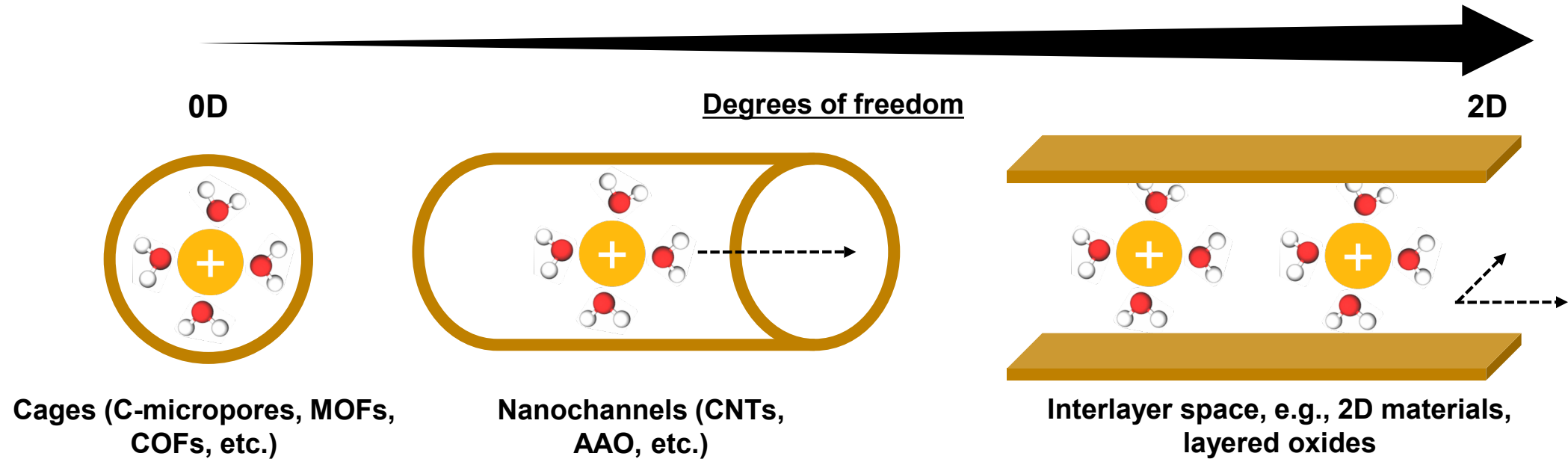


Simon Fleischmann – Principal Investigator and Group Leader at Helmholtz Institute Ulm (HIU)

How nanoconfinement shapes electrochemical interfaces: Insights from *operando* characterization

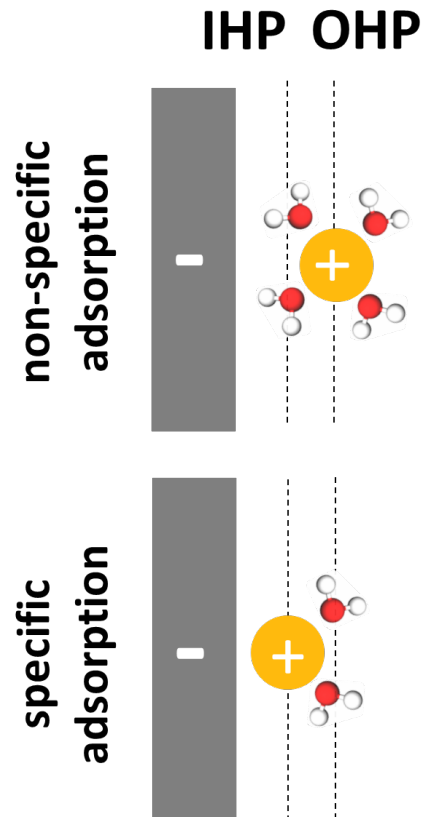
Webinar Series “Time and Length-Scale Operando Bridging Techniques to Study Battery Interfaces”,
22/01/2026

(Nano-)confinement is spatial restriction exerted by a solid-state host material onto a guest species (ions, molecules, fluids) in the dimension of guest size



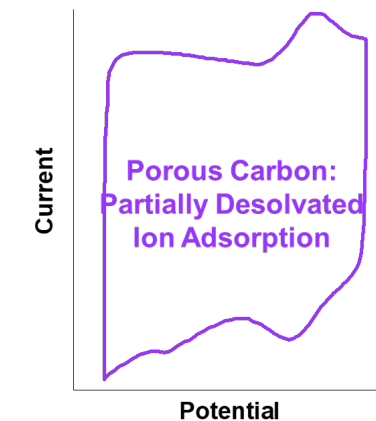
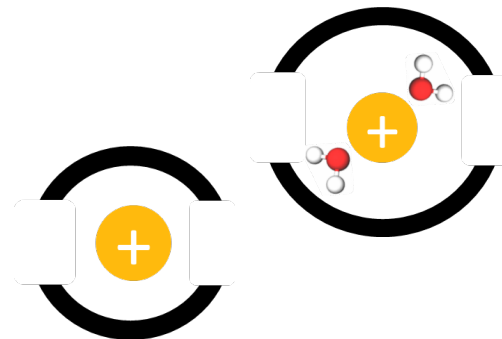
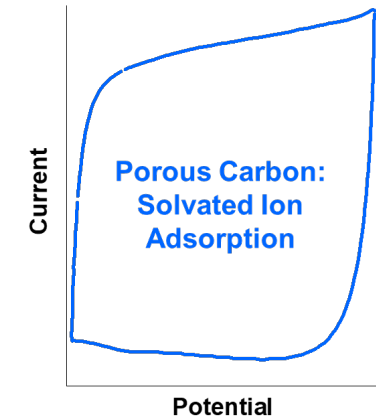
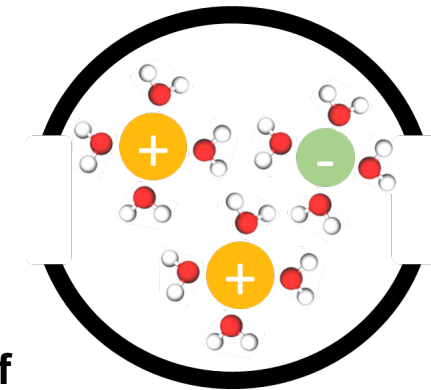
- **Long- and short-range order** of guest species is disrupted
- **Host-guest interaction altered**
- **Geometry**, but also **chemical composition** and **chemo-mechanics** of nanoconfined space determine **host-guest interaction** and drive **functionality**
- Different from “nanosizing-effects” by emphasis on spatial restriction, but both effects often overlap

Electrosorption at Planar Interface



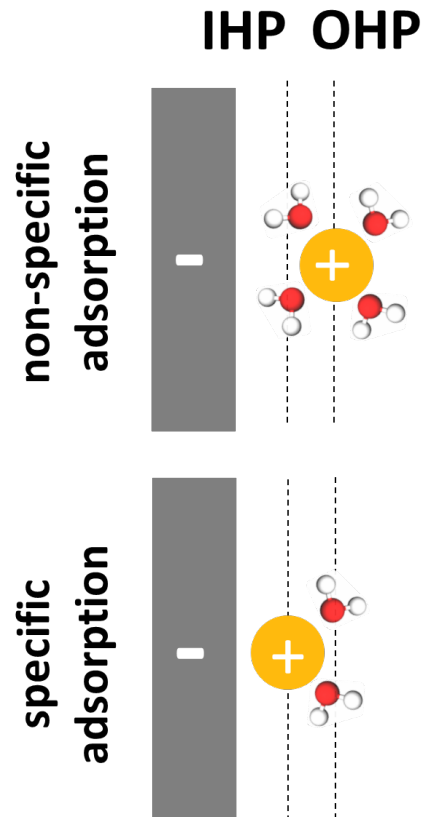
Electrosorption in carbon nanopores

Increased degree of
electrolyte confinement

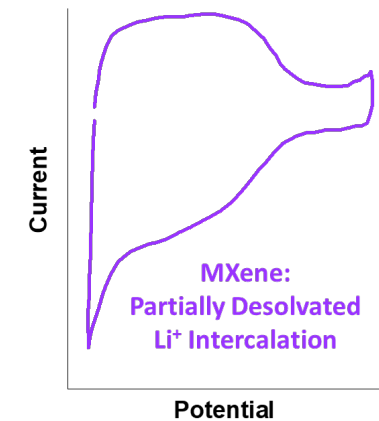
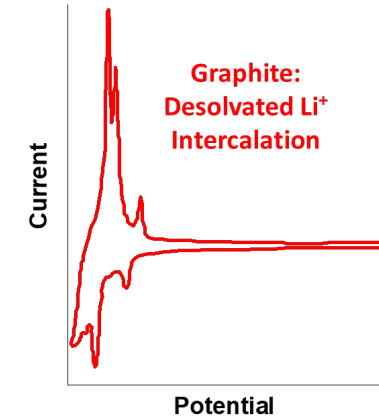
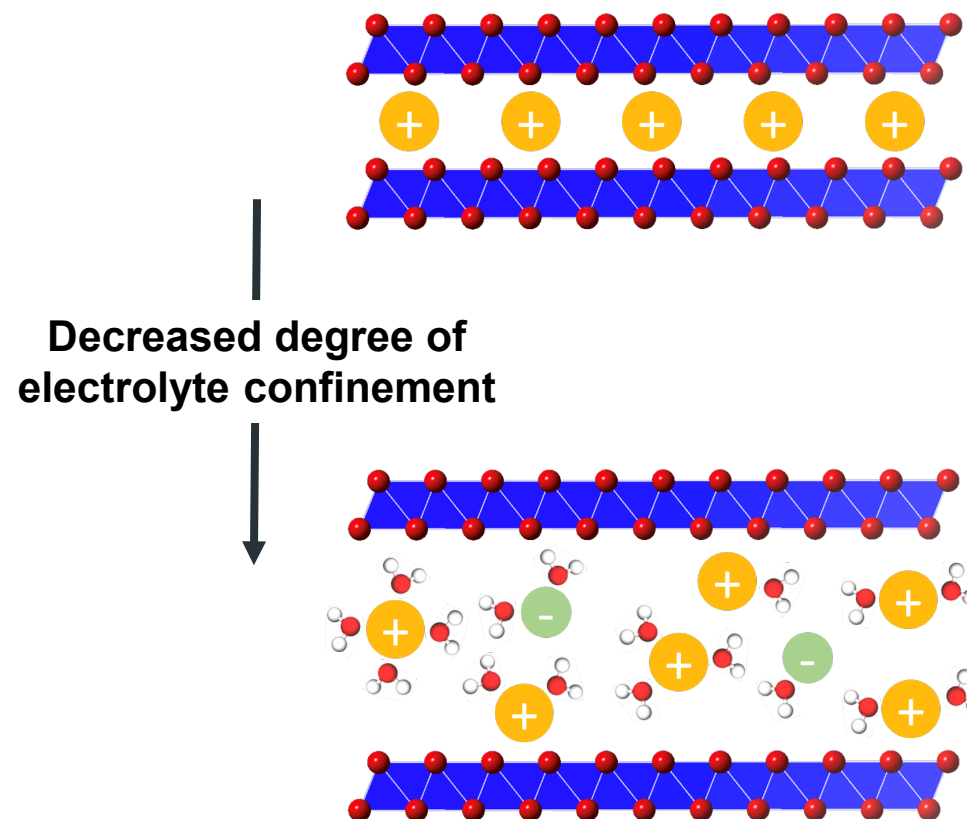


R. Lin, P. Simon, et al., *Electrochim. Acta*, **2009**, 54, 7025-7032

Electrosorption at Planar Interface

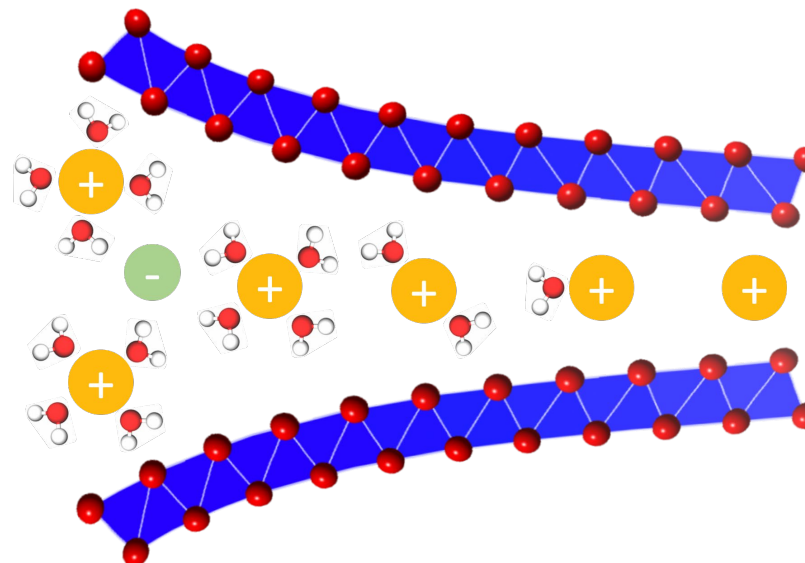


“Electrosorption” in 2D / layered materials



Hypothesis: Nanoconfinement properties of interlayer dictate the nature of intercalant

*Can we achieve solvent
co-intercalation by
materials design?*



*What are the resulting
electrochemical
properties?*

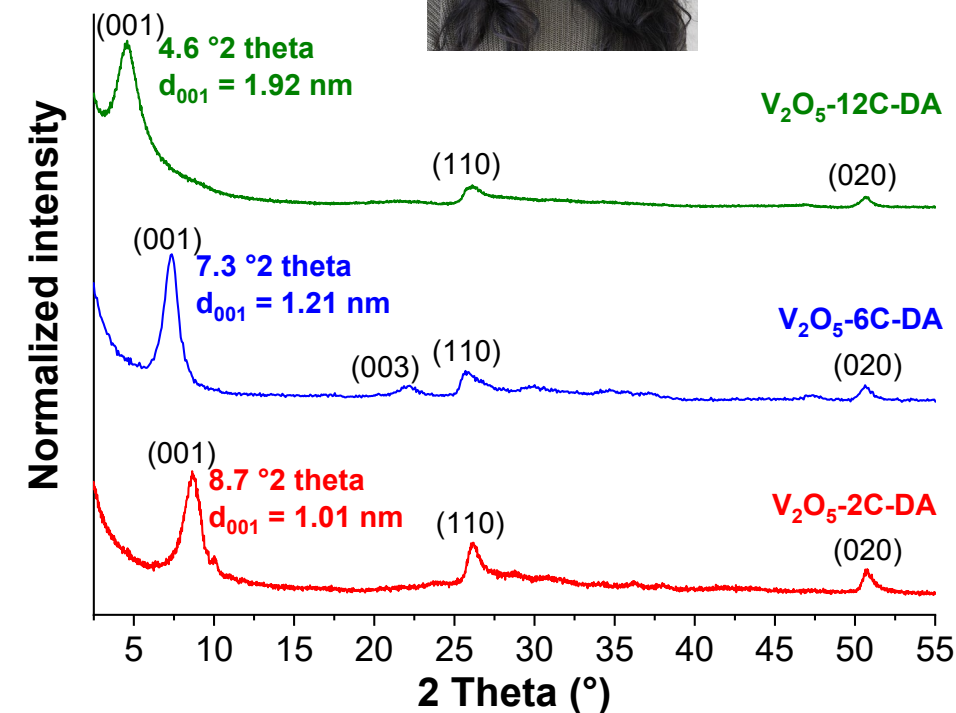
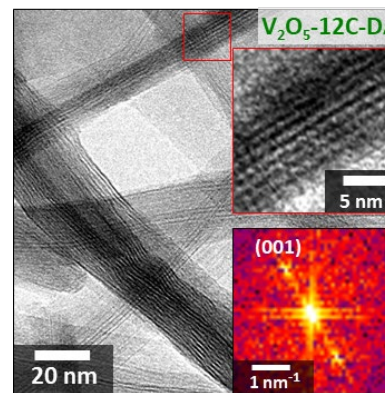
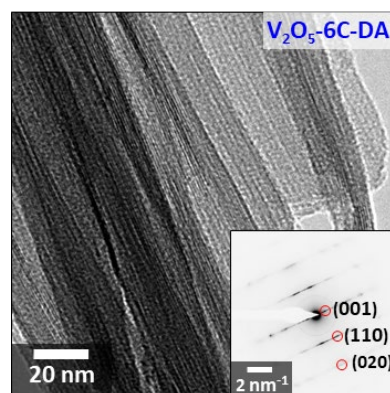
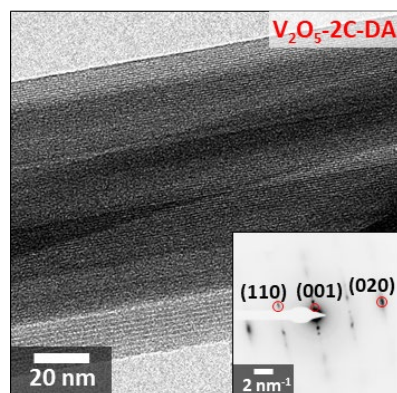
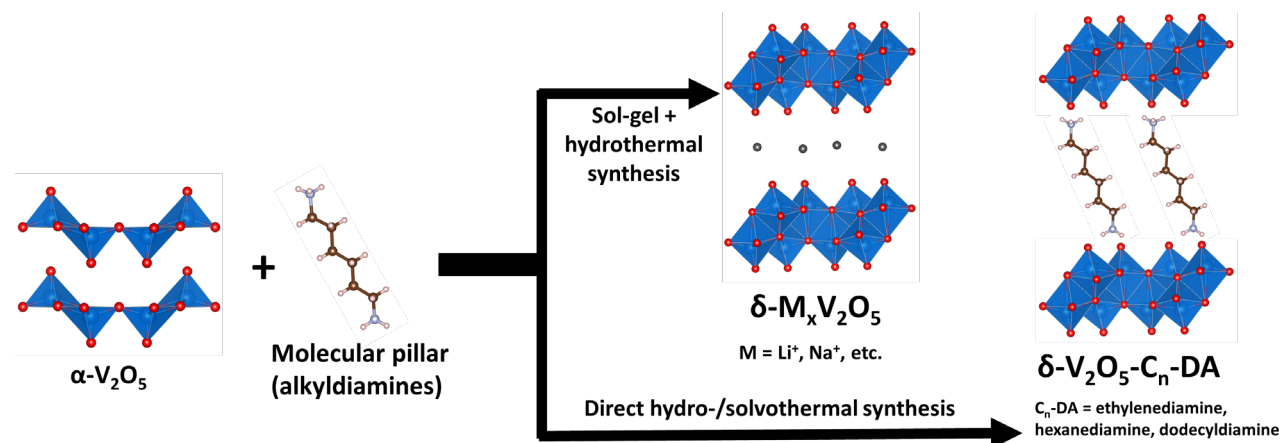
Fleischmann-Lab approach:

- ✓ Control degree of ion solvation by nanoconfinement design
- ✓ Understand and optimize **electrochemistry of nanoconfined solvated ions**



Jameela Karol

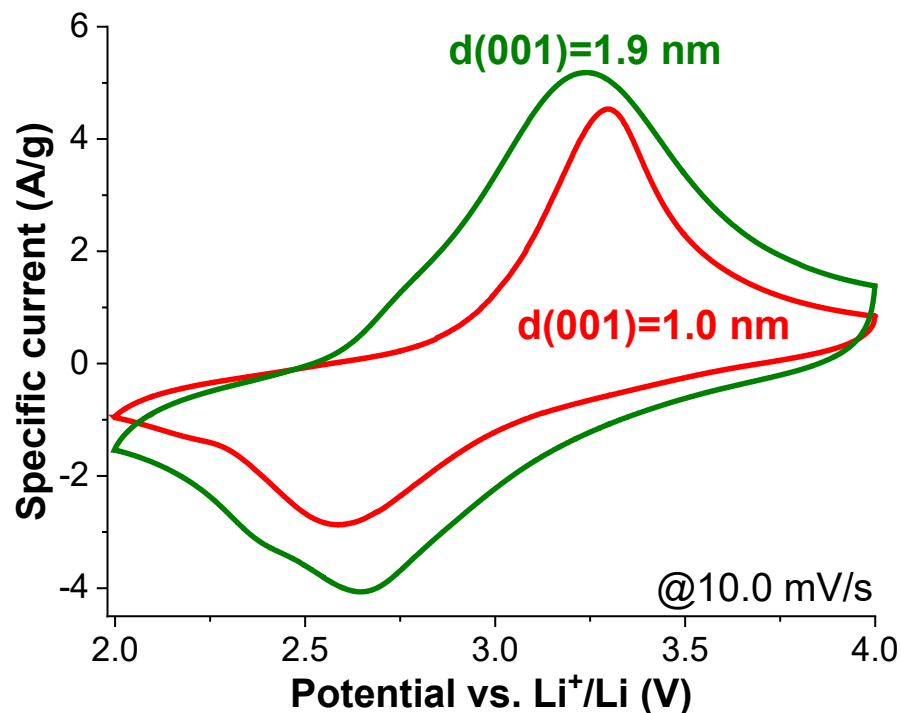
Interlayer-expanded δ - V_2O_5 using alkyldiammonium pillars



- XRD / TEM-SAED: bilayered δ - V_2O_5 host structure
- d-spacing variation from 1.0 – 1.9 nm
- **Nanoconfinement geometry control via pillaring**

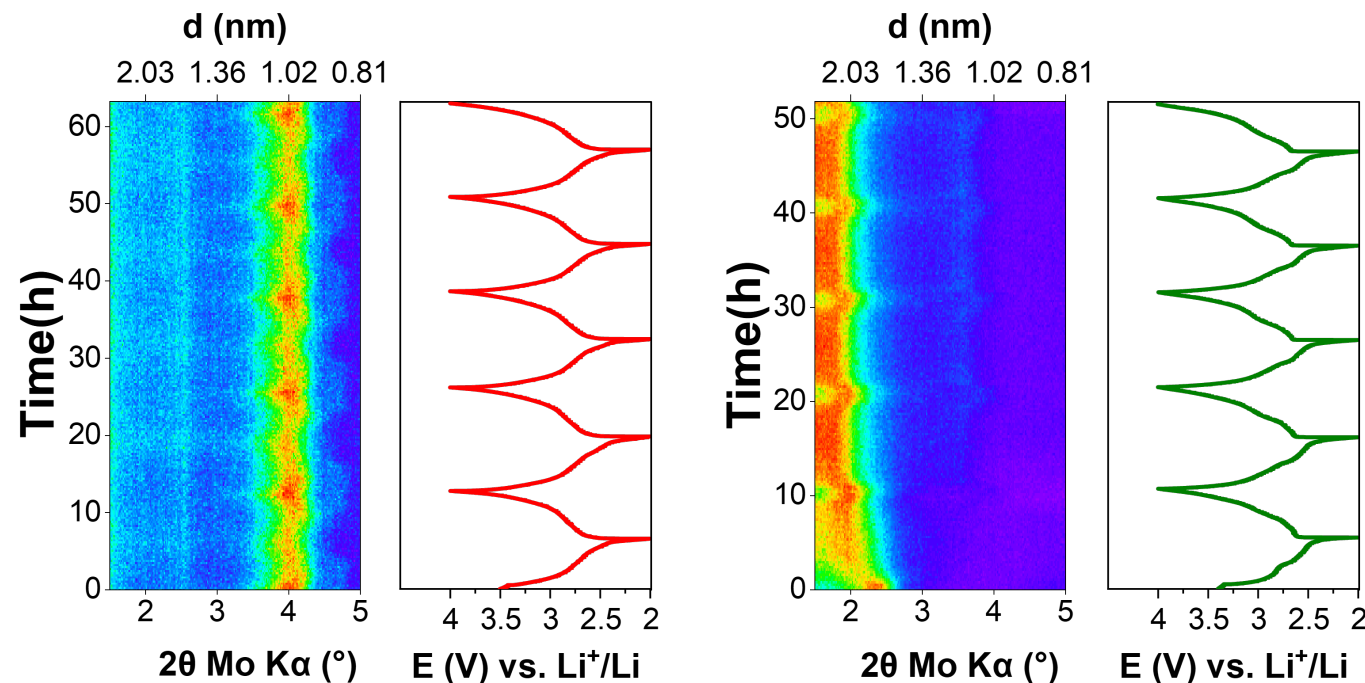
Nanoconfinement-induced change in charge storage mechanism

CV in coin cells vs. Li metal,
1M LiPF₆ in EC/DEC electrolyte



- With larger d-spacing: Broadening of redox peaks & improved capacity at high sweep rates

Operando XRD (transmission) in customized coin cells

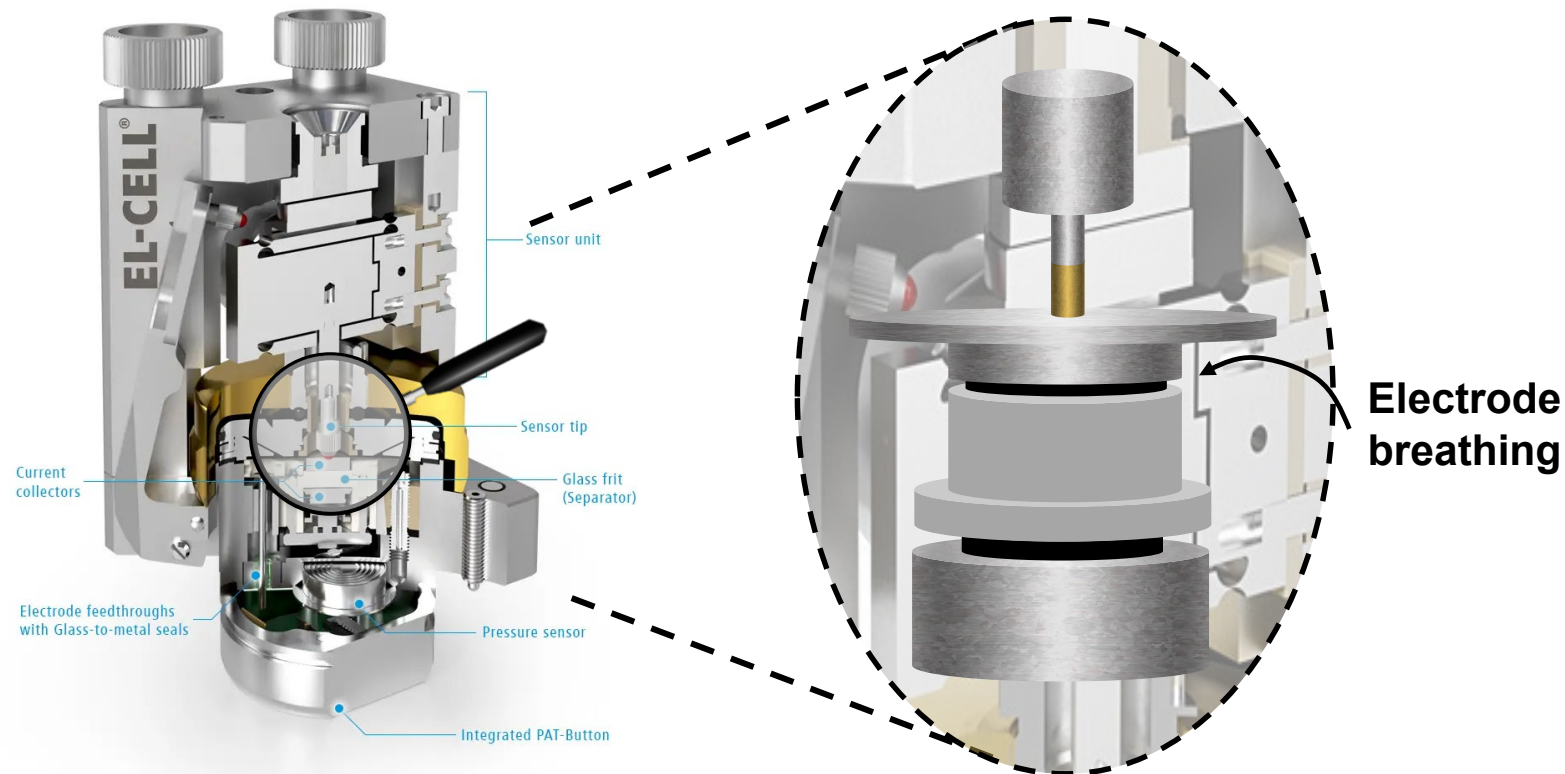


- Solid-solution with min. expansion in V₂O₅ with small d-spacing
- Strong further expansion in V₂O₅ with large d-spacing, co-intercalation
- **Nanoconfinement-dependent charge storage mechanism**

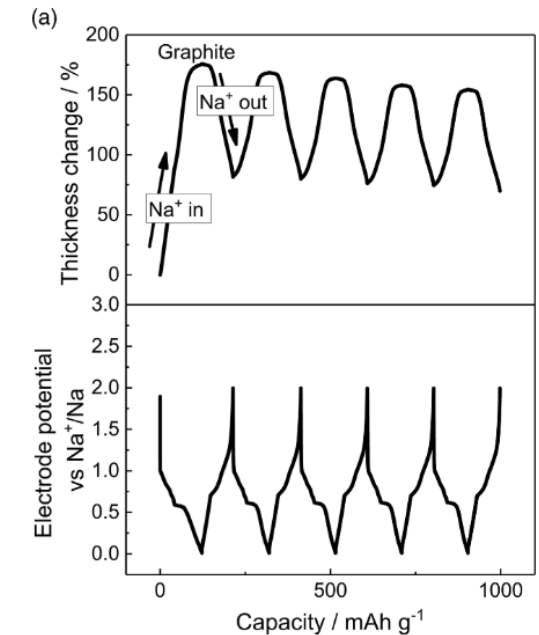
Electrochemical dilatometry (ECD)



Dr. Maciej Tobis



EL-Cell – ECD 4-nano

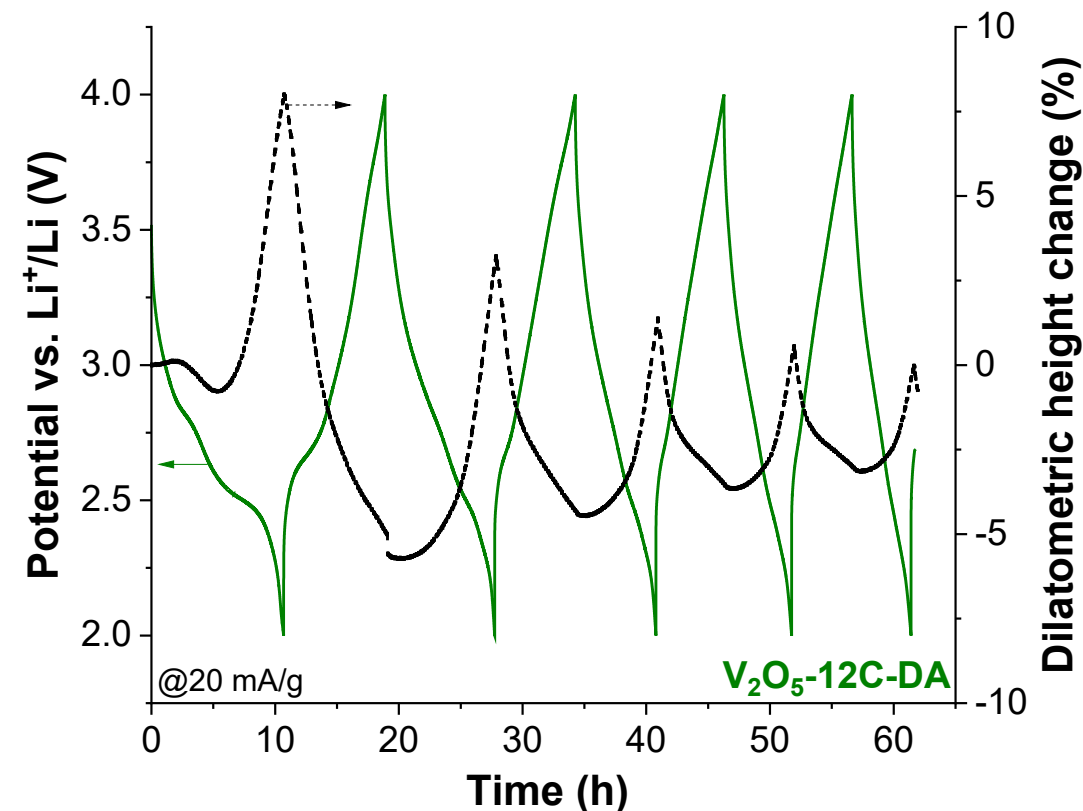
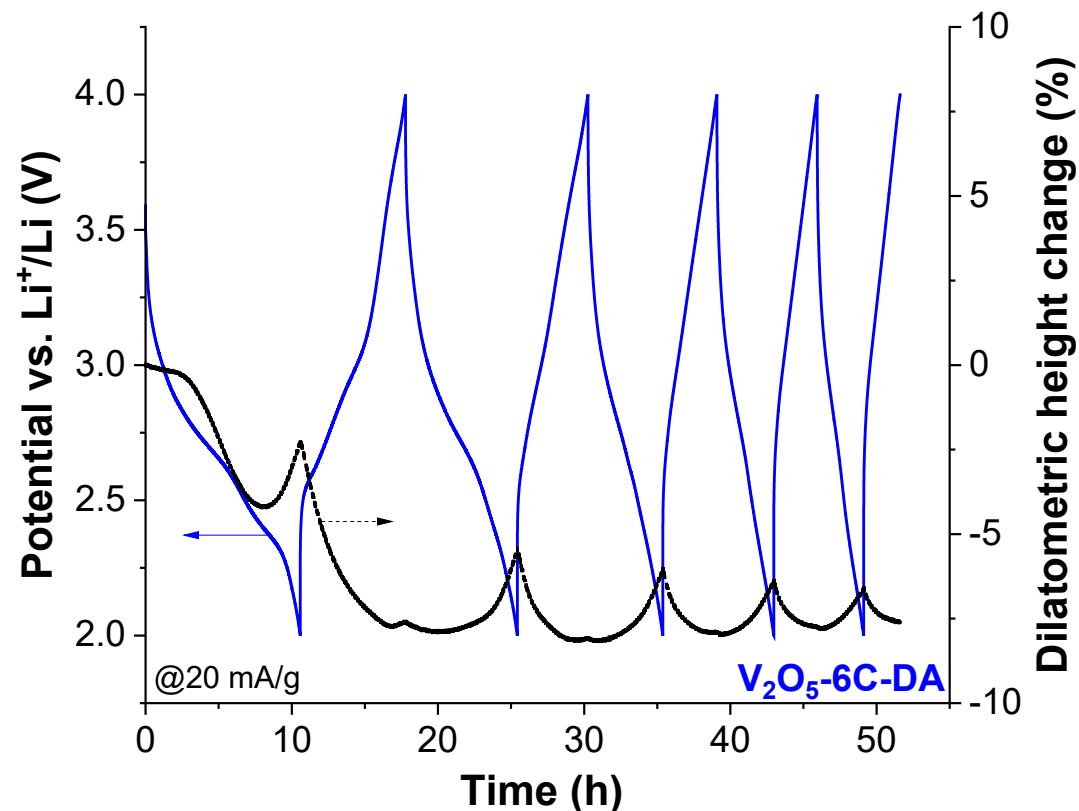


Energy Technology, **2021**, 9, 2000880

Dilatometer allows for tracking the (macroscopic) electrode **thickness** change during electrochemical operation

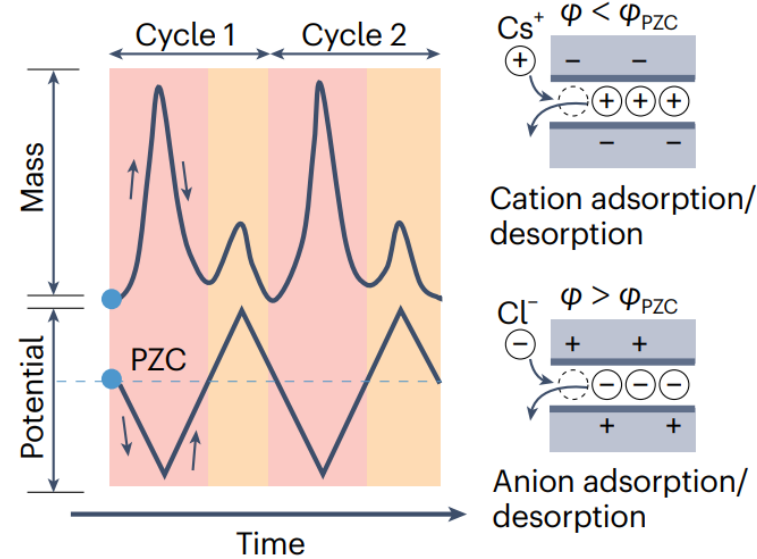
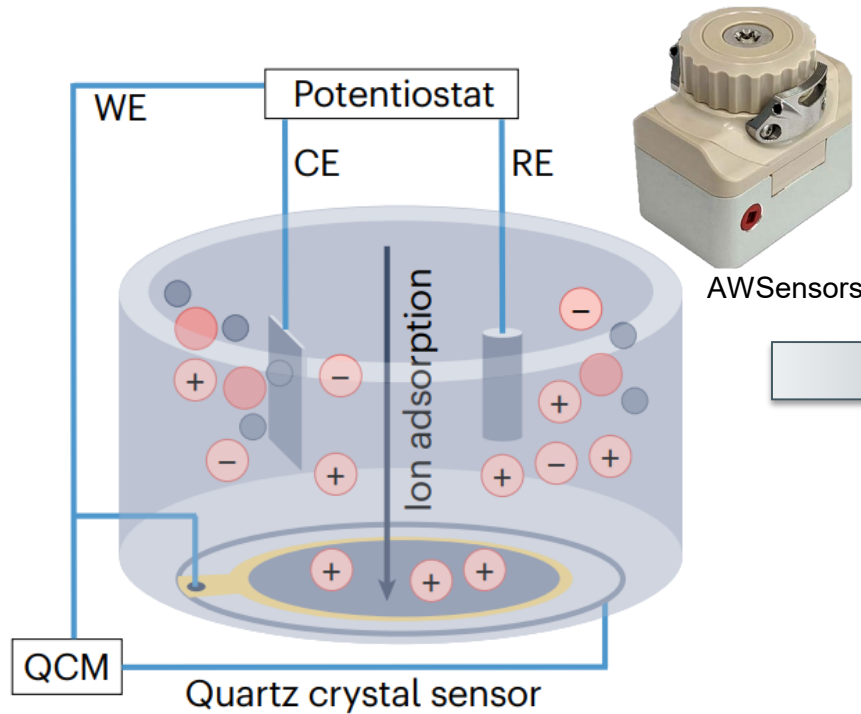
Verification of co-intercalation mechanism via electrochemical dilatometry

Galvanostatic cycling in EL-Cell dilatometer (ECD-4-nano); PTFE-bound electrode



- Significantly increased thickness changes in V_2O_5 -12C-DA electrode supports solvent co-intercalation

Electrochemical quartz crystal microbalance (EQCM)



Sauerbrey equation: $\Delta m = -C \frac{\Delta f}{n}$

Condition for validity: Rigidity of coating

Overtone analysis



$n=1$



$n=3$

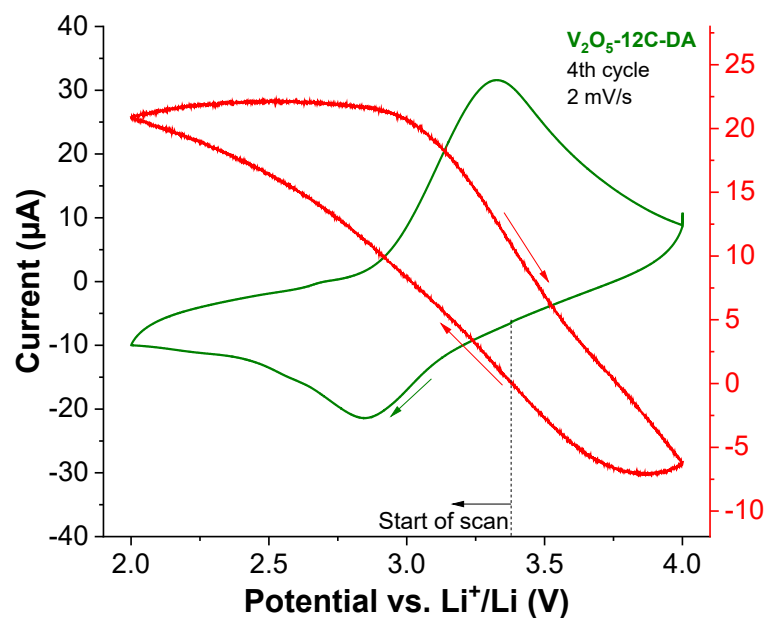
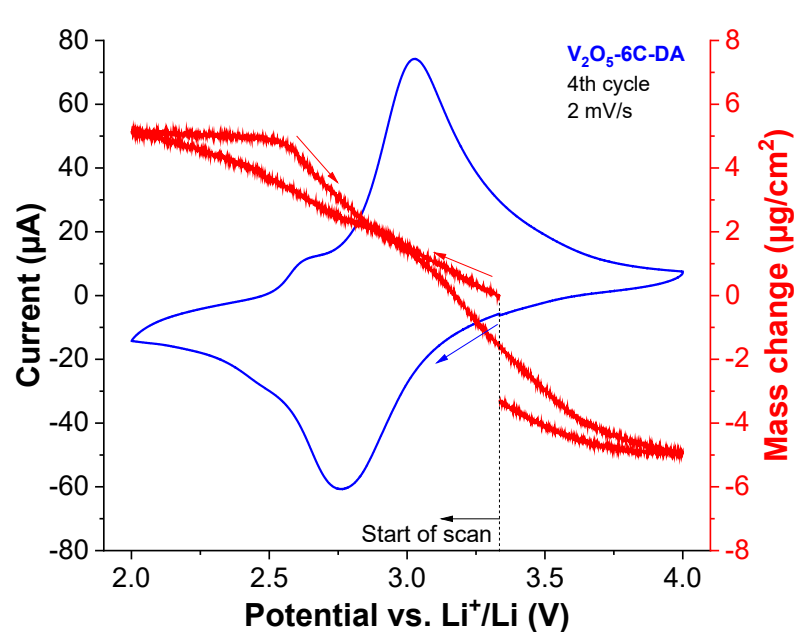
Condition: $\frac{\Delta f}{n} = \text{const.}$

Figure credit: BioLogic

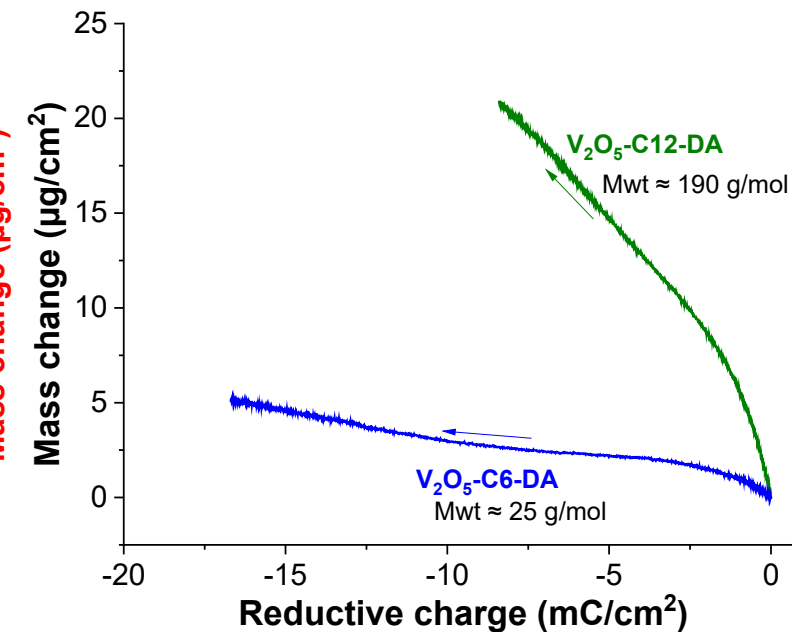
EQCM allows for tracking the electrode **mass** change during electrochemical operation

Verification of co-intercalation mechanism via electrochemical quartz crystal microbalance (EQCM)

CV in EQCM cell vs. Li metal, 1M LiClO₄ in EC/DEC electrolyte



Charge vs. Mass change plot

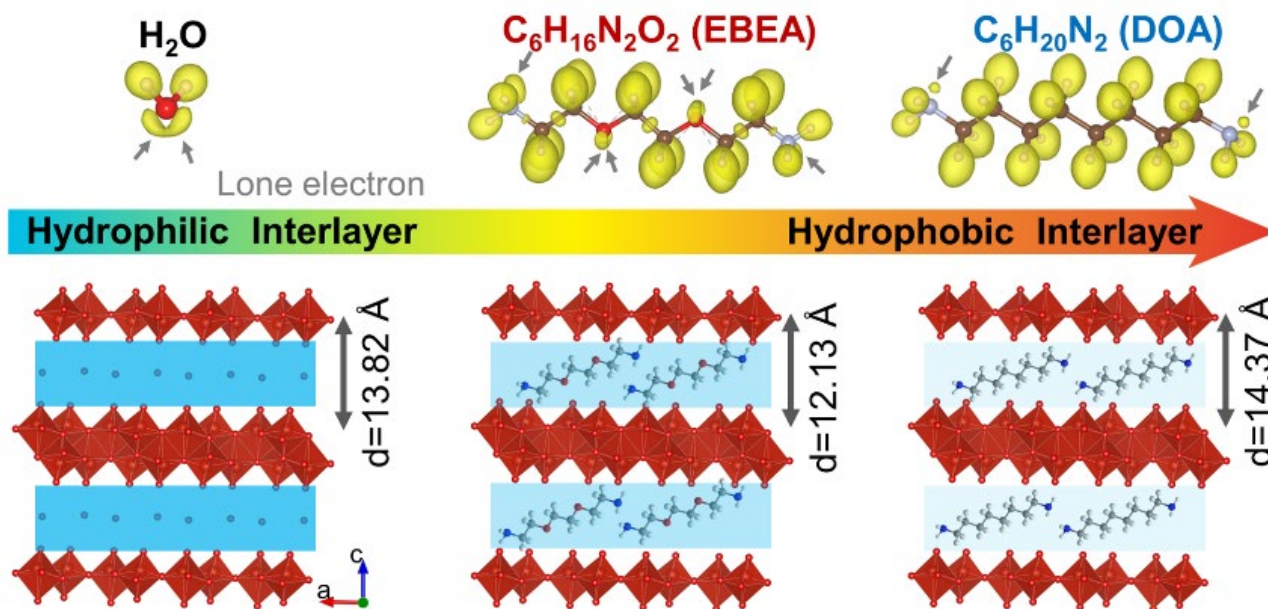
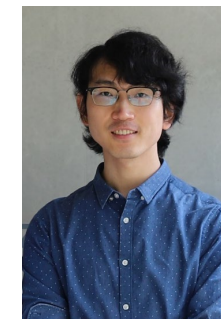


- Deposition of thin layer of active material on Au-coated quartz sensor (spray coating)
- Molar mass of intercalant is ca. 6 times larger in V₂O₅ with largest d-spacing
- **EQCM supports nanoconfinement geometry-induced co-intercalation mechanism**

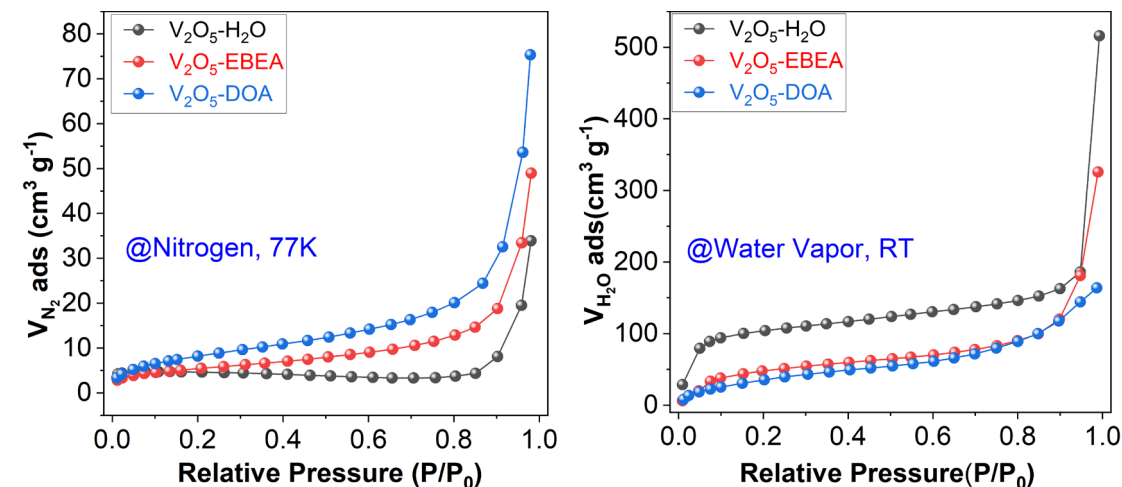
Nanoconfinement engineering to enable sustainable post-Li storage

- Safe and sustainable: Zn-ion batteries can use aqueous electrolytes
- How does water interact with electrode?
- **Our hypothesis: Hydration of Zn^{2+} determines charge storage!**

Dr. Haocheng Guo
Humboldt Fellow

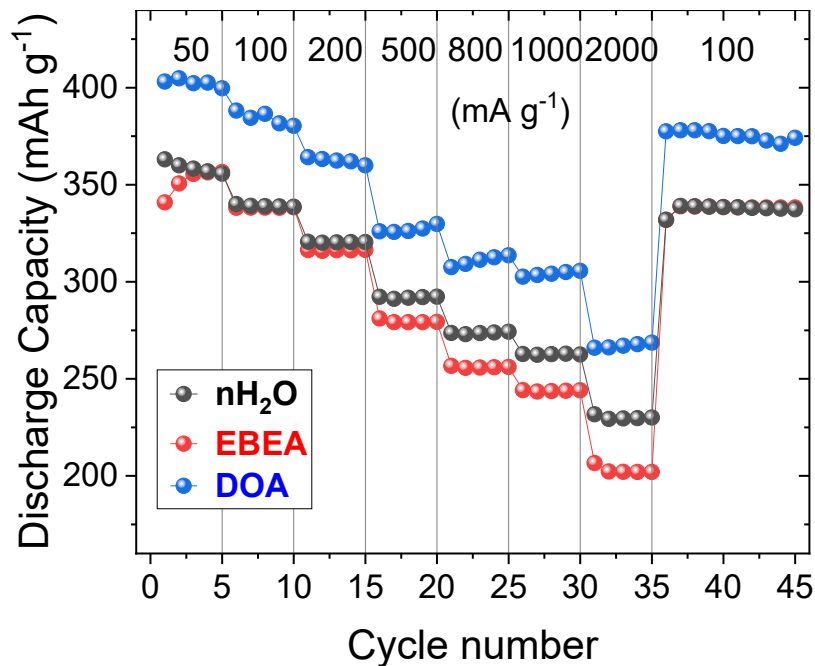


N₂ and H₂O adsorption isotherms



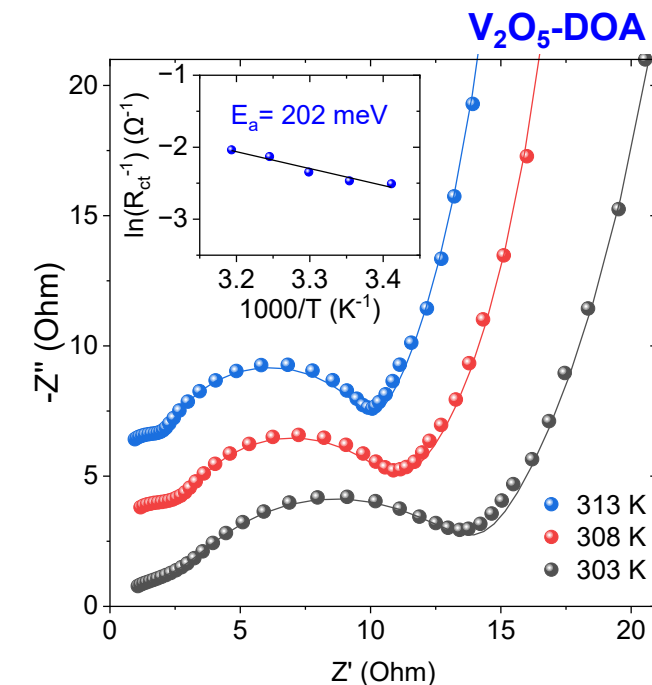
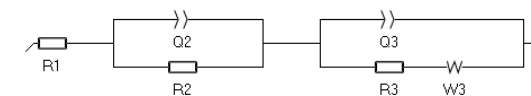
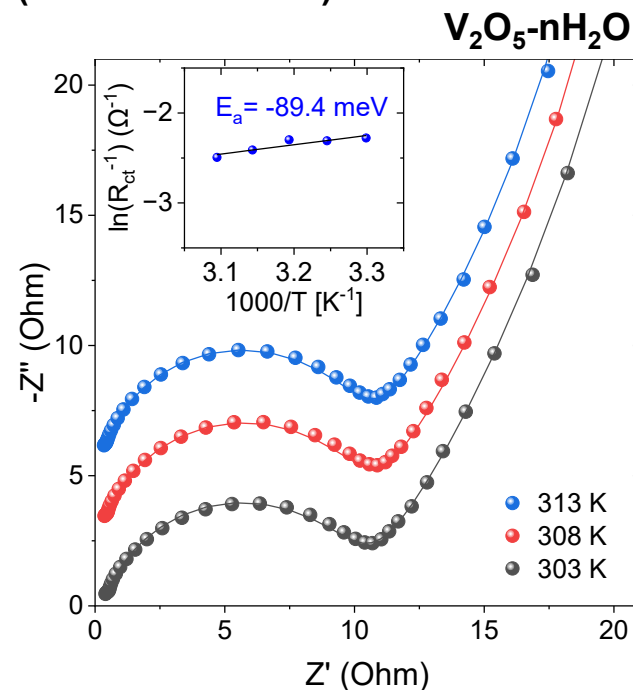
- Nanoconfinement chemistry determines H₂O sorption capacity
- **Effect on interfacial process in aqueous electrolyte?**

Electrochemistry in 2-electrode cells vs. Zn metal, 3.0M $\text{Zn}(\text{OTf})_2$



- Difference in specific capacity per V_2O_5 : DOA ($3.33 e^-$) > EBEA ($3.10 e^-$) > nH_2O ($2.57 e^-$)

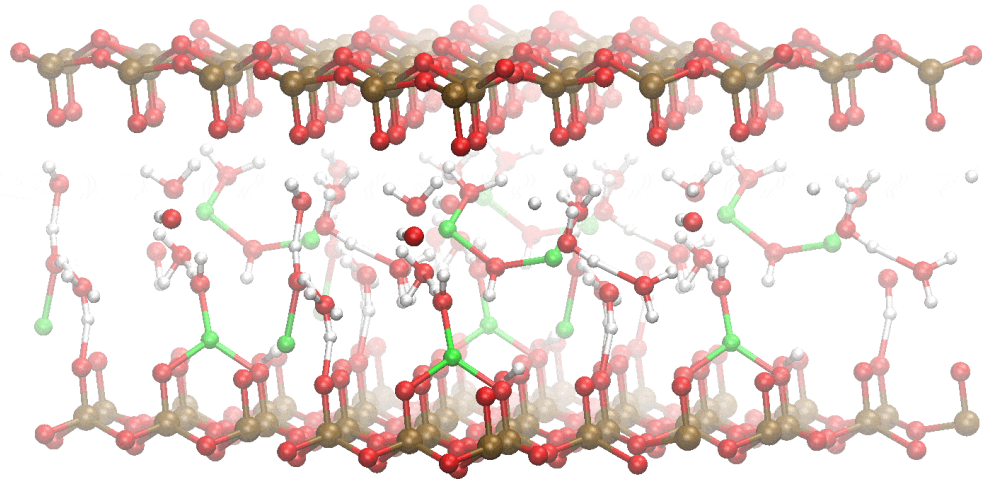
Activation energy from EIS (3-electrode cells)



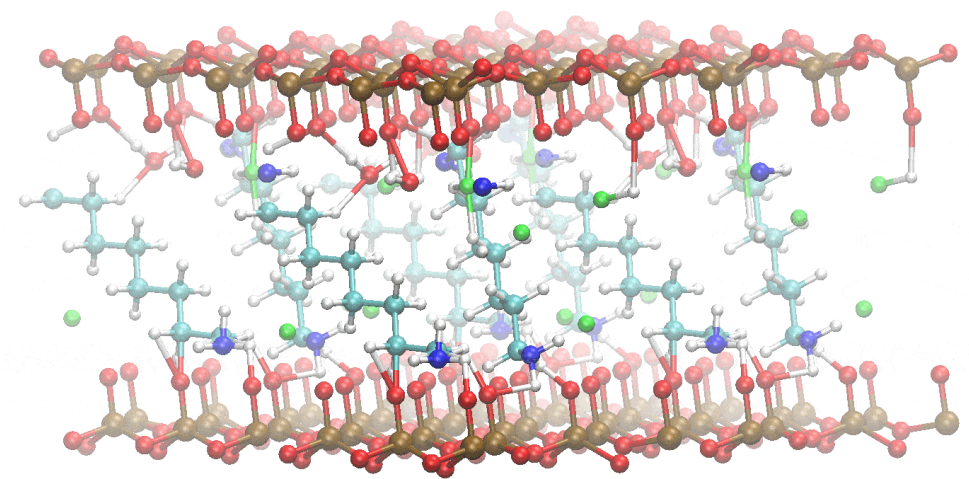
- Activation-less intercalation in $\text{V}_2\text{O}_5\text{-nH}_2\text{O}$; indicative of desolvation-free process
- Arrhenius-behavior in $\text{V}_2\text{O}_5\text{-DOA}$, indicative of ion desolvation

➤ **Nanoconfinement chemistry dictates charge storage mechanism**

$\text{V}_2\text{O}_5\text{-nH}_2\text{O}$



$\text{V}_2\text{O}_5\text{-DOA}$



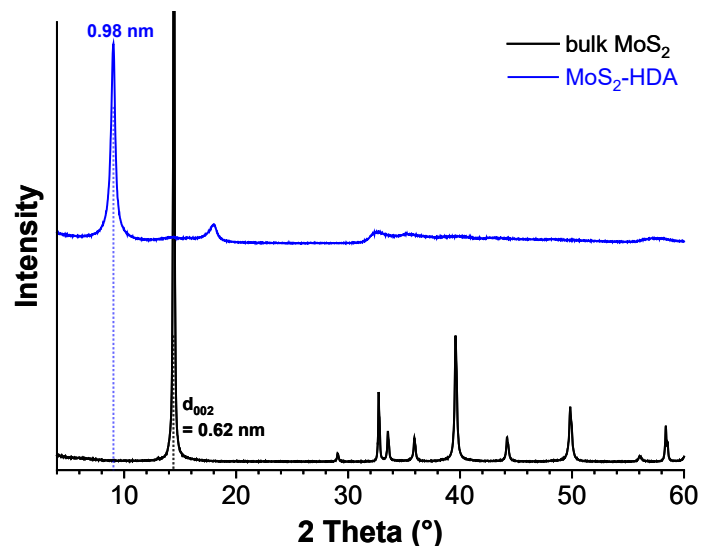
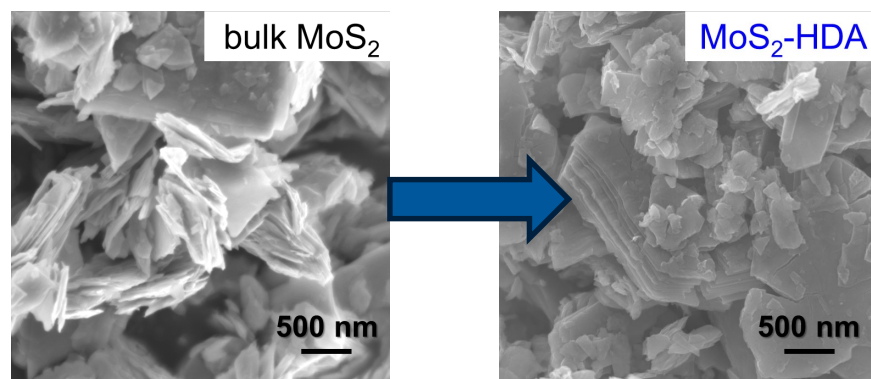
Collaboration w/ Dr. Mohsen Sotoudeh, Prof. Axel Groß, Ulm University

- AIMD simulation indicates hydrated Zn^{2+} in center of $\text{V}_2\text{O}_5\text{-nH}_2\text{O}$ interlayer, but dehydration of Zn^{2+} in $\text{V}_2\text{O}_5\text{-DOA}$

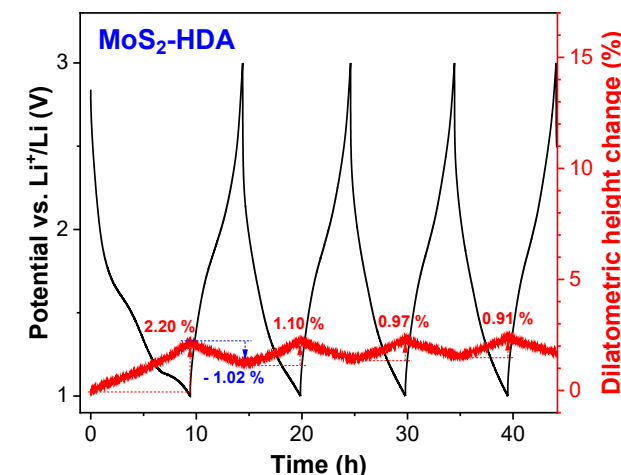
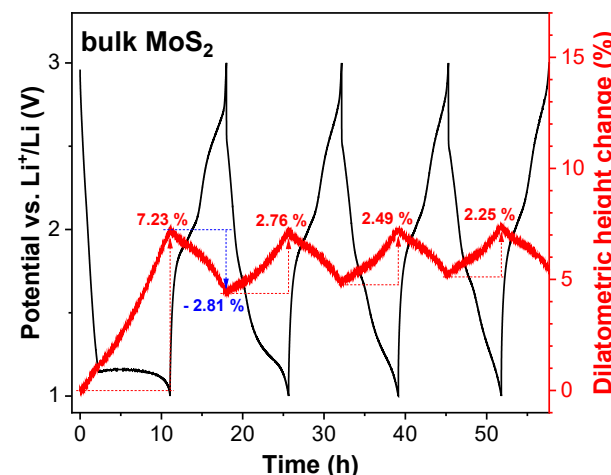
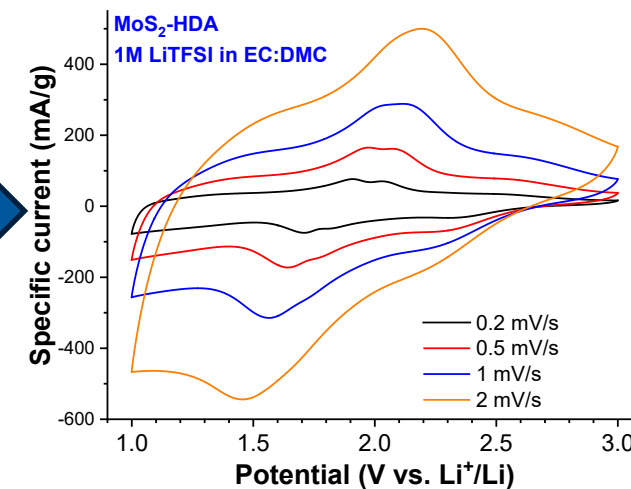
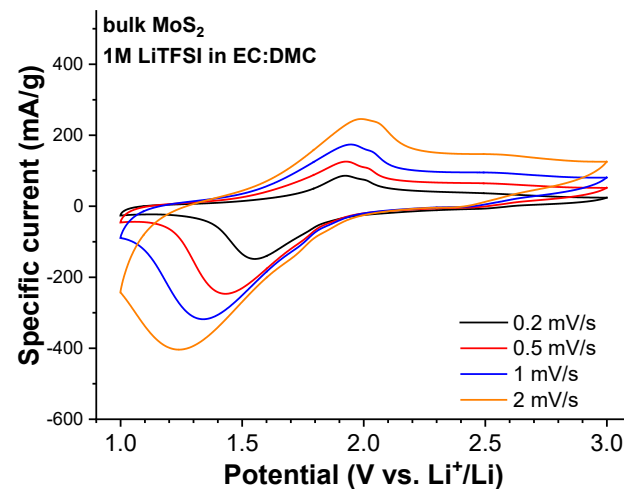


Diamine-pillaring of bulk-MoS₂

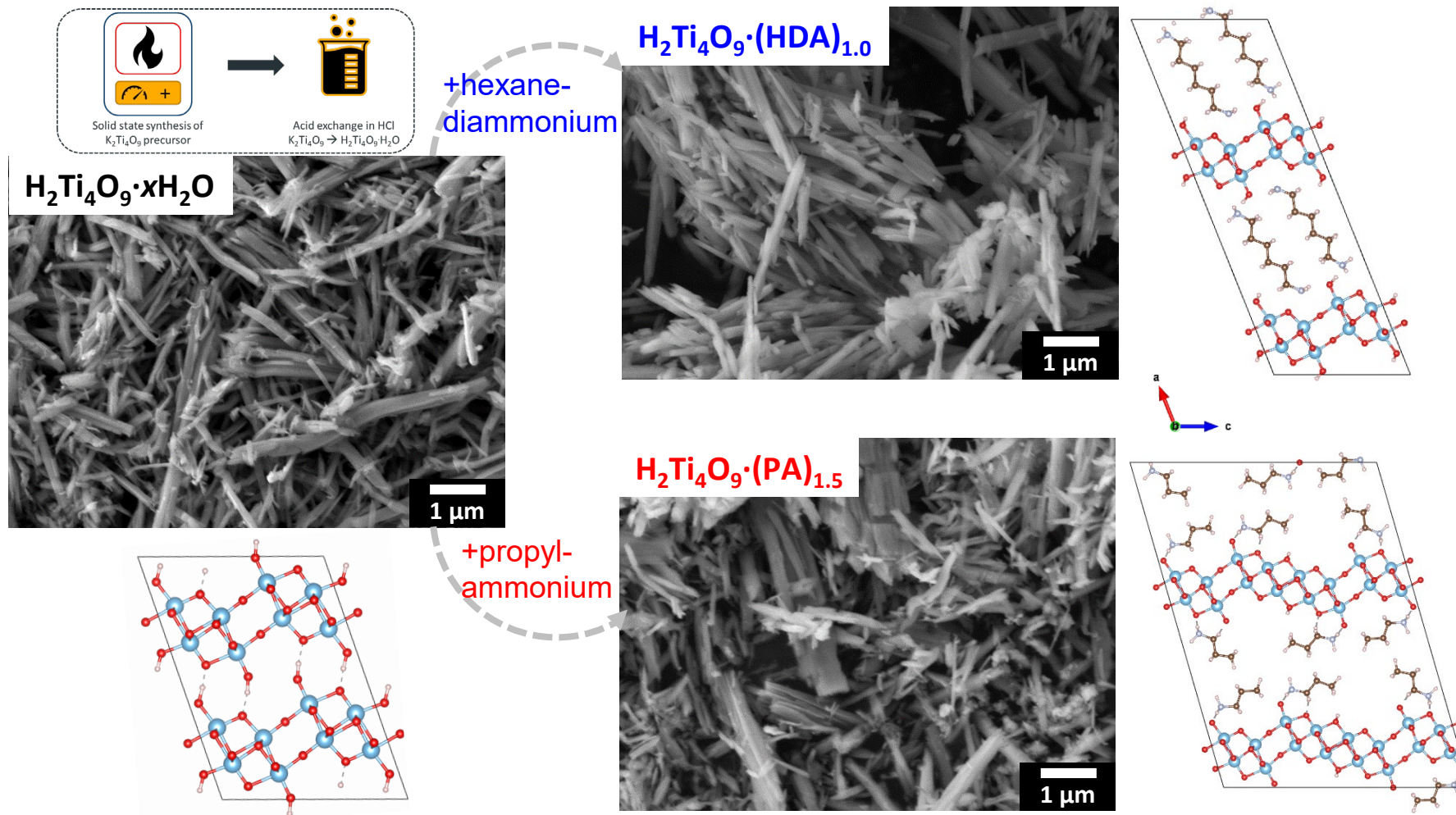
- Chemical reduction; pillaring in suspension



Transforming kinetics and chemo-mechanics of bulk host material



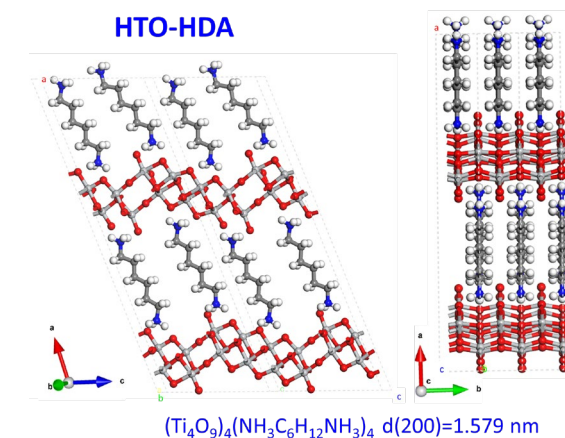
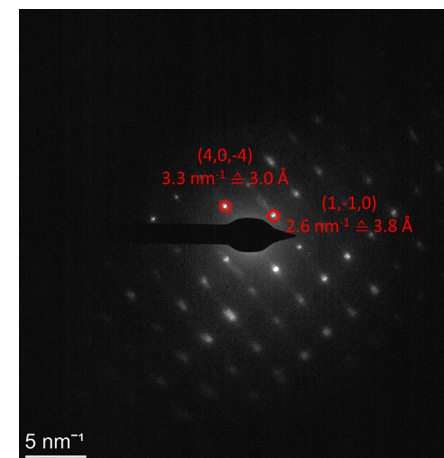
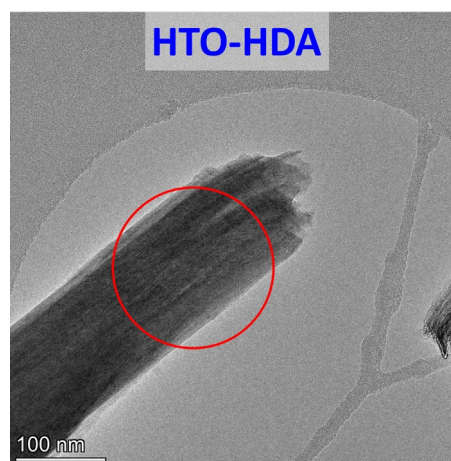
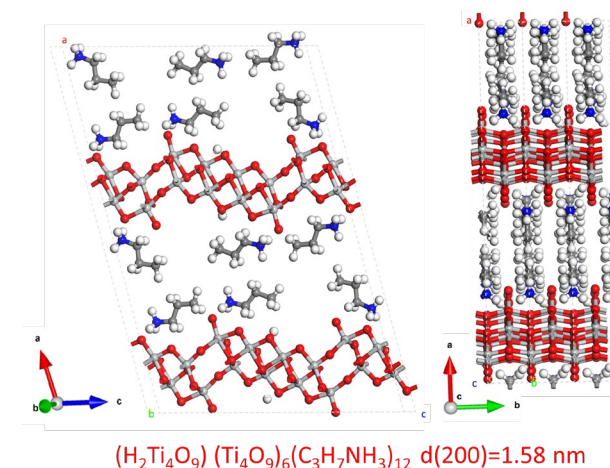
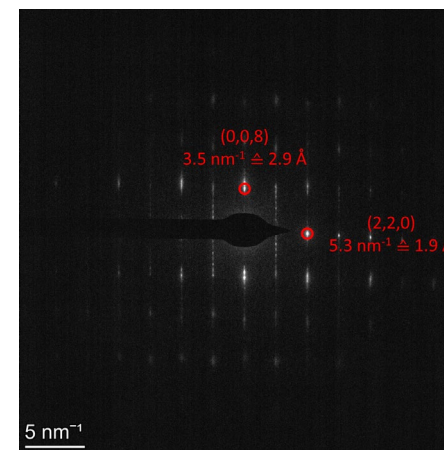
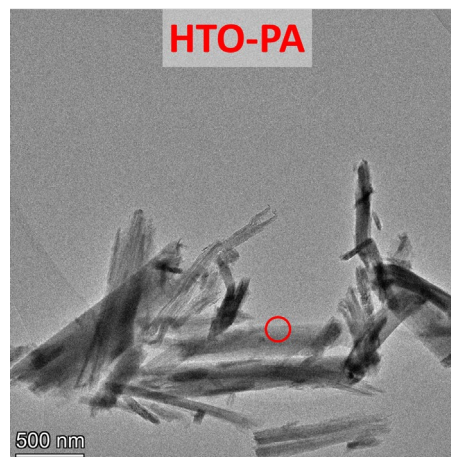
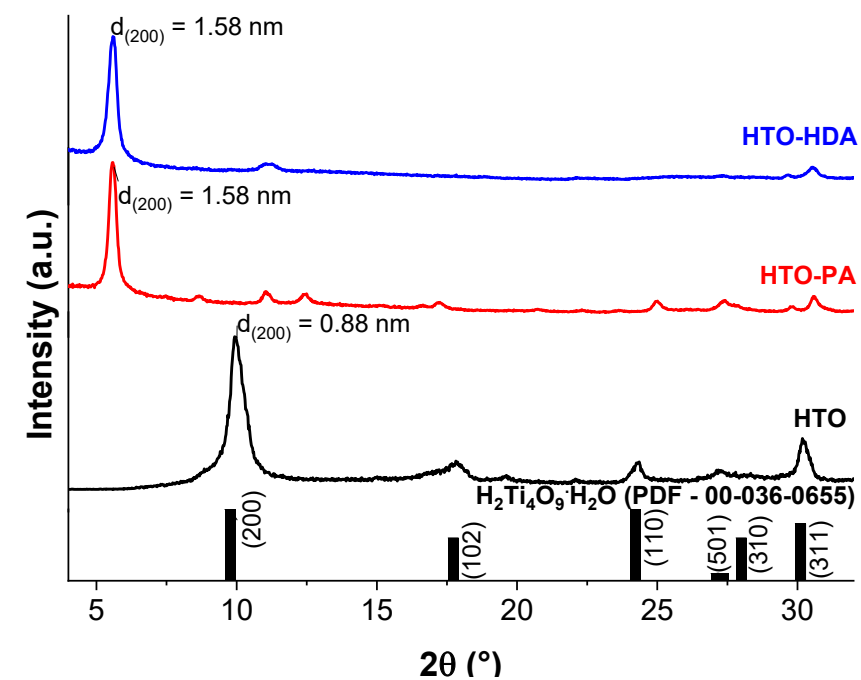
Synthesis by guest exchange: functionalization of the layered titanate system



Dr. Mennatalla Elmanzalawy

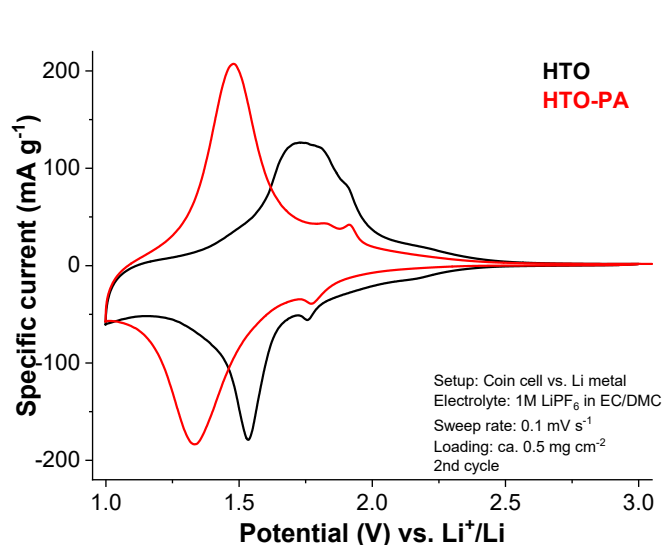
X-ray diffraction and selected area electron diffraction combined w/ DFT

w/ Haohong Song, Prof. De-en Jiang, Vanderbilt University

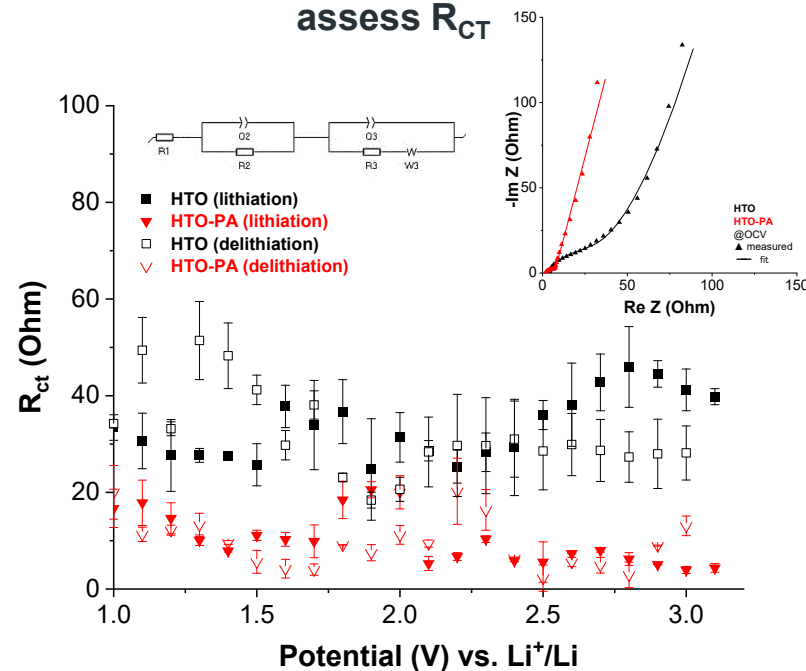


Electrochemical lithiation as a function of HTO nanoconfinement properties

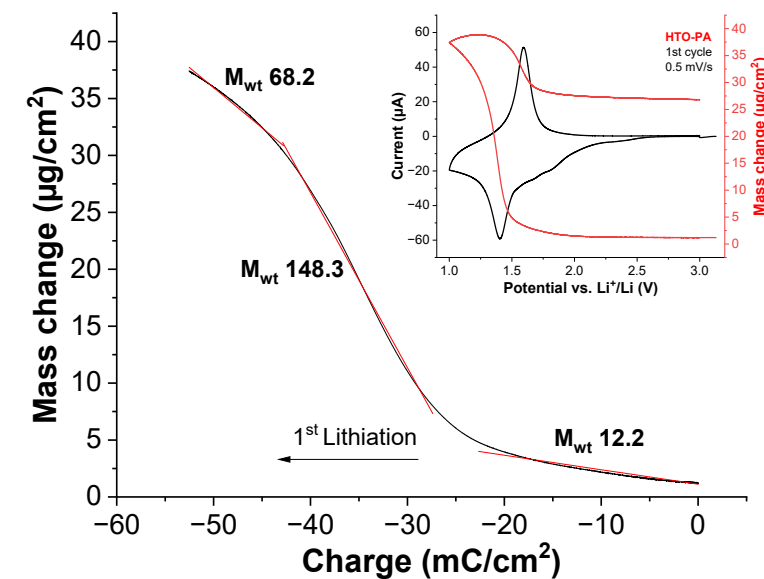
Cyclic voltammetry in organic LP30 electrolyte



Potential-dependent EIS to assess R_{CT}

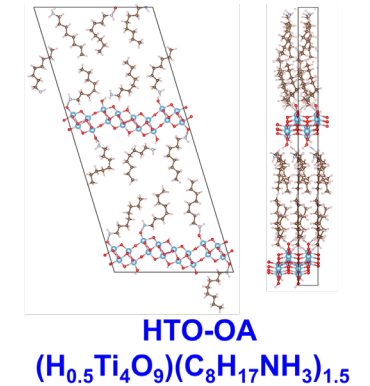
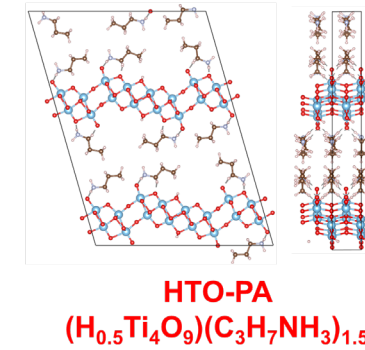
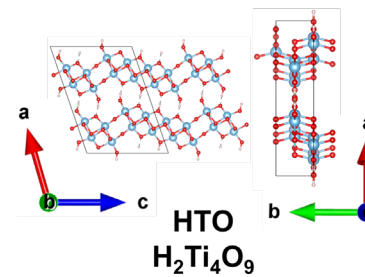
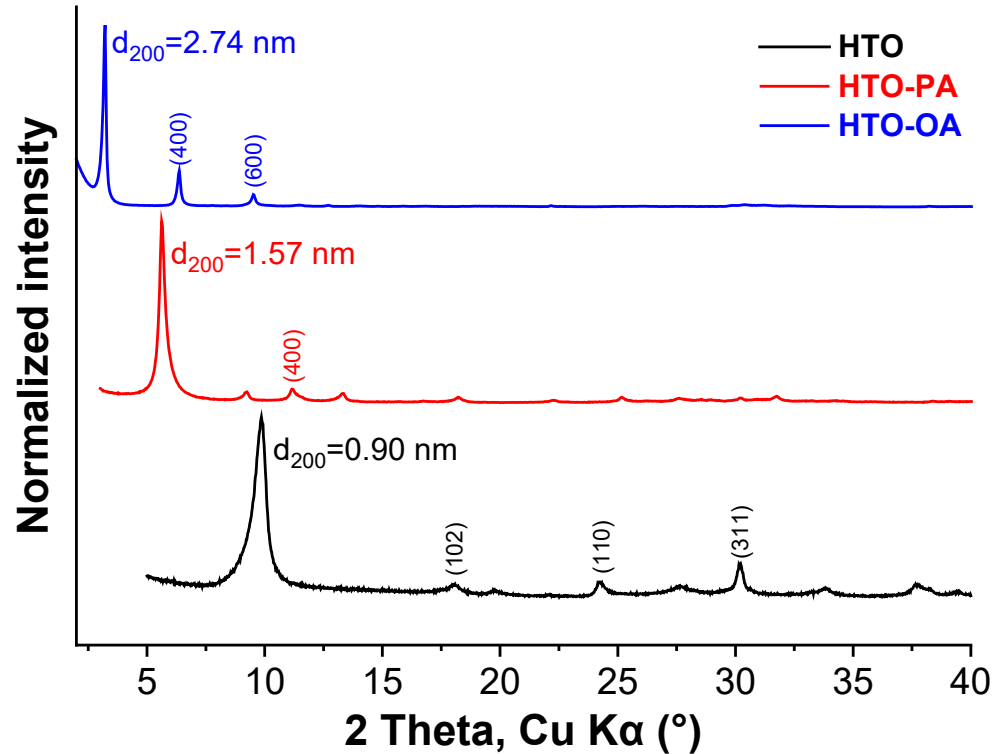


Electrochemical quartz crystal microbalance (EQCM)



- **Redox potential & maximum capacity** affected by nanoconfinement structure
 - **Solvent co-intercalation with improved kinetics** for **HTO-PA**
- Expanded interlayer yields co-intercalation with favorable Li⁺ storage performance

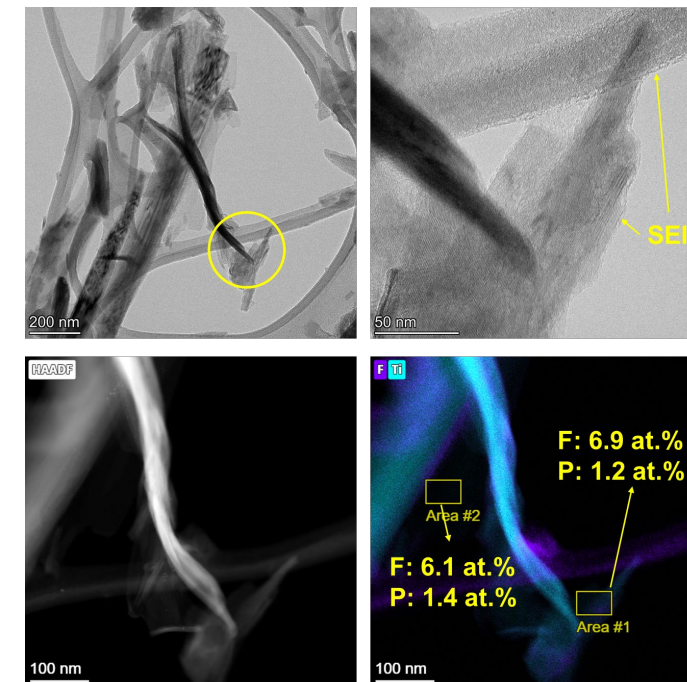
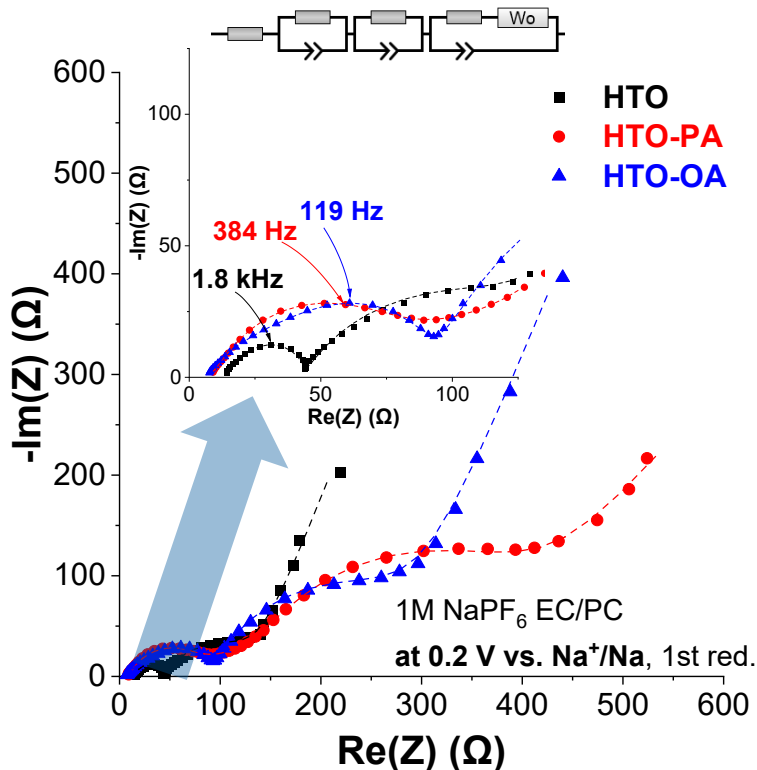
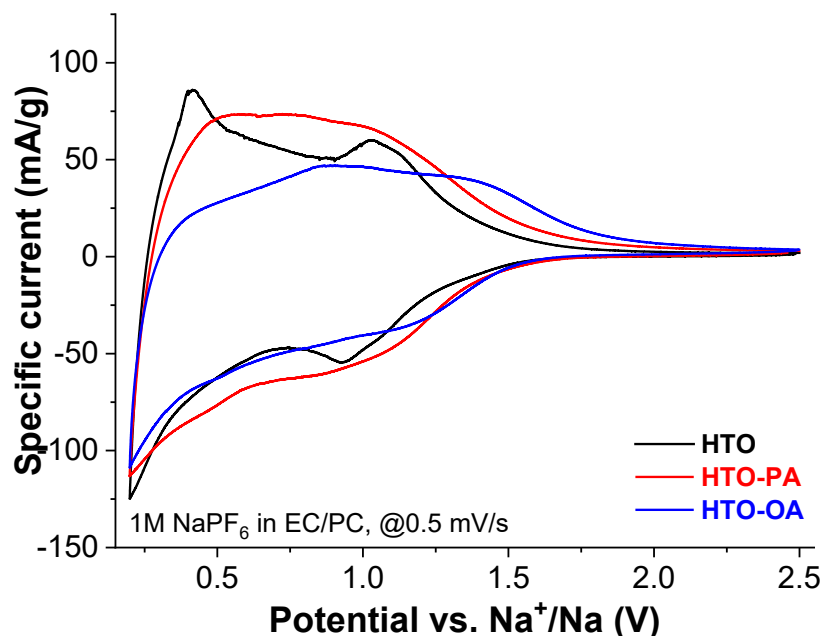
Does further expansion of HTOs benefit solvent co-intercalation?



- Expansion of HTO interlayer spacing up to >2.7 nm with octylammonium pillars
- **Suitable materials for Na^+ intercalation anodes? Alternatives for hard carbon?**

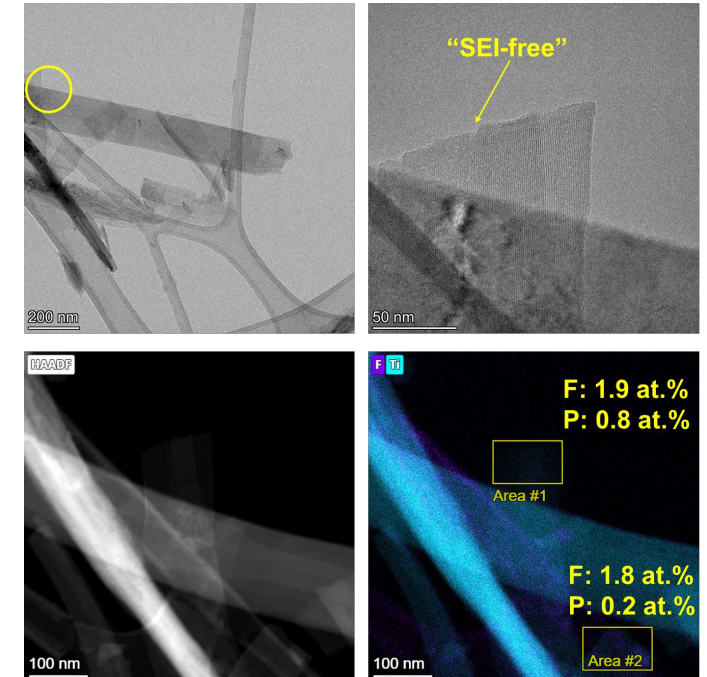
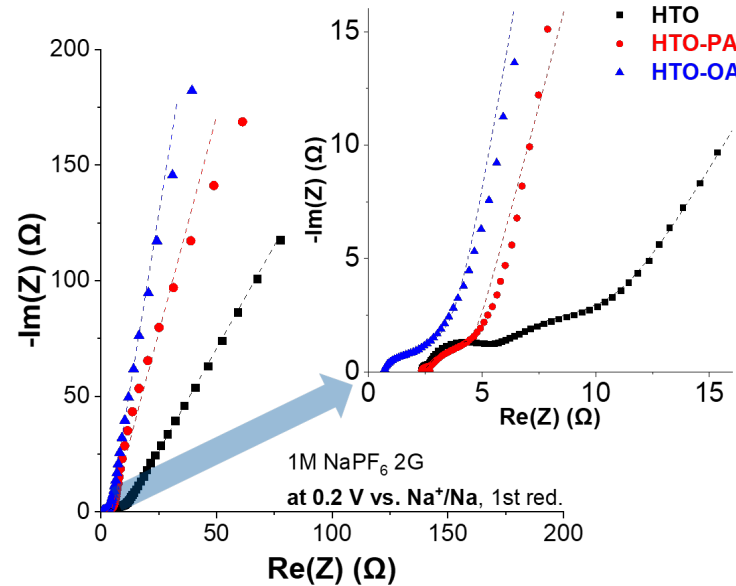
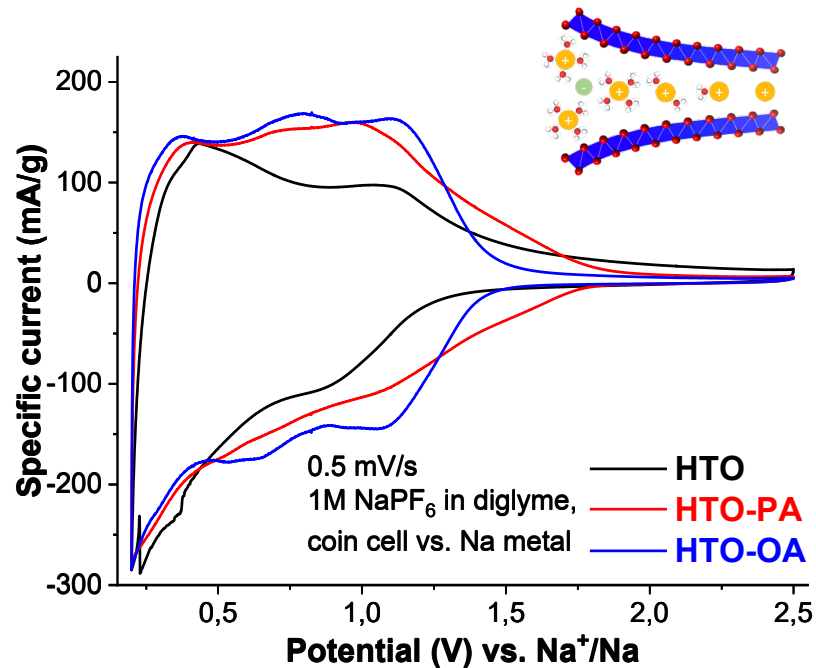
Influence of HTO interlayer spacing and electrolyte on Na⁺ intercalation properties

“Standard” 1M NaPF₆ in EC/PC



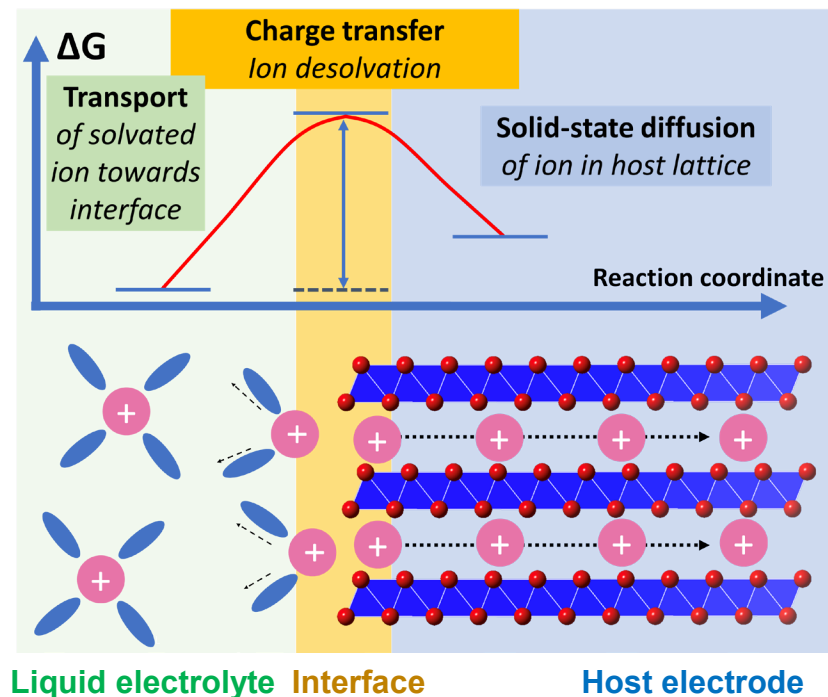
- Poor reversibility of sodiation in carbonate electrolyte
- SEI formation with inorganic components
- **Unfavorable voltage region for carbonate solvent co-intercalation**

Replacing carbonates with strongly solvating diglyme (2G)



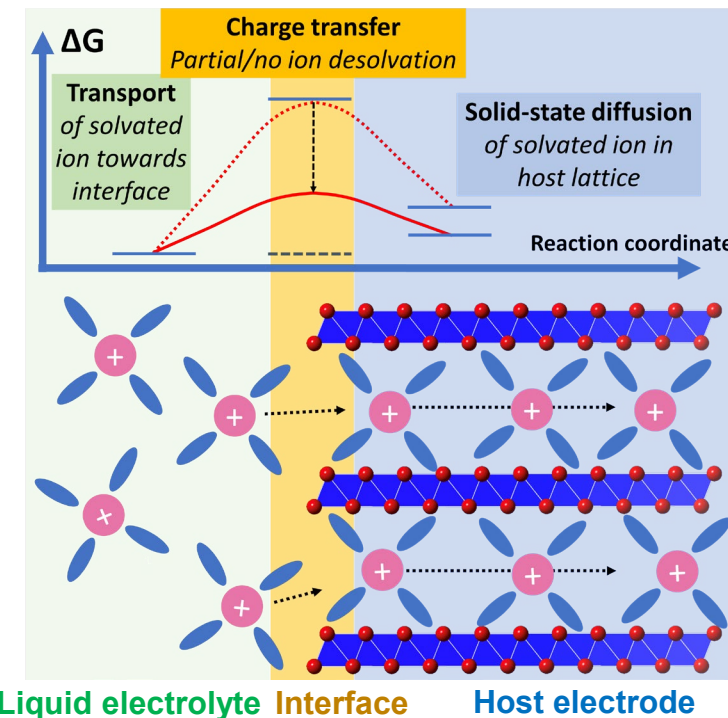
- Pseudocapacitive sodiation in diglyme electrolyte
- Increased interlayer spacing leads to amplified capacitor-like response
- Hypothesis: **SEI-free Na⁺/diglyme co-intercalation in HTO-OA** enables high power capability

Intercalation of a bare ion in layered host electrode



Intercalation of a (partially) solvated ion into layered host lattice

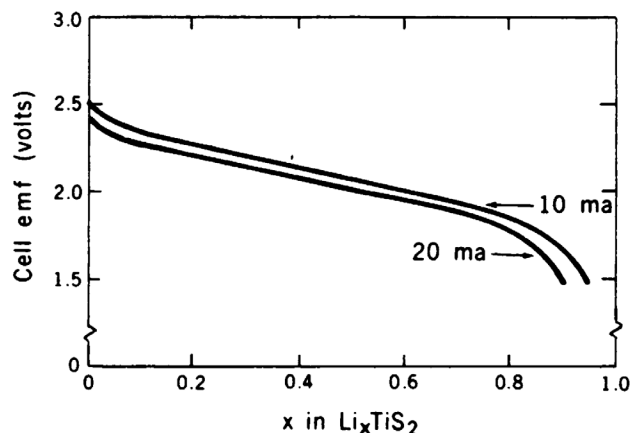
Solvent co-intercalation
reduces charge transfer
resistance



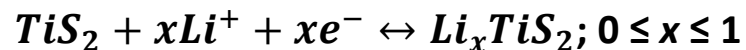
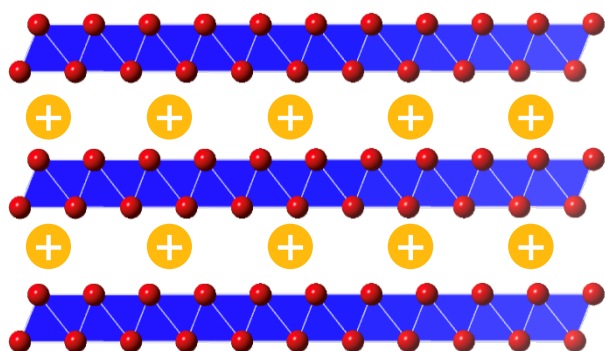
Co-intercalation is usually achieved via **electrolyte formulation**, e.g., use of strong solvents ($E_{des} > \sim 2\text{eV}$), or **changed solvation sheath chemistry** (e.g., water-in-salt electrolytes)

- Controlling ion-solvent co-intercalation feasible via electrode nanoconfinement design
- Promising for multivalent cell chemistries

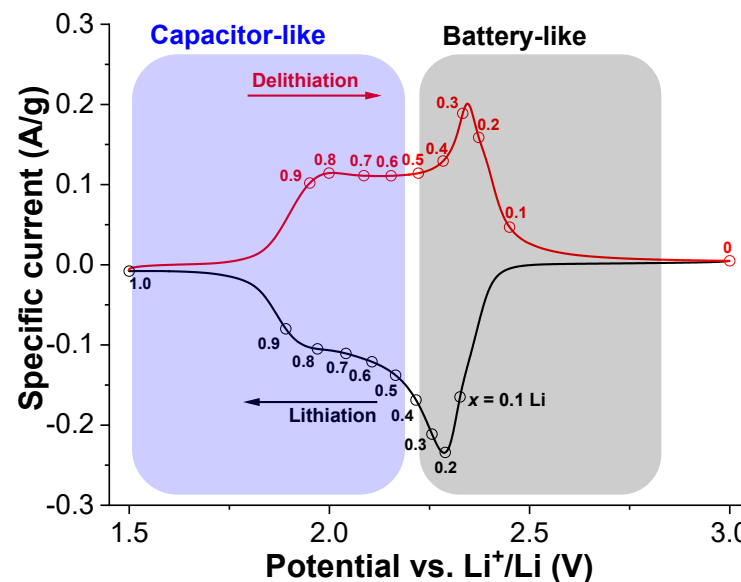
Electrochemical Li⁺ (de)intercalation in TiS₂



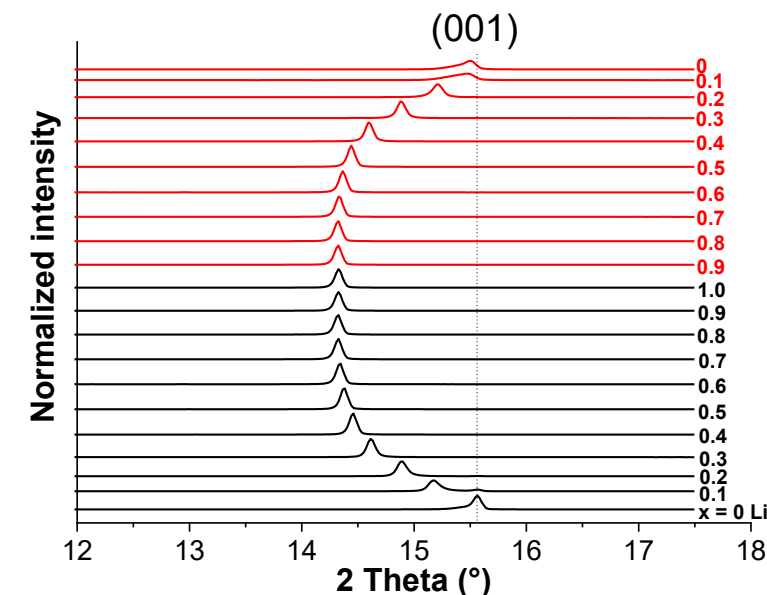
M.S. Whittingham, *Science*, **1976**, 192, 1126-1127



Our data: Cyclic voltammogram in LP30 electrolyte, 0.1 mV/s



In situ X-ray diffraction (galvanostatic intermittent titration technique)



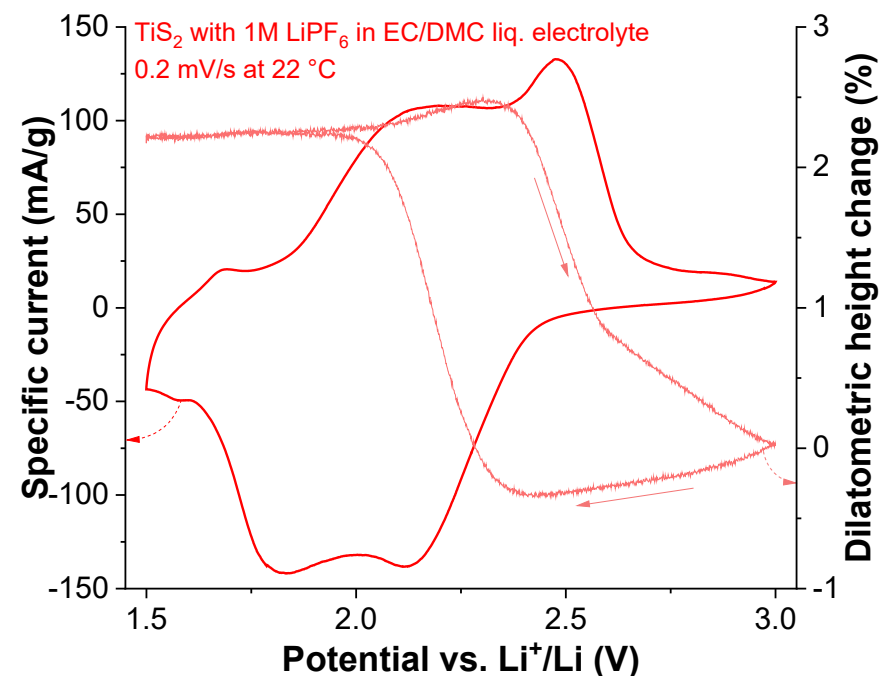
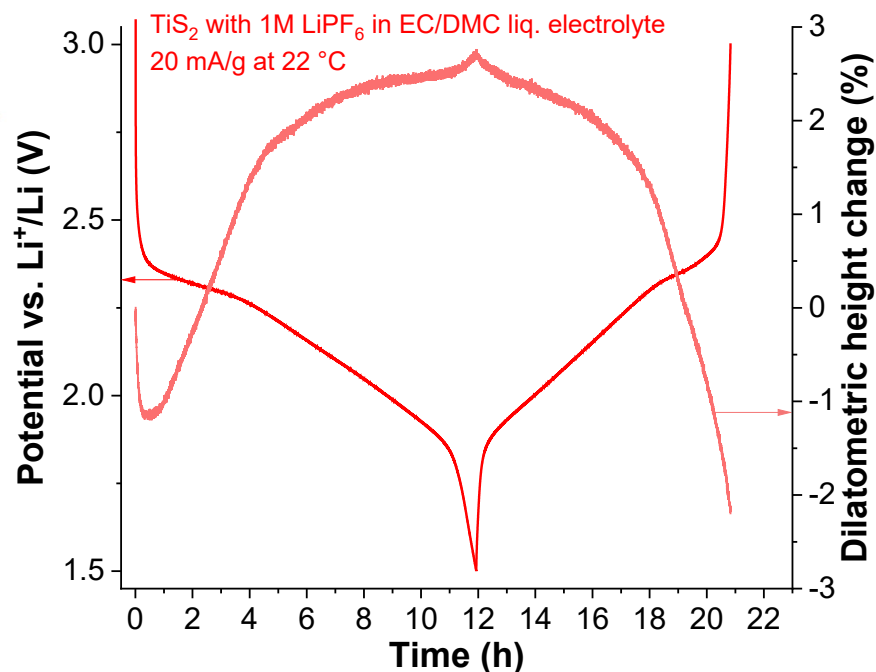
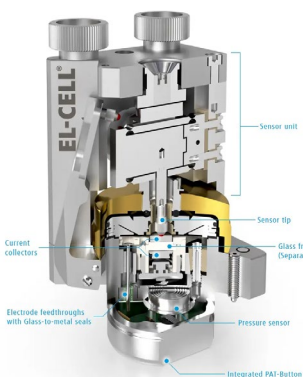
- Solid-solution intercalation with two distinct electrochemical signatures
- Voltage profile directly linked to evolution of Li_xTiS₂ d-spacing
- Apparent diffusion coefficient scales with d-spacing

➤ Echem response is coupled to chemo-mechanics in TiS₂

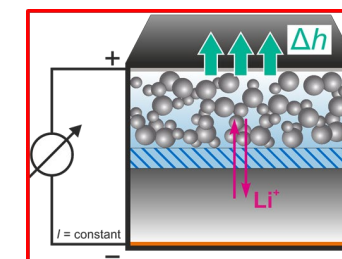


Yoga Malik

Electrochemical dilatometry in galvanostatic- and CV-mode



- Battery-like (region I) and capacitor-like (region II) also identified via operando dilatometry (macroscopically)

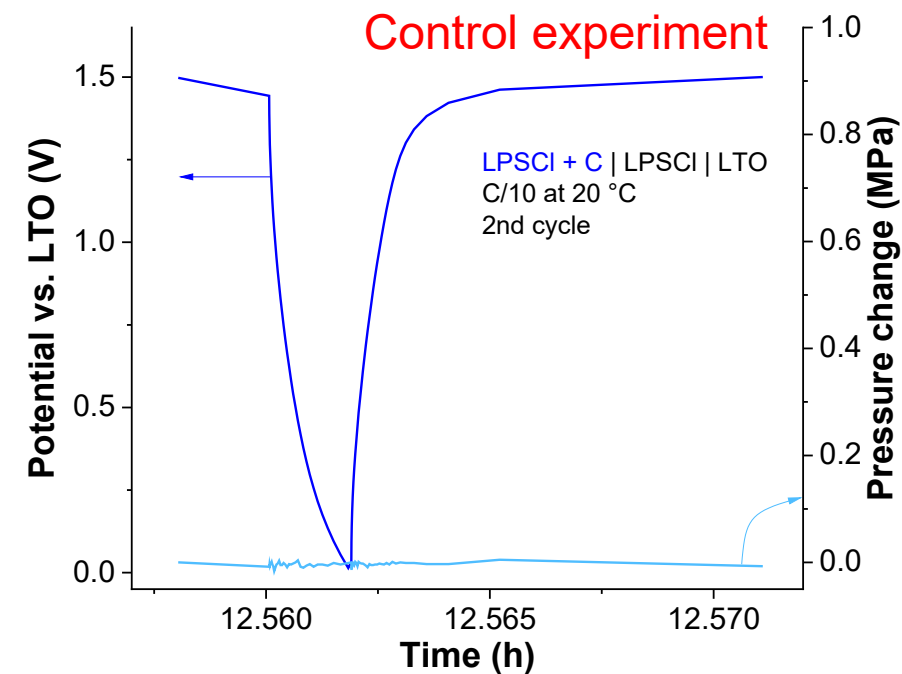
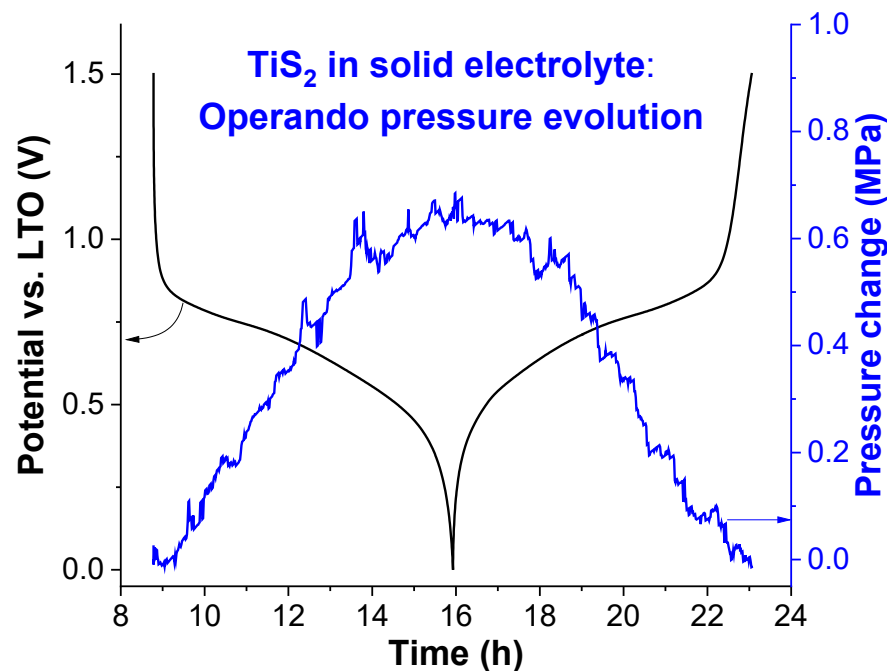
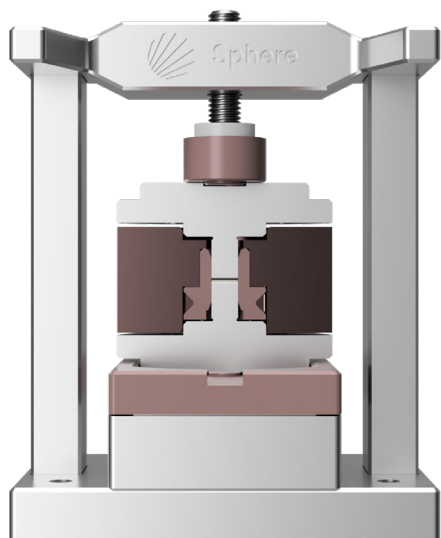


Liquid electrolyte

Operando
dilatometry

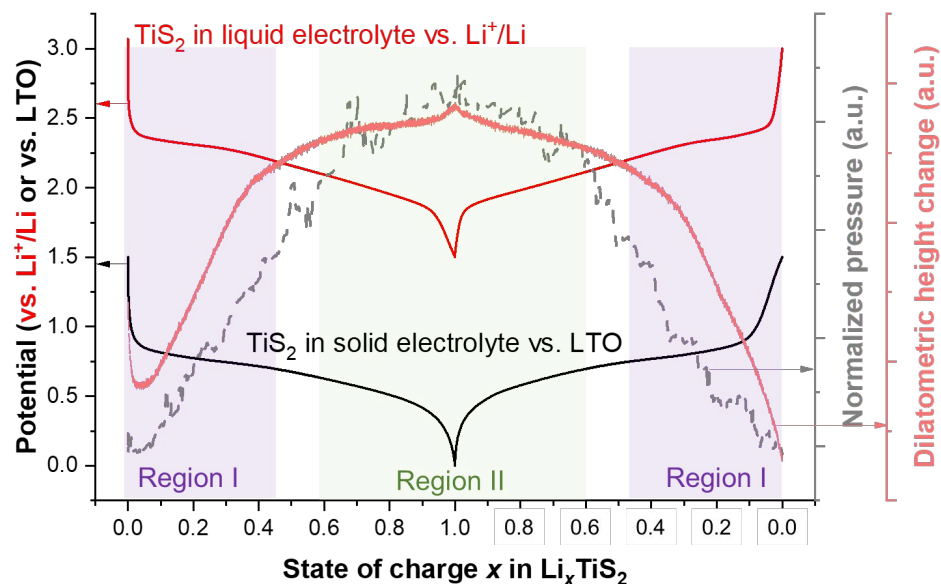
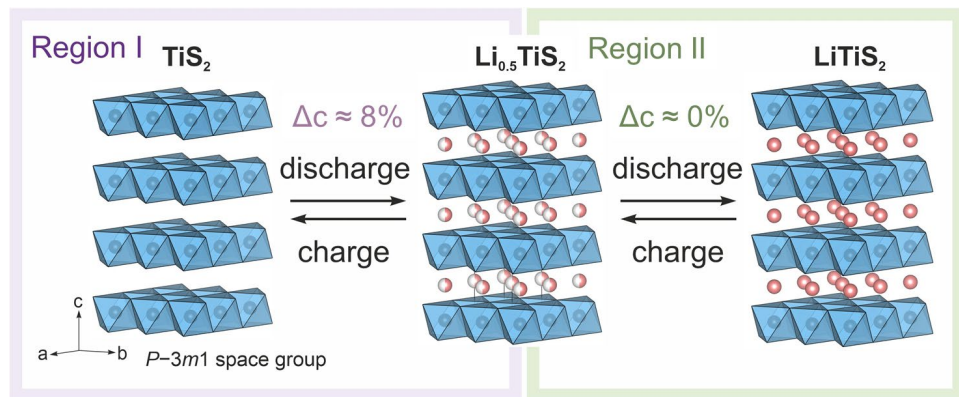
Height change Δh

What about tracking chemo-mechanics in solid-state batteries?

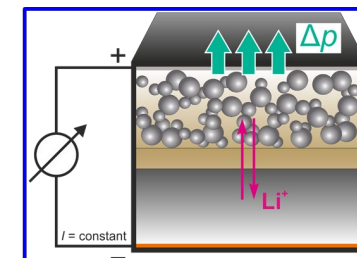


- Battery-like (region I) and capacitor-like (region II) also identified via **operando pressure evolution** (macroscopically)

Correlating chemo-mechanical coupling across liquid- and solid-state electrolytes



- **Qualitative agreement** between operando dilatometry and pressure monitoring!
- Dilatometry underestimates true crystallographic volume change by factor of ca. 2.5
- Operando pressure measurement underestimates by ca. 2 orders of magnitude!!



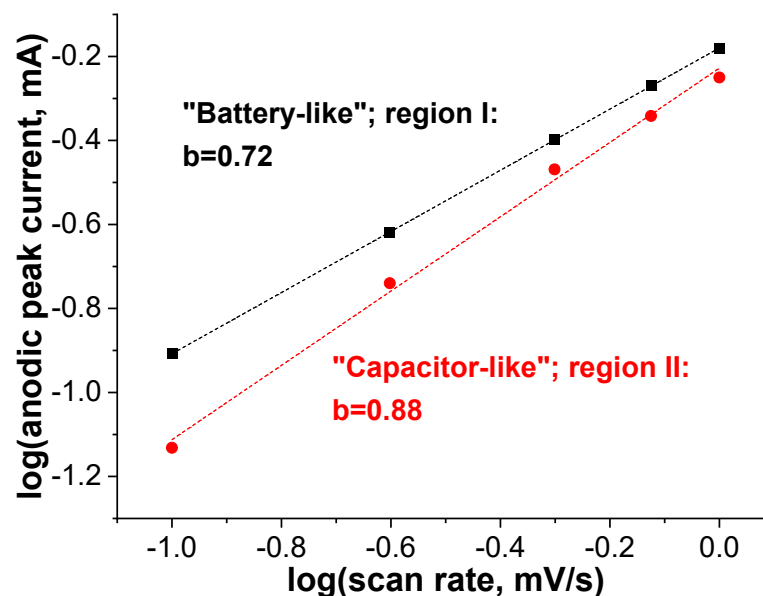
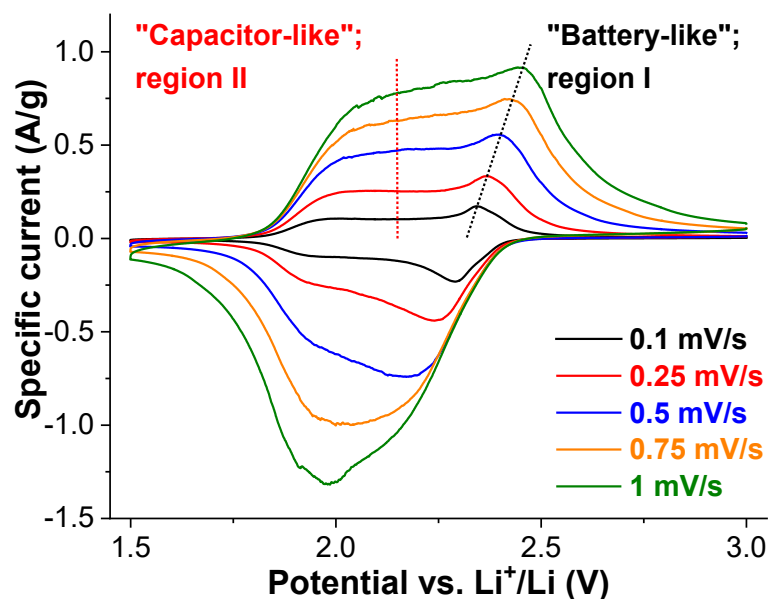
Solid electrolyte

Operando pressure
measurement

Pressure change Δp

“b” value analysis: Sweep rate-dependent redox peak current.

$$i(V) = a\nu^b$$



- The method analyses **kinetics** of charge storage process
- No information on charge storage mechanism (thermodynamic property)

Theoretical background

- When is b=1?

$$i = C_{DL}A\nu$$

Double-layer capacitance

$$i = \frac{nF^2}{4RT}A\Gamma^*\nu$$

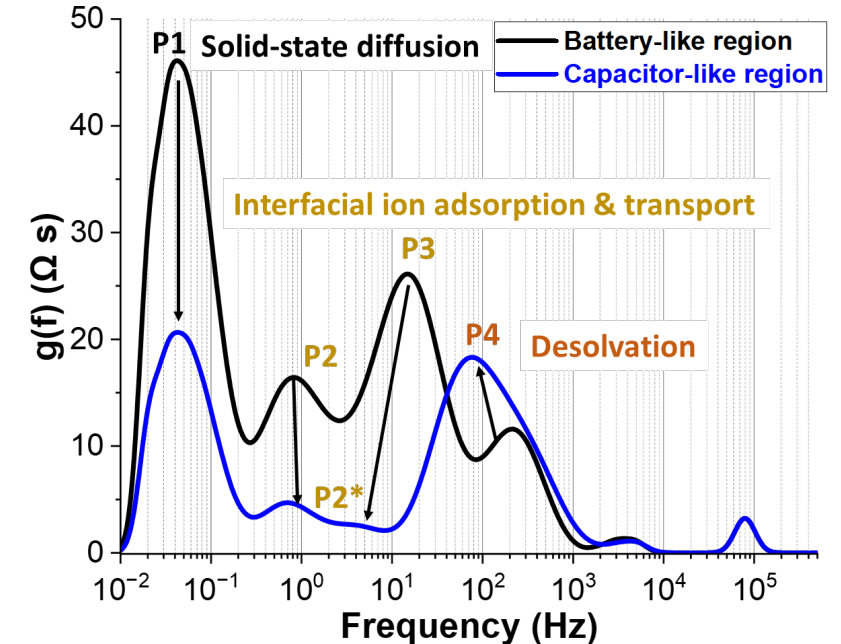
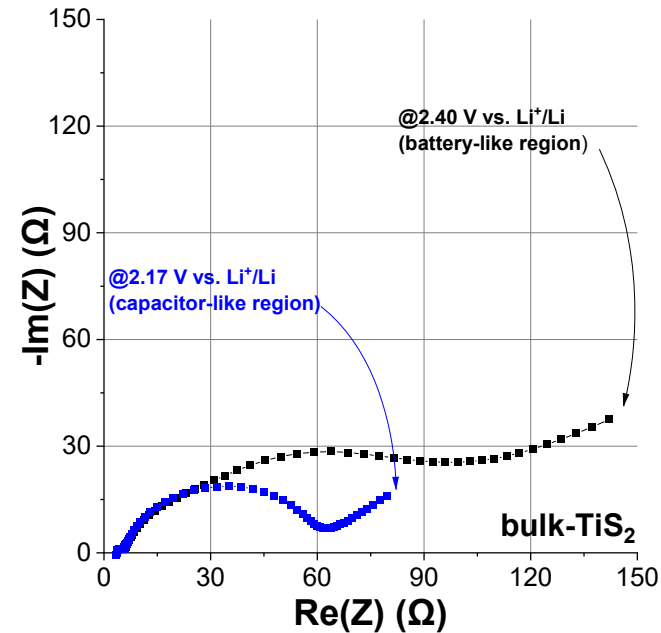
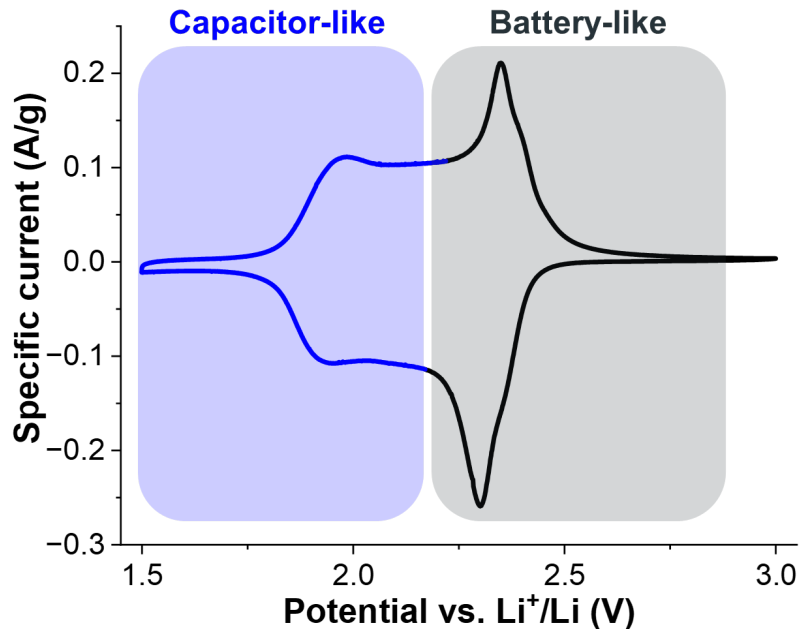
Surface confined redox
("modified thin-film electrodes")

- When is b=0.5?

$$i = 0.4958n \cdot FAC^* \cdot D^{1/2} \left(\frac{\alpha n F}{RT} \right)^{1/2} \nu^{1/2}$$

Semi-infinite diffusion control
(Randles–Ševčík Equation)

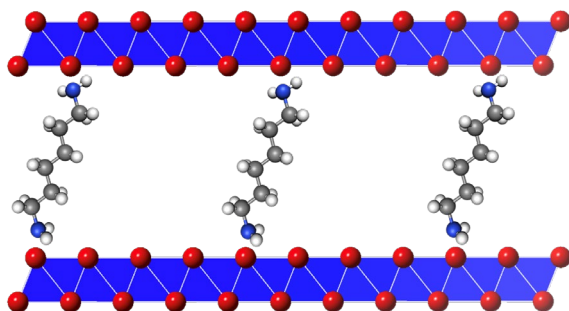
Identify and analyze various steps of the intercalation process



- DRT uses a distribution of RC-elements that represent relaxation processes
- DRT is assumption-free, i.e., no equivalent circuit necessary
- Clear visualization and separation of individual steps
- Potential-dependent measurements („in situ“ technique)

Nanoconfinement Engineering Approach

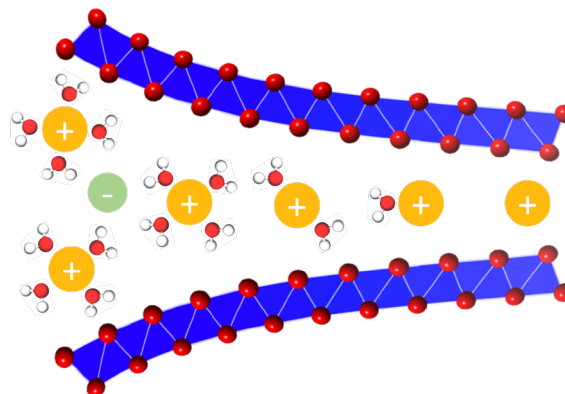
Nanoconfinement-Materials



Targeted synthesis...

- Unique library of layered model materials
- Universal concept, feasible with abundant elements

Fundamental insights



Mechanistic understanding...

- Reactivity in confined spaces
- Understand and tailor material-environment interaction

Sustainable energy storage and beyond



Sustainable applications...

- High power, safe batteries
- Sustainable, new cell chemistries
- (Electro-)catalysts, CO₂/H₂ capture/storage, etc.

Impact: fundamental understanding of (electro)chemistry in nanoconfinement & advance sustainable functional materials for energy/environmental applications

Thank you for your attention!



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