@adelhelm_group
philipp.adelhelm

POLiS
Post Lithium Storage
Cluster of Excellence

Electrode Materials for Na-ion batteries

Philipp Adelhelm and team

Humboldt-Universität zu Berlin
Helmholtz-Zentrum Berlin

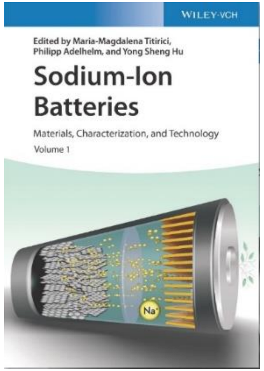
Photograph: Campus Mitte, Faculty of law

HZB Helmholtz Zentrum Berlin

POLiS Seminar Series, July 24 2024 (online)

Group activities

- Studies on Na-ion batteries since 2010
- Currently about 30 group members, most of them working on „Na-ion“ (liquid & SSB)
- Junior BMBF research group: Gustav Graeber
- Inorganic materials (oxides, sulfur & sulfides, carbons, metals, Prussian Blue/White)
- Operando methods


WILEY-VCH

Edited by Maria-Magdalena Titirici, Philipp Adelhelm, and Yong Sheng Hu

Sodium-Ion Batteries

Materials, Characterization, and Technology

Volume 1

Technology Park Berlin- Adlershof

HUMBOLDT-UNIVERSITÄT ZU BERLIN

HU Berlin, Chemistry

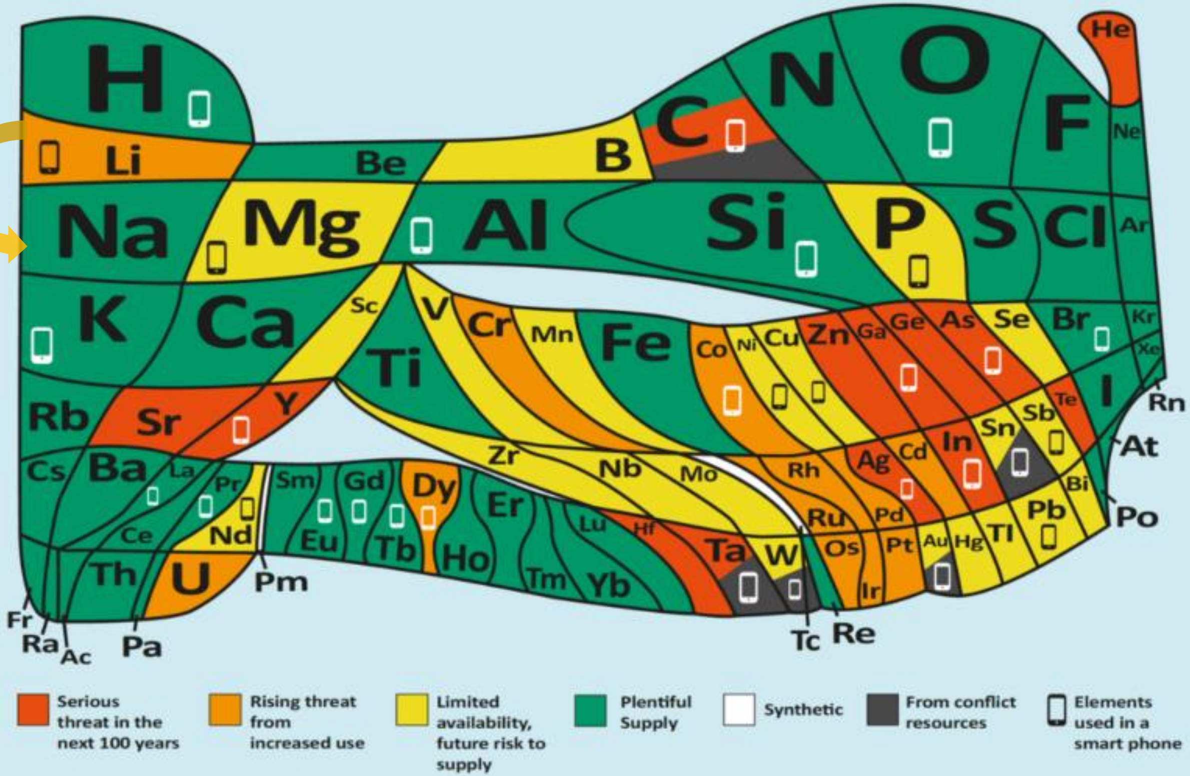
BESSY II Synchrotron / Helmholtz-Zentrum Berlin

HZB Helmholtz Zentrum Berlin

Ion size
+ 30%
good or bad?

The 90 natural elements that make up everything

How much is there? Is that enough? Is it sustainable?



Inspired by WF Sheehan's 'A Periodic Table with Emphasis' published in Chemistry, 1976, 49, 17-18

Read Support Notes and play the video game **http://bit.ly/euchems-pt**

Edition 3 (2023)

EuChemS
European Chemical Society

Today`s menu

Layered materials:

- Layered oxides and sulfides
- Graphite

Metals

- Na and Sn

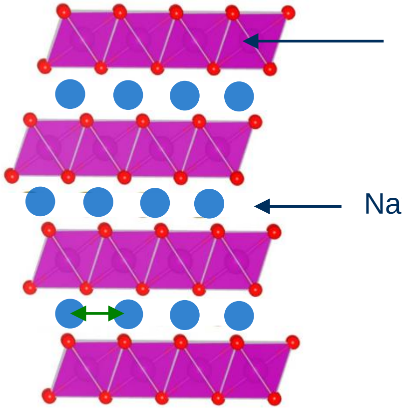
Conversion materials

- CuS – a unique electrode materials studied with tomography

Layered Materials

Strategies for tuning the properties of layered materials in Na-ion (and Li-ion) batteries

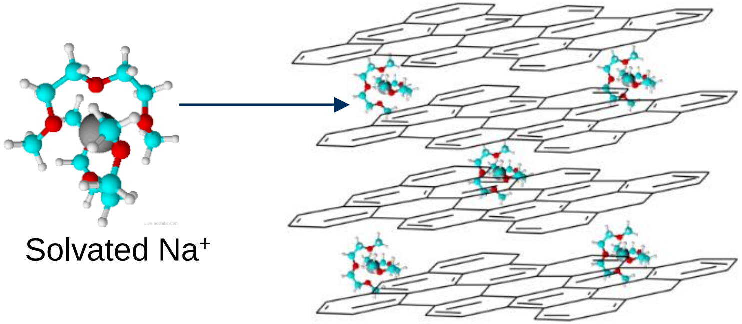
Tuning properties through adjusting transition metals and dopants



Type and ratios of
TM (Mn, Fe, Ni,….)
Dopants (Ti, Mg, Li,….

Na^+

Tuning properties through solvent co-intercalation



Solvated Na^+

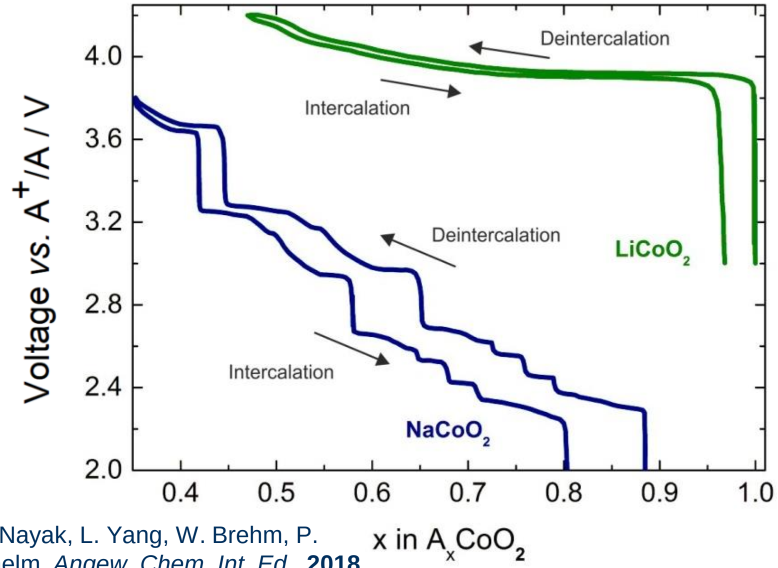
1) $Na_{0.67}[Ni_{0.33}Mn_{0.67}]O_2$ doped with Mg, Sc

2) New model for solvent co-intercalation

3) Apply solvent co-intercalation to cathode materials

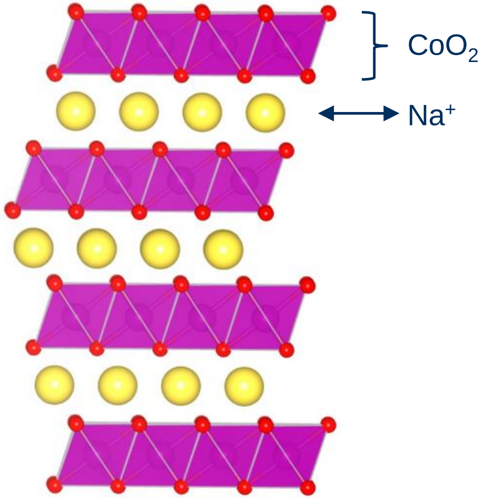
Cathode materials – Layered materials

„$LiCoO_2$ vs. $NaCoO_2$“



P. K. Nayak, L. Yang, W. Brehm, P. Adelhelm, *Angew. Chem. Int. Ed.*, **2018**

$$NaCoO_2 \underset{\text{discharging (intercalation)}}{\overset{\text{charging (deintercalation)}}{\rightleftarrows}} Na_xCoO_2 + (1-x)\cdot e^- + (1-x)\cdot Na^+$$



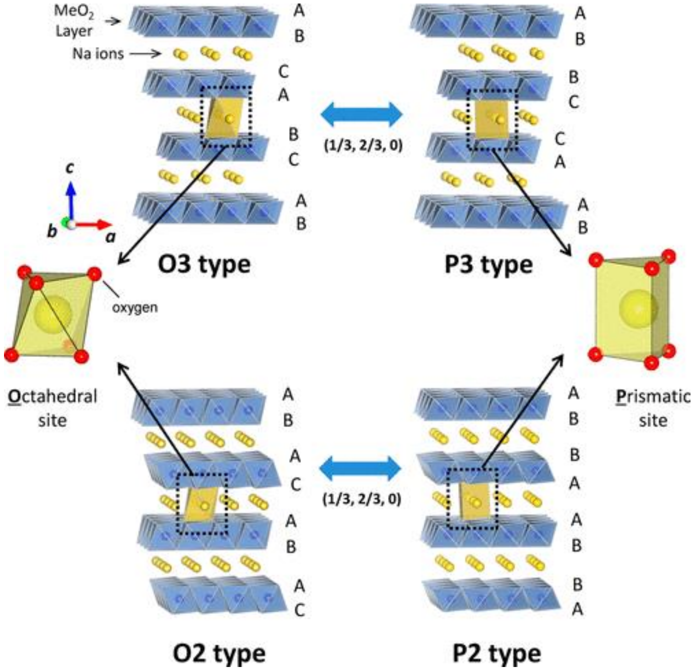
- Removing Na from layered oxides strongly depends on the SOC while the effect is much smaller for Li.
- Obviously the same materials behave quite different for Li and Na

→ **Why more complexity in case of sodium? Why is there a more diverse chemistry?**

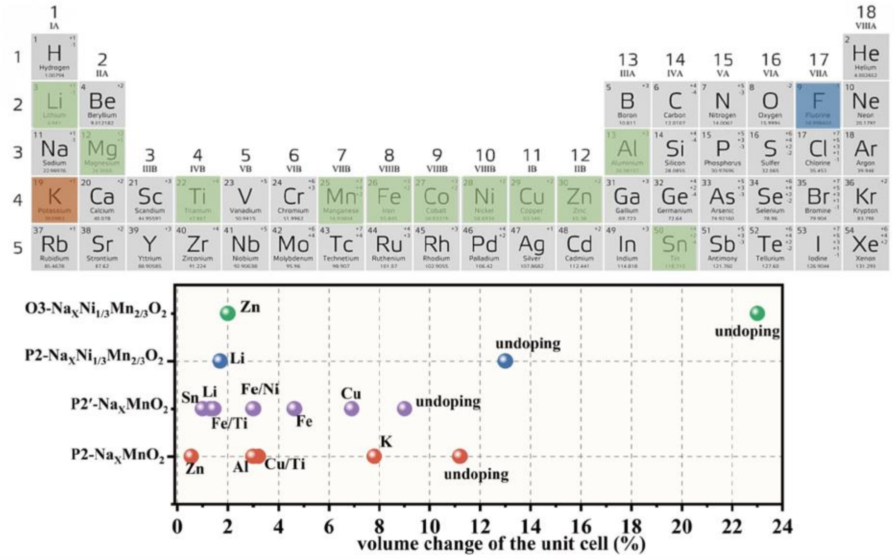
Layered oxides and tuning their properties

Na layered oxides with **one TM**, i.e. $NaTMO_2$

Na layered oxides with **several transition metals** $Na[TM_1TM_2TM_3,\ldots]O_2$ and **other substitutional elements** like Li^+, Mg^{2+},…

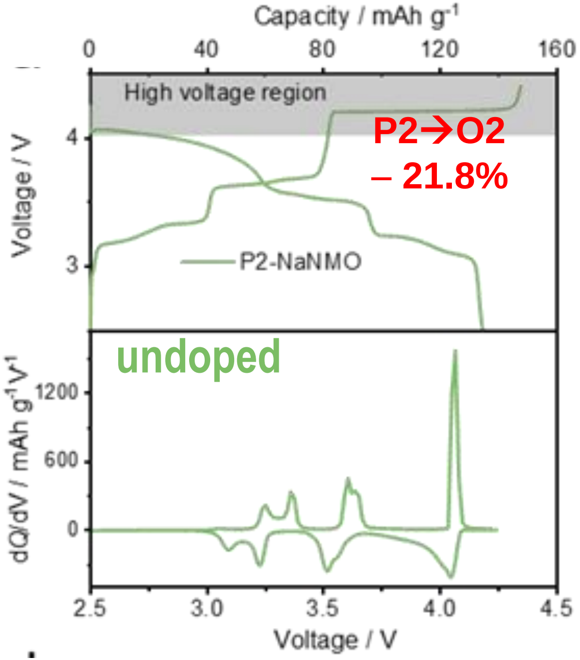


Yabuuchi/Komaba (2014) doi:10.1021/cr500192f



Jiang (2023) doi:10.1007/s40843-023-2617-5

Example: P2-$\mathbf{Na_{0.67}[Ni_{0.33}Mn_{0.67}]O_2}$ **doped with Mg or Sc**



Isovalent substitution of Ni^{2+} by Mg^{2+}

(similar radii, similar size)

Aliovalent substitution of Ni^{2+} by Sc^{3+}

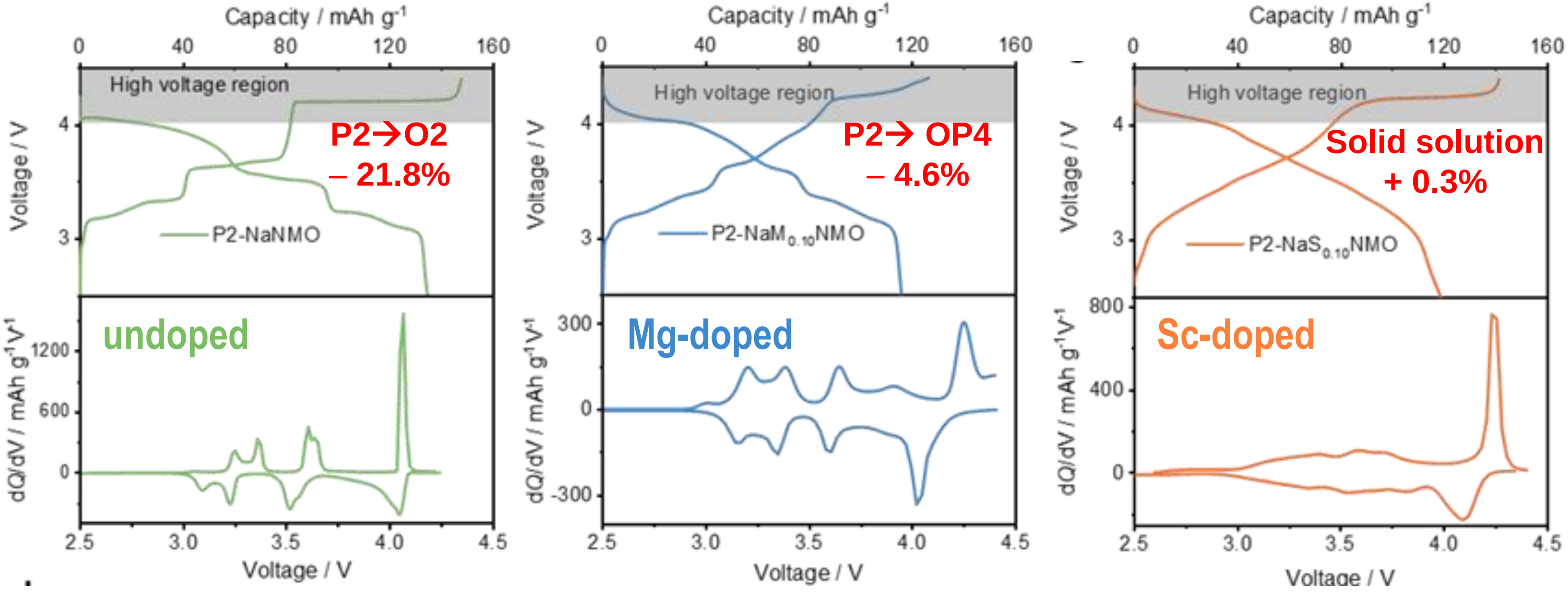
(similar radii, but different charges
→ requires charge compensation)

Capacity ↓ **Stability** ↑ **O-redox** ?

High voltage region: Phase transition causes strong decrease in interlayer spacing

Y. Li et al. / Competing mechanisms determine oxygen redox in doped Ni-Mn based layered oxides for Na-ion batteries, **2024 doi:** 10.1002/adma.202309842

Example: P2-$Na_{0.67}[Ni_{0.33}Mn_{0.67}]O_2$ doped with Mg or Sc



P2→O2
– 21.8%

P2→ OP4
– 4.6%

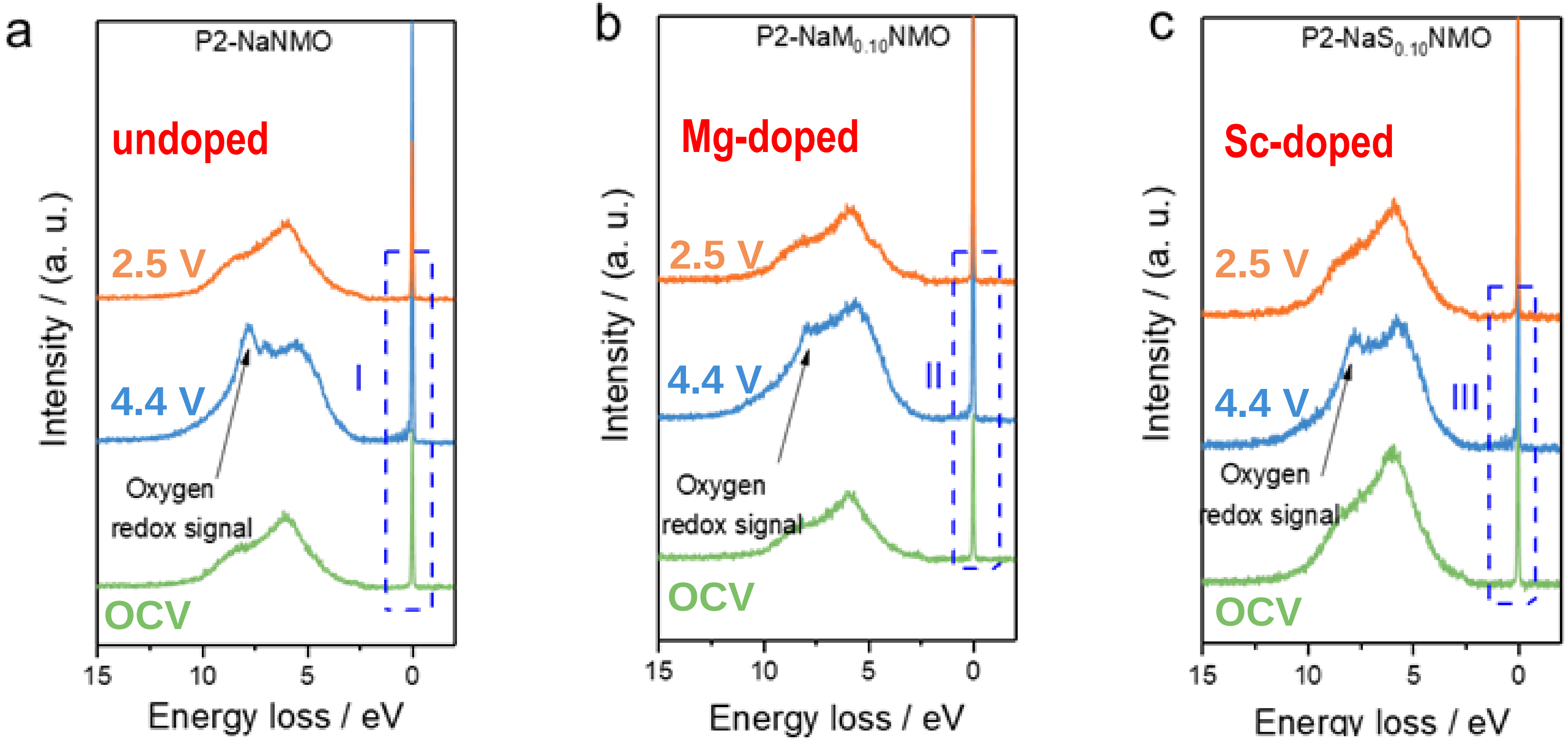
Solid solution
+ 0.3%

Sc doping: Most effective for smoothening the voltage profile and minimizing lattice changes.

Mg doping: Trunkates the high voltage plateau (less O redox?)

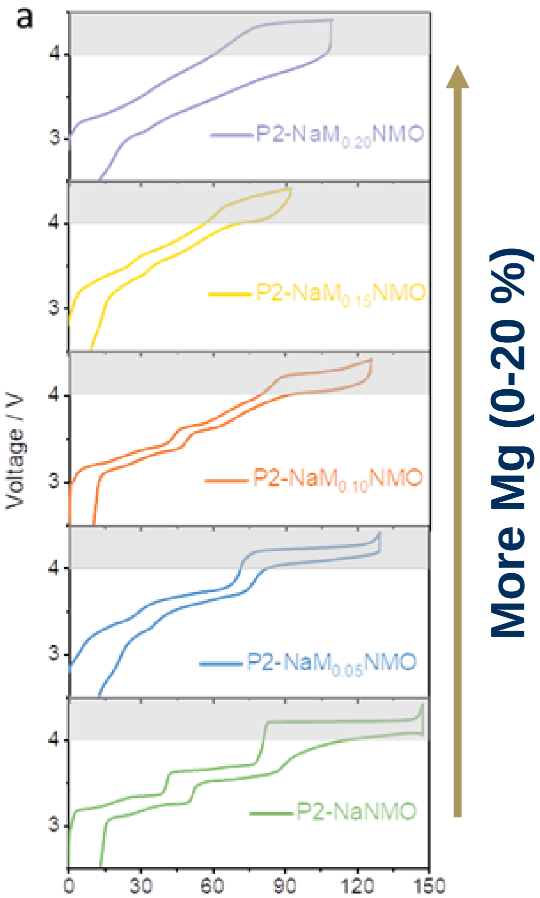
Y. Li et al. / Competing mechanisms determine oxygen redox in doped Ni-Mn based layered oxides for Na-ion batteries, **2024 doi:** 10.1002/adma.202309842

Example: P2-**$Na_{0.67}[Ni_{0.33}Mn_{0.67}]O_2$ doped with Mg or Sc**

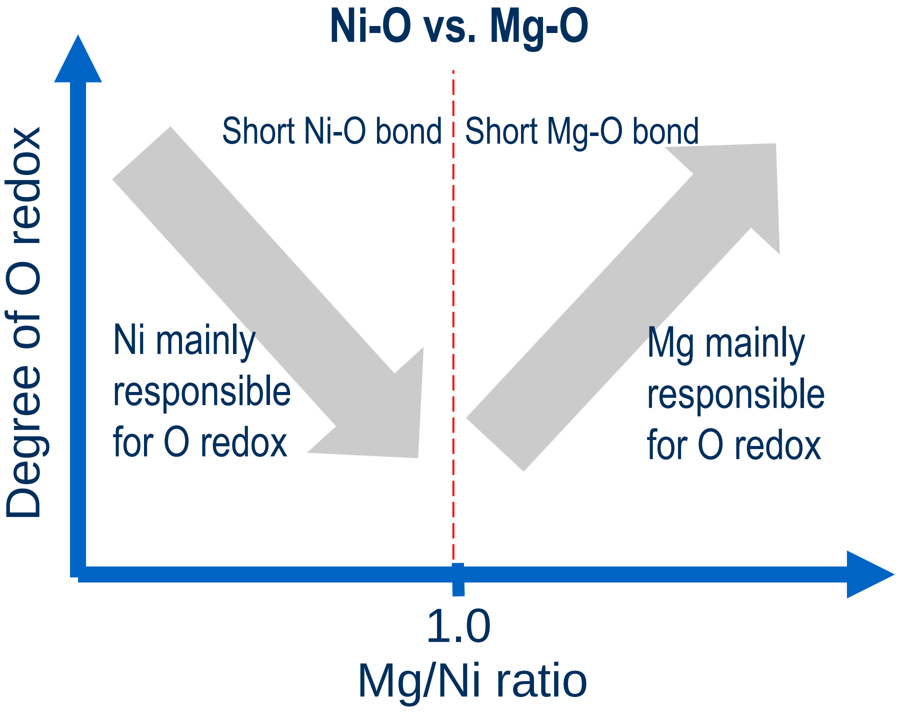


Mg doping: Most effective in mitigating O-redox (bit surprising at first!)

Example: P2-$Na_{0.67}[Ni_{0.33}Mn_{0.67}]O_2$ doped with Mg or Sc



Mg doped P2-$Na_{0.67}[Ni_{0.33}Mn_{0.67}]O_2$



Ni-O vs. Mg-O

Short Ni-O bond

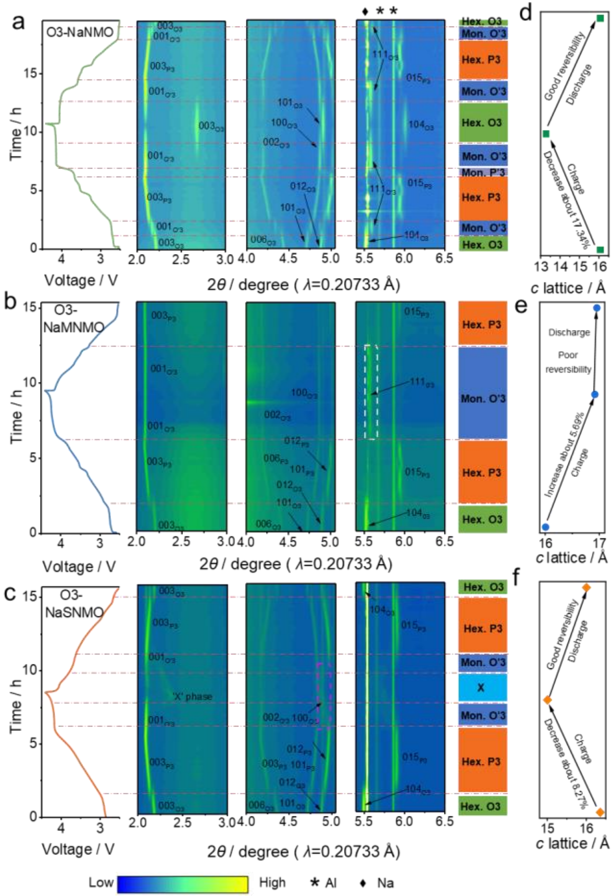
Short Mg-O bond

Ni mainly responsible for O redox

Mg mainly responsible for O redox

Y. Li et al. / Competing mechanisms determine oxygen redox in doped Ni-Mn based layered oxides for Na-ion batteries, **2024 doi:** 10.1002/adma.202309842

Example: O3-$\mathbf{Na_{1.0}[Ni_{0.50}Mn_{0.50}]O_2}$ **doped with Mg or Sc**



O3-$\mathbf{Na_{1.0}[Ni_{0.50}Mn_{0.50}]O_2}$
Many phase transitions, large shrinkage

O3-$\mathbf{Na_{1.0}[Mg_{0.1}Ni_{0.4}Mn_{0.5}]O_2}$
Less phase transitions, less shrinkage,
additional redox center, better cycle life

O3-$\mathbf{Na_{1.0}[Sc_{0.1}Ni_{0.4}Mn_{0.5}]O_2}$
Less phase transitions, less shrinkage,
no additional redox center, better cycle life

Y. Li et al. / 'Oxygen bound to Mg' as high voltage redox center causes sloping of the potential profile in Mg-doped layered oxides for Na-ion batteries, **2024 submitted**

Stability of electrolytes and electrodes: Gas analysis (DEMS)

Gas analysis

Determination of gas release during charging/ discharging of a battery (e.g. When does overcharging takes place?). Can be quantitative.

Our project

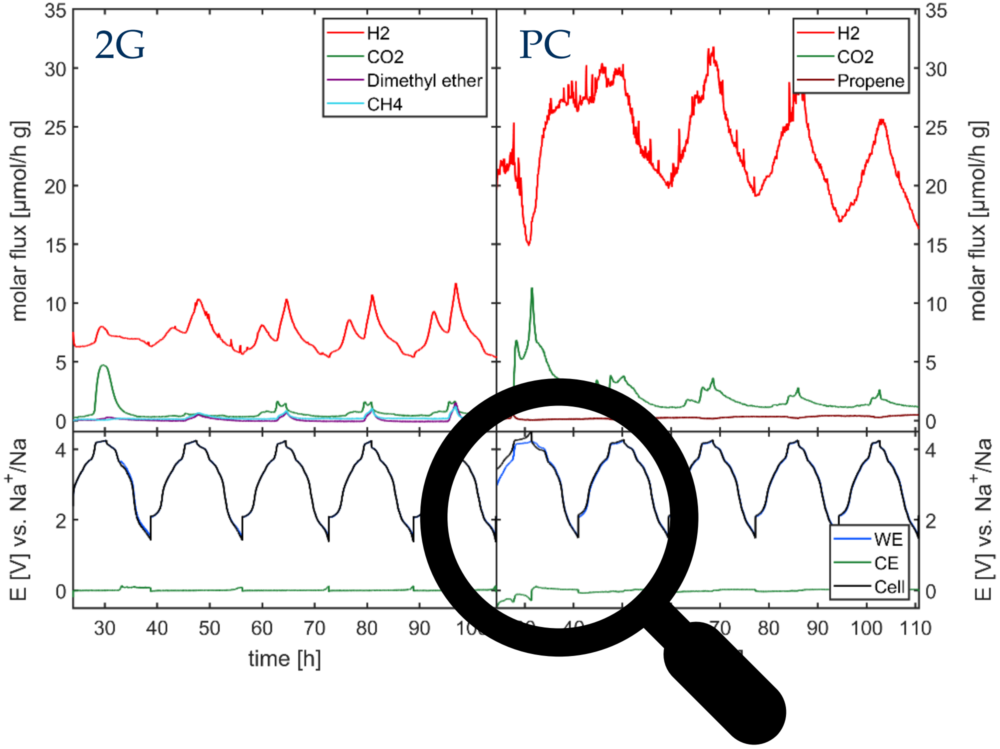
Improving data analysis
→ Analyzing the whole spectra instead of detecting only single masses. Improving quantification.

Improving cell design
→ Minimize artefacts, trapping of gas bubbles

J. Geisler, L. Pfeiffer, G. A. Ferrero, P. Axmann, P. Adelhelm *Batteries and Supercaps,* **2024**, doi: 10.1002/batt.202400006

Stability of Na-ion layered cathode active materials

Electrolyte stability in $Na_{0.67}[Mn_{3/4}Ni_{1/4}]O_2$ half-cells



- 1.5 – 4.25 V vs. Na^+ / Na
- More gas release in case of PC electrolyte!
- Validation with operando pressure measurements
- 3-electrode geometry important, especially when carbonates are used in half cells.

J. Geisler, L. Pfeiffer, G. A. Ferrero, P. Axmann, P. Adelhelm *Batteries and Supercaps*, **2024**, doi: 10.1002/batt.202400006

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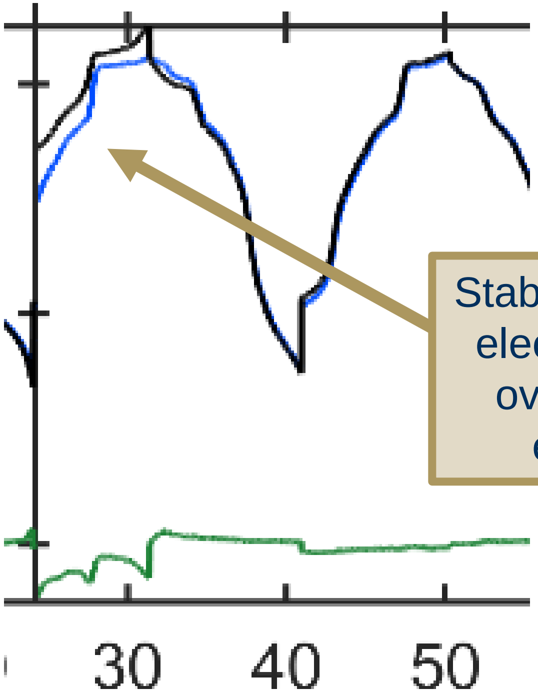

Stability of CAM in PC electrolyte would be overesimated in 2 electrode stall

- 1.5 – 4.25 V vs. Na^+ / Na
- More gas release in case of PC electrolyte!
- Validation with operando pressure measurements
- **3-electrode geometry important, especially when carbonates are used in half cells.**

J. Geisler, L. Pfeiffer, G. A. Ferrero, P. Axmann, P. Adelhelm *Batteries and Supercaps,* **2024**, doi: 10.1002/batt.202400006

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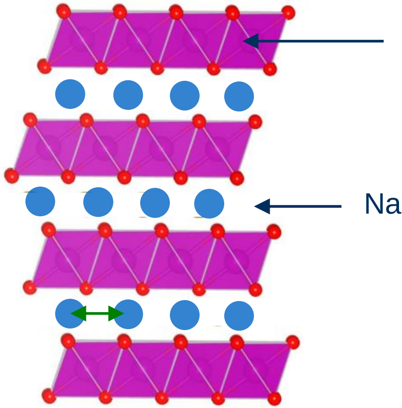
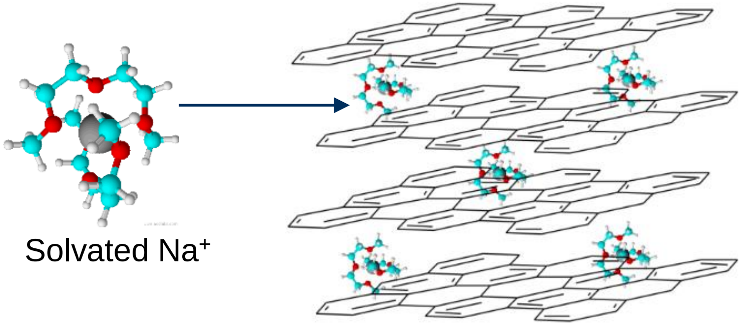


Type and ratios of
TM (Mn, Fe, Ni,….)
Dopants (Ti, Mg, Li,….

Na^+

Tuning properties through solvent co-intercalation



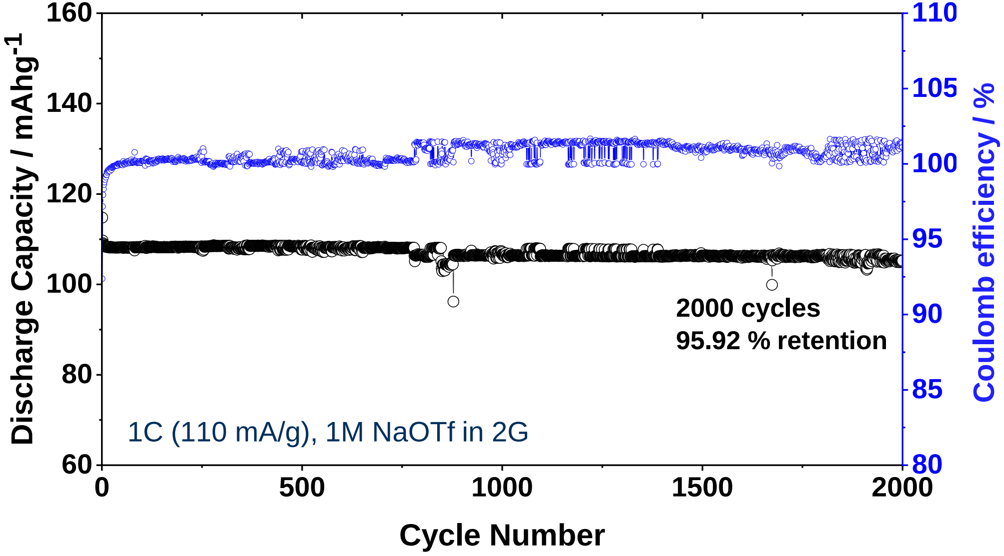
Solvated Na^+

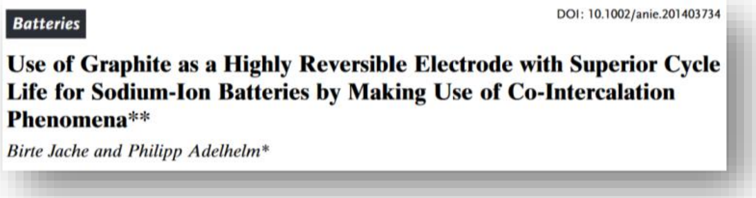
Co-intercalation reactions: Intercalation of solvated ions

Y. Kravets / I. Escher (own data)

Extreme volume expansion

Co-intercalation reactions: Intercalation of solvated ions





Batteries

DOI: 10.1002/anie.201403734

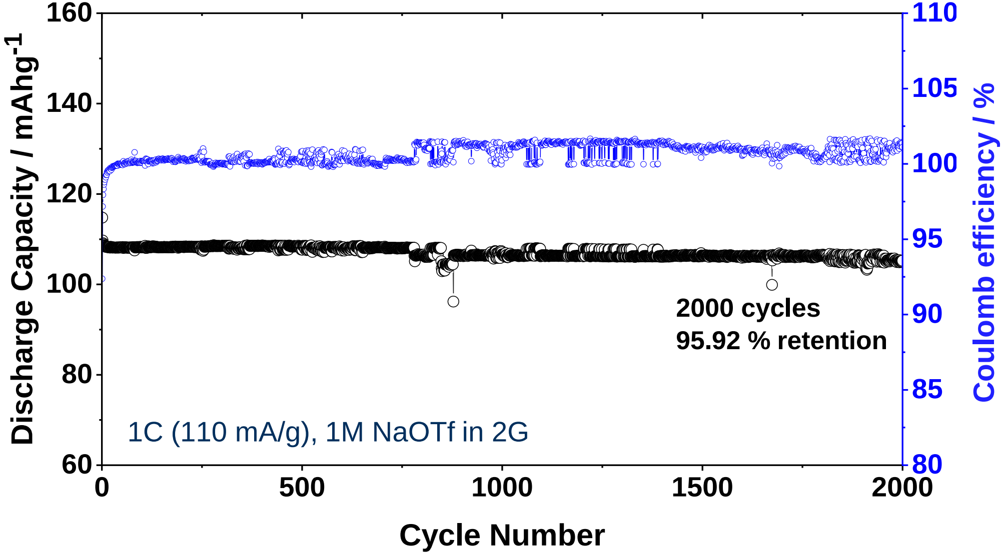
Use of Graphite as a Highly Reversible Electrode with Superior Cycle Life for Sodium-Ion Batteries by Making Use of Co-Intercalation Phenomena**

*Birte Jache and Philipp Adelhelm**

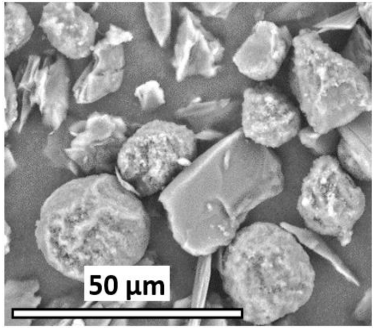
2014, *Angew. Chemie. Int. Ed.*, doi:10.1002/anie.201403734

Intercalation of solvated ions can be highly reversible despite large volume change
Exfolation but no delamination occurs (the structure remains crystalline!)
Concept minimizes charge transfer resistance (= high energy efficiency, fast charging)

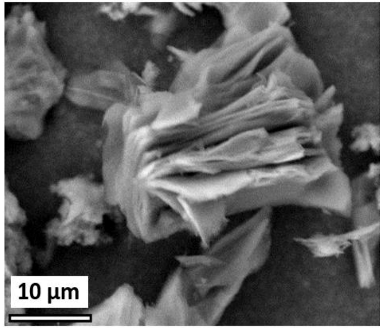
Co-intercalation reactions: Intercalation of solvated ions



before intercalation



after cycling



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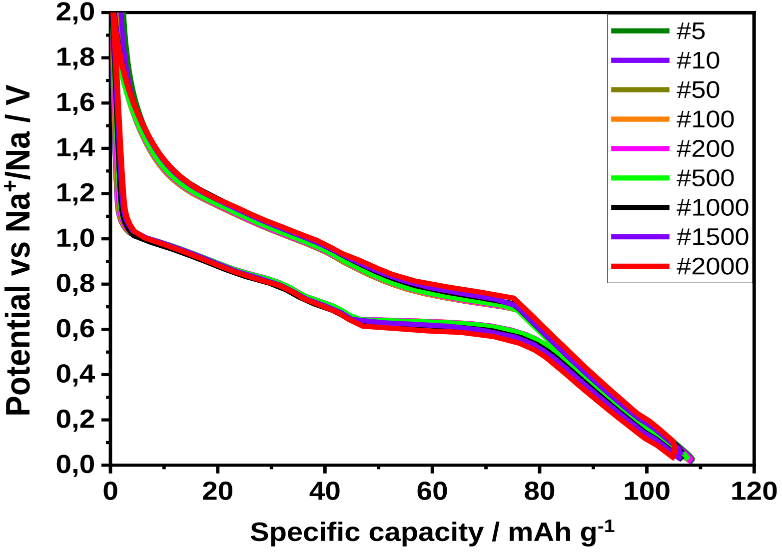
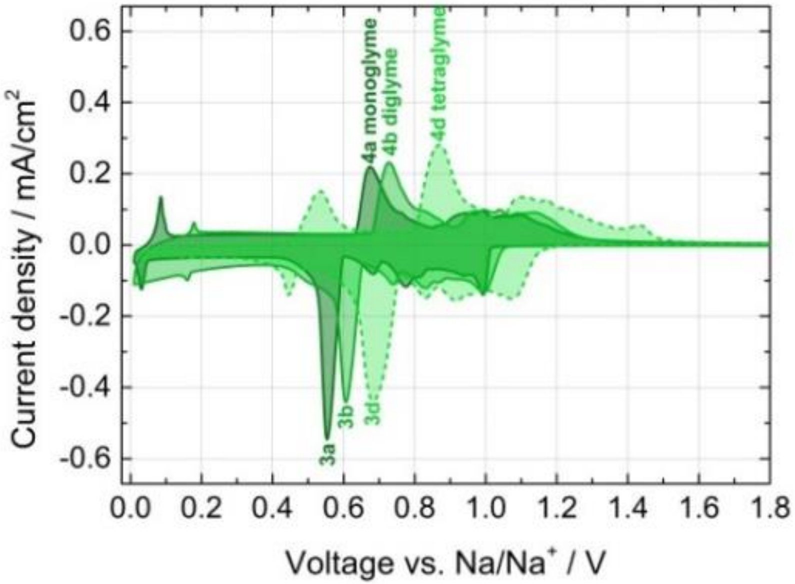
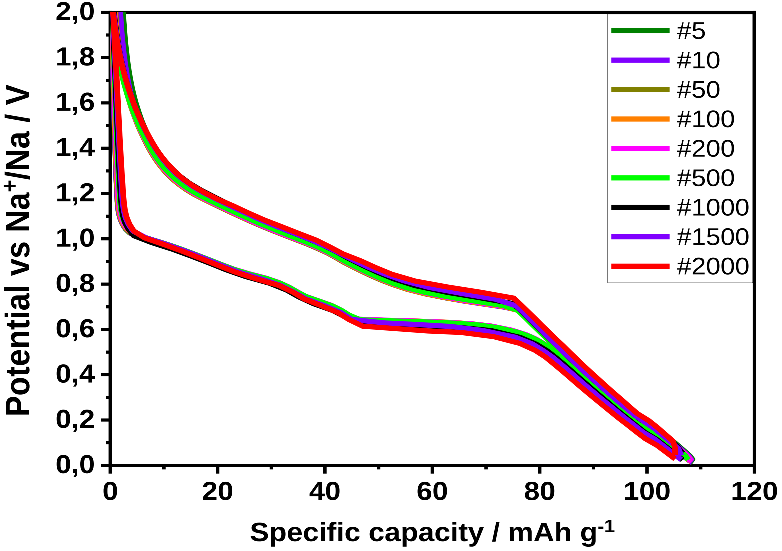


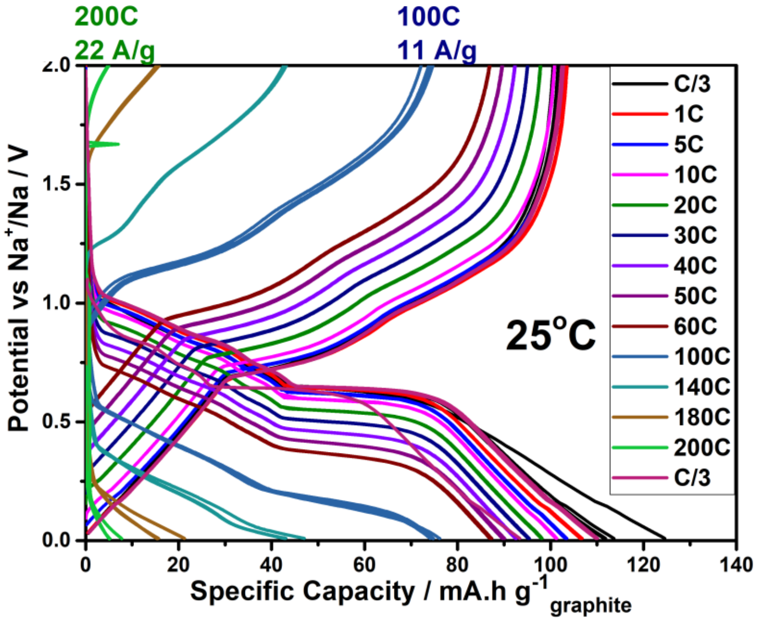


Voltage profile indicate that crystalline structure is preserved
Redox potential can be changed by changing the co-intercalating solvent (up to a few hundred mV)

Phys. Chem. Chem. Phys., doi: 10.1039/C6CP00651E

Co-intercalation reactions: Intercalation of solvated ions





Rate tests indicate very fast kinetics despite the large size of the solvated ions.

Theory* and NMR** suggest high mobility of solvated Na$^+$ in graphite lattice (D=1.1·10^{-8} cm^2/s).

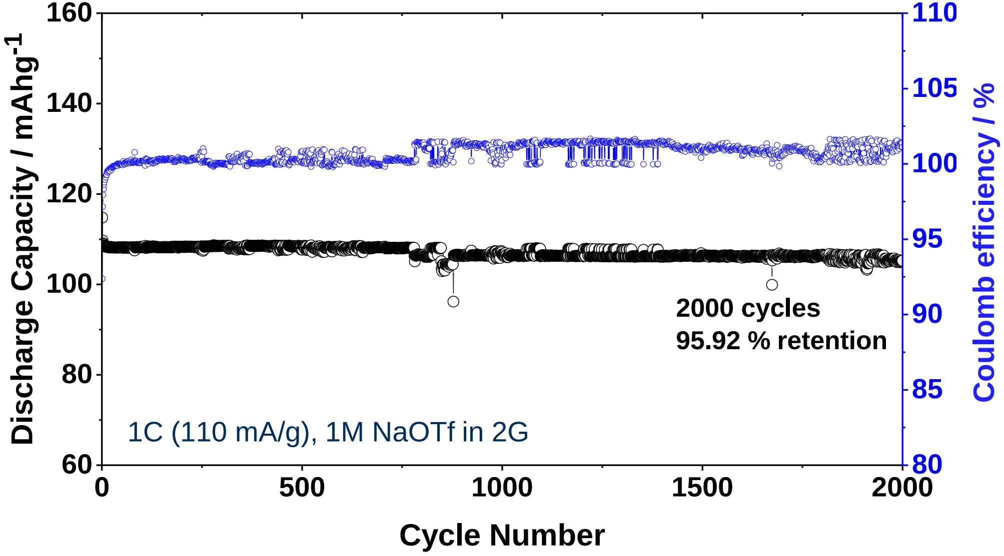
Activation energy for charge transfer < 10 kJ/mol as compared to around 60 kJ/mol for normal intercalation***

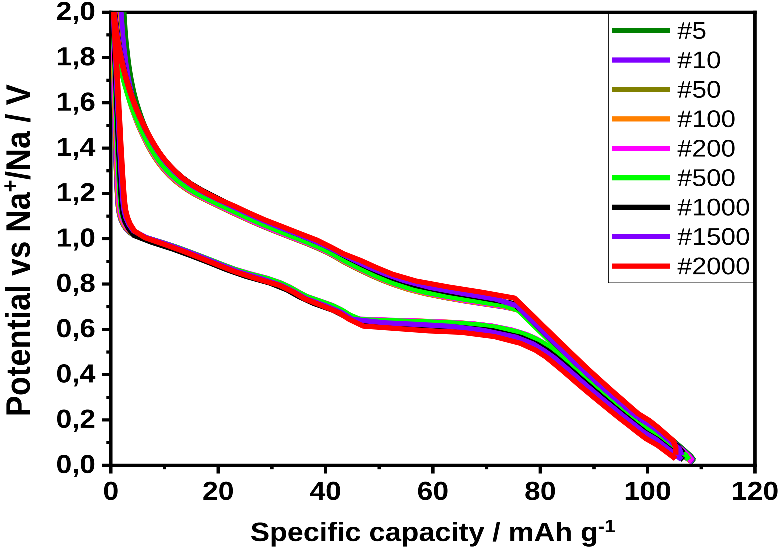
*** K. Janßen et al. / to be published

* SC Jung et al., *Nano Energy*, 2017 DOI: 10.1016/j.nanoen.2017.03.015

** K Gotoh et al., *J. Phys. Chem. C.*, 2016, DOI: 10.1021/acs.jpcc.6b10962

Co-intercalation reactions: Intercalation of solvated ions



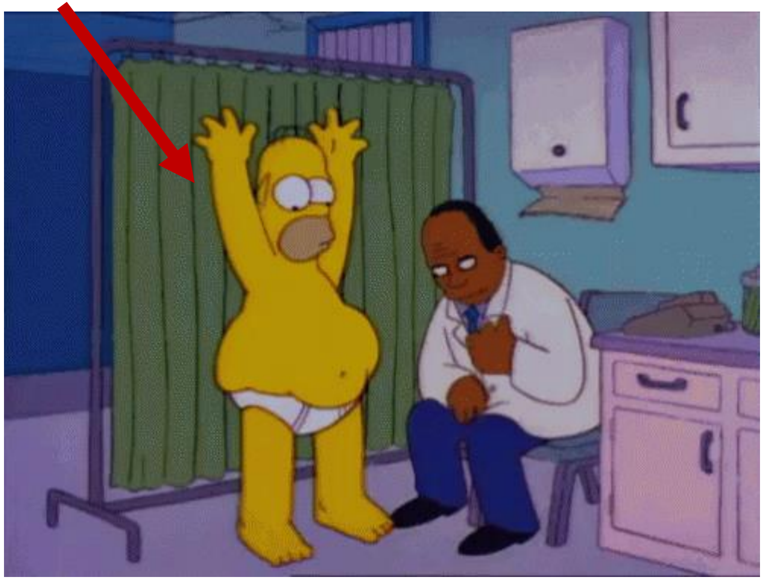


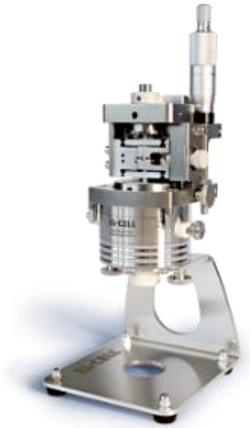
Intercalation of solvated ions can be highly reversible despite large volume change
Concept minimizes charge transfer resistance (= high energy efficiency, fast charging)

M. Goktas et al – *Adv. Energy Materials,* **2018,** 1702724
M. Goktas et al., *J. Phys. Chem. C.*, **2018**, 122, 47, 26816-26824
I. Escher et al. *Energy Technology*, **2021**, 2000880
G. Ferrero et al. *Adv. Energy Materials*, **2023,** 2202377 (full cell, co-intercalation battery)

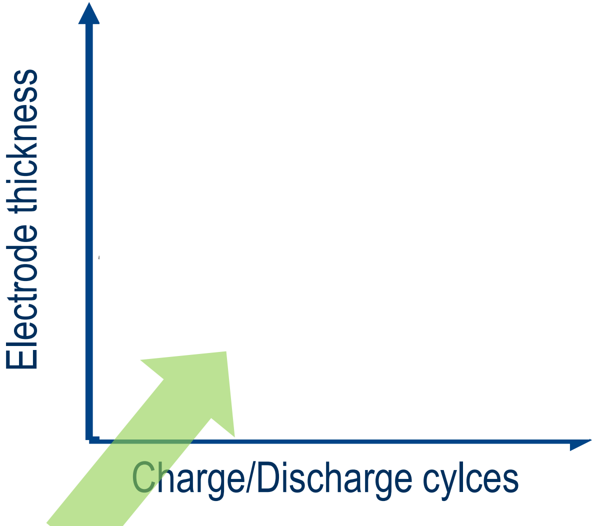
Operando electrochemial dilatometry

Quite similar to this situation, batteries and electrodes change their size during charging and discharging, they are „breathing“





nm resolution

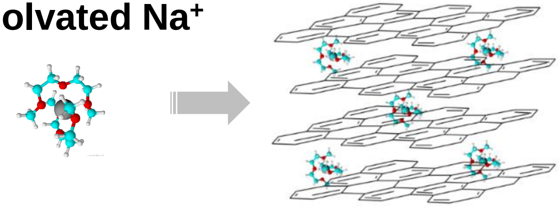


Shape contains information on storage mechanism

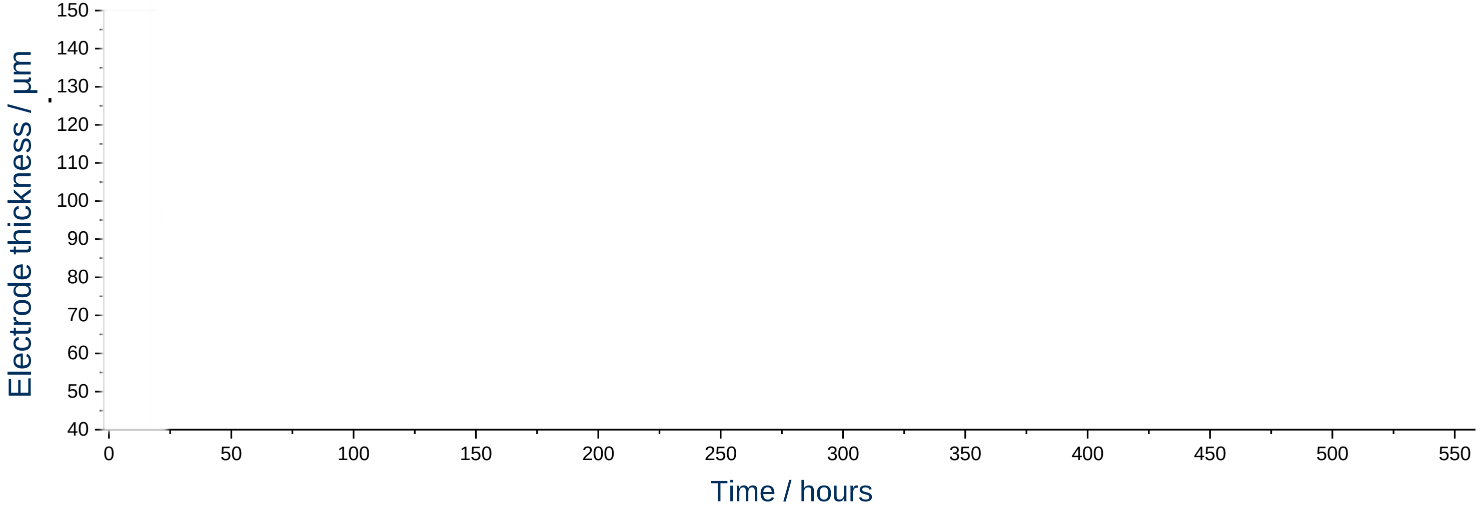
Review on operando dilatometry:
I. Escher et al., Energy Technology, 2022, doi: 10.1002/ente.202101120

Applying operando electrochemical dilatometry

Solvated Na$^+$



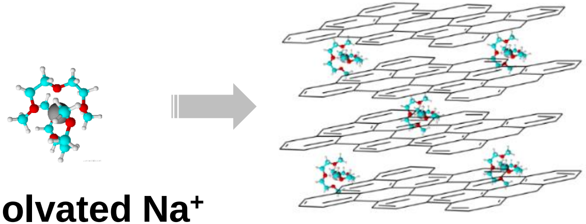
Graphite electrode
1M $NaPF_6$ in diglyme



M. Gotkas et al., Avanced Energy Materials, 2018, doi: 10.1002/aenm.201702724

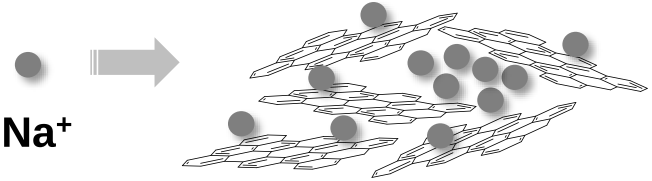
Applying operando electrochemical dilatometry

Graphite



Solvated Na$^+$

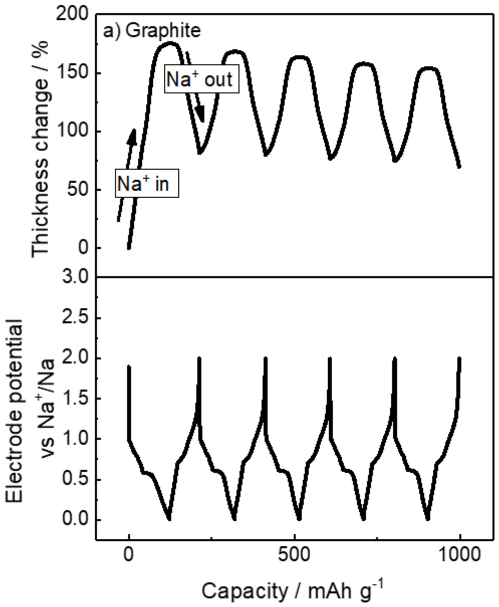
Hard carbon



Na$^+$

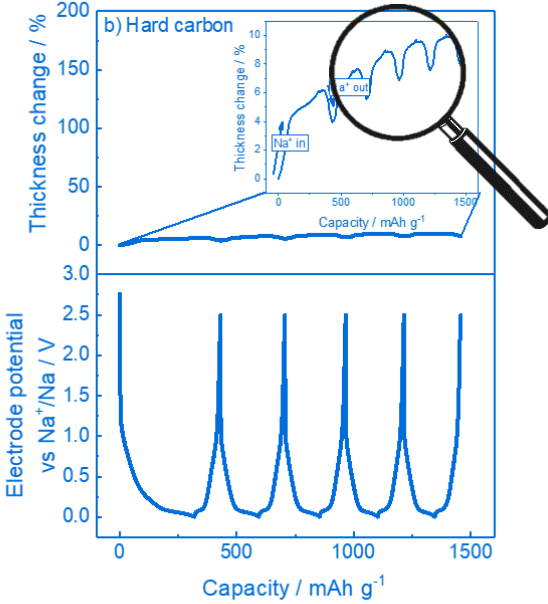
Graphite

Breathing > 50 %



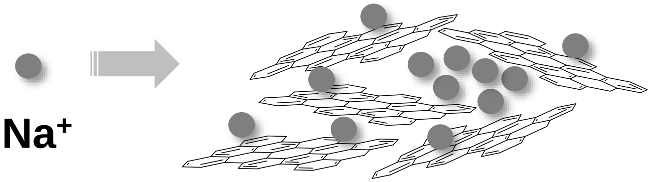
Hard carbon

Breathing around ≤ 2 %

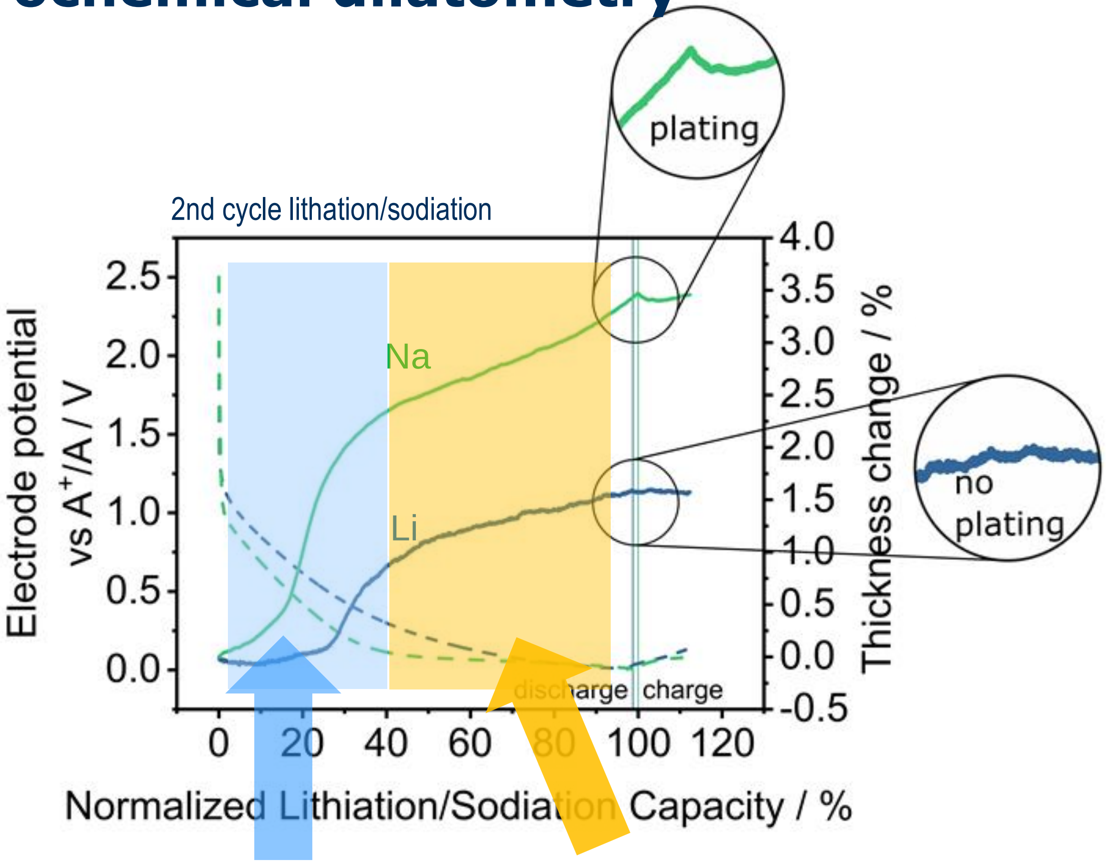


I. Escher et al., Adv. Materials Interfaces, 2021, 2100596
Review: I. Escher et al., *Energy Technology*, 2022, 10, *5*, DOI: 10.1002/ente202101120

Applying operando electrochemical dilatometry



- **Operando dilatometry can be used to identify different storage mechanisms in hard carbons: intercalation, cluster formation, metal plating**
- **For Na/hard carbon, underpotential Na plating takes place (dendrites may form above 0 V!)**



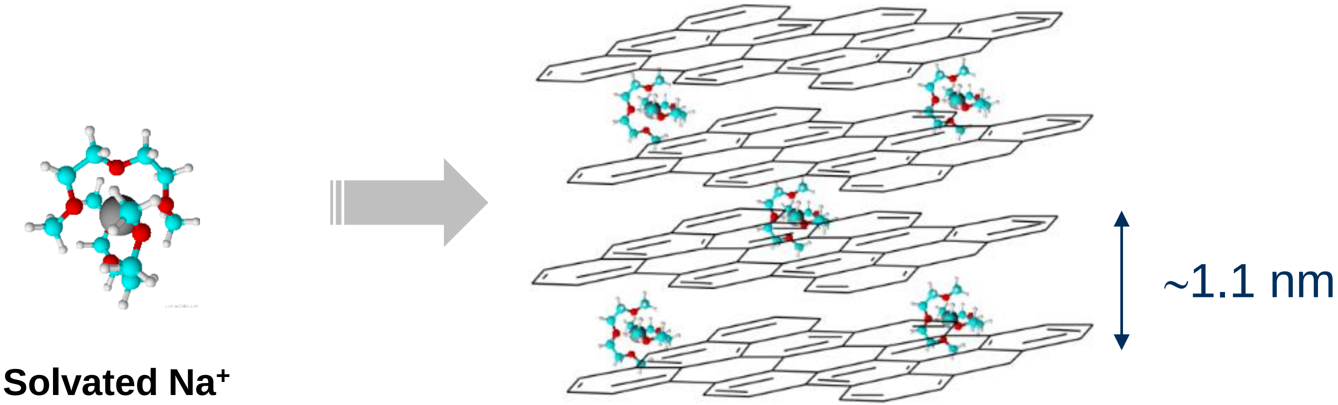
Ion intercalation
Rapid thickness increase

Formation of „metal clusters“
Slow tickness increase

I. Escher et al., Adv. Materials Interfaces, 2021, 2100596
Review: I. Escher et al., *Energy Technology*, 2022, 10, *5*, DOI: 10.1002/ente202101120

…we had learned a lot but a major question was still unclear:

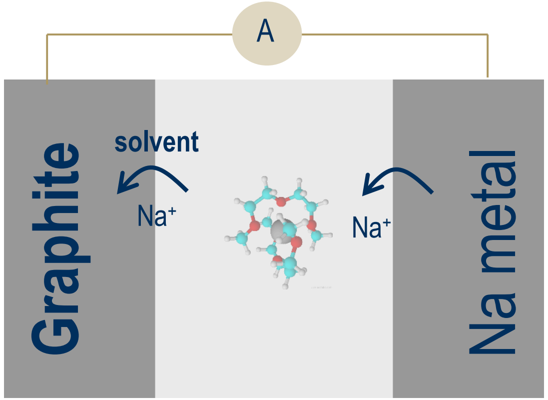
How many solvent molecules co-intercalate into graphite and what is the formation process?



$$\mathrm{Na}^{+}\left(diglyme\right)_{n}+x\cdot\mathrm{C}+e^{-}\rightleftarrows\mathrm{Na}\left(diglyme\right)_{n}\mathrm{C}_{x}$$

Illustration too simple!

How many solvent molecules co-intercalate into graphite?



What experiments can be made to answer this question?

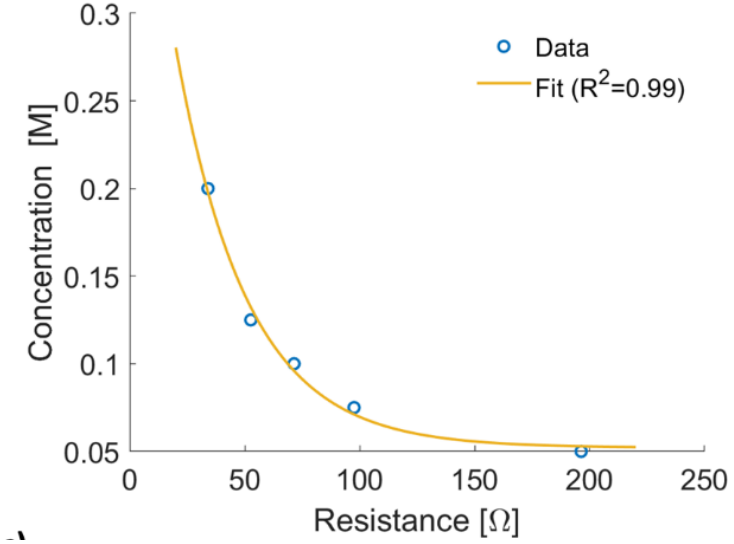
XRD, Dilatometry,….
Change of electrode mass
Change of electrolyte conductivity
Change of optical properties
Change in entropy
Change in ssNMR spectra
Theory

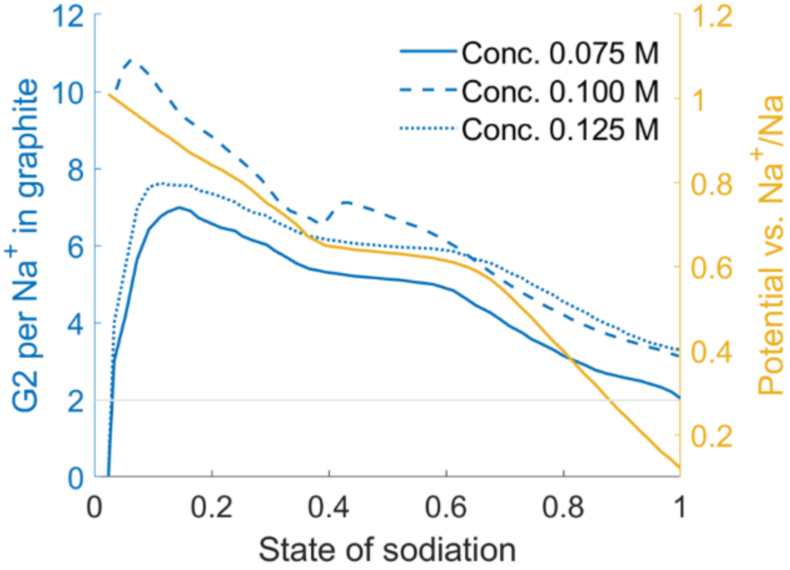
New model for the co-intercalation process

G. Avall et al., Adv. Energy Materials, **2023**, doi: 10.1002/aenm.202301944

Change in electrolyte conductivty during solvent co-intercalation:

Idea: Measure conductivity change of the electrolyte during the reaction and calculate how much solvent is co-intercalating

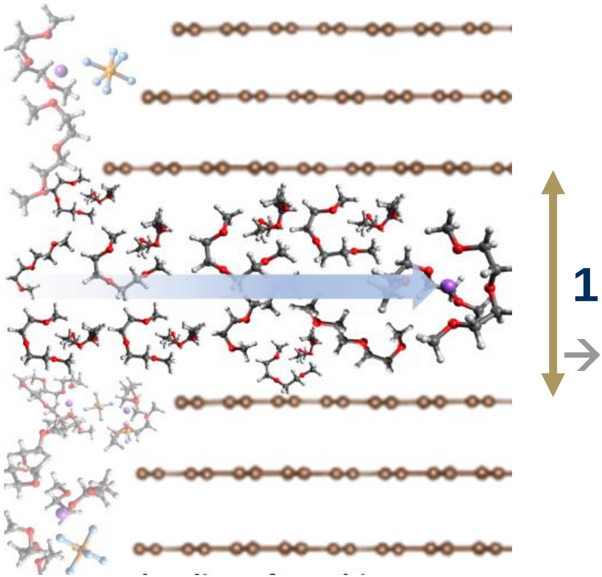




As soon as the first Na^+ intercalates, the electrolyte concentration rapidly increases. This means that many solvents enter the graphite structure, up to approx. 7 diglyme molecules for every Na^+!

New model for the formation of *t*-GICs

Step 1:
pore formation &
pore filling



1.1 nm

→ 2,600 m^2/g?

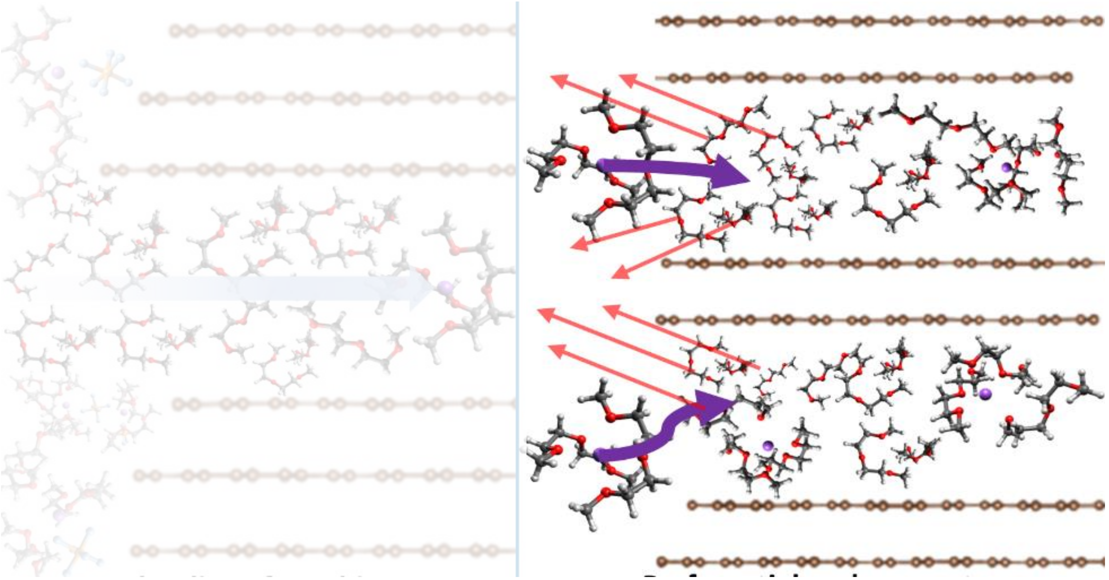
~ 7 molecules per Na^+

G. Avall et al., In situ pore formation in graphite through solvent co-intercalation: A new model for the formation of ternary graphite intercalation compounds bridging batteries and supercapacitors, Adv. Energy Mater., 2023, doi: 10.1002/aenm.202301944

New model for the formation of *t*-GICs

Step 1:
pore formation & pore filling

Step 2:
Replacement of free solvents



~ 7 molecules per Na^+

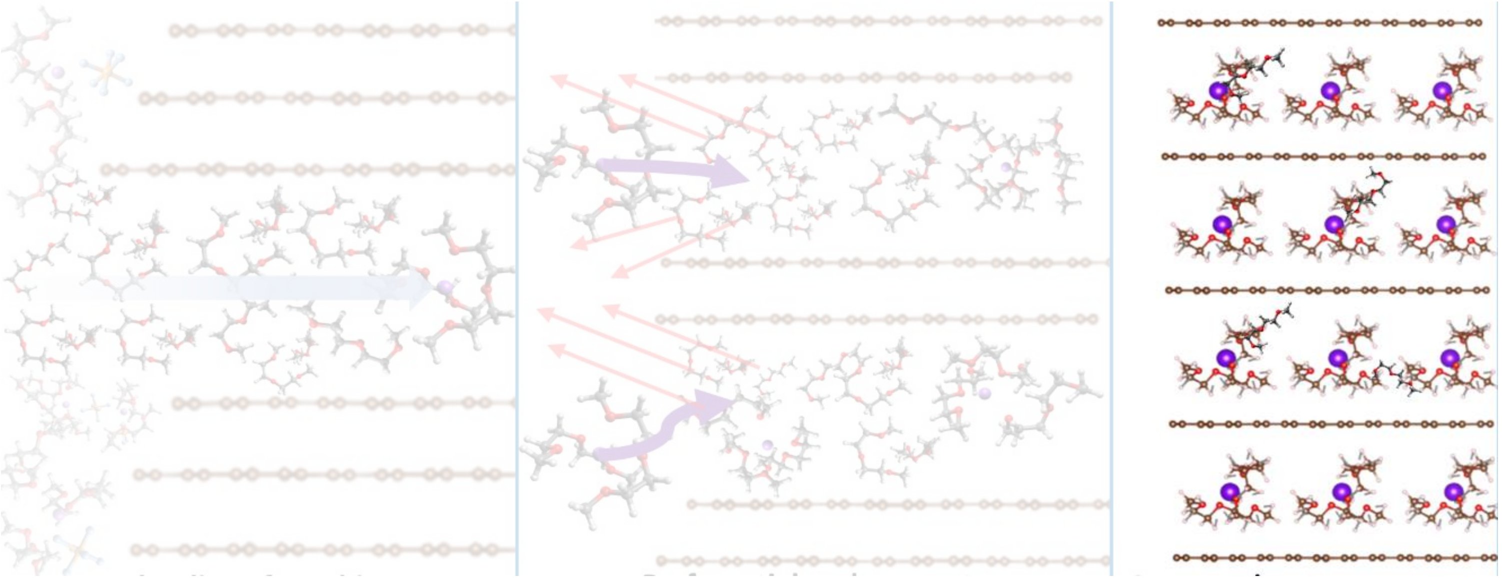
G. Avall et al., In situ pore formation in graphite through solvent co-intercalation: A new model for the formation of ternary graphite intercalation compounds bridging batteries and supercapacitors, Adv. Energy Mater., 2023, doi: 10.1002/aenm.202301944

New model for the formation of *t*-GICs

Step 1:
pore formation & pore filling

Step 2:
Replacement of free solvents

Step 3:
Geometric optimization

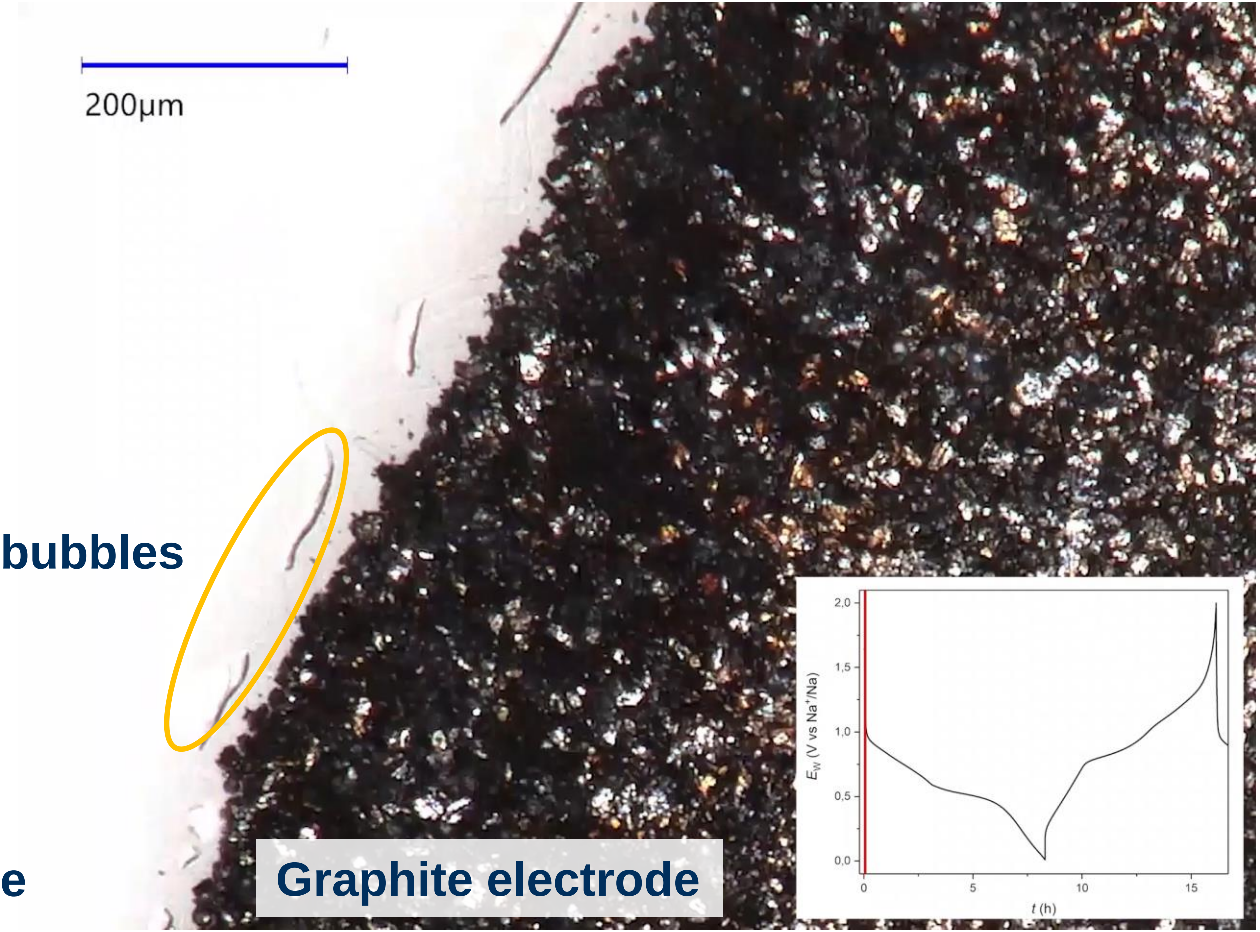


~ 7 molecules per Na^+

~ 2 molecules per Na^+

G. Avall et al., In situ pore formation in graphite through solvent co-intercalation: A new model for the formation of ternary graphite intercalation compounds bridging batteries and supercapacitors, Adv. Energy Mater., 2023, doi: 10.1002/aenm.202301944

Solvent co-intercalation: operando optical microscopy

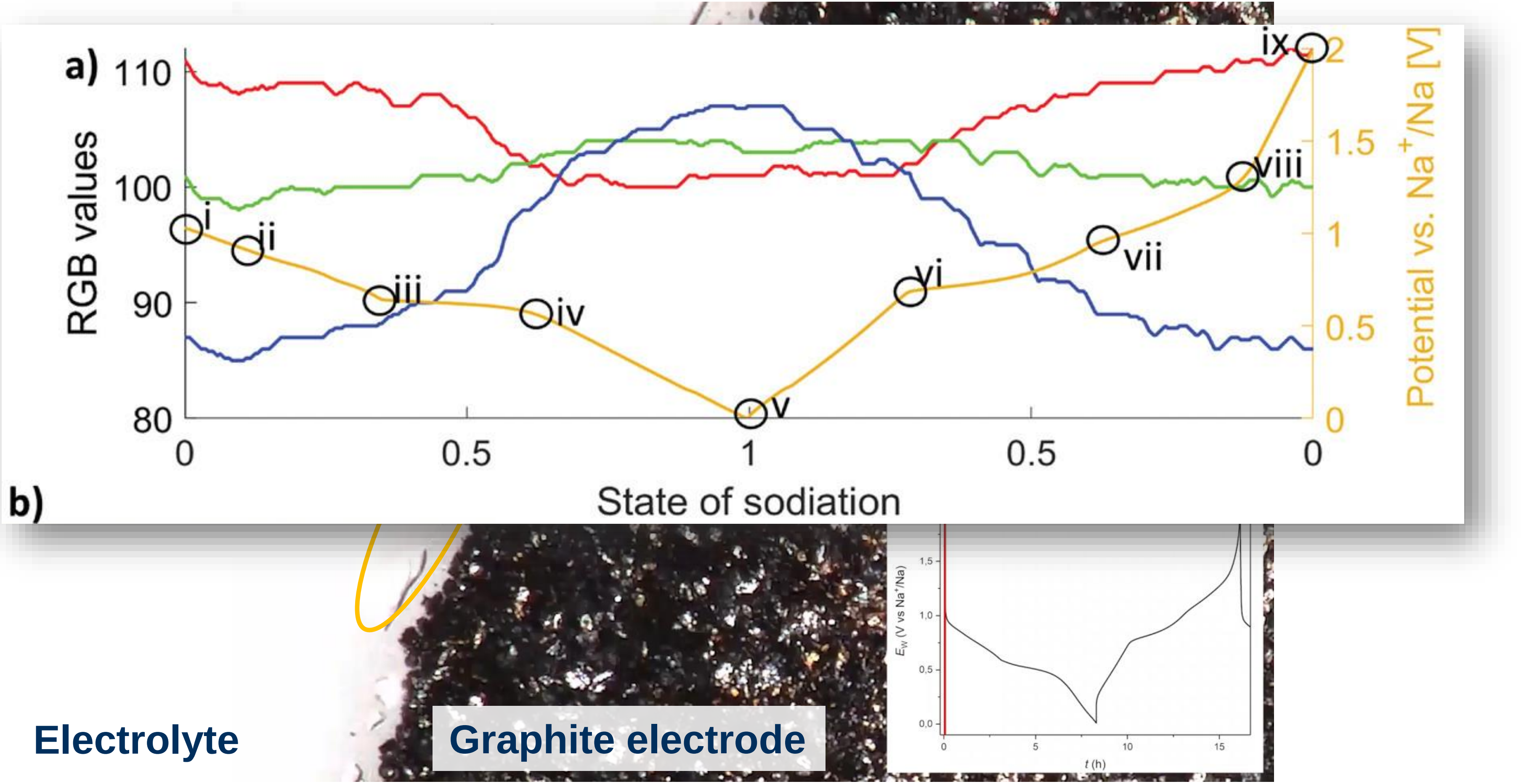


bubbles

Electrolyte

Graphite electrode

Solvent co-intercalation: operando optical microscopy

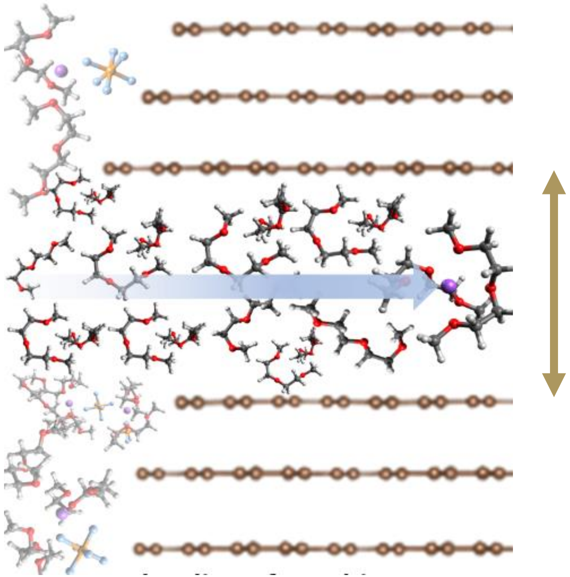


Electrolyte

Graphite electrode

New model for the formation of *t*-GICs

Step 1:
pore formation &
pore filling



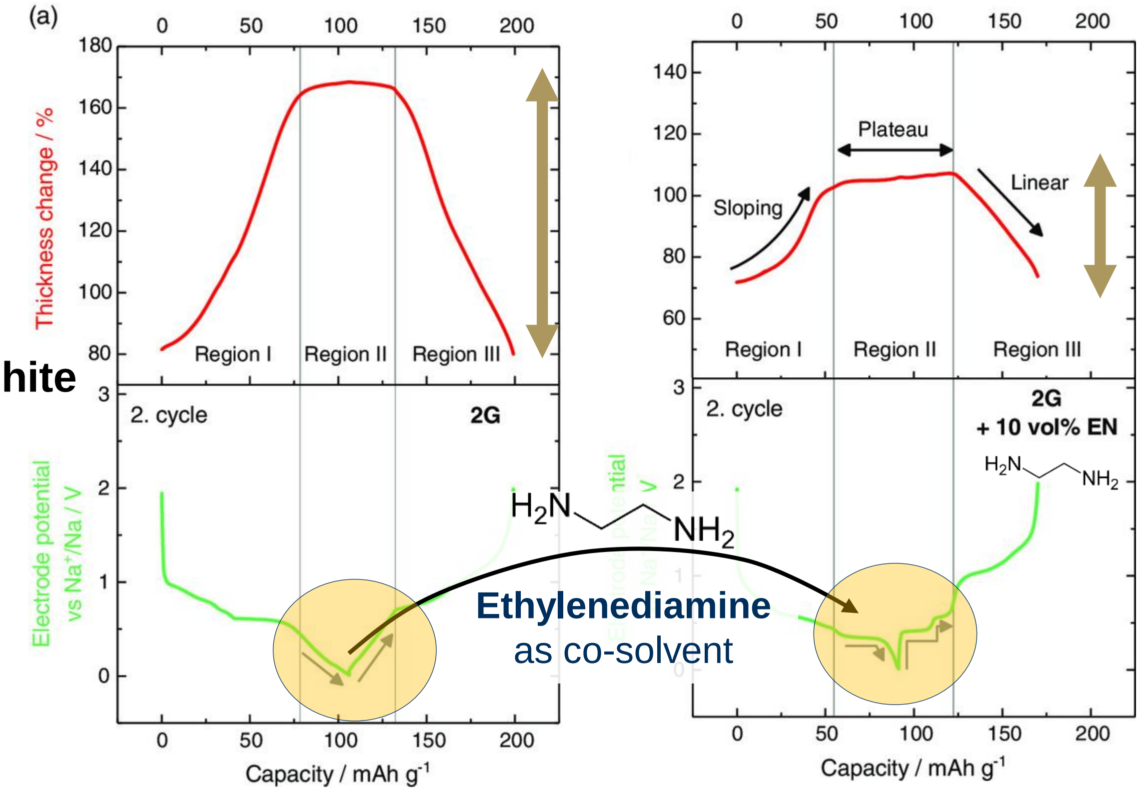
~ 7 molecules per Na$^+$

If pore filling takes place, additional solvents may be co-intercalated.

…from ternary, to quarternary intercalations, to quinary etc. compounds?

G. Avall et al., In situ pore formation in graphite through solvent co-intercalation: A new model for the formation of ternary graphite intercalation compounds bridging batteries and supercapacitors, Adv. Energy Mater., 2023, doi: 10.1002/aenm.202301944

From ternary to quarternary intercalation compounds



Graphite

Ethylenediamine
as co-solvent

Adding ethylene diamine as co-solvent:

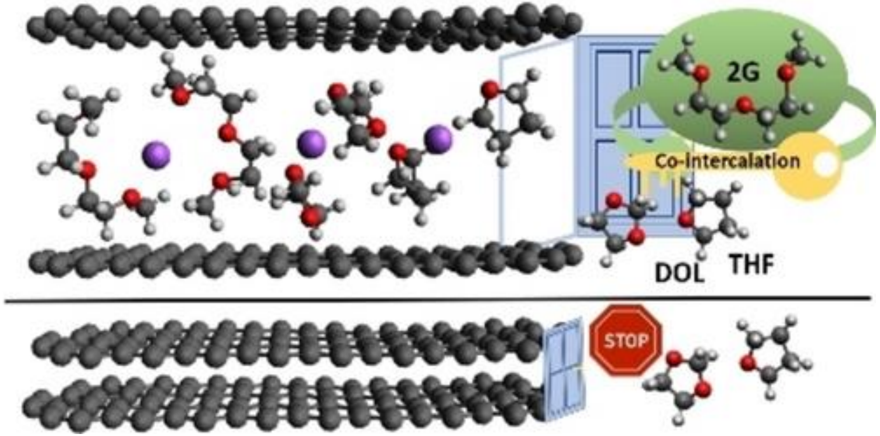
1) Changes the reaction mechanism and leads to a quarternary GIC (*q*-GIC), i.e. graphite intercalated by Na^+ and two different solvents

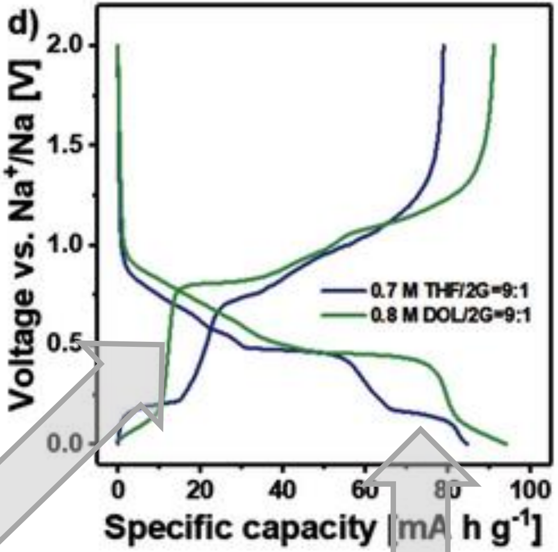
2) Significantly reduces the interlayer spacing (from 1.1 nm to 0.7 nm)[1] and the electrode breathing (from 40-60 % to around 15-20 %)[2]

1) Zhang/Lerner Nanotechnology, 2018, 325402
2) I. Escher, *Energy Technology*, 2021, doi:10.1002/ente.202000880

From ternary to quarternary intercalation compounds

Diglyme can promote the co-intercalation of others solvents too (DOL and THF)





New Quartenary Graphite Intercalation Compounds!

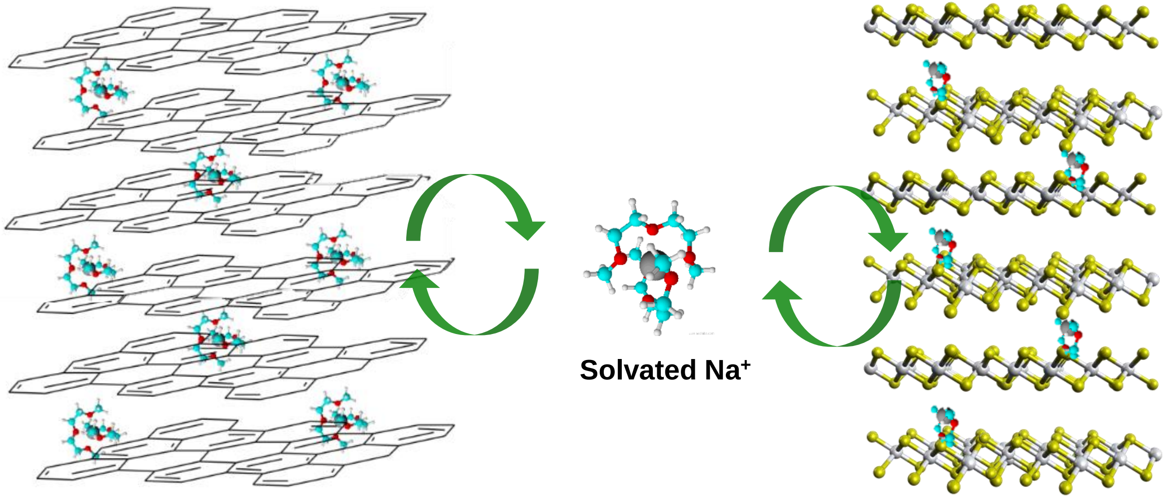
High voltage:
Na$^+$ and diglyme enter the structure

Low voltage:
Na$^+$ and diglyme+THF/DOL enter the structure

Y. Son et al., Diglyme as a promoter for the electrochemical formation of quaternary graphite intercalation compounds containing two different types of solvents, *Batteries & Supercaps*., **2024**, doi: 10.1002/batt.202300506

Can we build a co-intercalation battery?

Negative electrode **Positive electrode**

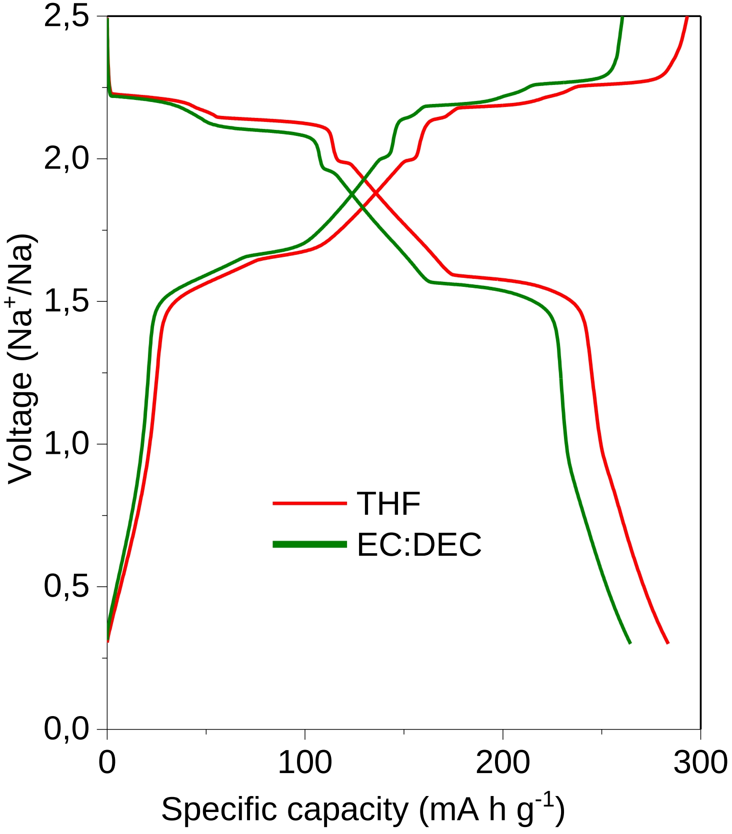


Adv. Energy Mater. (2022)

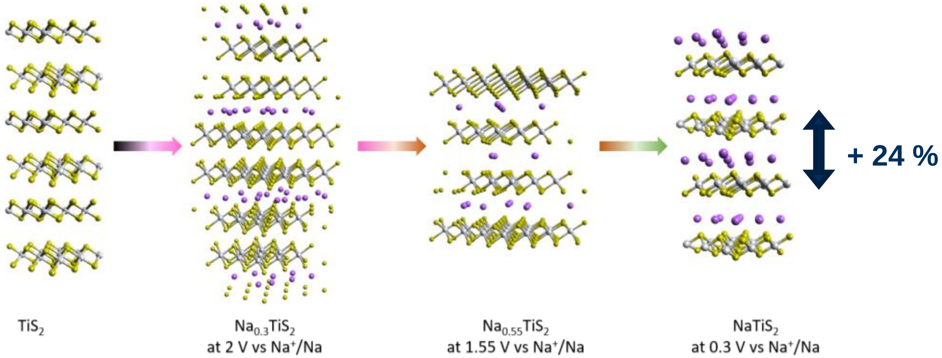
G. Alvarez et al. *Advanced Energy Materials,* 2023, 2202377, DOI:10.1002/aenm.202202377

erc
European Research Council
ERC Consolidator Grant
SEED

TiS_2 - Intercalation of solvated Na-ions

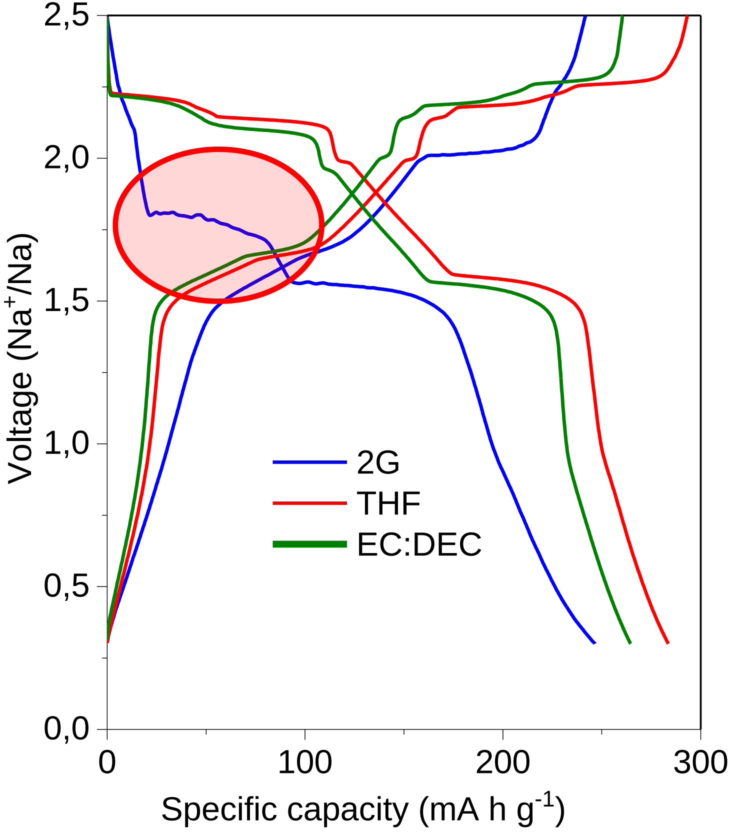


THF or EC:DEC as solvents: no solvent co-intercalation

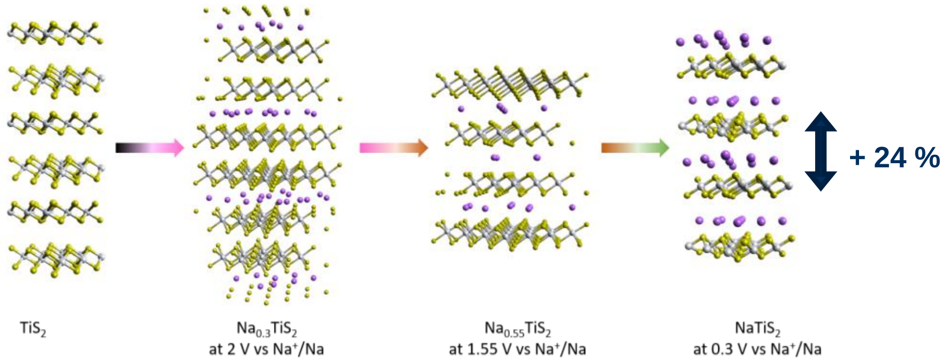


G. Alvarez *Advanced Energy Materials, 2022,* 2202377, DOI:10.1002/aenm.202202377

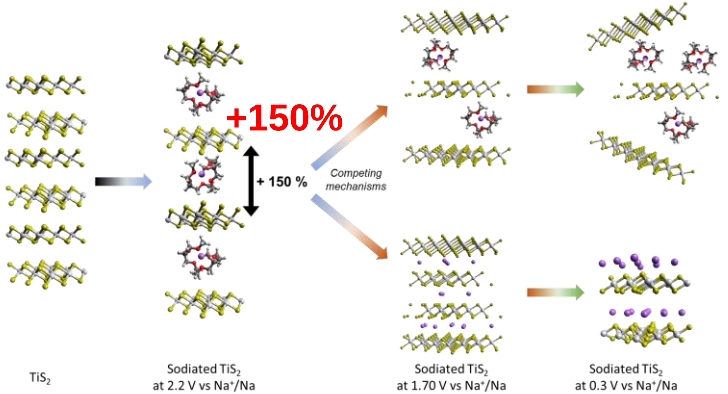
TiS_2 - Intercalation of solvated Na-ions



THF or EC:DEC as solvents: no solvent co-intercalation



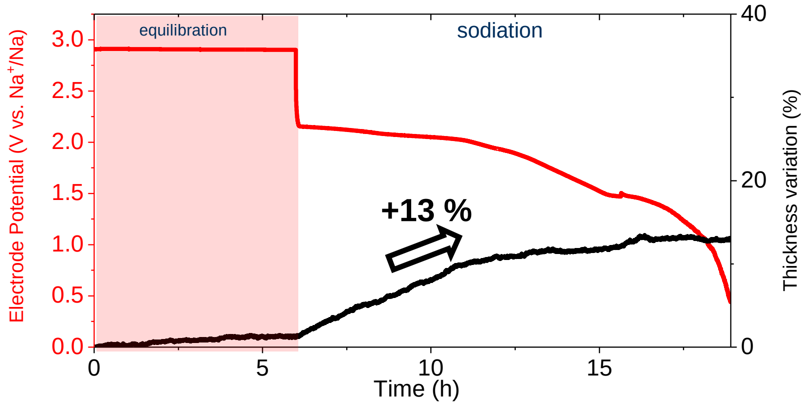
Diglyme as solvent: (partial) co-intercalation

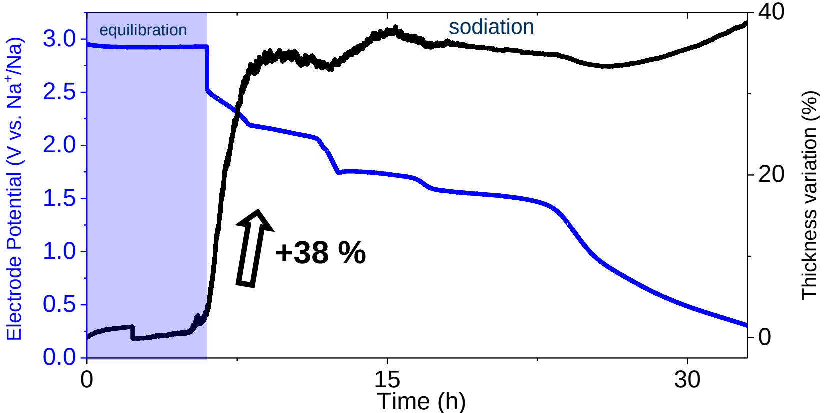


G. Alvarez *Advanced Energy Materials, 2022,* 2202377, DOI:10.1002/aenm.202202377

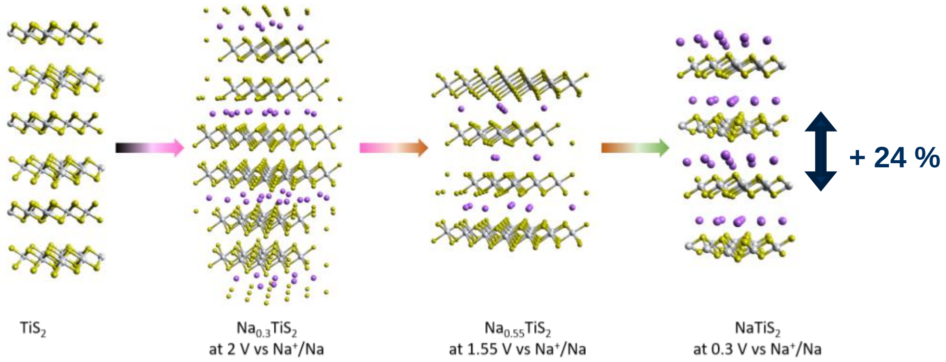
TiS_2 - Intercalation of solvated Na-ions

Operando dilatometry

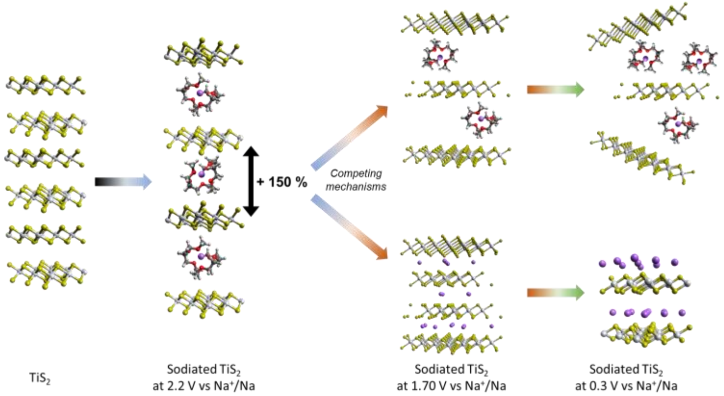




THF or EC:DEC as solvents: no solvent co-intercalation



Diglyme as solvent: (partial) co-intercalation



What about solvent co-intercalation in Na_xTiS_2

Y. Sun et al. Preprint: doi: 10.21203/rs.3.rs-4564500/v1

Today‵s menu

Layered materials:

- Layered oxides and sulfides
- Graphite

Metals

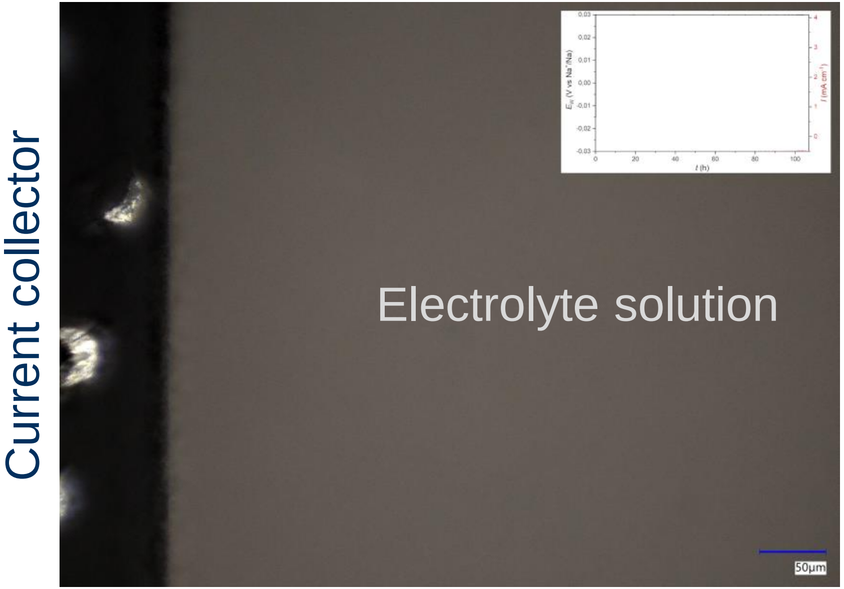
- Na and Sn

Conversion materials

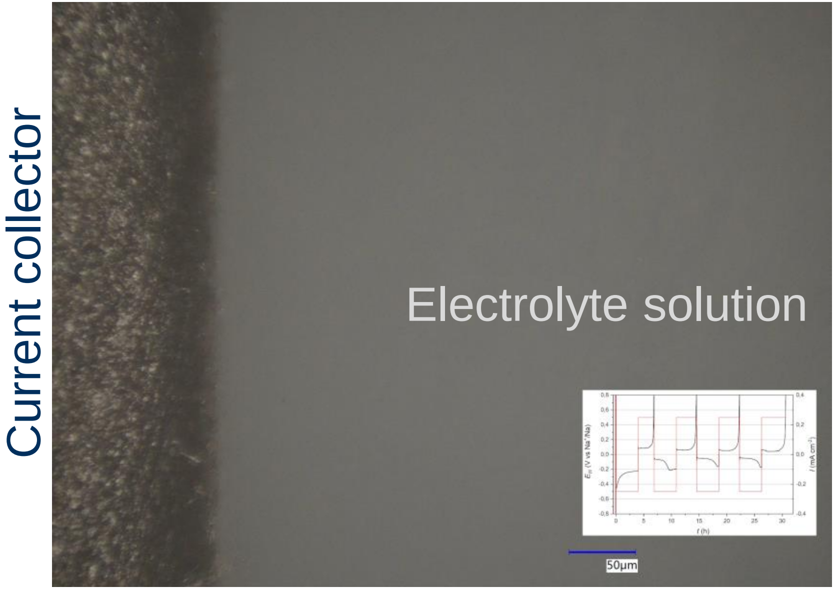
- CuS – a unique electrode materials studied with tomography

Anode materials: Sodium

$$\mathrm{Na} \underset{\text{charge (plating)}}{\overset{\text{discharge (stripping)}}{\rightleftharpoons}} \mathrm{Na}^{+} + e^{-}$$



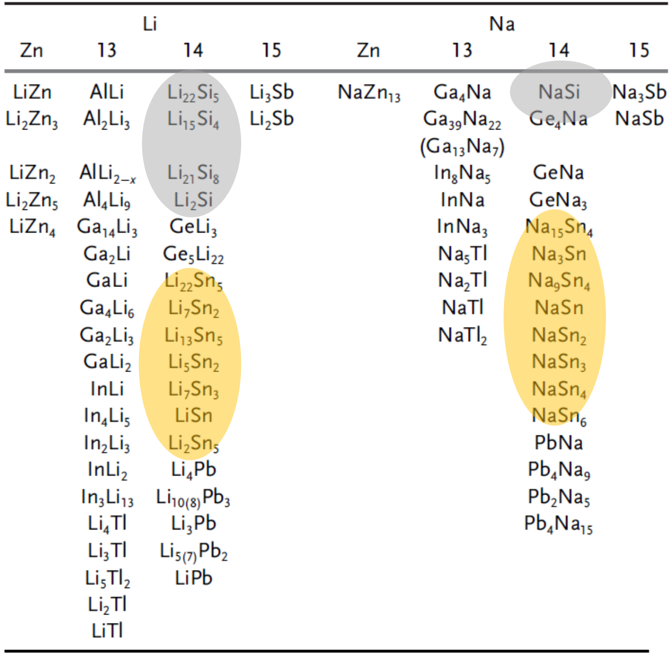
Plating on current collector
Different currents for 1 mAh cm^{-2}
1M $NaPF_6$ in Diglyme
→ **Tip growth mechanism**



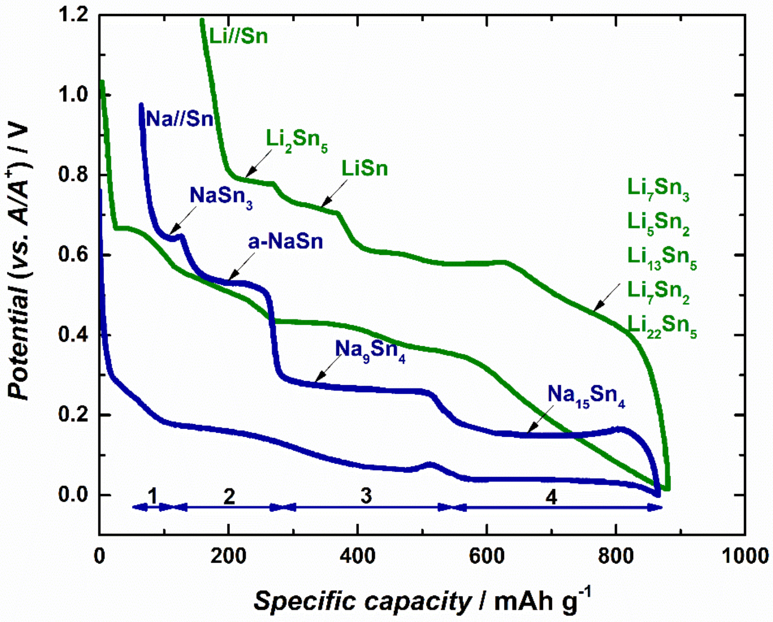
Plating on current collectore
0.25 mA for 1 mAh cm^{-2}
Alternative electrolyte
→ **Root growth mechanism**

Unpublished results

Anode materials: Alloys



Li				Na			
Zn	13	14	15	Zn	13	14	15
LiZn	AlLi	$Li_{22}Si_5$	Li_3Sb	$NaZn_{13}$	Ga_4Na	NaSi	Na_3Sb
Li_2Zn_3	Al_2Li_3	$Li_{15}Si_4$	Li_2Sb		$Ga_{39}Na_{22}$	Ge_4Na	NaSb
					$(Ga_{13}Na_7)$		
$LiZn_2$	$AlLi_{2-x}$	$Li_{21}Si_8$			In_8Na_5	GeNa	
Li_2Zn_5	Al_4Li_9	Li_2Si			InNa	$GeNa_3$	
$LiZn_4$	$Ga_{14}Li_3$	$GeLi_3$			$InNa_3$	$Na_{15}Sn_4$	
	Ga_2Li	Ge_5Li_{22}			Na_5Tl	Na_3Sn	
	GaLi	$Li_{22}Sn_5$			Na_2Tl	Na_9Sn_4	
	Ga_4Li_6	Li_7Sn_2			NaTl	NaSn	
	Ga_2Li_3	$Li_{13}Sn_5$			$NaTl_2$	$NaSn_2$	
	$GaLi_2$	Li_5Sn_2				$NaSn_3$	
	InLi	Li_7Sn_3				$NaSn_4$	
	In_4Li_5	LiSn				$NaSn_6$	
	In_2Li_3	Li_2Sn_5				PbNa	
	$InLi_2$	Li_4Pb				Pb_4Na_9	
	In_3Li_{13}	$Li_{10(8)}Pb_3$				Pb_2Na_5	
	Li_4Tl	Li_3Pb				Pb_4Na_{15}	
	Li_3Tl	$Li_{5(7)}Pb_2$					
	Li_5Tl_2	LiPb					
	Li_2Tl						
	LiTl						



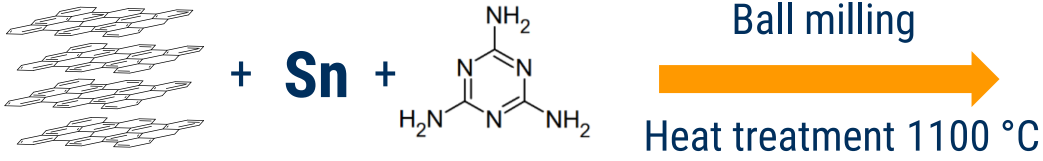
Metals: Lithium generally forms more intermetallic phases than Na

→ Using Si in SIBs fails so far, Al can be used as current collector!

P. K. Nayak, L. Yang, W. Brehm, P. Adelhelm, *Angew. Chem. Int. Ed.*, **2018**

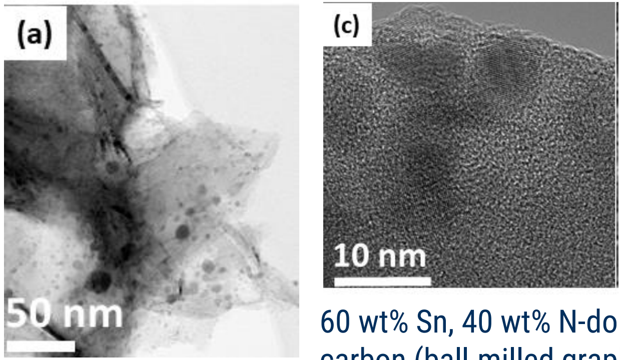
Tin as anode for sodium-ion batteries

$\mathrm{Sn} + 3.75\,\mathrm{Na}^{+} + 3.75\,e^{-} \rightleftarrows \mathrm{Na}_{3.75}\mathrm{Sn}$ $q_{th} = 874\ \mathrm{mAh/g}$



Ball milling

Heat treatment 1100 °C



60 wt% Sn, 40 wt% N-doped carbon (ball-milled graphite)

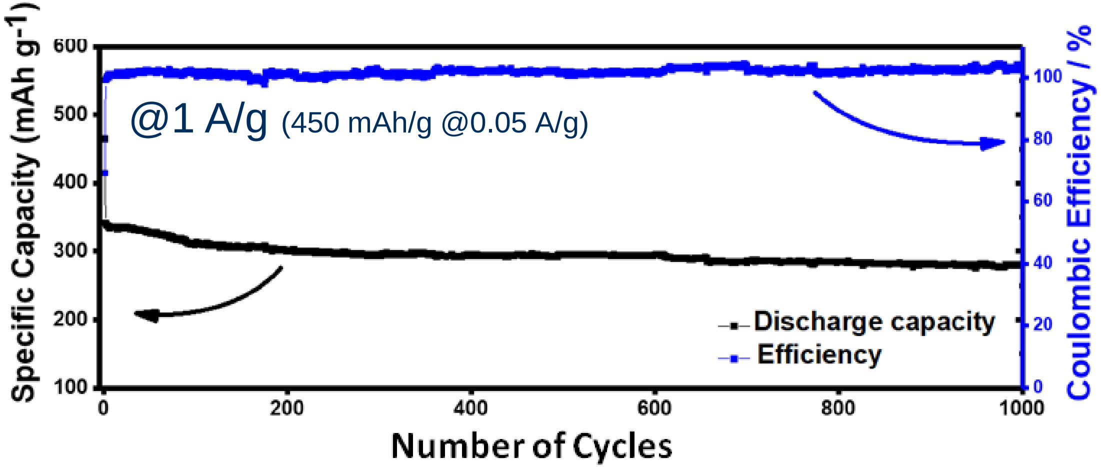
T. Palaniselvam et al., *Adv. Funct. Materials*, **2019**, DOI: 10.1002/adfm.201900790

Tin as anode for sodium-ion batteries

$$Sn + 3.75\,Na^{+} + 3.75\,e^{-} \rightleftarrows Na_{3.75}Sn$$

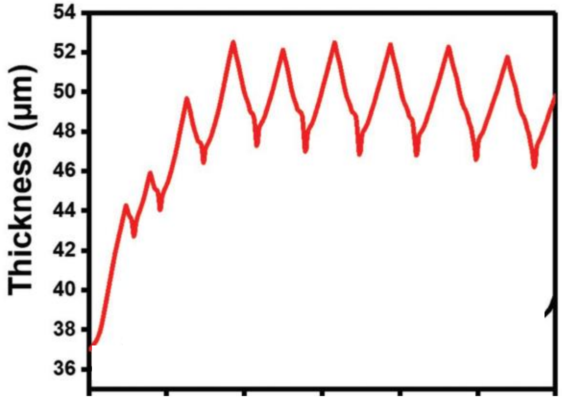
q_{th}= 874 mAh/g

Sn → $Na_{3.75}Sn$: ΔV= + 420 %



@1 A/g (450 mAh/g @0.05 A/g)

Operando electrochem. dilatometry



ΔV=
+ 14 %

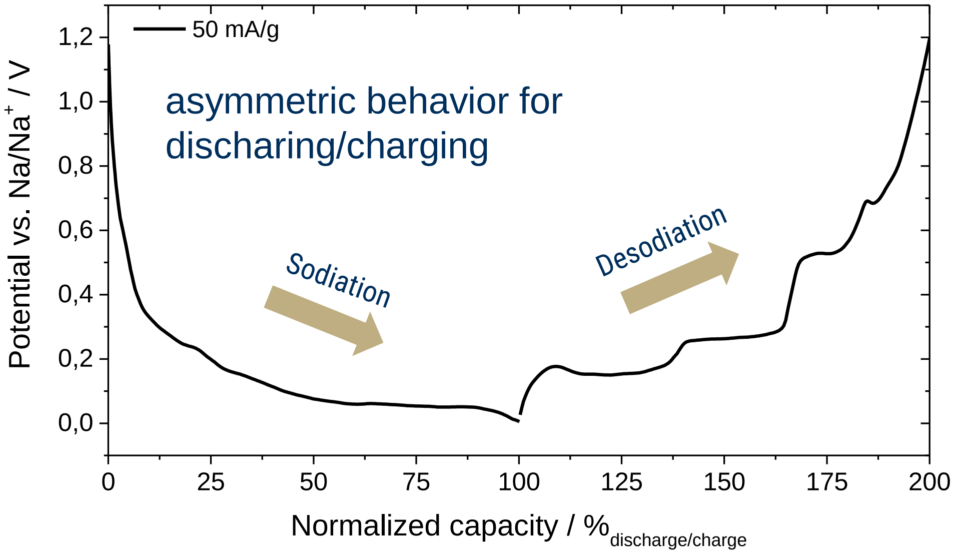
All electrodes:
60wt% Sn, 40wt% C,
q_{th}≈1.5 mAh/cm^2.

Electrode „breathes“ only by about 14%! → good cycle life

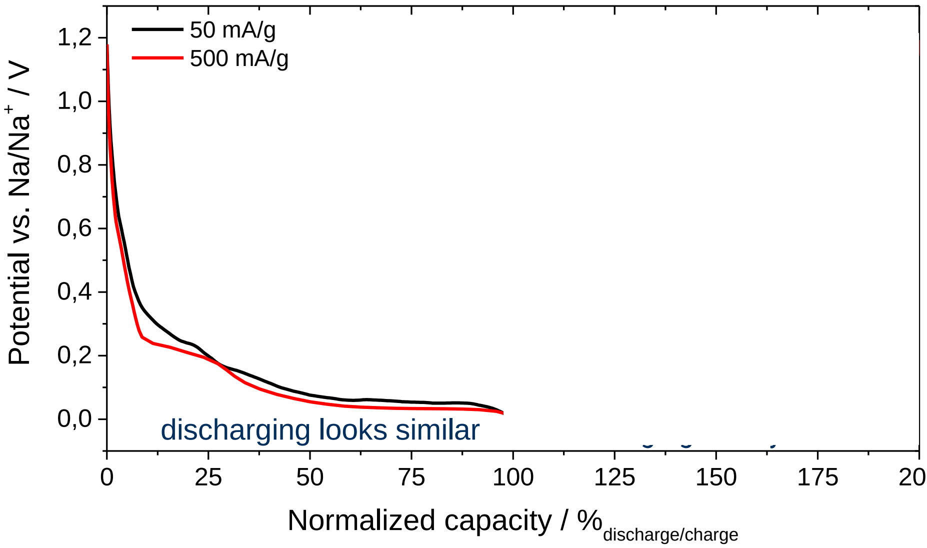
T. Palaniselvam et al., *Adv. Funct. Materials*, **2019**, DOI: 10.1002/adfm.201900790

Tin as anode for sodium-ion batteries

A closer look on the surprises when sodiating Sn



2nd cycle, 1M $NaPF_6$ in diglyme
q_{dis}(50 mA/g)= 437 mAh/$g_{composite}$
q_{ch}(50 mA/g)= 435 mAh/$g_{composite}$

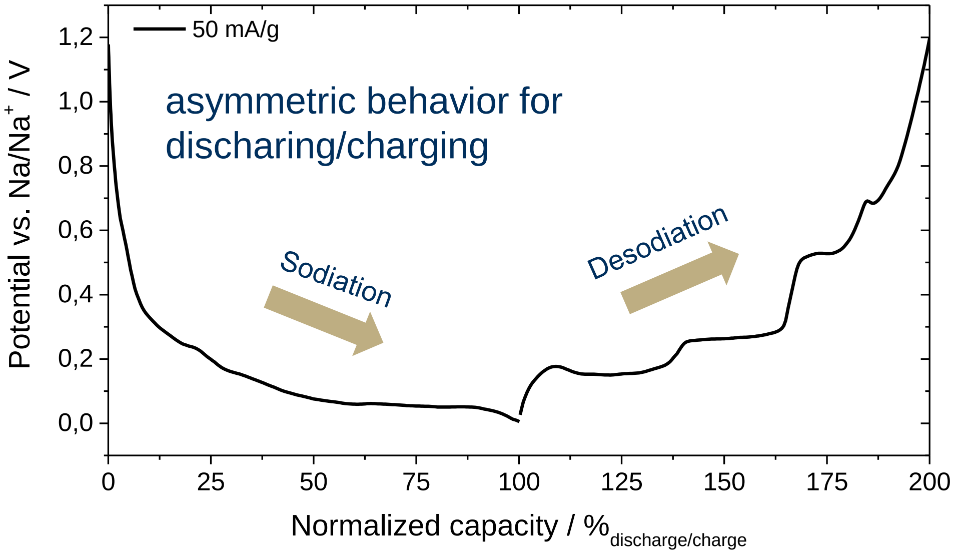


2nd cycle, 1M $NaPF_6$ in diglyme
q_{dis}(50 mA/g)= 437 mAh/$g_{composite}$
q_{ch}(50 mA/g)= 435 mAh/$g_{composite}$
q_{dis}(500 mA/g)= 386 mAh/$g_{composite}$
q_{ch}(500 mA/g)= 385 mAh/$g_{composite}$

T. Palaniselvam et al., *Adv. Funct. Materials*, **2019**, DOI: 10.1002/adfm.201900790

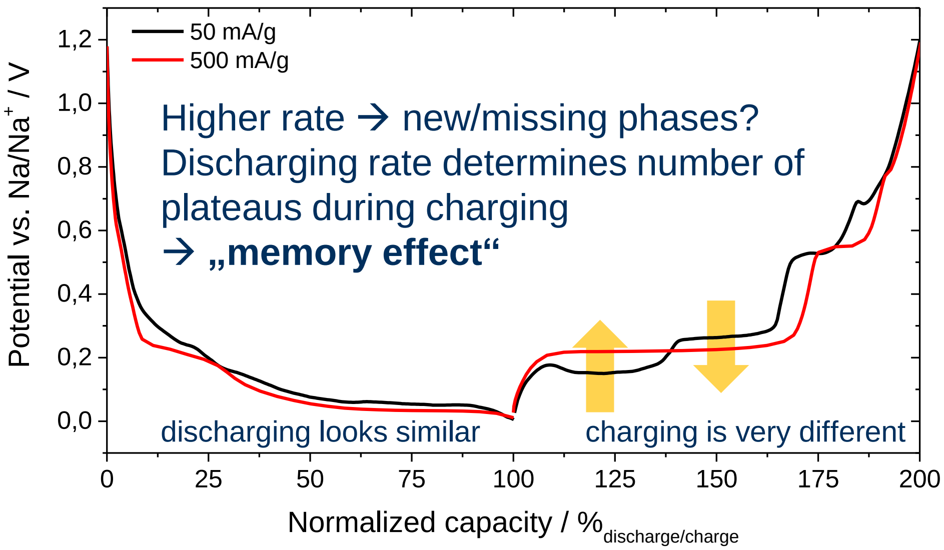
Tin as anode for sodium-ion batteries

A closer look on the surprises when sodiating Sn



asymmetric behavior for discharing/charging

2nd cycle, 1M $NaPF_6$ in diglyme
q_{dis}(50 mA/g)= 437 mAh/$g_{composite}$
q_{ch}(50 mA/g)= 435 mAh/$g_{composite}$



Higher rate → new/missing phases?
Discharging rate determines number of plateaus during charging
→ **„memory effect“**

discharging looks similar

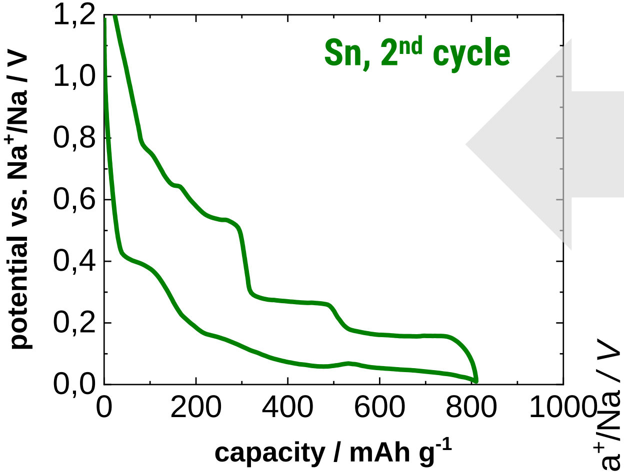
charging is very different

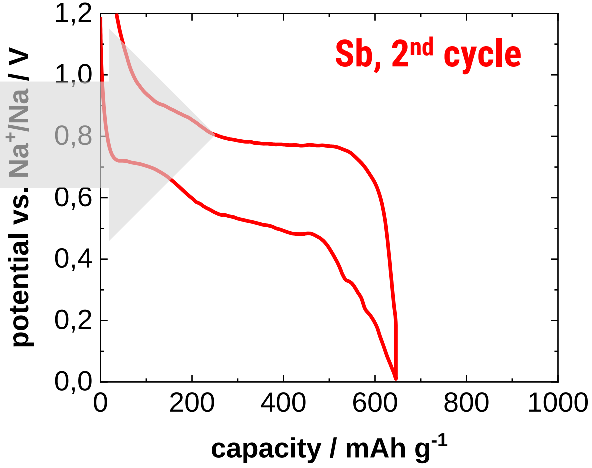
2nd cycle, 1M $NaPF_6$ in diglyme
q_{dis}(50 mA/g)= 437 mAh/$g_{composite}$
q_{ch}(50 mA/g)= 435 mAh/$g_{composite}$
q_{dis}(500 mA/g)= 386 mAh/$g_{composite}$
q_{ch}(500 mA/g)= 385 mAh/$g_{composite}$

T. Palaniselvam et al., *Adv. Funct. Materials*, **2019**, DOI: 10.1002/adfm.201900790

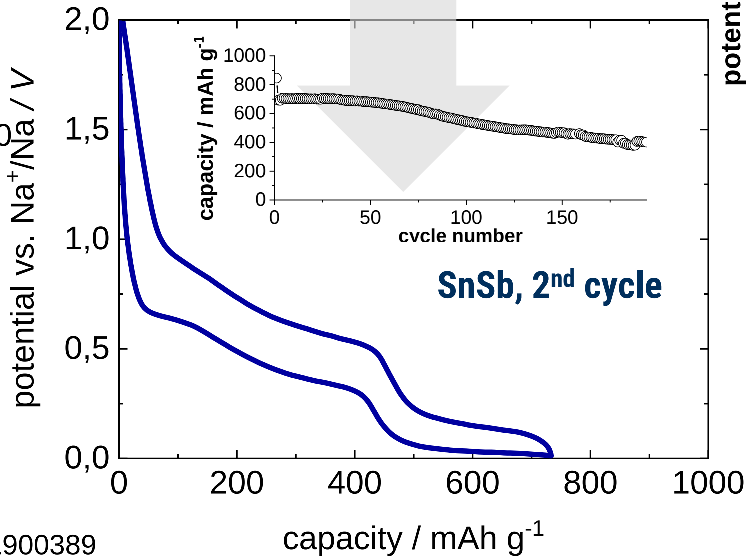
Tin as anode for sodium-ion batteries

Tailoring the voltage profile: From Sn to SnSb





All electrodes:
70 wt% metal, 30 wt%
C, q_{th}≈1.5 mAh/cm^2.



W. Brehm *et al.*, *Energy Technology*., **2019**, 1900389

Today‵s menu

Layered materials:

- Layered oxides and sulfides
- Graphite

Metals

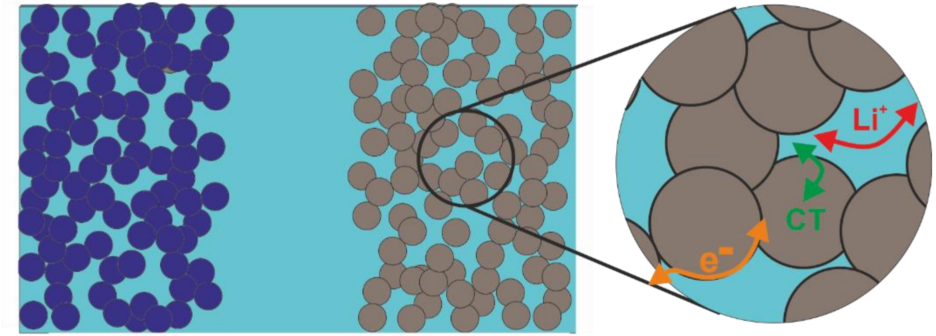
- Na and Sn

Conversion materials

- CuS – a unique electrode materials studied with tomography

From Li/Na-ion batteries to Li/Na **solid-state batteries**

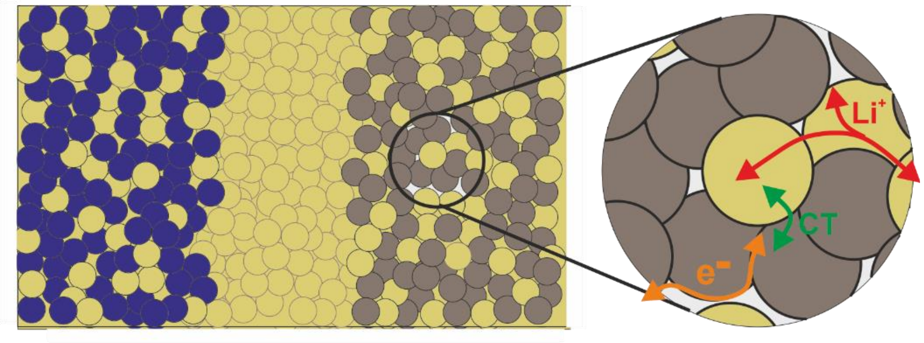
Negative electrode **Liquid electrolyte** **Positive electrode**



~ 50-80 µm ~ 50-80 µm

Liquid/solid interfaces
All voids filled with
electrolyte

Negative electrode **Solid electrolyte** **Positive electrode**



Solid/Solid interfaces
Voids remain

Solidifying batteries:

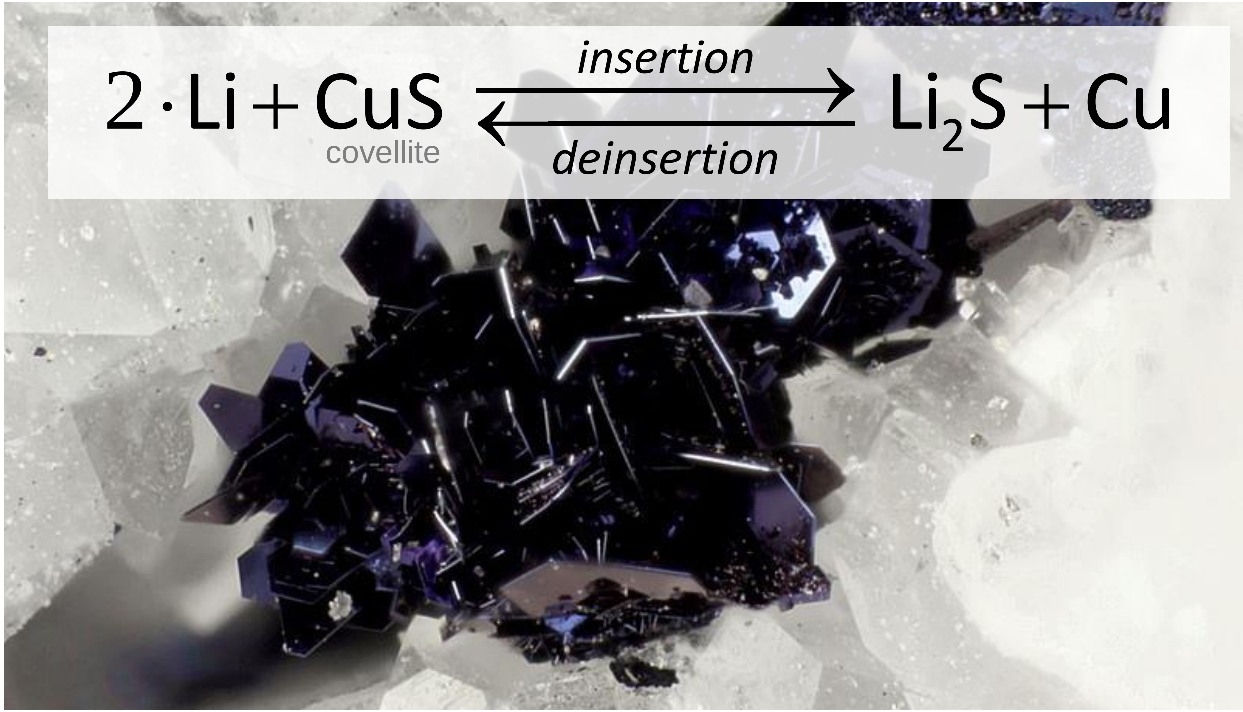
Main motivation: Higher energy density, better safety

Main difference: Mechanical properties become much more important

Copper sulfide – CuS (covellite)

Covellite: A naturally occuring mineral. Source: Mineralienatlas.de; Grube Clara, Black forest.

Copper sulfide – CuS (covellite)



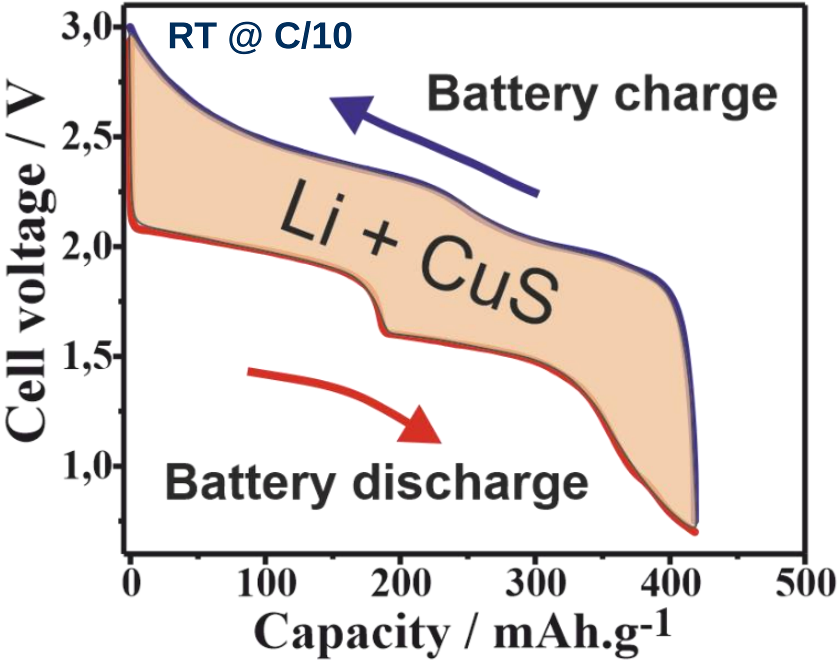
$$2\cdot\mathrm{Li}+\underset{\text{covellite}}{\mathrm{CuS}}\ \underset{\textit{deinsertion}}{\overset{\textit{insertion}}{\rightleftarrows}}\ \mathrm{Li_2S}+\mathrm{Cu}$$

Covellite: A naturally occuring mineral – even in Germany. Source: Mineralienatlas.de; Grube Clara, Black forest.

Mixed conductor (Cu^+, e^-)

Cell voltage	**q_{th}(CuS)**	**Energy**	**Vol. expansion**	**Conductivity**
1.96 V	561 mAh/g	961 Wh/kg	+ 75 %	760 S/cm

CuS as electrode for solid state batteries

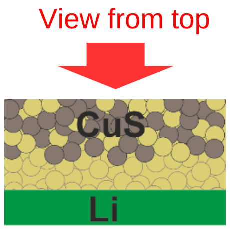


ICE: 95%
310 mAh/g after 100 cycles
q_{th}= 4.9 mAh/cm^2
Cathode: 70wt% CuS, 30 wt% Li_3PS_4,
no conductive additive

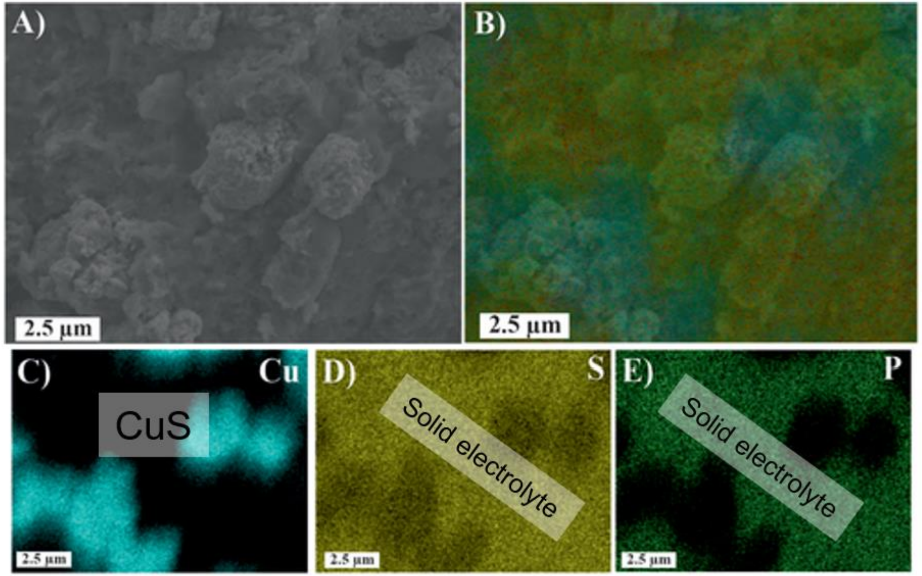
A. L. Santosha *et al.*, *Adv. Energy Materials*., **2020**, DOI: 10.1002/aenm.202002394

CuS as electrode for solid state batteries

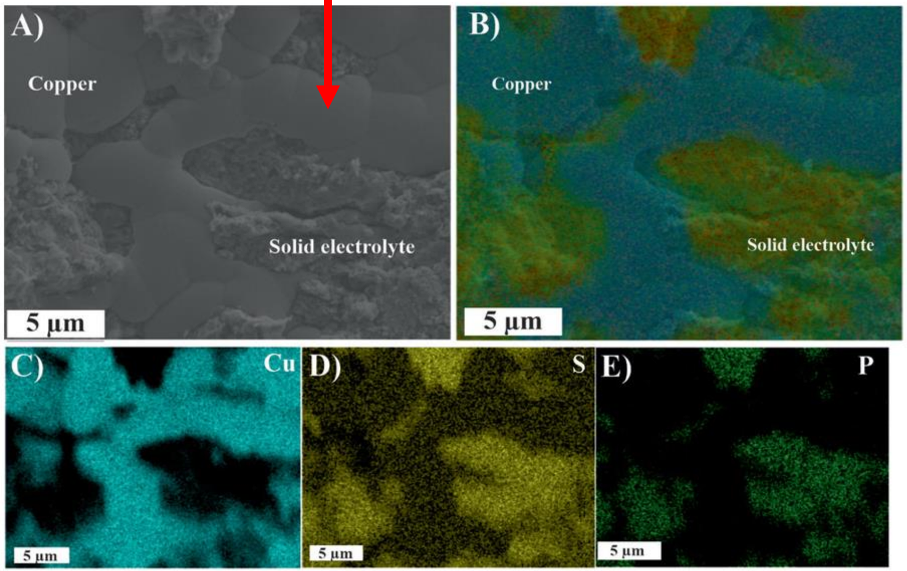
Very large crystals form during discharge.
Ideal case for tomography!



Before discharge



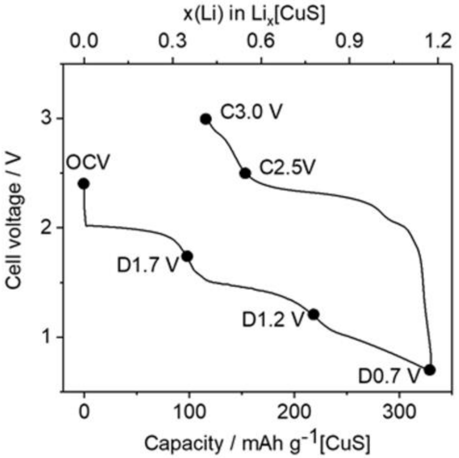
After discharge



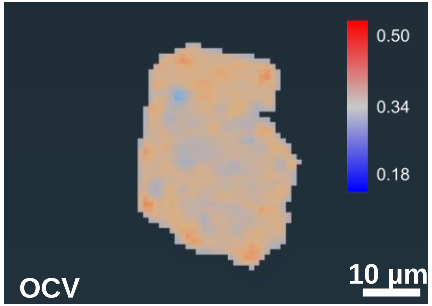
A. L. Santosha *et al.*, *Adv. Energy Materials*., **2020**, DOI: 10.1002/aenm.202002394 (cooperation with JLU Giessen, BASF)

CuS as electrode for solid state batteries

Tomography study

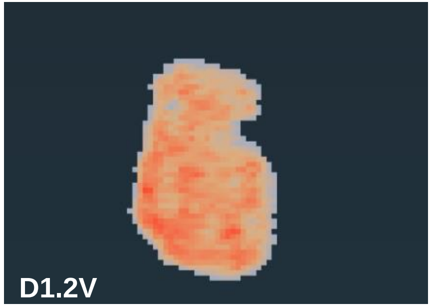


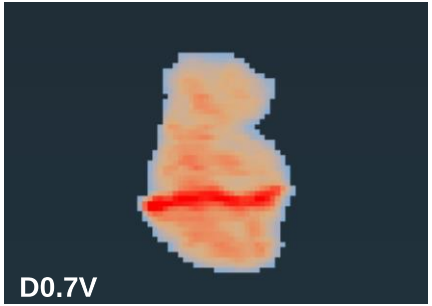
Before lithiation - CuS



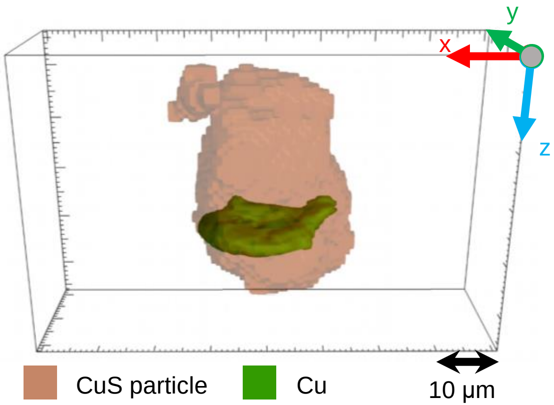
Formation of Cu_2S and Li_2S

Formation of Cu_2S and Li_2S





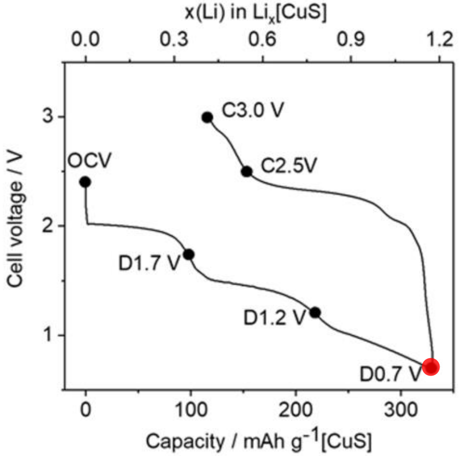
Formation of Cu and Li_2S

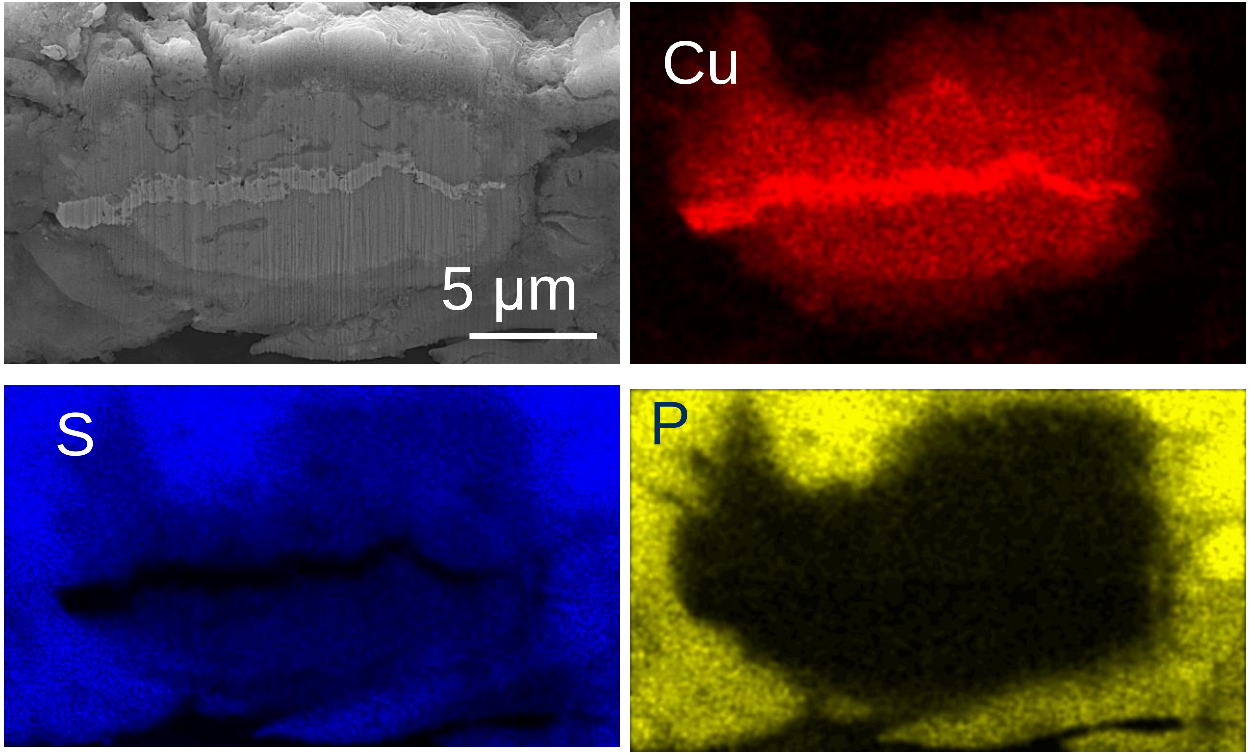


Zhenggang Zhang *et al.*, *Adv. Energy Materials*., **2022**, DOI: 10.1002/aenm.202203143
In cooperation with Ingo Manke group at HZB

CuS as electrode for solid state batteries

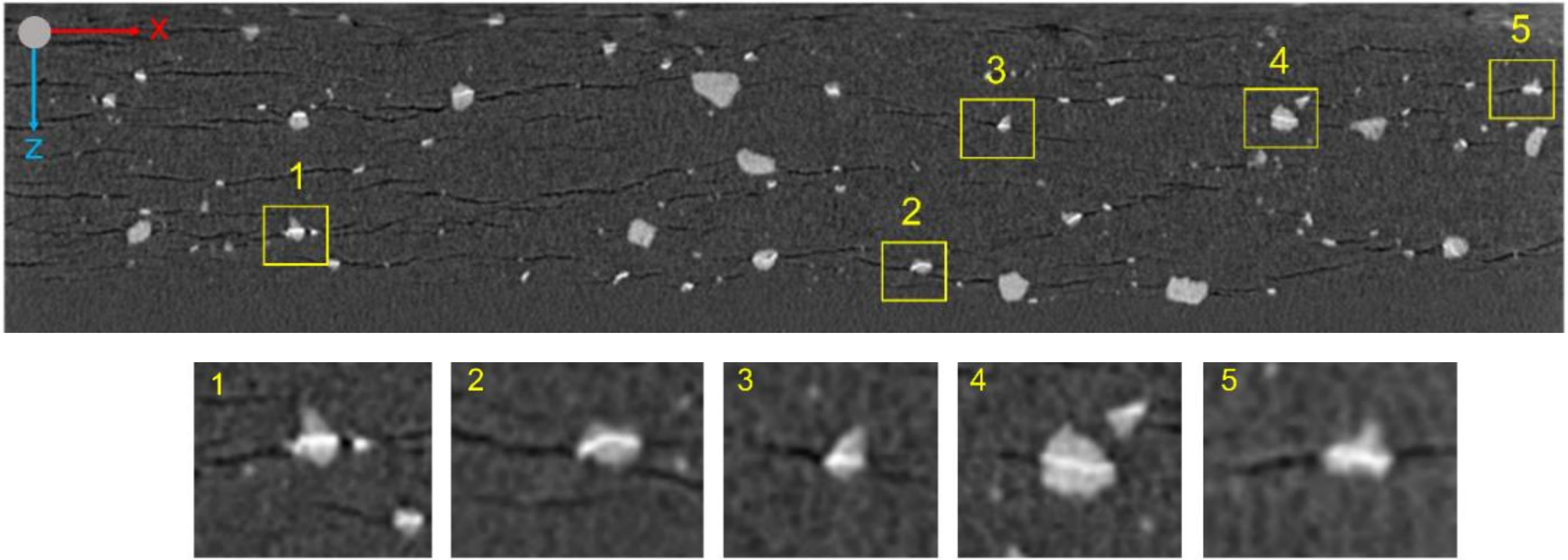
FIB/SEM study





CuS as electrode for solid state batteries

Tomography study



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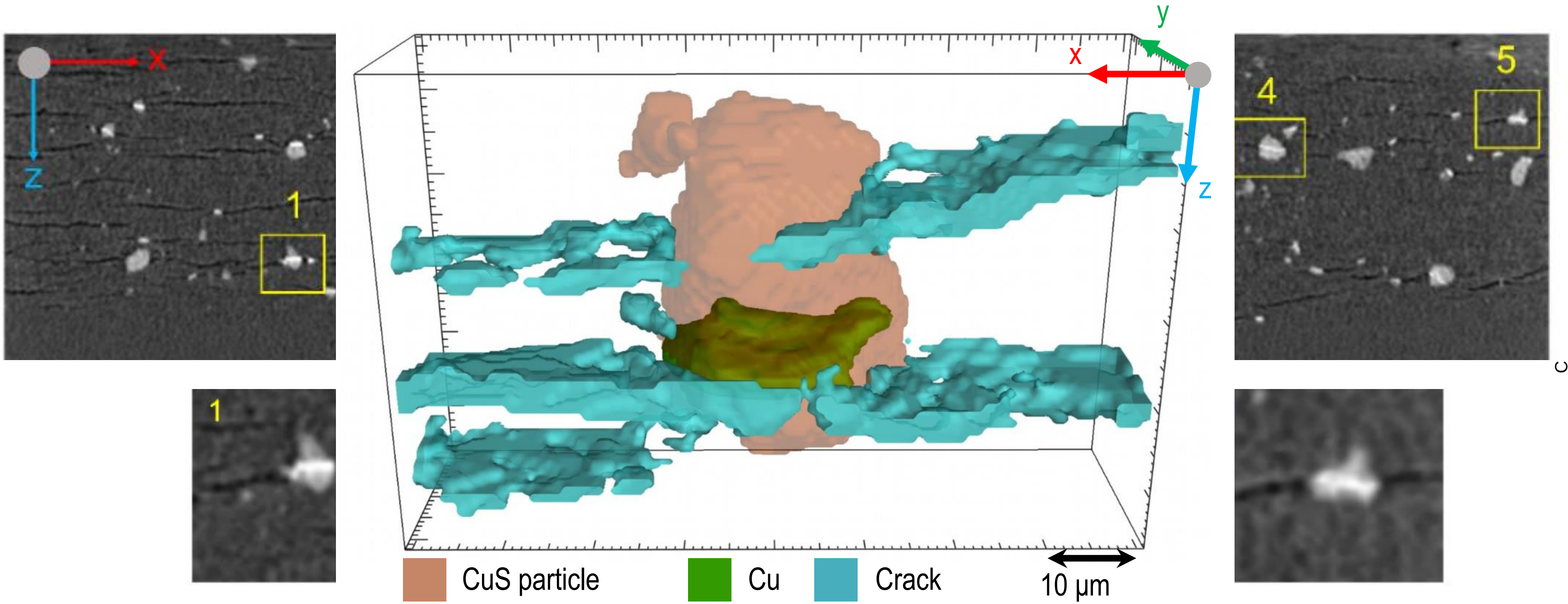

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Take home message

- Na-ion batteries are entering the market! There is great potential for improving electrode materials.

- Intercalation of solvated ions into solid host structures enriches the chemical space of battery materials

- Understanding electrode materials requires many analytical tools and input from different science disciplines. Important contributions can be made through operando studies and synchrotron / neutron facilities.

- Solid-state batteries are another technology of great interest. Mechanical properties (crack formation, contact loss,….) add to the complexity

Questions?

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Cooperation partners of results from this talk: Giessen (Janek), Jülich (Kaghazchi), ZSW (Axmann), HZB (Manke), BESSY/DESY synchrotrons

Postdoc position available

Na-sulfur solid state battery project
(Deadline July 26), 2 years

Sodium Battery Symposium (SBS-5)

Berlin, Sept 23-25 2024 (updates on Linkedin)
https://www.helmholtz-berlin.de/events/international-sodium-battery-symposium/index_en.html