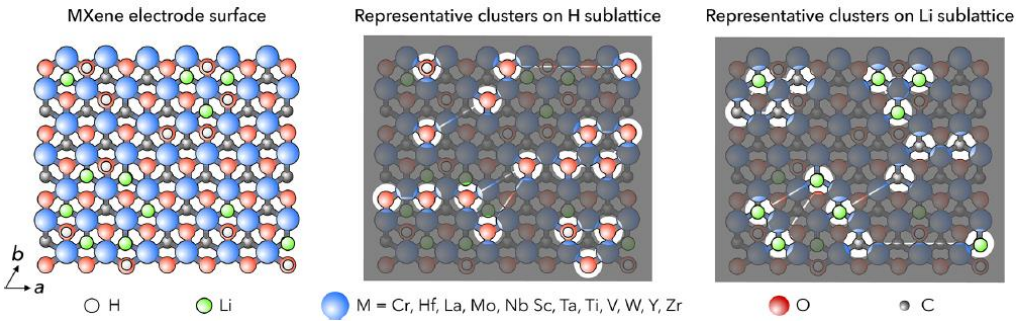
ACS Nano 2019, 13, 8, 8491–8494

Considerable number of researches on MXenes have been made so far to investigate the properties deeply and to explore new applications

MXenes as Pseudocapacitive Electrode



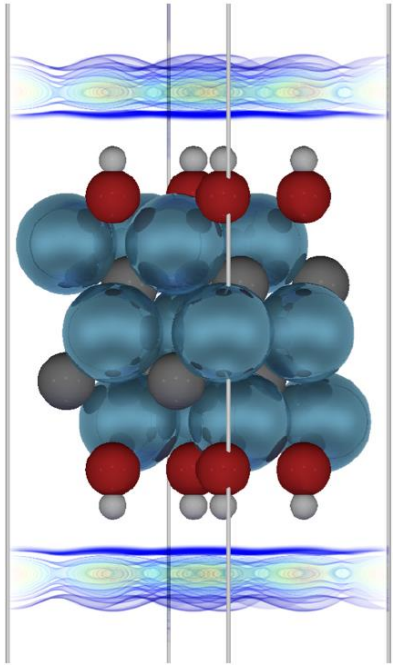
Charge storage mechanisms of pseudocapacitive electrode is explained as reversible redox reactions at the surface of the electrode material



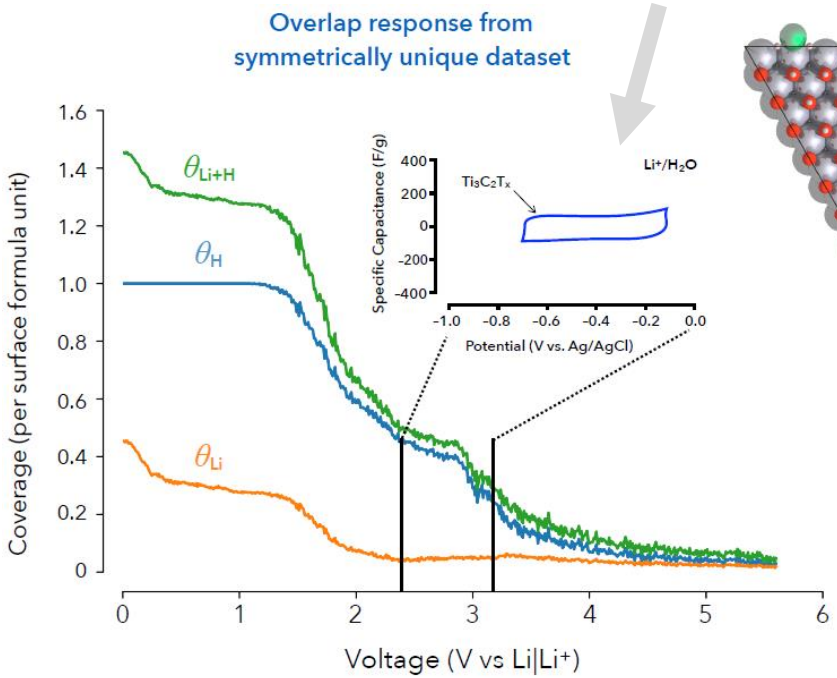
Hydrogen and Li have different adsorption sites on $Ti_3C_2O_2$ MXene

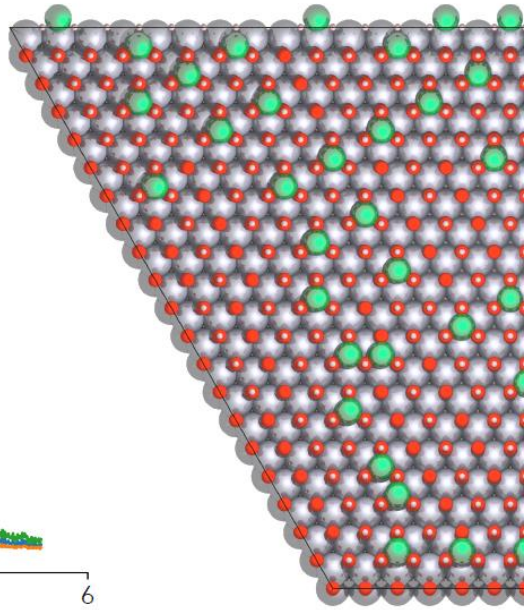
*ACS Appl. Energy Mater. 2021, **4**, 3151−3159.*

Computational Method (DFT + GCMC)



Okubo *et al.*, *Accounts of Chemical Research* **51**, 591 (2018)





Grand-canonical Monte Carlo snapshot at 2.5 V

Voltage dependent adsorption energy

$$\Delta F^{\mathrm{ads}}(\phi) = \Delta F^{\mathrm{ads}}(q) - q\phi$$

$$\Delta F(\mathrm{Li}^*)^{\mathrm{solv}} = E(\mathrm{Li}^*) - E_{\mathrm{MXene}} - N_{\mathrm{Li}}(\mu_{\mathrm{Li}^+} + \mu_{\mathrm{e}^-})$$

$$\mu_{\mathrm{Li}^+} = E(\mathrm{Li}) + k_{\mathrm{B}}T\ \ln(a_{\mathrm{Li}}) + \mathrm{e}\phi_{\mathrm{Li|Li}^+}$$

(DFT + GCMC) method can predict charge-discharge behavior of pseudo-capacitive MXene electrode reactions

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Computational Method (Cluster-Expansion)

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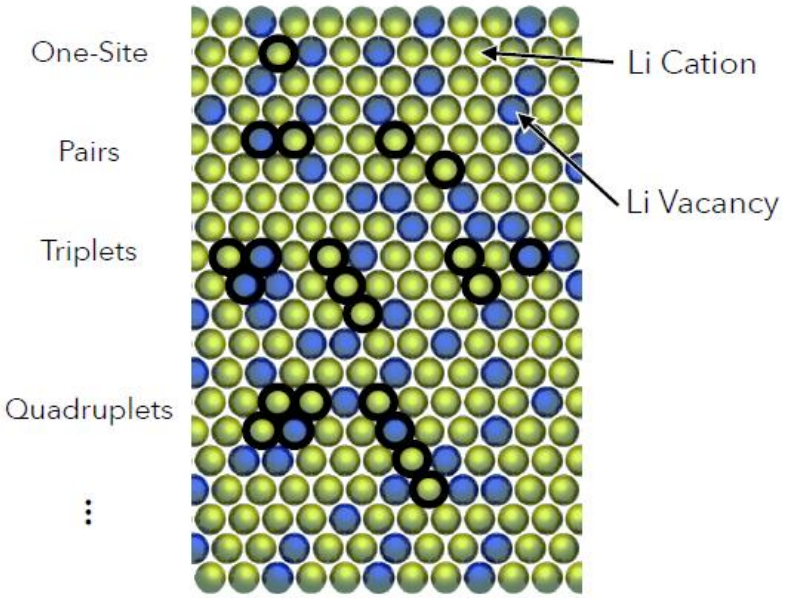
Cluster-expansion methods are used to generate voltage-dependent adsorption energy dataset for GCMC sampling

CASM
A Clusters Approach to Statistical Mechanics

Expansion of adsorption energies
(Lithium sub-lattice example)

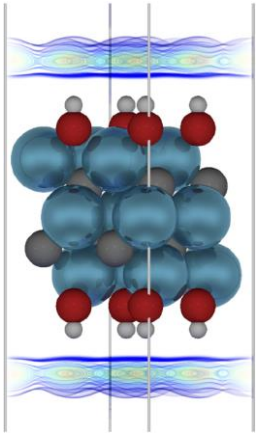


$$F^{ads}(\sigma) = F_0^{ads} + \sum_i \sigma_i J_i + \sum_i \sum_j \sigma_i \sigma_j J_{ij} + \sum_i \sum_j \sum_k \sigma_i \sigma_j \sigma_k J_{ijk} + \ldots$$

The symmetrically distinct adsorption configurations (supercells up to 6 times larger surface area, 184 configurations) were generated by the CASM code

Then, DFT calculations were performed using Quantum ESPRESSO for all the generated configurations (the training set to fit the cluster-expansion model)

Calculation Conditions



MXene system : $M_2X_1T_2$ and $M_3X_2T_2$

M-element : Cr, Hf, La, Mo, Nb, Sc, Ta, Ti, V, W, Y, and Zr

X-element : C

T-element (terminal-group) : O, Adsorbent : H, Li

184 configurations for each M-element generated by CASM code

DFT code : Quantum ESPRESSO

Functional : GGA-PBE, Energy cutoff : 120 Ry

K-mesh : 11/n × 11/m × 1 (depend on supercell)

Implicit solvent : Organic solvent ($\varepsilon_0 = 12$)

http://www.quantum-espresso.org/
http://www.quantum-environ.org/

GCMC code : CASM

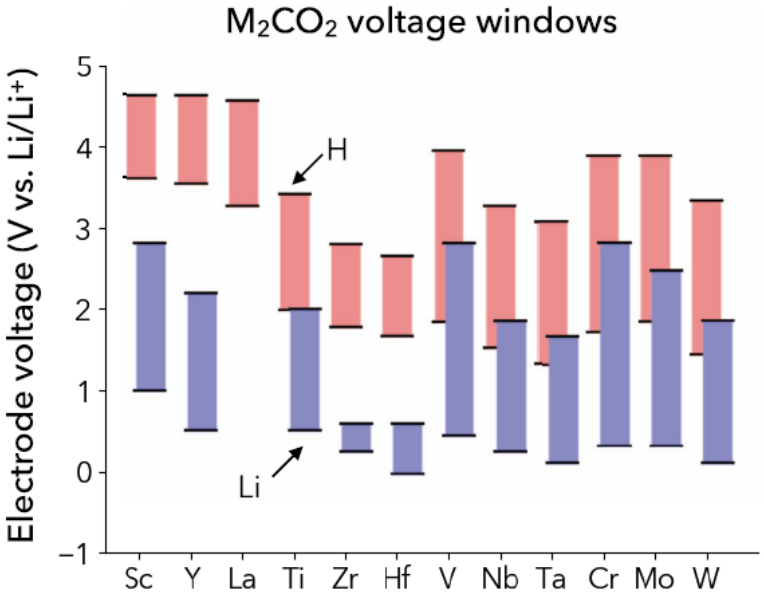
Monte Carlo simulations with grand-canonical ensemble

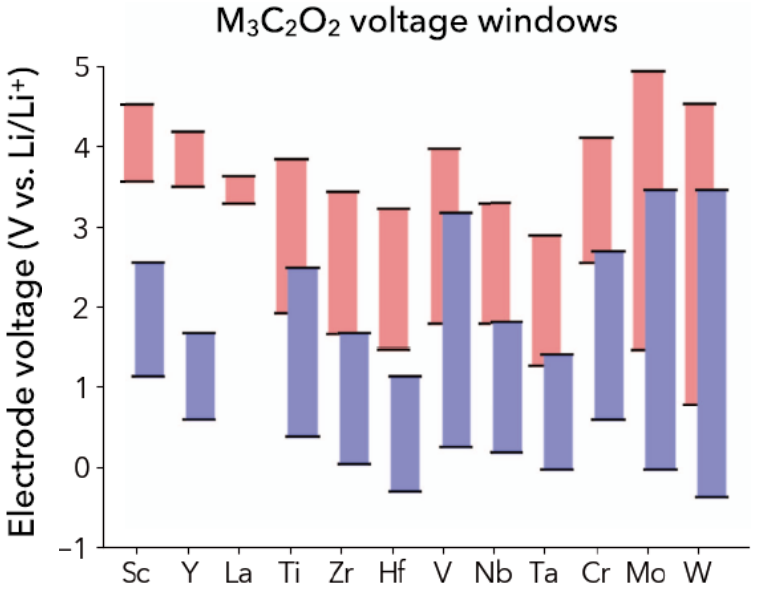
Surface-cell : 30 × 30, Voltage-range : −1.5 ~ 5.5V (vs. Li/Li^+)

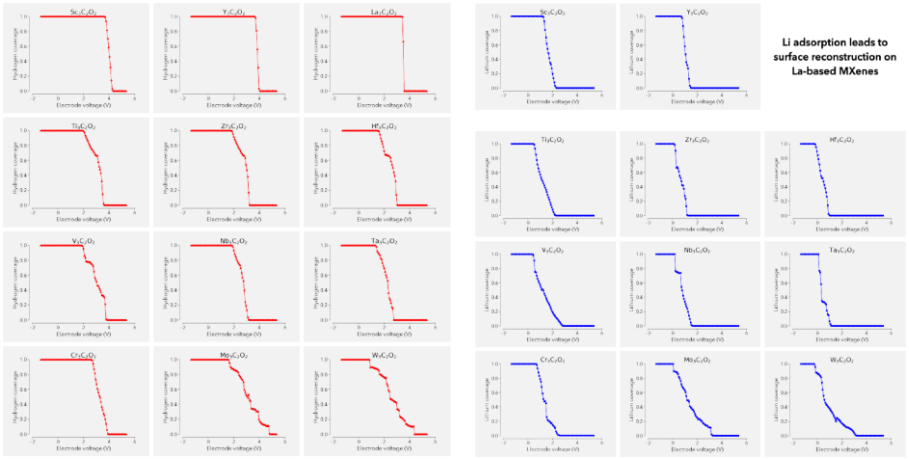
Number of MC trials : 10,000 steps for each voltage

https://prisms-center.github.io/CASMcode_docs/

Results (Voltage Window)







The group-VI MXene compositions show large voltage windows for both H and Li pseudocapacitance

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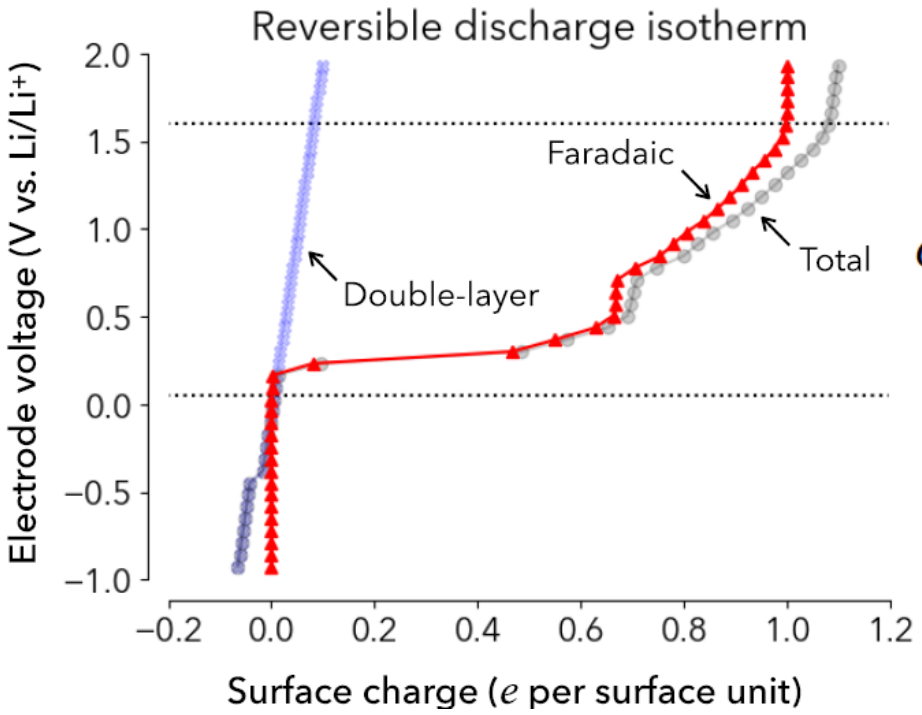
Results (Pseudocapacitance)



$$C = \left\langle \frac{dq_{surf}}{dV} \right\rangle$$

Pseudocapacitances were calculated on average taking the derivative of the stored charge with respect to voltage over the voltage window

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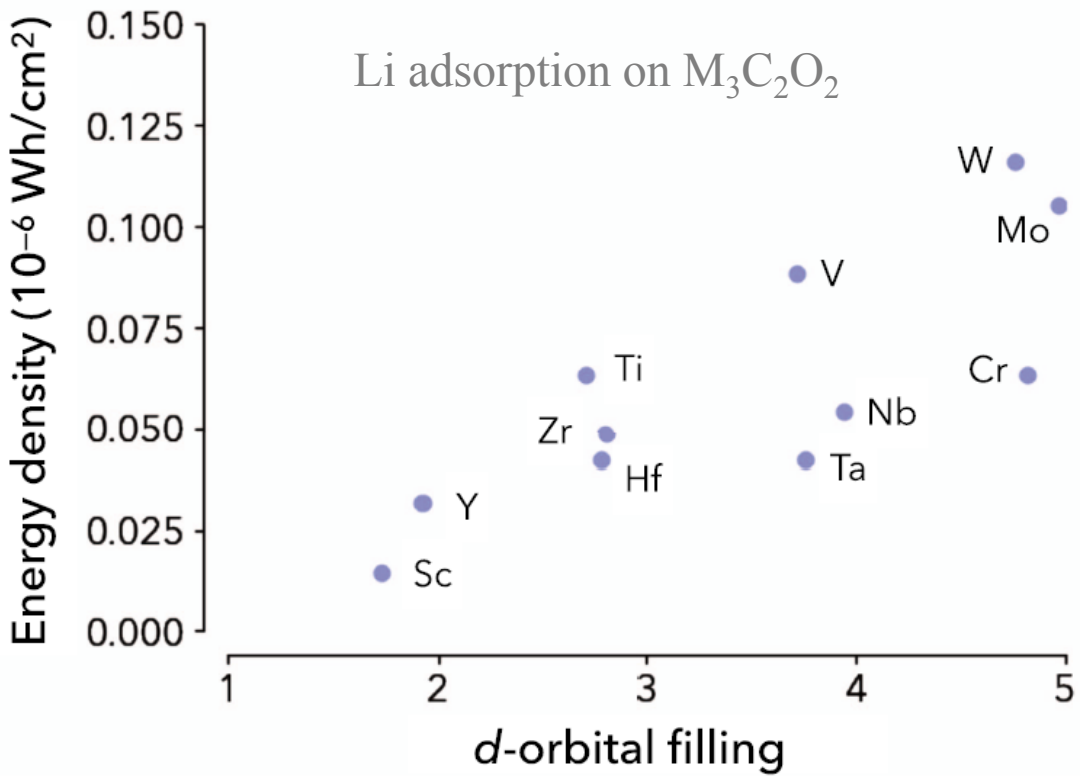
Results (Energy Density)



The pseudocapacitive energy densities by Li adsorption are associated with the valence of transition metal in MXene. Generally, group-VI MXene seem to be suitable for high energy density pseudocapacitor

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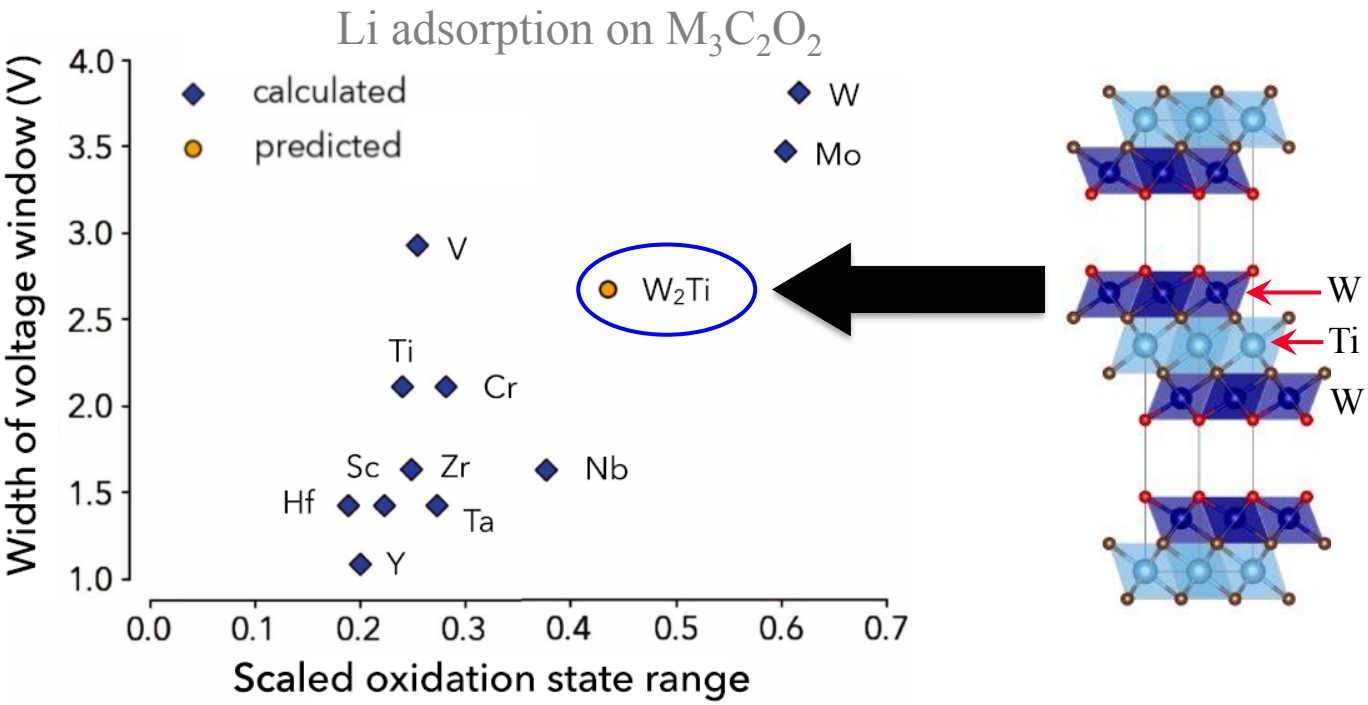
Results (Voltage Window and Prediction)



Generally, the oxidation state ranges of transition metal in MXenes (except for magnetic MXenes) seem to be associated with voltage window. However, the group-VI MXenes are not typically stable. Therefore, $(W_2Ti)C_2O_2$ MXene is one of the promising candidates for pseudocapacitive electrode

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Summary

- We performed high-throughput calculations of MXene by changing transition metals, composition ratio, and adsorbent types. DFT and GCMC calculations combined with voltage-dependent 2D cluster expansion models can predict charge-discharge behavior of pseudocapacitive MXene electrode
- The group-VI MXene compositions show large voltage windows for both H and Li pseudocapacitance
- The pseudocapacitive energy densities by Li adsorption are associated with the valence of transition metal in MXene. Generally, group-VI MXene seem to be suitable for high energy density pseudocapacitor
- The group-VI MXenes are not typically stable. Therefore, $(W_2Ti)C_2O_2$ double-transition-metal type MXene is one of the promising candidates for pseudocapacitive electrode since Ti in center layer significantly stabilize MXene structure

Acknowledgments

I'd like to appreciate all the collaborators shown below

Sandia National Laboratories

Dr. James M. Goff

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PennState

Dabo Research Group

Thank you for your kind attention