3rd Minisymposium on Materials, Characterization and Modelling

TECHNISCHE UNIVERSITÄT DRESDEN

cfaed CENTER FOR ADVANCING ELECTRONICS DRESDEN

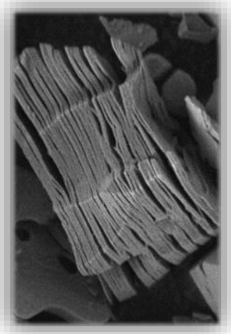
2D layered materials for fast-kinetics energy storage

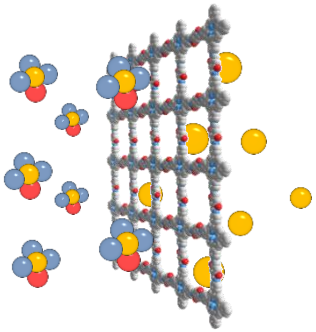
Dr. Minghao Yu

PI, Group Leader

Technische Universität Dresden

minghao.yu@tu-dresden.de





Freistaat SACHSEN

DFG Deutsche Forschungsgemeinschaft

CRC 1415

Funded by the European Union

LEAF project

Funded by the European Union

erc European Research Council Established by the European Commission

BattSkin project

About Dresden

TECHNISCHE UNIVERSITÄT DRESDEN

cfaed CENTER FOR ADVANCING ELECTRONICS DRESDEN

- Beautiful tourism city, **'Florence on the Elbe'**

TU Dresden Campus

About Dresden

- Science & technology center, 'German Silicon Valley'

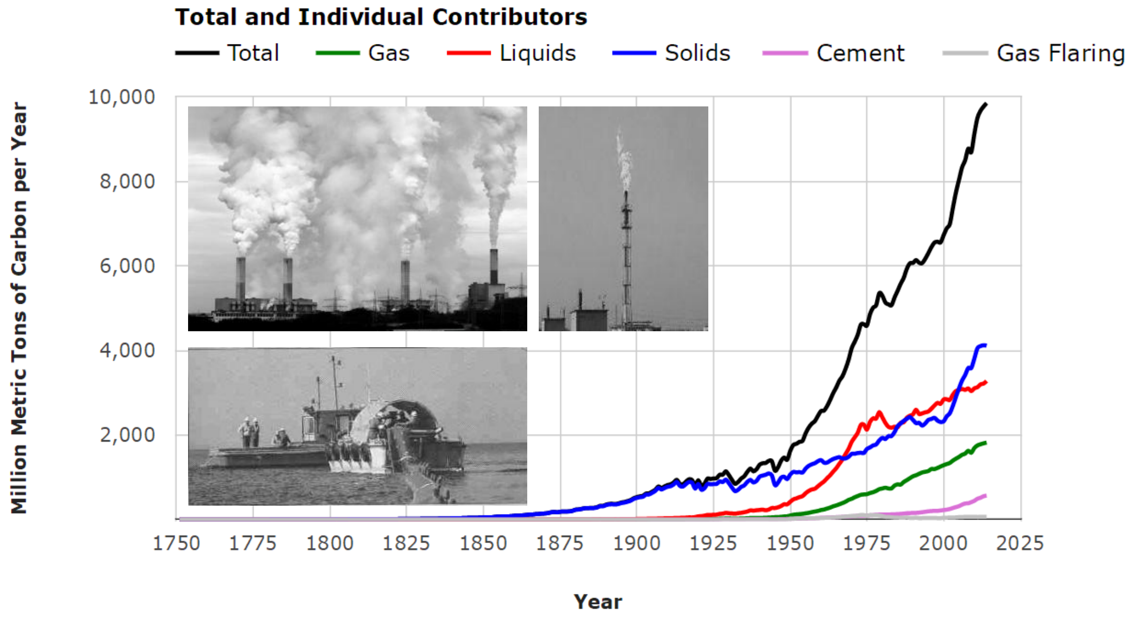
TU Dresden

- ➢ 28,952 students
- ➢ 8,303 employees
- ➢ TU9
- ➢ Universities of Excellence (1/11)

CRC 1415 **Chemistry of synthetic two-dimentional materials**

Research Background

- **Sustainable energy transition**



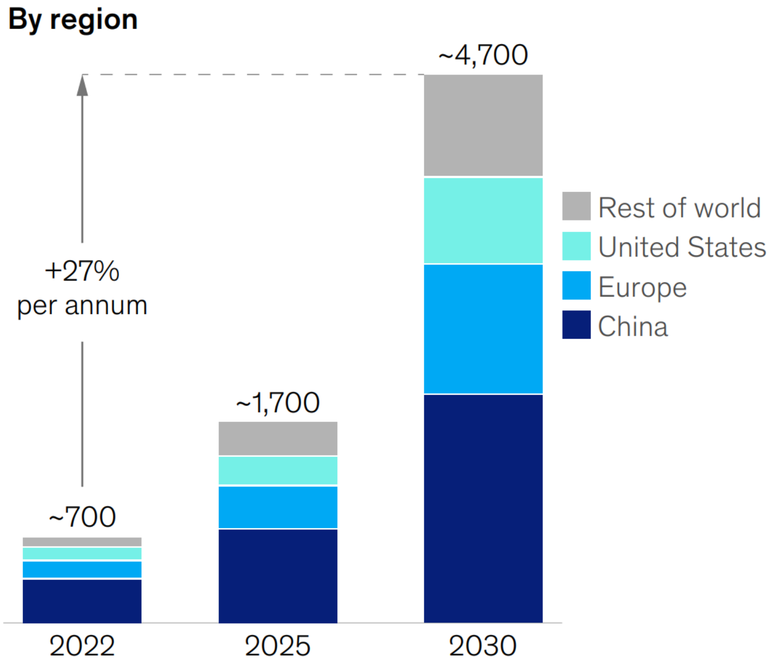
https://cdiac.ess-dive.lbl.gov/trends/emis/glo_2014.html

Generated by ChatGPT

Energy storage devices provide an efficient solution to
flexibly store, transport, and deliver intermittent sustainable energies.

Research Background

Battery demand will grow by 27% annually to reach 4,700 GWh by 2030.

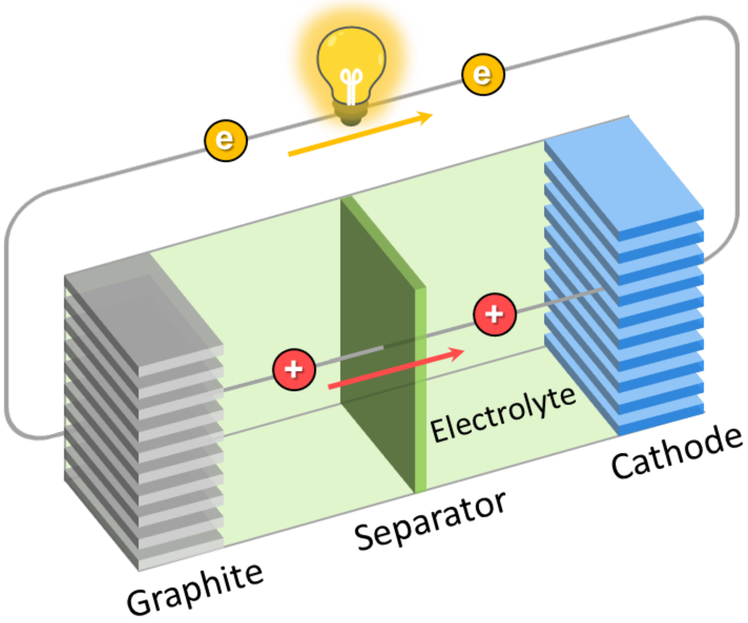


Source: McKinsey Battery Insights

Diverse energy storage markets

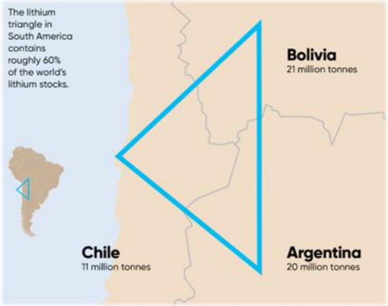
Research Background

- **State-of-the art Li-ion batteries**



Store/release charges/ions simultaneously

Safety: Li-ion battery fire in Neermoor Germany, May 2024



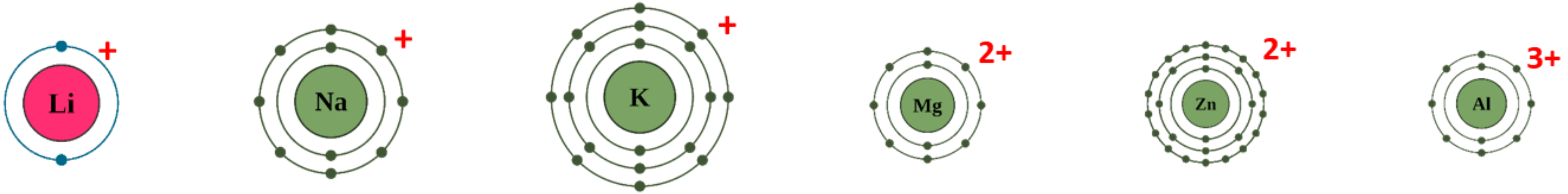
***Resource:* Li triangle**

***Recyclability:* tera-Wh market**

Research Background

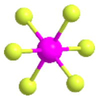
- **Future sustainable battery concepts**

  - Cheap cations

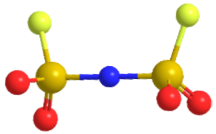


  - Metal-free anions

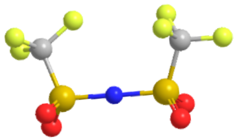
Halogen anion



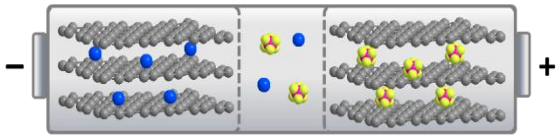
PF_6^-



FSI^-



$TFSI^-$

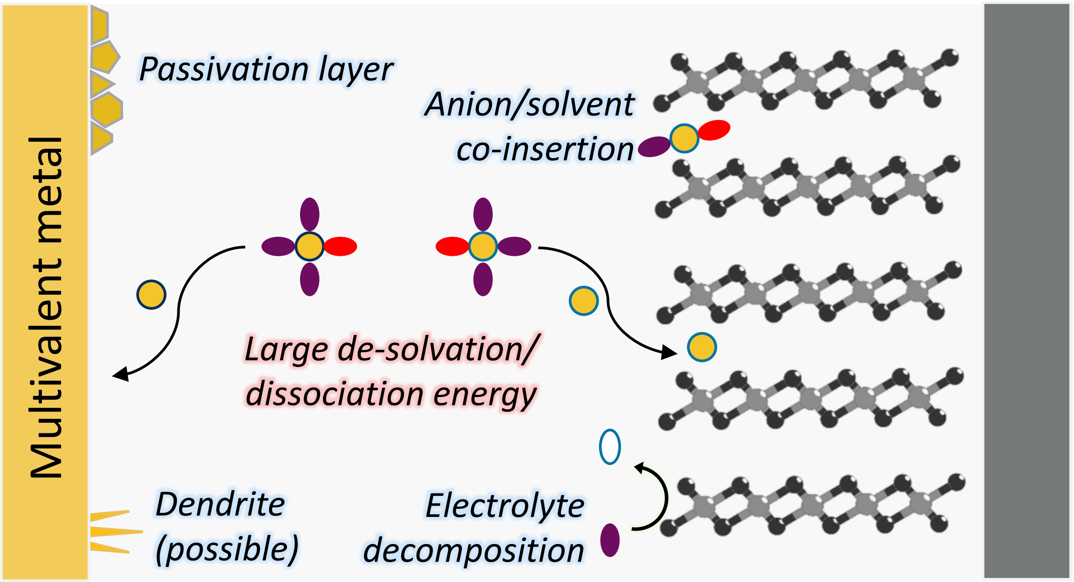


Dual-ion batteries

What material structures enable fast, reversible, and high-capacity storage of sustainable ion species?

Grand challenges

- **Sustainable battery electrochemistry**



Anode chemistry *Cathode chemistry*

Electrode

- ➢ Sluggish electrochemical kinetics.
- ➢ Limited ion-hosting capability.

Electrode/electrolyte interface

- ➢ Side reactions on electrode surface.
- ➢ Anion/solvent co-insertion.

Electrolyte

- ➢ Intense ion solvation.
- ➢ Strong anion-cation pairing.

Battery devices: low efficiency, capacity, energy, cycling life…

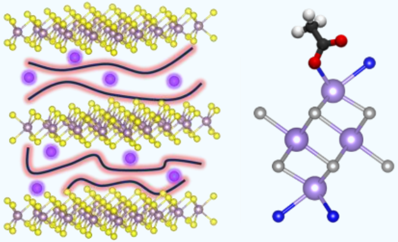
Our Research Interests

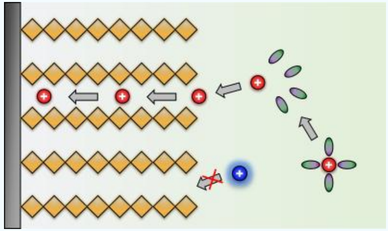
TECHNISCHE UNIVERSITÄT DRESDEN

cfaed CENTER FOR ADVANCING ELECTRONICS DRESDEN

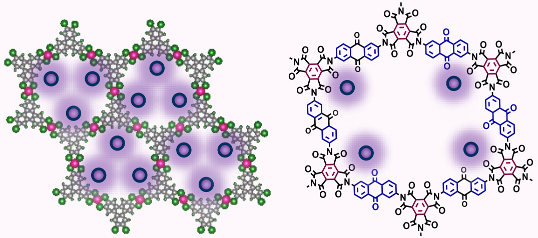
Key materials & **electrochemistry** in sustainable energy storage devices

2D layered transition metal compounds (TMCs)



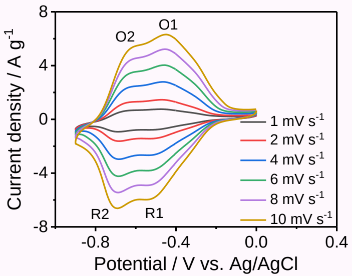


Redox 2D frameworks

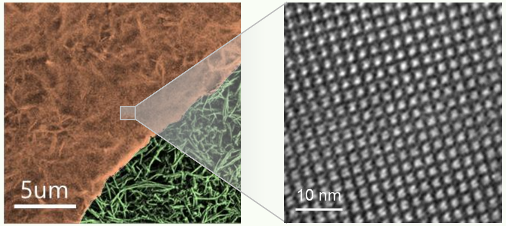


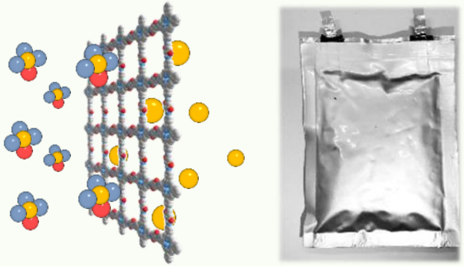
2D COFs

2D c-MOFs



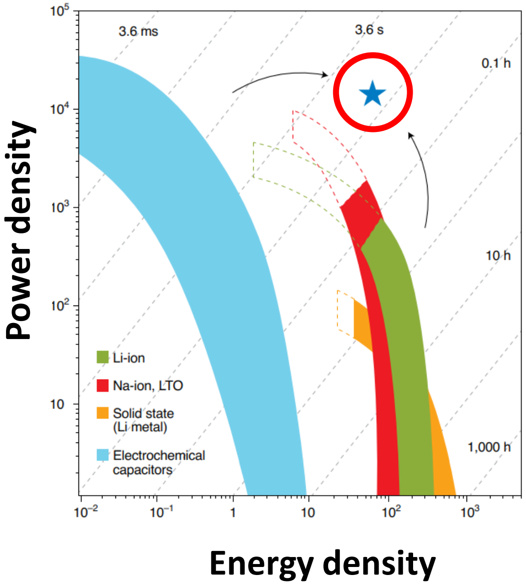
Polymeric artificial interphase





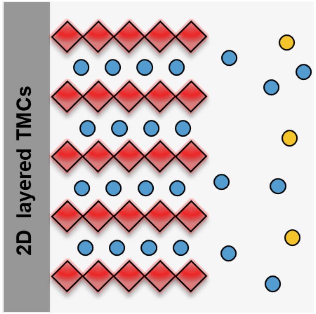
1. 2D layered TMCs

- **Energy-power tradeoff**

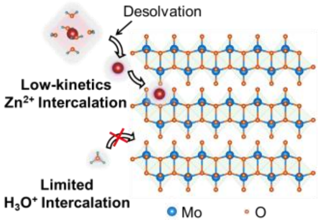


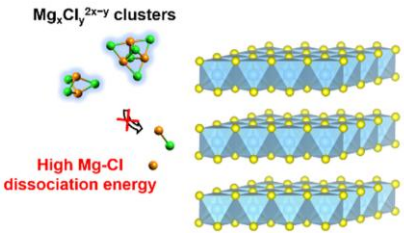
Simon & Gogotsi, Nat. Mater., **2020**, *19*, 1151

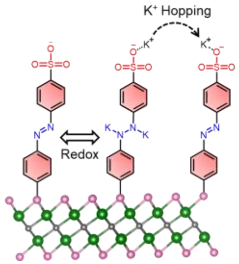
How to store ions more and faster?



- Highly tailorable interlayer structure
- Flexibly tunable surface chemistry



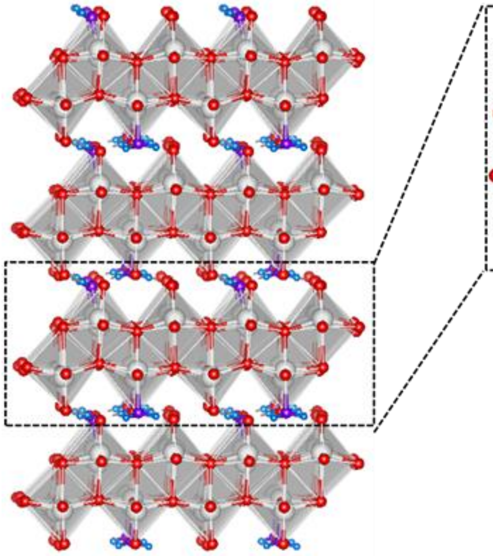


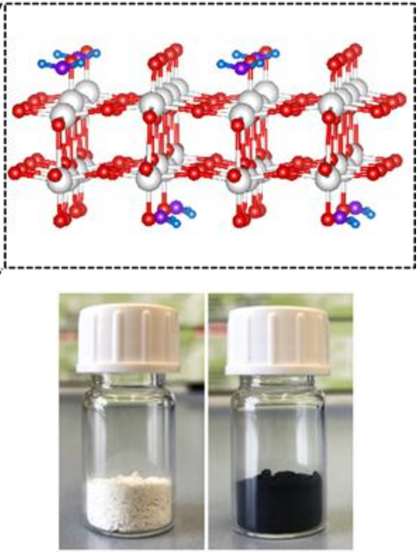


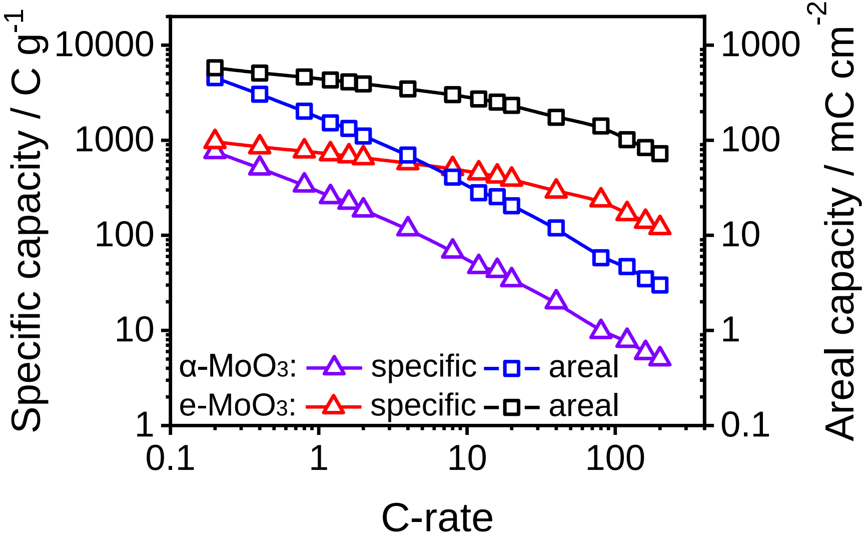
Nat. Mater. ***2024***; *Adv. Energy Mater.* **2023**; *Adv. Mater.* **2022**; *Angew. Chem.* **2021**; *Nat. Commun.* **2020** ; *Joule* **2019**

MoO_3 with lattice H_2O

- **Replacing lattice O with H_2O molecules**







Lattice oxygen replaced by H_2O:

$MoO_{2.7} \cdot 0.3H_2O$

➤ 4.4% *vs.* 40.2% , from 0.1 to 10 mV s^{-1}

Nat. Commun. **2020**, 11, 1348.

MoO_3 with lattice H_2O

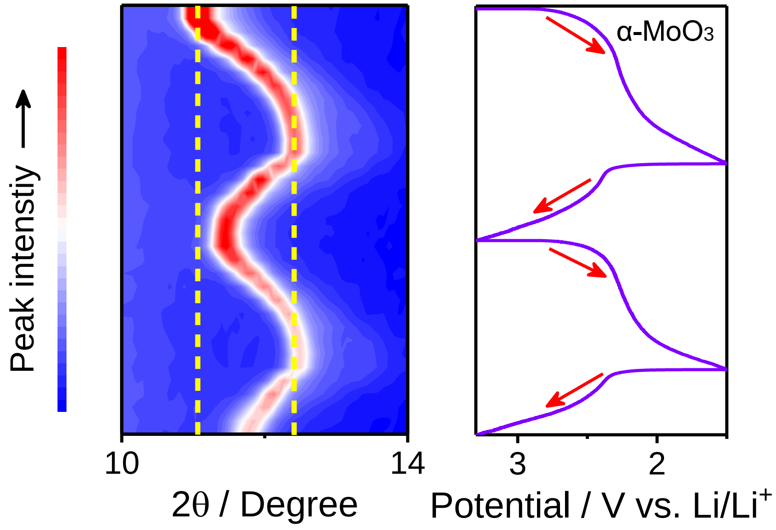
TECHNISCHE UNIVERSITÄT DRESDEN

cfaed CENTER FOR ADVANCING ELECTRONICS DRESDEN

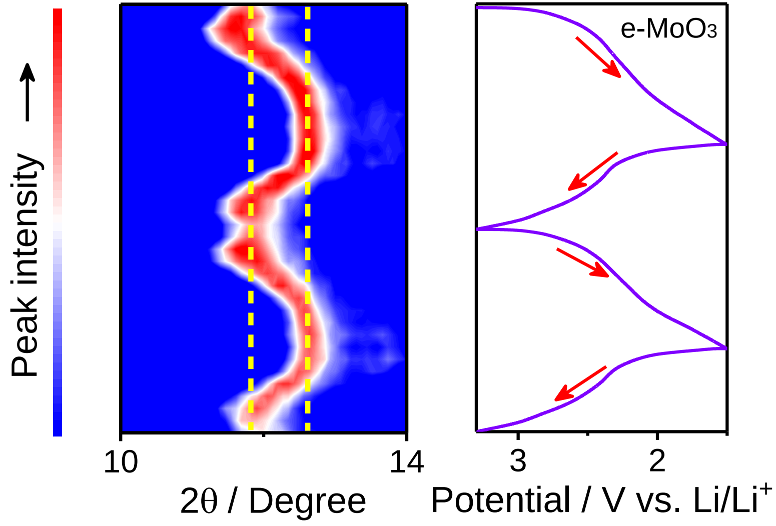
- α-MoO_3 with expanded vdW gap

Co. with **Prof. Patrice Simon**

1.3°



0.8 °



➢ Less volume change.

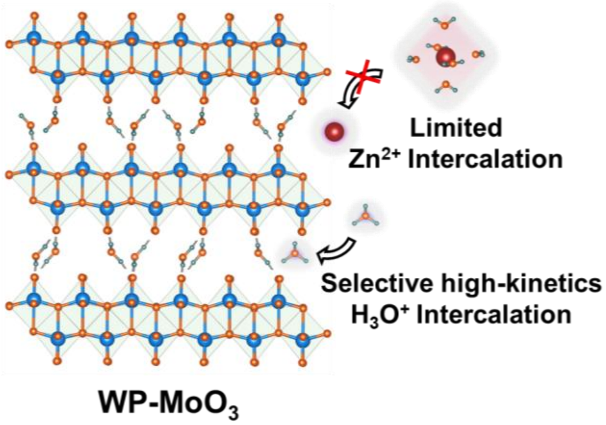
➢ Better lattice change reversibility.

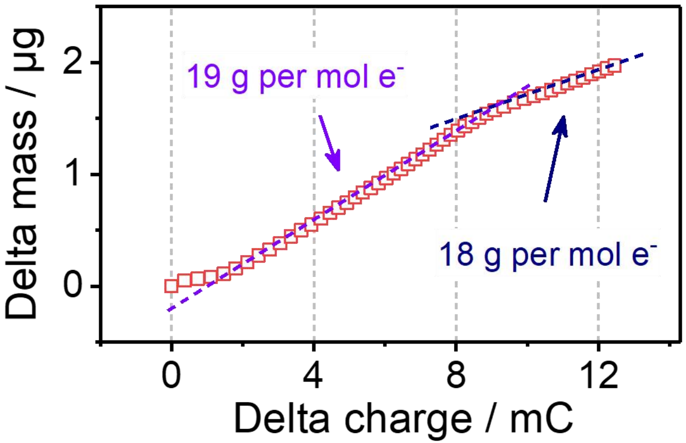
Nat. Commun. **2020**, 11, 1348.

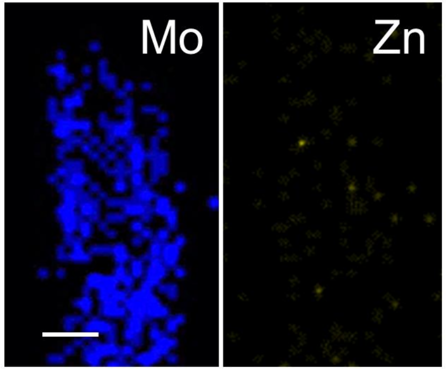
1. 2D layered TMCs

- **Performance in the Zn battery electrolyte**

  2 M $ZnCl_2$ aqueous electrolyte (pH 4.3)







- ➢ 356.8 *vs.* 184.0 mA h g^{-1}
- ➢ 77.5% *vs.* 42.4%, from 0.4 to 4.8 A g^{-1}

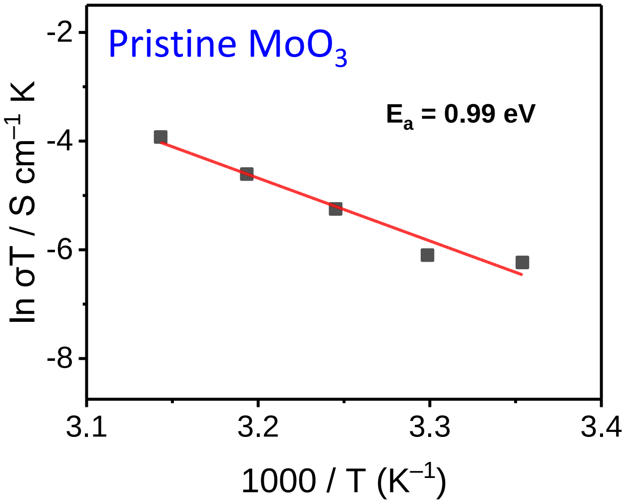
Selective H_3O^+-intercalation chemistry

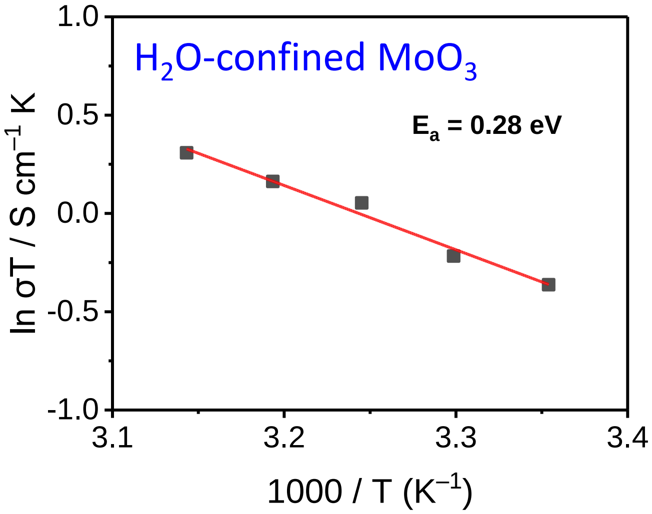
Angew. Chem. Int. Ed. **2021**, 60, 896-903.

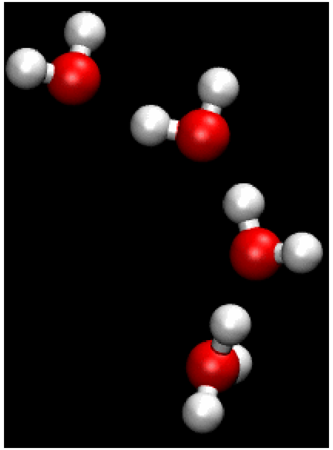
1. 2D layered TMCs

- **H_3O^+-insertion mechanism**

Temperature-dependent EIS measurement







E_a = 0.28 eV for proton transport

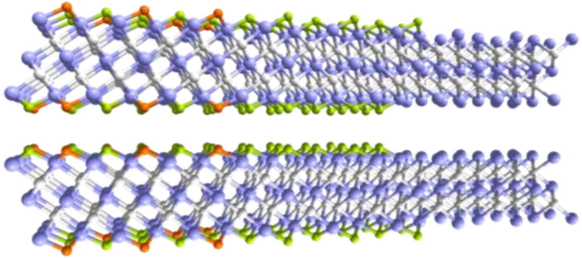
E_a < 0.4 eV: Grotthuss conduction

Grotthuss proton-conduction mechanism

Angew. Chem. Int. Ed. **2021**, 60, 896-903.

1. 2D layered TMCs

- $M_{n+1}X_nT_x$ (n = 1-4, T_x: terminal groups)



Wet-chemistry etching

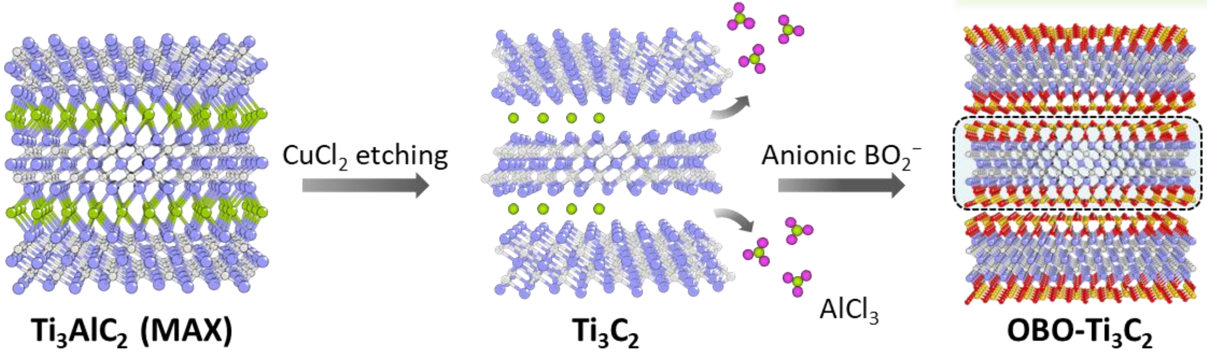
Mixing termination (-F/-Cl, -O, -OH)

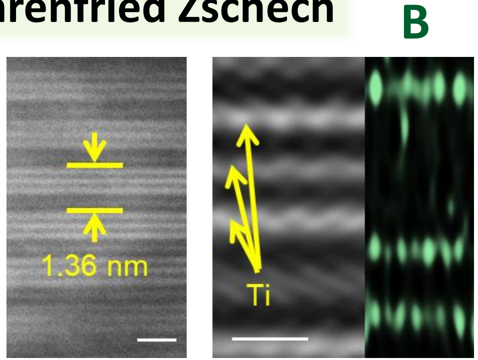
Molten-salt etching

Mixing termination (-Cl, -O)

Flux-assisted eutectic molten etching

Co. with **Prof. Ehrenfried Zschech**



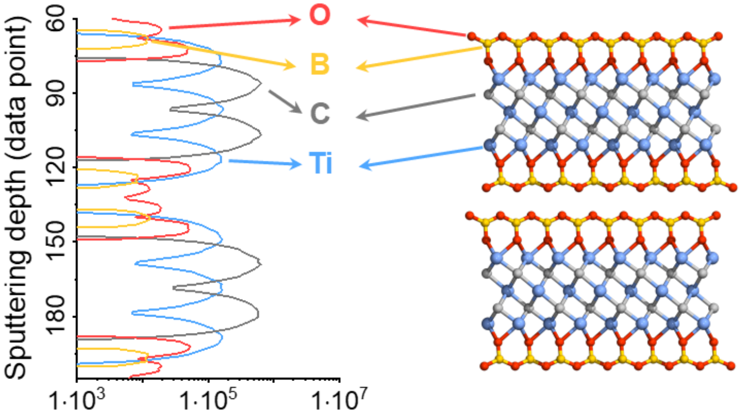


Nat. Mater. **2024**, *23*, 1085.

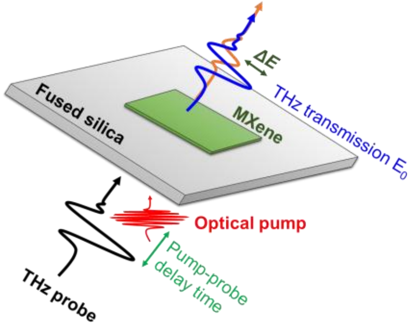
1. 2D layered TMCs

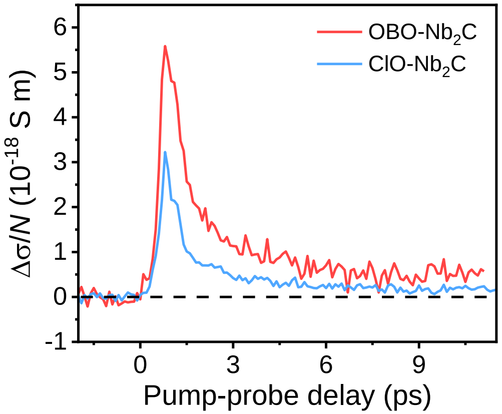
- **MXenes with OBO-termination**

Triatomic-layer borate polyanion terminations



Ultralow-energy SIMS





Co. with **Prof. Mischa Bonn**

Van der Pauw:
15-fold enhancement in conductivity.

THz spectroscopy:
Carrier mobility by 10-fold improvement

Nat. Mater. **2024**, *23*, 1085.

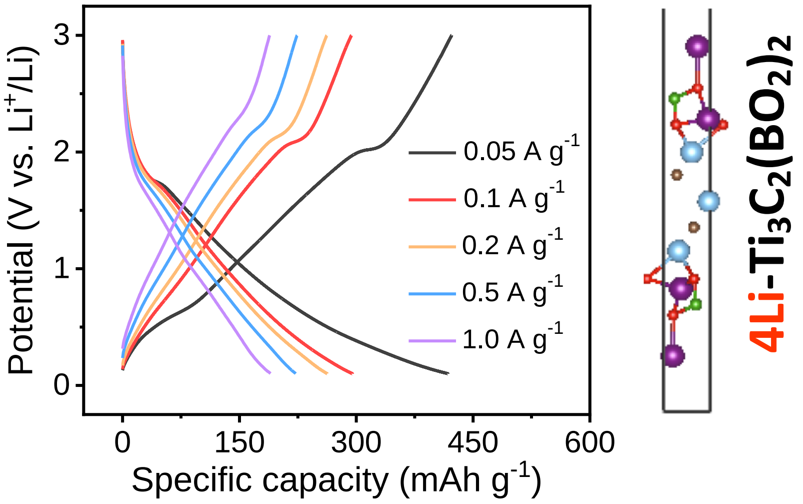
1. 2D layered TMCs

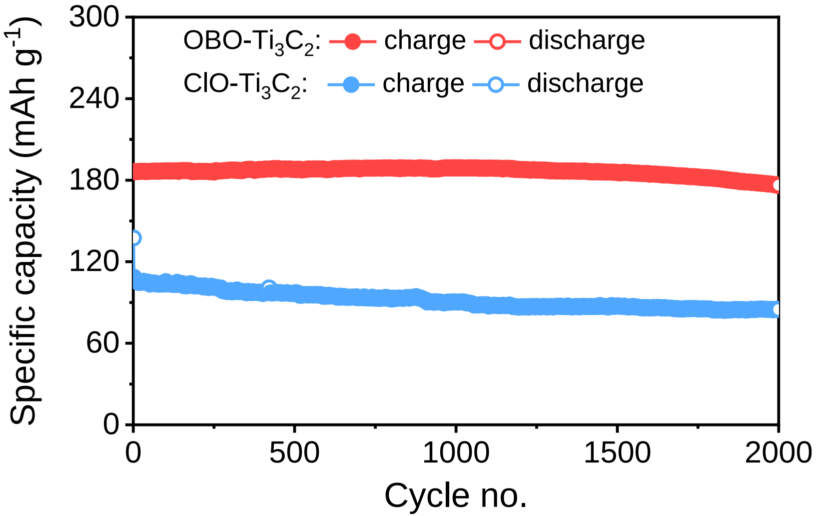
TECHNISCHE UNIVERSITÄT DRESDEN

cfaed CENTER FOR ADVANCING ELECTRONICS DRESDEN

- **MXenes with OBO-termination**

Charge storage properties





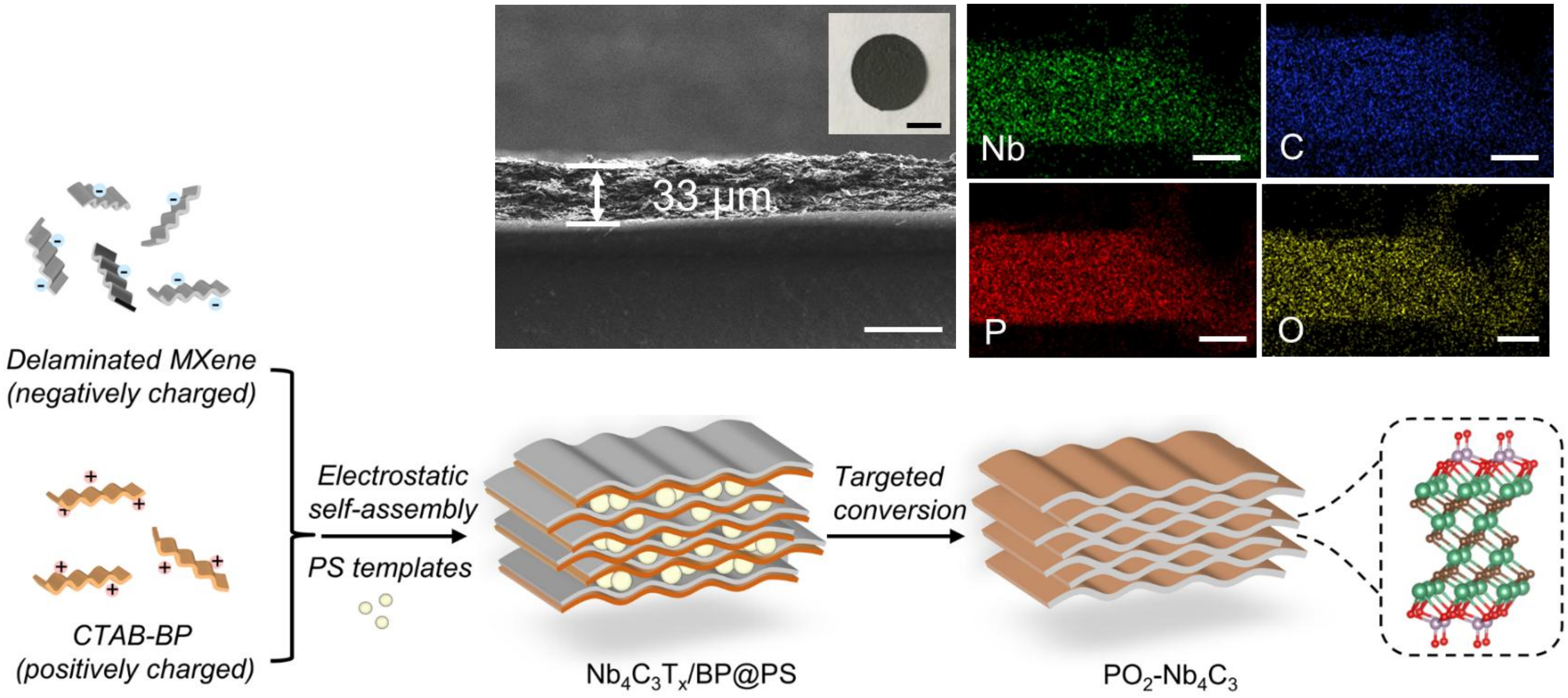
➢ **OBO-Ti_3C_2 vs. ClO-Ti_3C_2**: 423.2 mAh g^{-1} *vs.* 224.6 mAh g^{-1}.

➢ More Li^+-storage sites: **on-top sites** and **OBO-cage sites.**

Nat. Mater. **2024**, *23*, 1085.

MXenes with PO_2-termination

- **Targeted termination conversion**

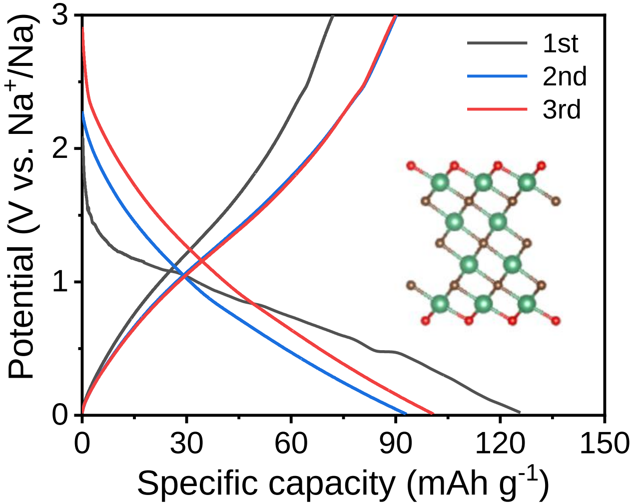


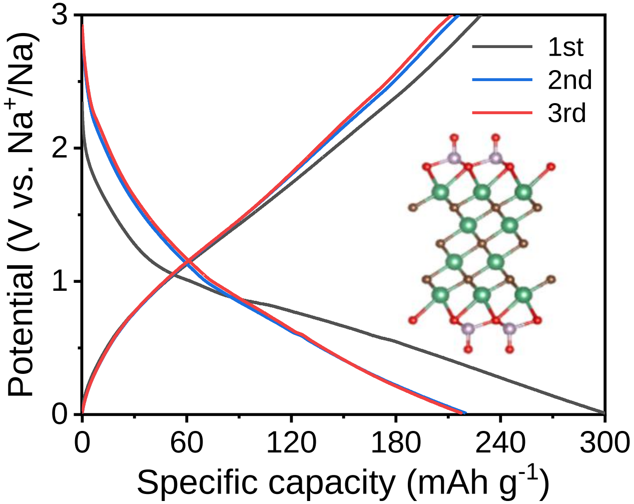
Adv. Mater. **2022**, 34, 2108682

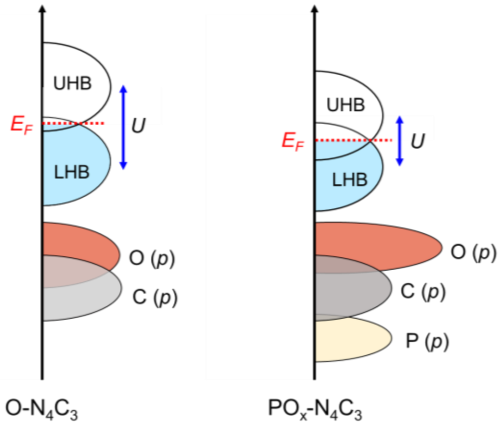
MXenes with PO_2-termination

- **As Na^+-hosting anode**

  Doubled Na^+-storage capacity







➢ 221.0 *vs.* 96.5 mA h g^{-1}

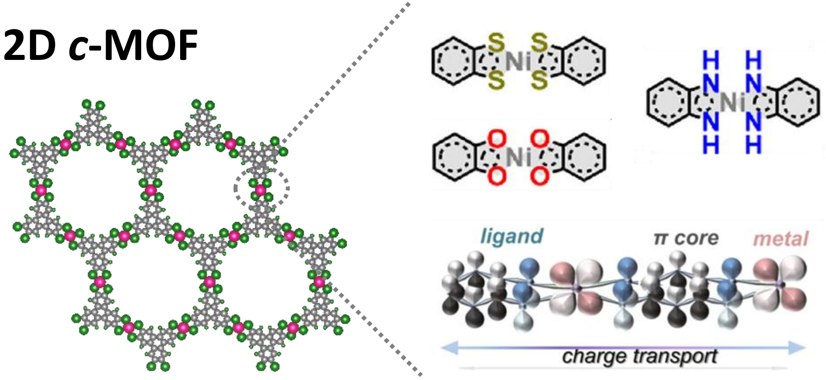
1. Additional Na^+-adsorption sites provided by PO_2-terminals.
2. Enhanced redox depth of surface Nb atoms.

Adv. Mater. **2022**, 34, 2108682

2. 2D carbon-rich frameworks

- **Emerging synthetic layered functional materials**

2D *c*-MOF



- ➢ ***π*-ligand + square-planar Metal-X_4** linkage
- ➢ Extended π–d-conjugated planes
- ➢ **Pseudocapacitive material** construction

2D COFs

- ➢ Polymerization under **thermodynamic control**.
- ➢ **Self-correction** toward layered crystals
- ➢ Particular desired for **multivalent ion storage**

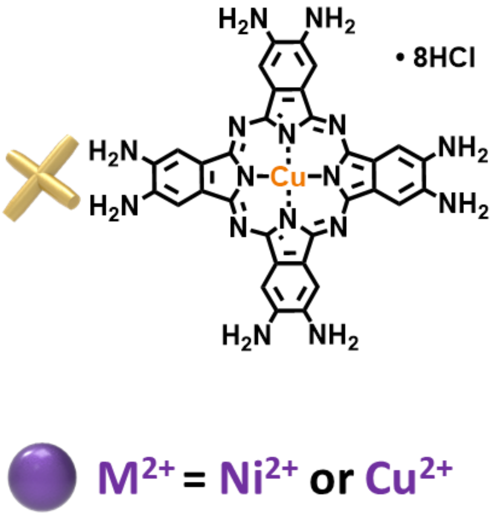
How to design redox and stable molecules with framework chemistries?

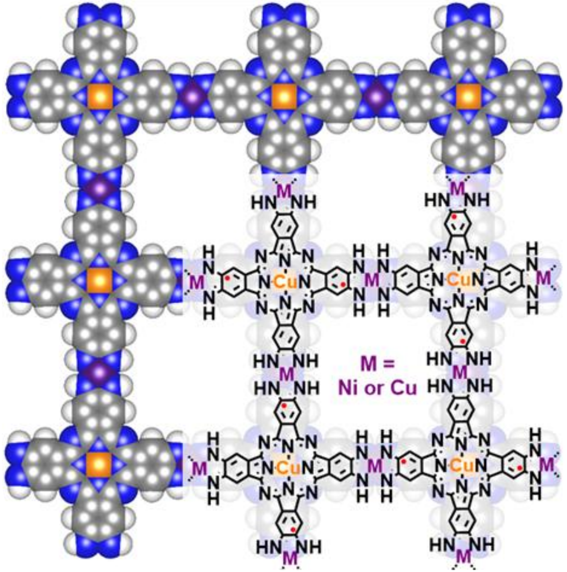
Angew. Chem. **2025**; *Angew. Chem.* **2023**; *JACS* **2023**; *JACS* **2021**; *JACS* **2020**; *JACS* **2020**;

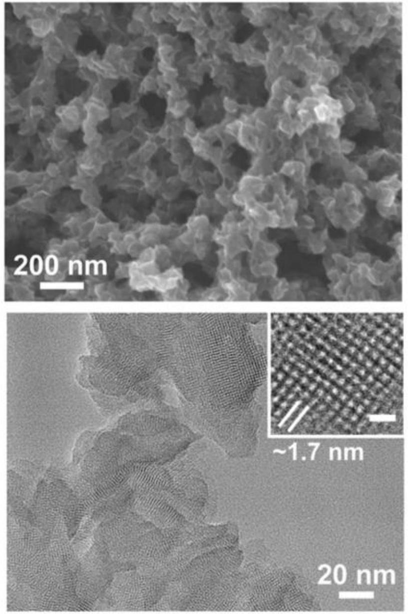
2. 2D carbon-rich frameworks

- **Dual-redox-site 2D *c*-MOFs**

  Phthalocyanine-based 2D c-MOF







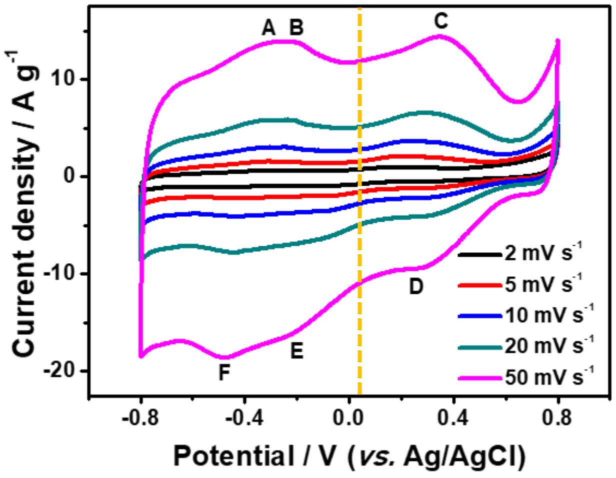
J. Am. Chem. Soc. **2021**, 143, 10168.

2. 2D carbon-rich frameworks

- **Dual-redox-site 2D *c*-MOFs**

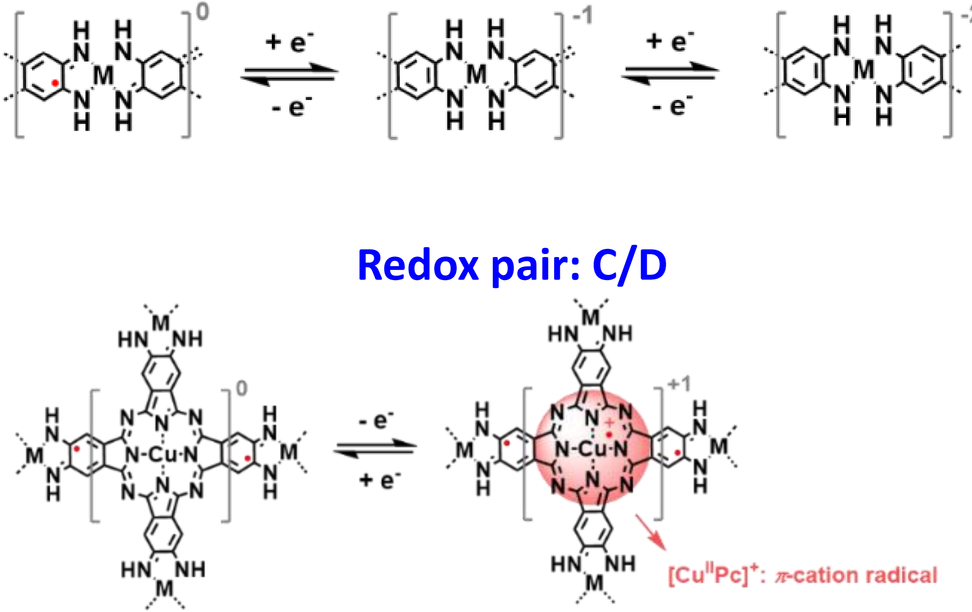
Phthalocyanine-based 2D c-MOF

1 M Na_2SO_4 aqueous electrolyte



Redox pairs: A/F, B/E

Redox pair: C/D



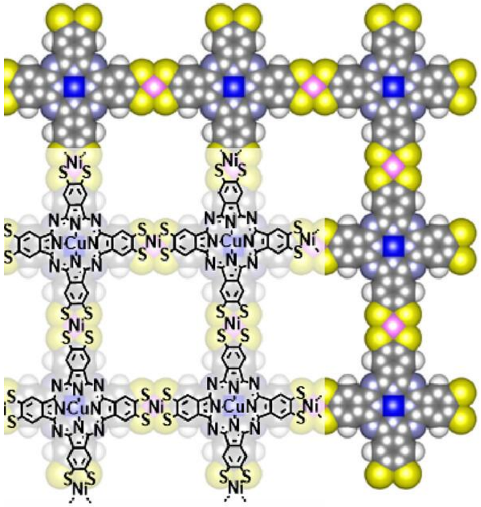
✓ −0.8 ~ 0.8 V *vs.* Ag/AgCl

✓ 400 F g^{-1} at 0.5 A g^{-1}

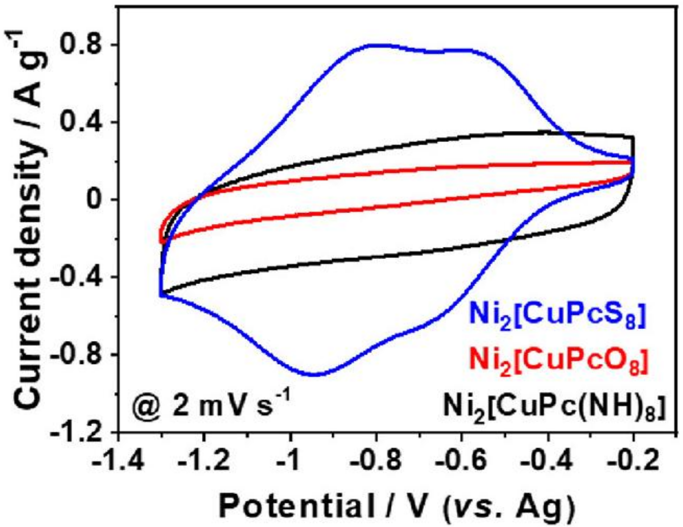
J. Am. Chem. Soc. **2021**, 143, 10168.

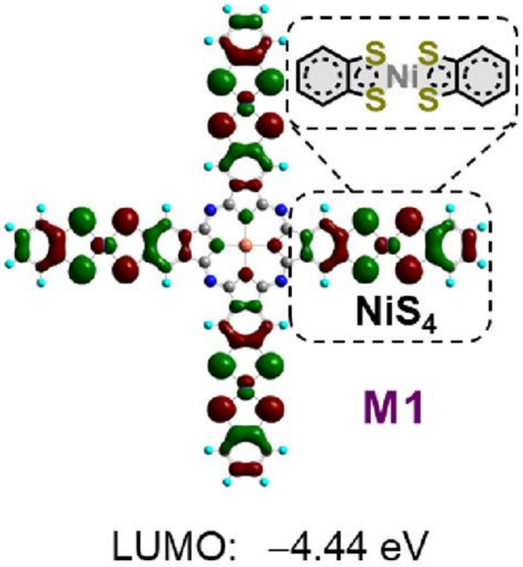
2. 2D carbon-rich frameworks

- **Linkage-dependent pseudocapacitive behaviours**



1 M TEABF$_4$/acetonitrile





Only NiS_4 linkages exhibit apparent pseudocapacitive charge storage.

✓343 C g^{-1} at 0.5 A g^{-1}

J. Am. Chem. Soc. **2023**, 145, 6247.

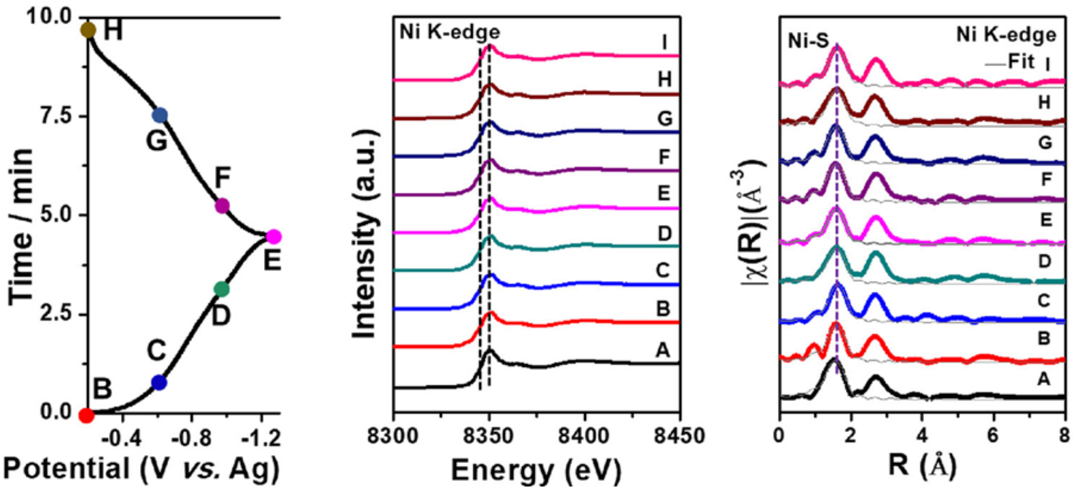
2. 2D carbon-rich frameworks

TECHNISCHE UNIVERSITÄT DRESDEN

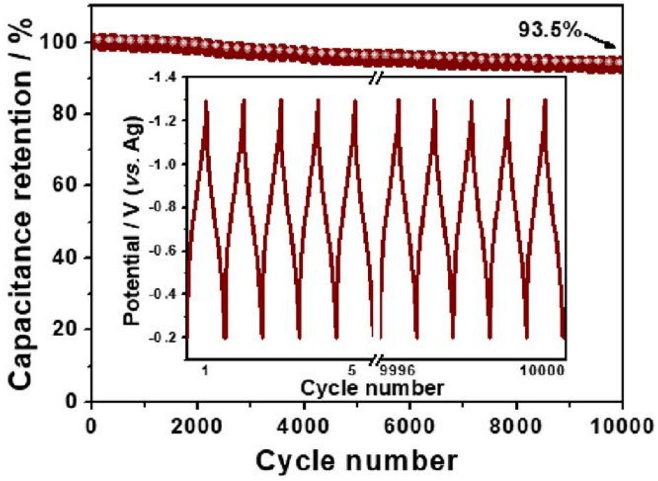
cfaed CENTER FOR ADVANCING ELECTRONICS DRESDEN

- **Linkage-dependent pseudocapacitive behaviours**

In situ X-ray absorption spectra



Long-term cycling



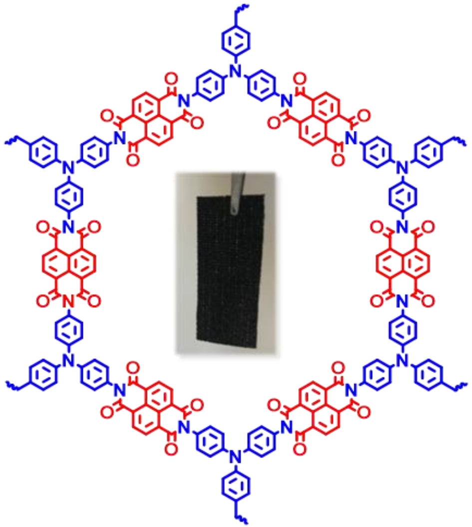
Pseudocapacitance is not from the valence change of metal (Ni) atoms.

J. Am. Chem. Soc. **2023**, 145, 6247.

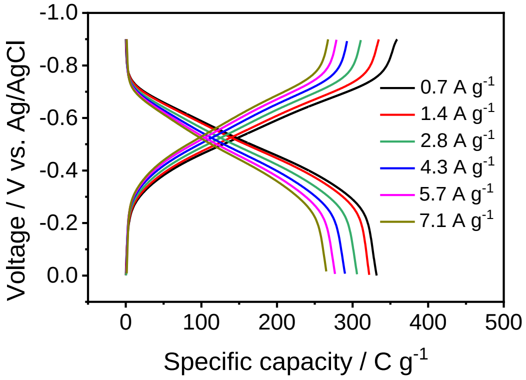
2. 2D carbon-rich frameworks

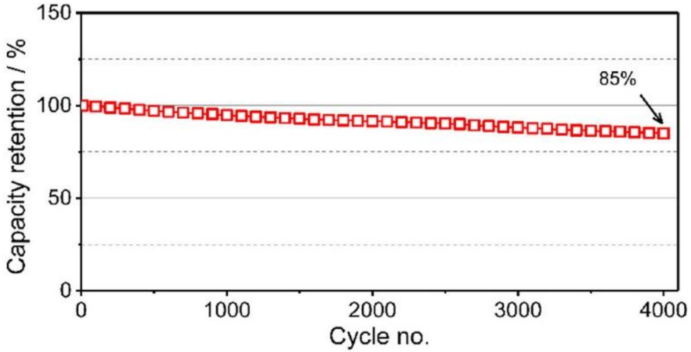
- **Polyimide 2D COF for multivalent ion storage**

  The first COF for Zn^{2+} storage



2 M $ZnSO_4$ aqueous electrolyte





Highly accessible redox-active sites

➢ 92 mAh g^{-1} at 0.7 A g^{-1}

➢ 85% capacity retention over 4,000 cycles

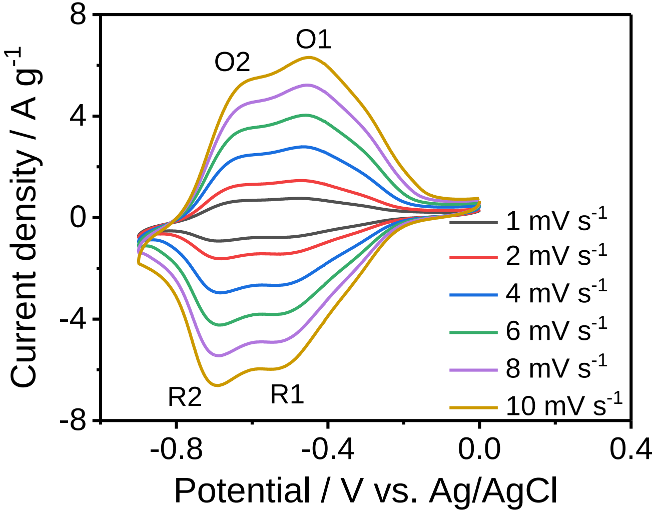
J. Am. Chem. Soc. **2020**, 142, 19570.

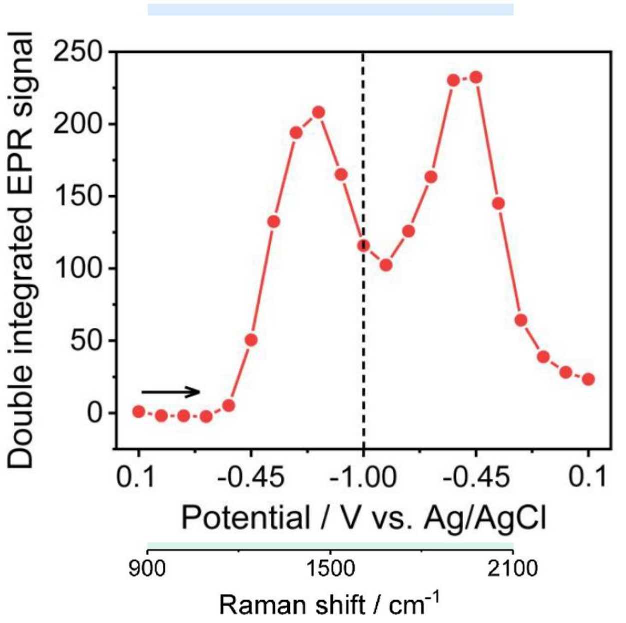
2. 2D carbon-rich frameworks

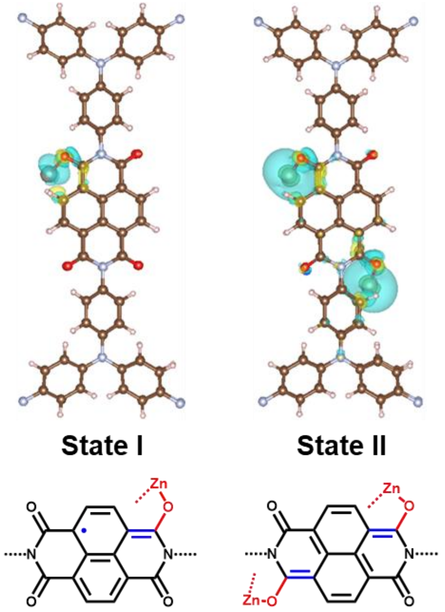
- **Polyimide 2D COF for Zn^{2+} storage**

Two-step Zn^{2+} storage

Co. with **Prof. Inez Weidinger**







➢ Two-step redox reaction

➢ Stepwise carbonyl-enolate conversion.

J. Am. Chem. Soc. **2020**, 142, 19570.

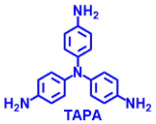
2. 2D carbon-rich frameworks

TECHNISCHE UNIVERSITÄT DRESDEN

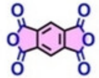
cfaed CENTER FOR ADVANCING ELECTRONICS DRESDEN

- **Redox-bipolar polyimide 2D COFs for Al batteries**

  Structure design: n type imide + p type triazine moieties



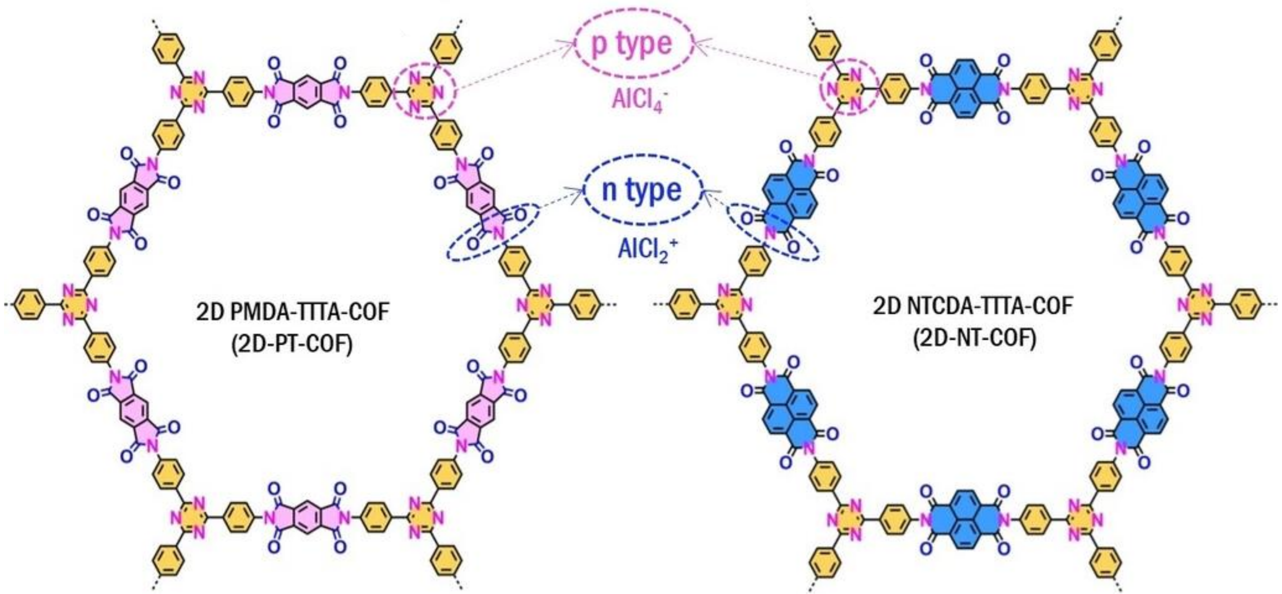
Non-redox active



PMDA

TTTA

NTCDA

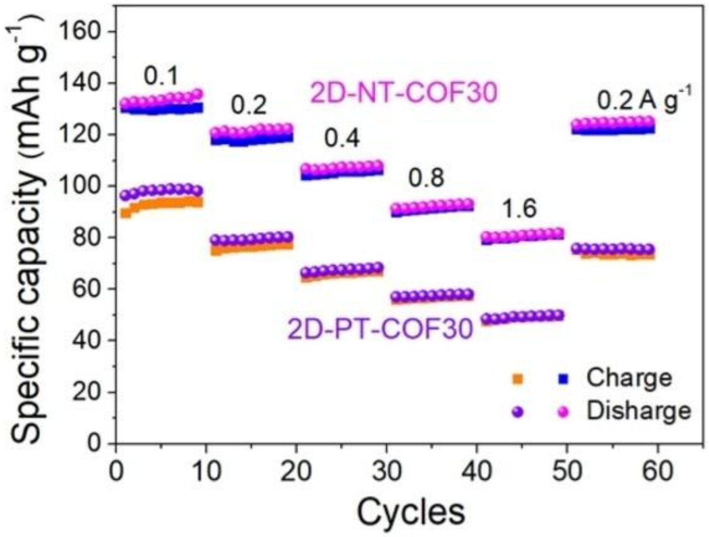


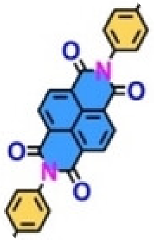
Angew. Chem. Int. Ed. **2023**, *62*, e202306091.

2. 2D carbon-rich frameworks

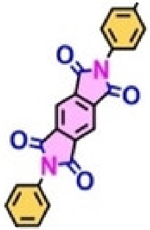
- **Redox-bipolar polyimide 2D COFs for Al batteries**

Al-COF batteries: EMIMCl/$AlCl_3$

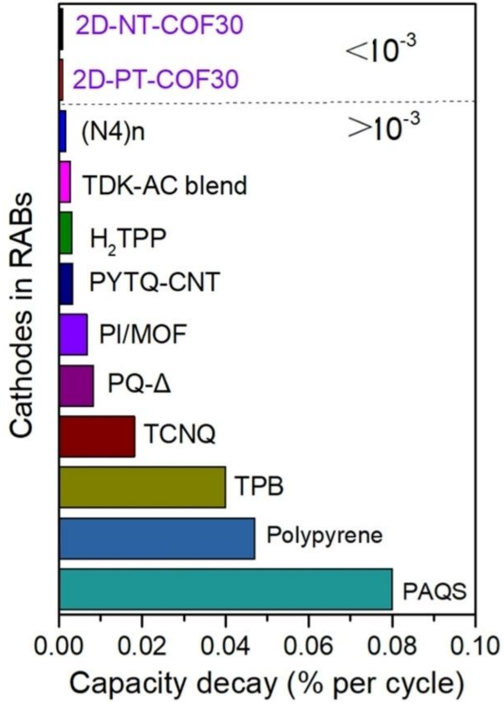




High efficiency



Low efficiency



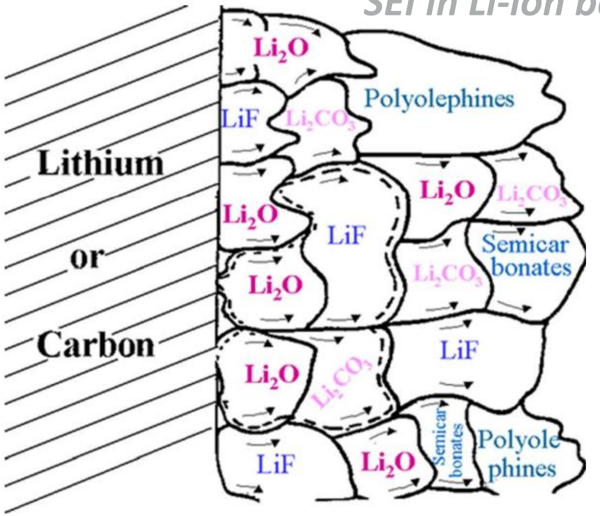
Angew. Chem. Int. Ed. **2023**, *62,* e202306091.

Stable for 4,000 cycles.

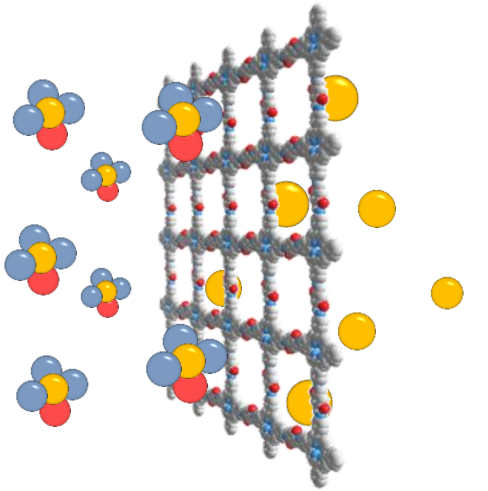
3. Polymeric artificial interphase

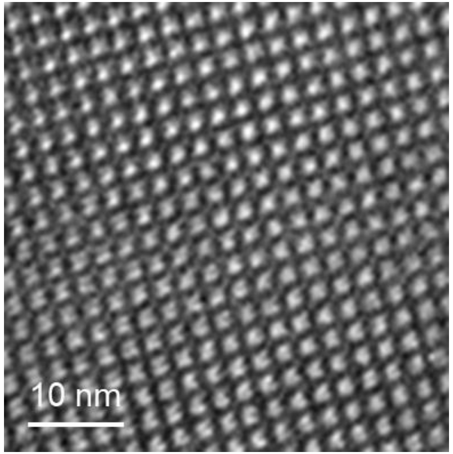
- **Interphase in emerging batteries**

SEI in Li-ion batteries



Peled *et al. J. Electrochem. Soc.* **2017**, *164*, A1703





- Dense direct nanochannels.
- Allow rapid and homogeneous ion flux in.
- Keep **harmful solvent/ion** out.

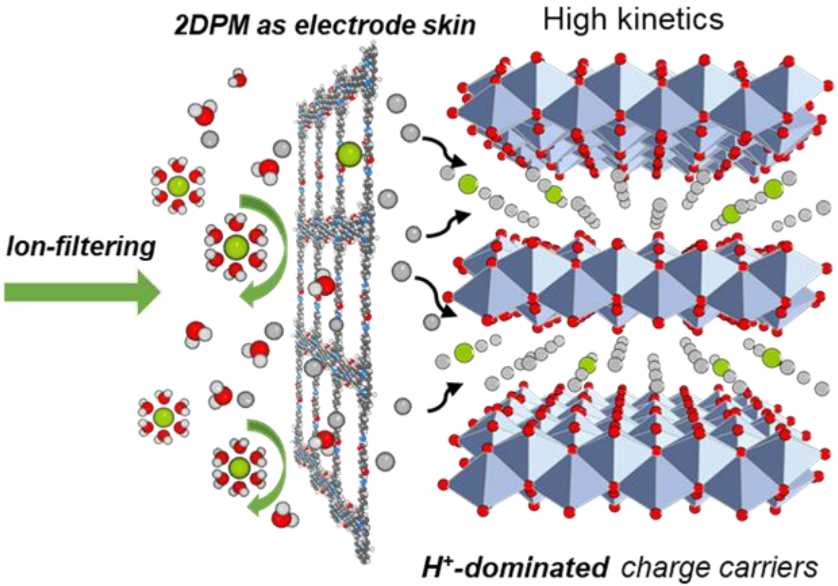
Nat. Commun. **2024**; *Angew. Chem.* **2024**; *Nat. Commun.* **2023**;

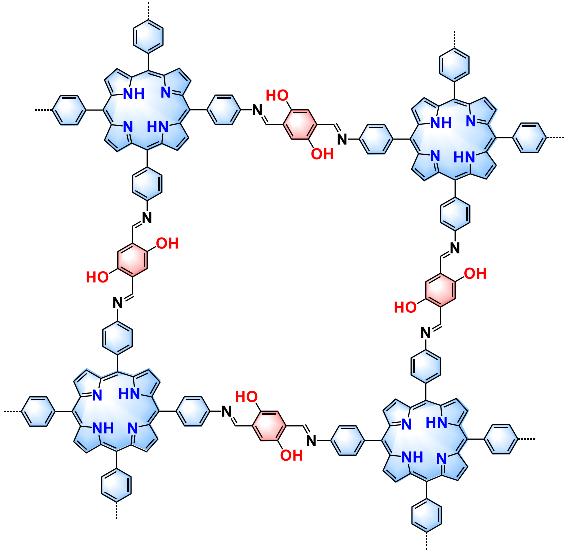
Can one construct artificial interphase for emerging battery chemistries?

3. Polymeric artificial interphase

- **Proton-selective interphase for aqueous batteries**

Sluggish Zn^{2+}-dominated *vs.* fast H^{+}-involved cathode chemistry





Dense proton-conduction groups

-OH, imine, and porphyrin pyrrole units.

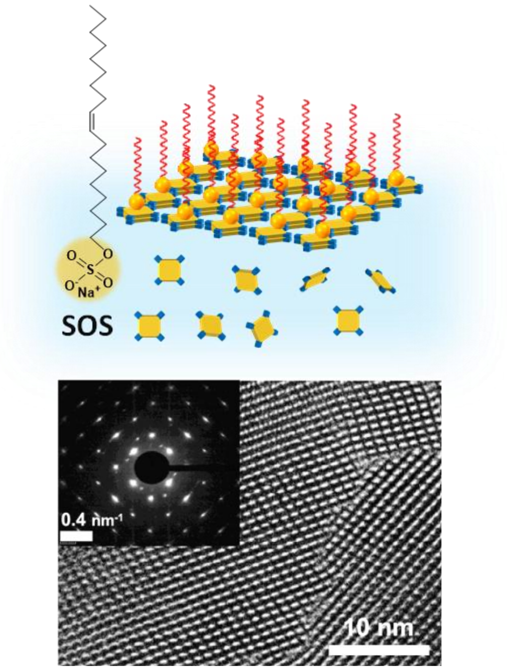
➢ **Filtering ions at the electrode-electrolyte interphase**

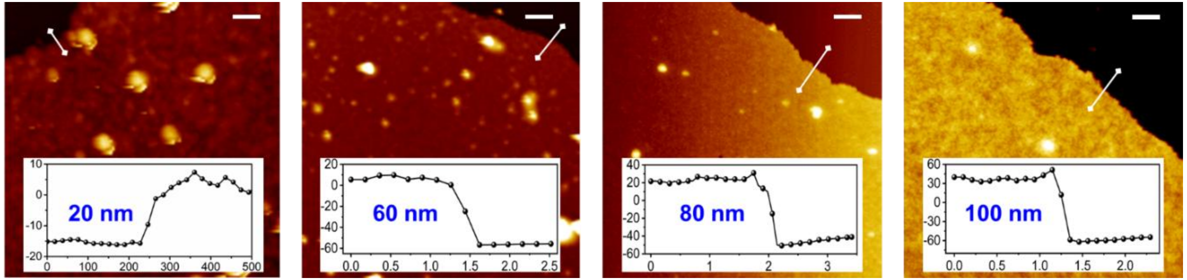
Nat. Commun. **2024**, *15,* 2139.

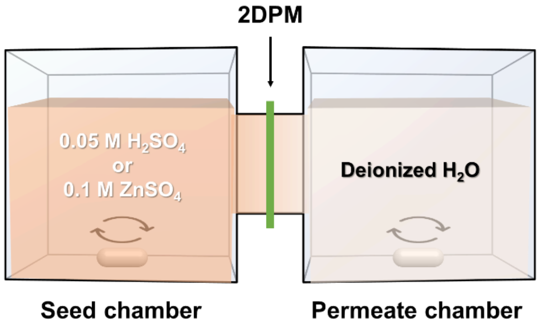
3. Polymeric artificial interphase

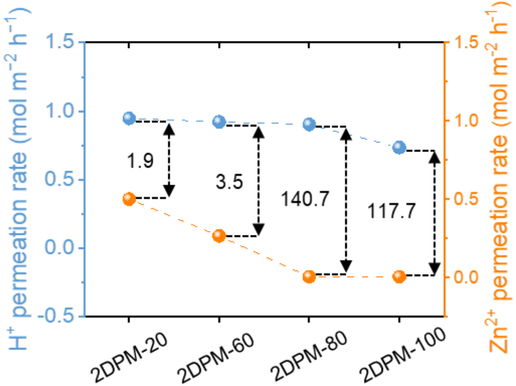
- **2D crystalline polyimine membrane**

H$^+$ selectivity over Zn^{2+}









➢ The highest H$^+$/Zn^{2+} selectivity reaches > 140.

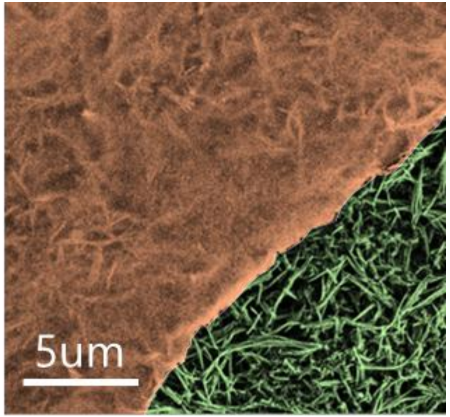
Nat. Commun. **2024**, *15*, 2139.

3. Polymeric artificial interphase

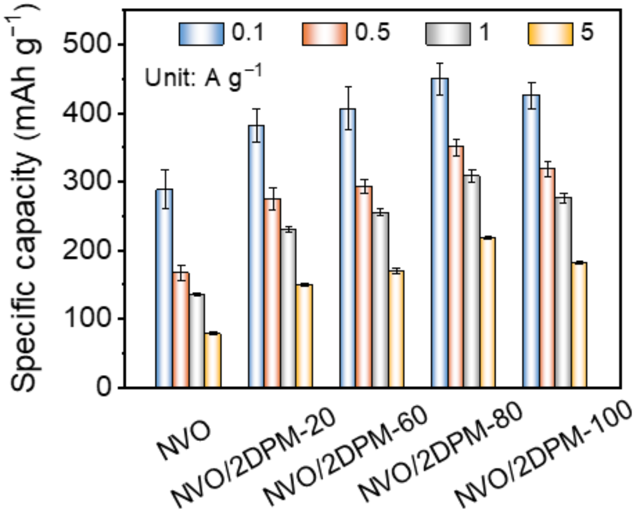
- **2D crystalline polyimine membrane**

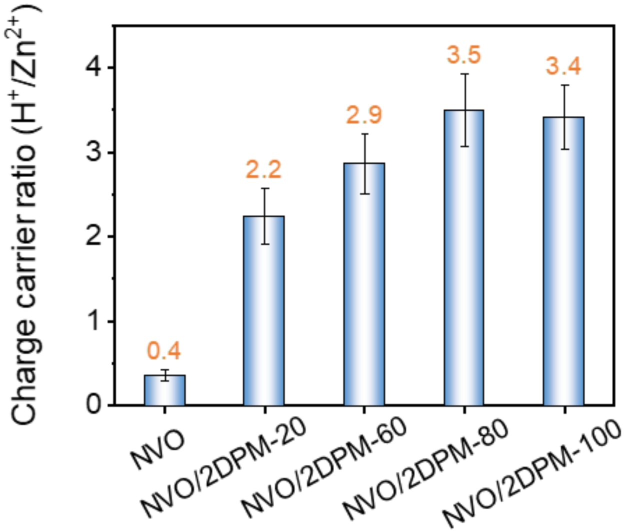
Coating for high-loading cathodes

2 M $ZnSO_4$, pH = 4.3



$NaV_3O_8 \cdot 1.5H_2O$
(10 mg cm^{-2})





➢ Electrochemistry transition from Zn^{2+}- to H^+-dominated

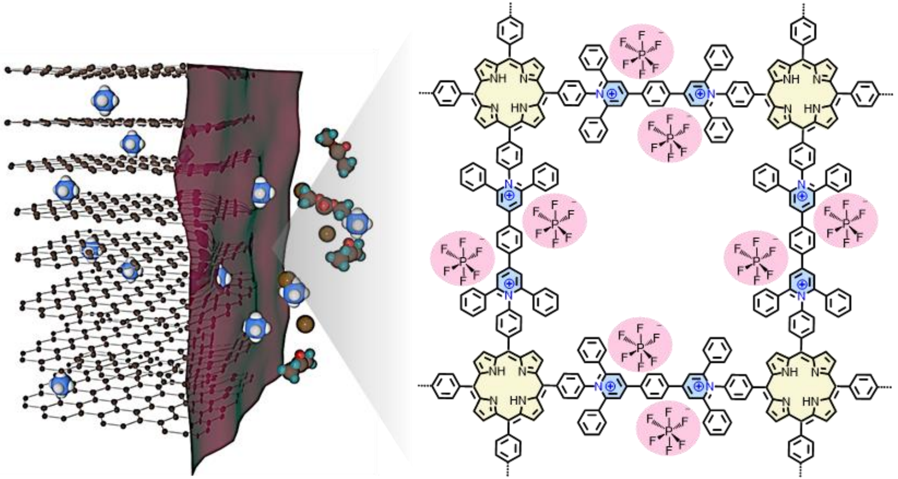
➢ **4.5 mAh cm^{-2}** and **33.8 Wh m^{-2}**

Nat. Commun. **2024**, *15*, 2139.

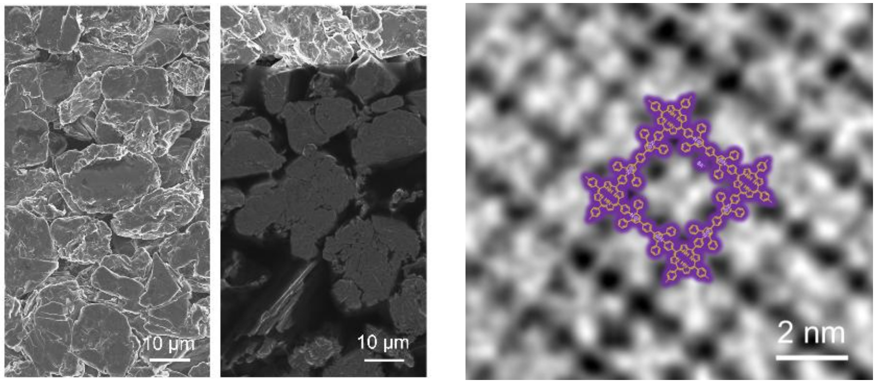
3. Polymeric artificial interphase

- **Anion-selective electrode skin**

Stable pyridinium salt linkage with cationic backbone



Conformal coating as the ‘skin’.



Anion intercalation

2 M $LiPF_6$ in DMC, 3.5~5.1 V

Face-on crystals with dense 1D nanochannels directly across the memberane

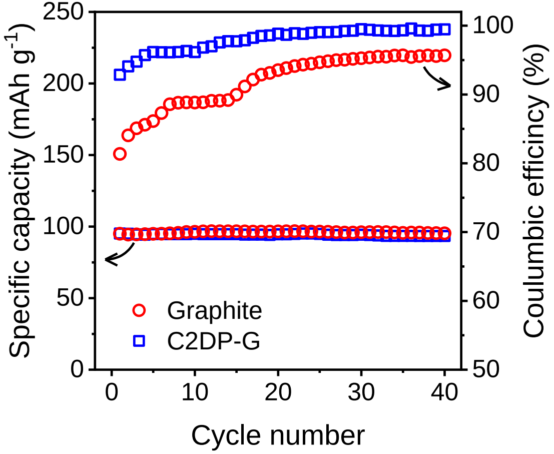
Nat. Commun. **2023**, *14*, 760.

3. Polymeric artificial interphase

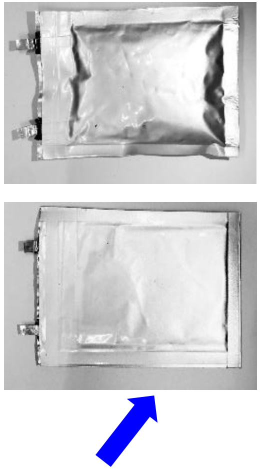
- **2D crystalline poly(pyridinium salt) membrane**

Electrode skin for graphite cathodes

Promoted CEs

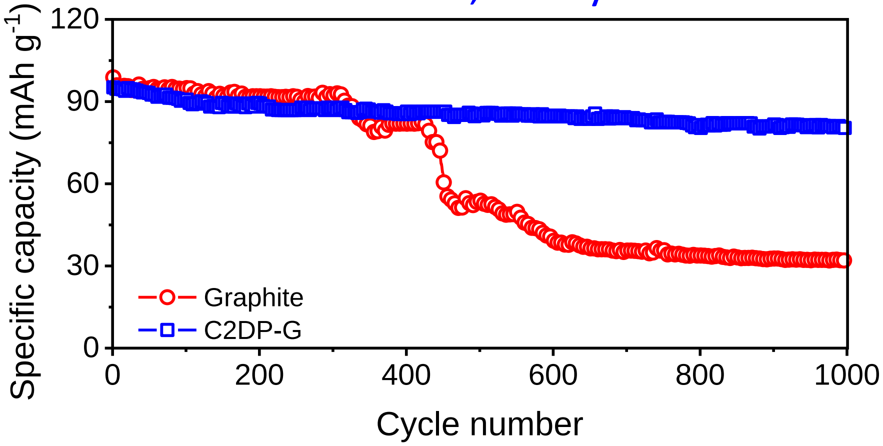


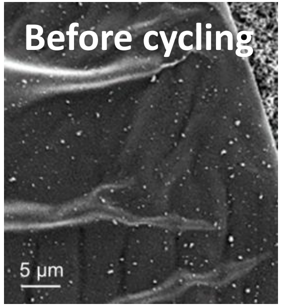
Gas formation

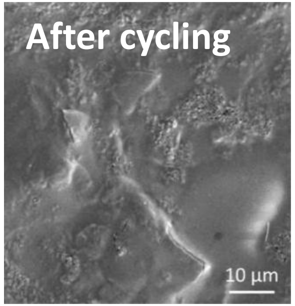


Electrolyte decomposition inhibited

92.8% over 1,000 cycles at 1 C.





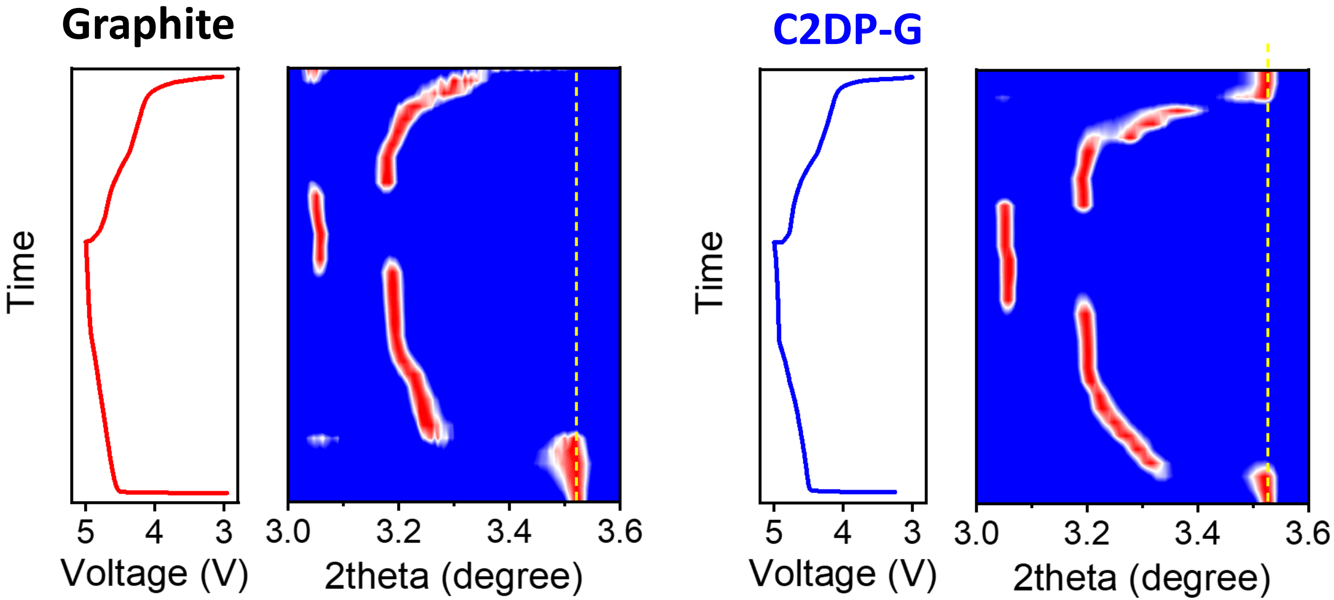


Nat. Commun. **2023**, *14*, 760.

3. Polymeric artificial interphase

- **2D crystalline poly(pyridinium salt) membrane**

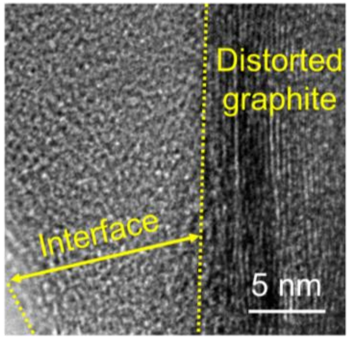
Synchrotron operando X-ray diffraction



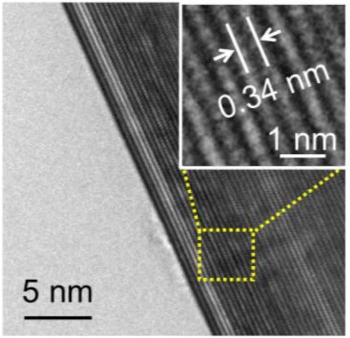
Inhibiting CEI formation and graphite structure degradation

Nat. Commun. **2023**, *14*, 760.

Graphite

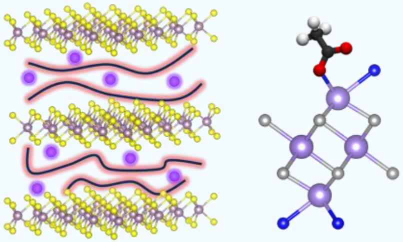


C2DP-G



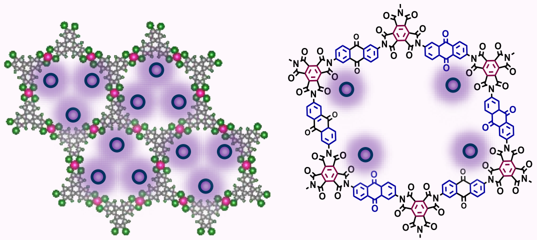
What we have learned…

2D layered TMCs



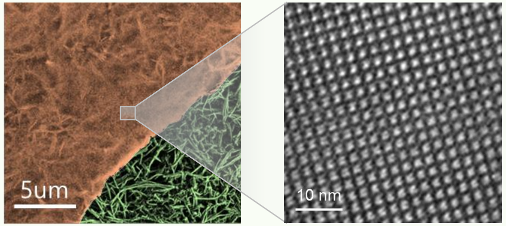
- Interlayer space and surface chemistry
- Controlling ion transport and storage behaviors

2D carbon-rich frameworks



- Design of stable linkages and dual redox sites
- Potential applications in supercapacitors and multivalent batteries

Polymeric artificial interphase



- Constructing stable ion-selective interphase for emerging batteries
- Enable high battery reaction kinetics and reversibility

TECHNISCHE UNIVERSITÄT DRESDEN

cfaed CENTER FOR ADVANCING ELECTRONICS DRESDEN

Former members:

Dr. Faxing Wang, Dr. Panpan Zhang

Dr. Xia Wang, Dr. Boya Sun

New comers:

Dr. Tian Sun, Dr. Xinmei Song

Ruofan Yin, Yuhang Zhuang, Imran Khan

Collaborators: **TUD:** Prof. Xinliang Feng, Prof. Thomas Heine, Prof. Stefan Kaskel, Prof. Thomas D. Kühne, Prof. Eike Brunner, Prof. Inez M. Weidinger. **MPI Mainz:** Prof. Mischa Bonn. **MPI Dresden:** Prof. Claudia Felser. **IFW Dresden:** Prof. Axel Lubk, Prof. Kornelius Nielsch. **KIT:** Prof. Daria Mikhailova, **HZDR:** Dr. Arkady Krasheninnikov. **Argonne National Lab:** Prof. Tao Li. **U Ulm:** Prof. Ute Kaiser. **UPS:** Prof. Patrice Simon. **UCT Prague:** Prof. Zdenek Sofer. **TU Brno:** Prof. Tomáš Šikola. **U Utrecht:** Prof. Hai Wang. **U Warsaw:** Prof. Ehrenfried Zschech. **U Mons:** Prof. David Beljonne. **U Leiden:** Prof. Grégory Schneider

Freistaat SACHSEN

DFG Deutsche Forschungsgemeinschaft

CRC 1415

Funded by the European Union

LEAF project

Funded by the European Union

erc European Research Council Established by the European Commission

BattSkin project

Thank you for your attention.