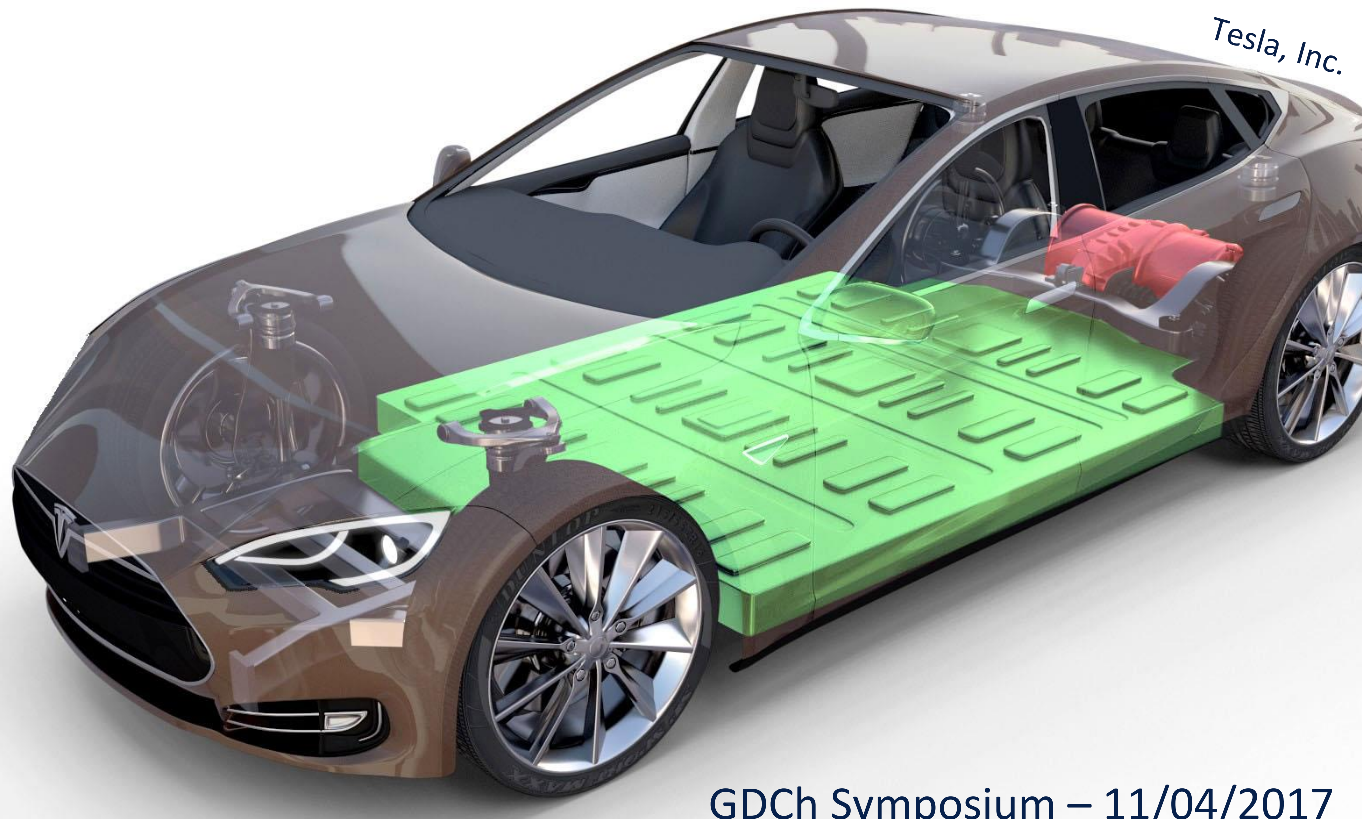
Understanding Lithium-ion Batteries –
Cryo and *in situ* TEM for Materials Science

Prof. Dr. Benjamin Butz

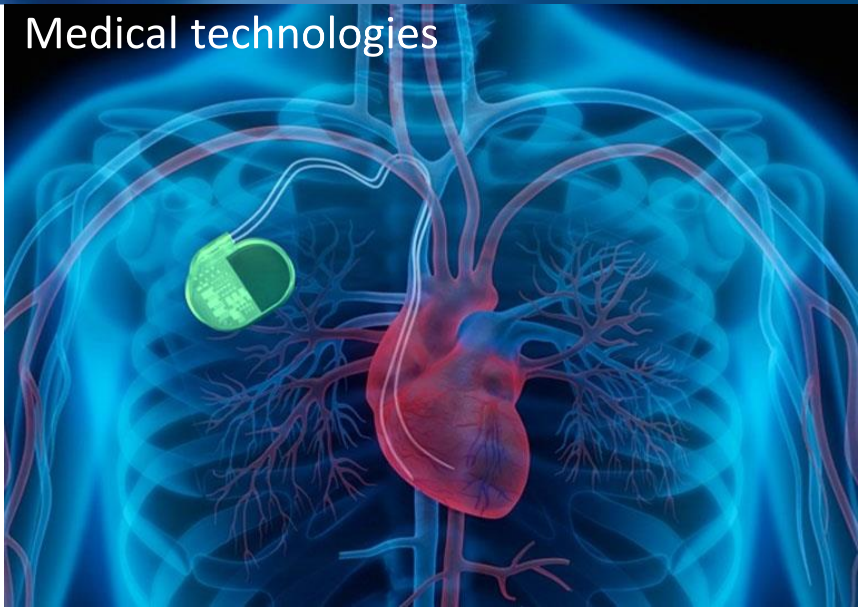
Micro- and Nanoanalytics & –Tomography Group
University of Siegen, Germany



UNIVERSITÄT SIEGEN

GDCh Symposium – 11/04/2017

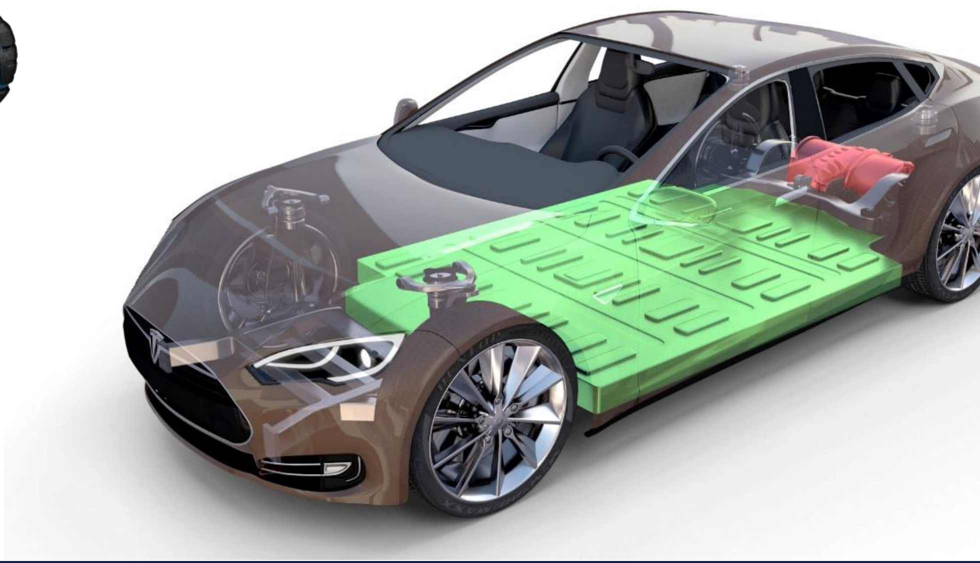
Battery Applications



Devices

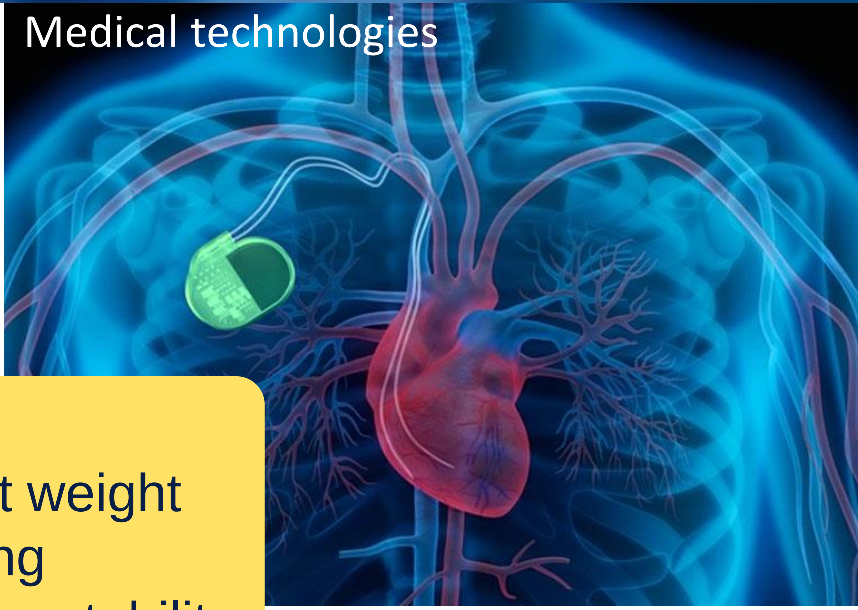
Power tools

Vehicles



Tesla, psdesign1/Fotolia.de, Samsung, Asus, Bosch

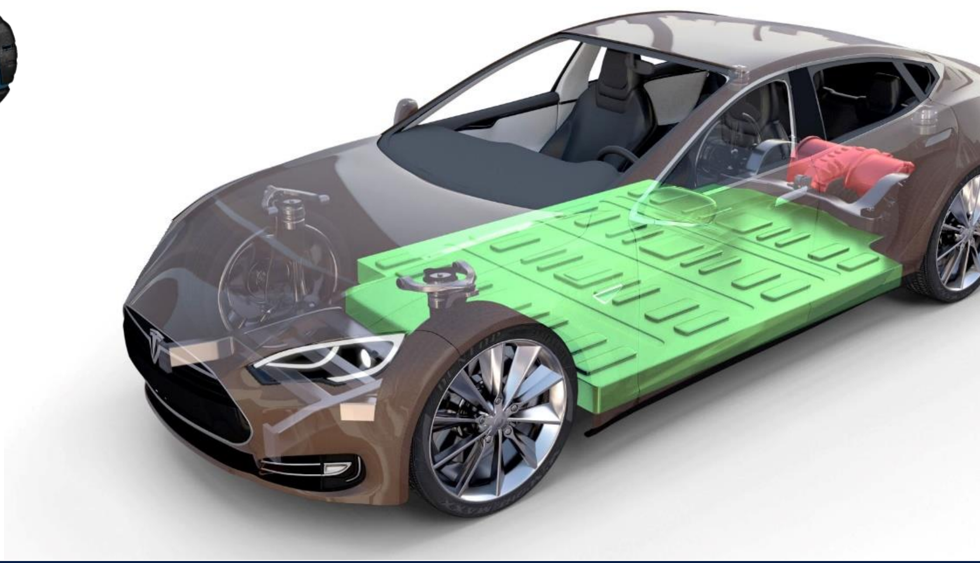
Battery Applications



Safety
Capacity – Light weight
Fast charging
Durability – Cycling stability

Devices

Vehicles



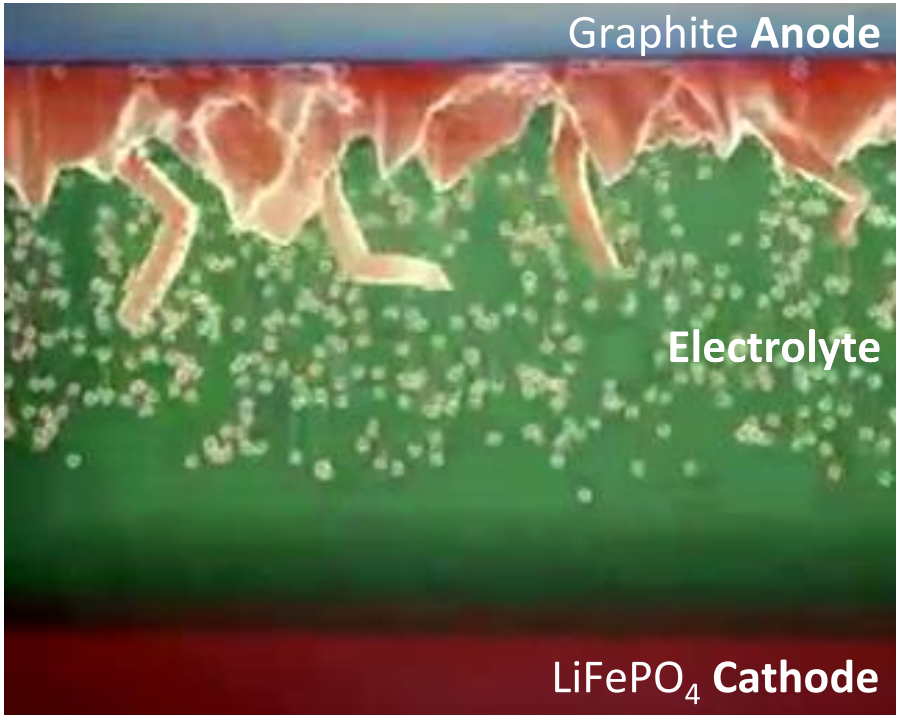
Tesla, psdesign1/Fotolia.de, Samsung, Asus, Bosch

Safety Issues & Degradation

Intended failure of LiPo battery

Real battery

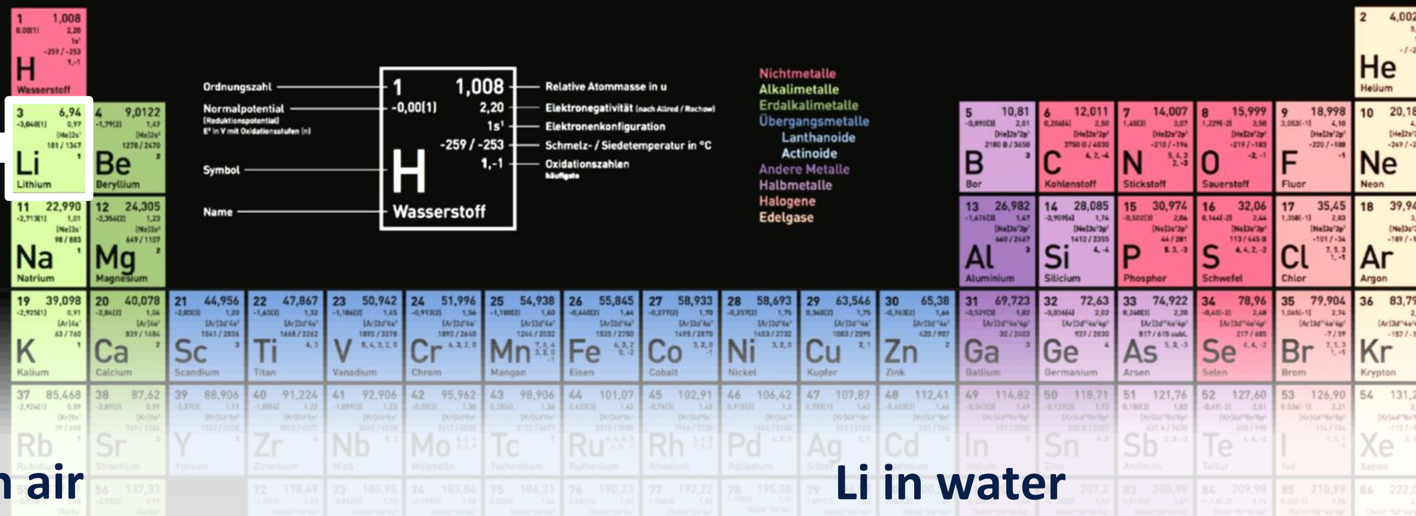
Charging
Deposition of Li at anode
Li-dendrite formation
Internal short circuit



NewsD2 & Oak Ridge National Laboratory/Youtube.com

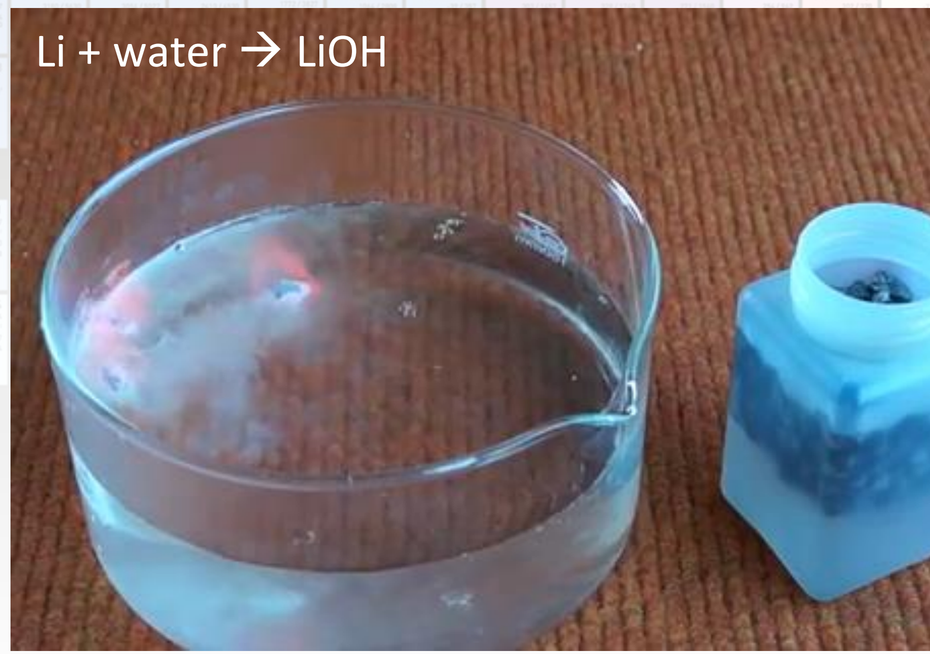
Extreme Reactivity of Lithium

- **Lightest** solid element/metal
  0.5 g/cm³
- **One of the most reactive elements**



Li in air

Li in water



Science247/TeacherTube.com

Thoisoi2/Youtube.com

Targeted Materials Development

Preventing battery failure

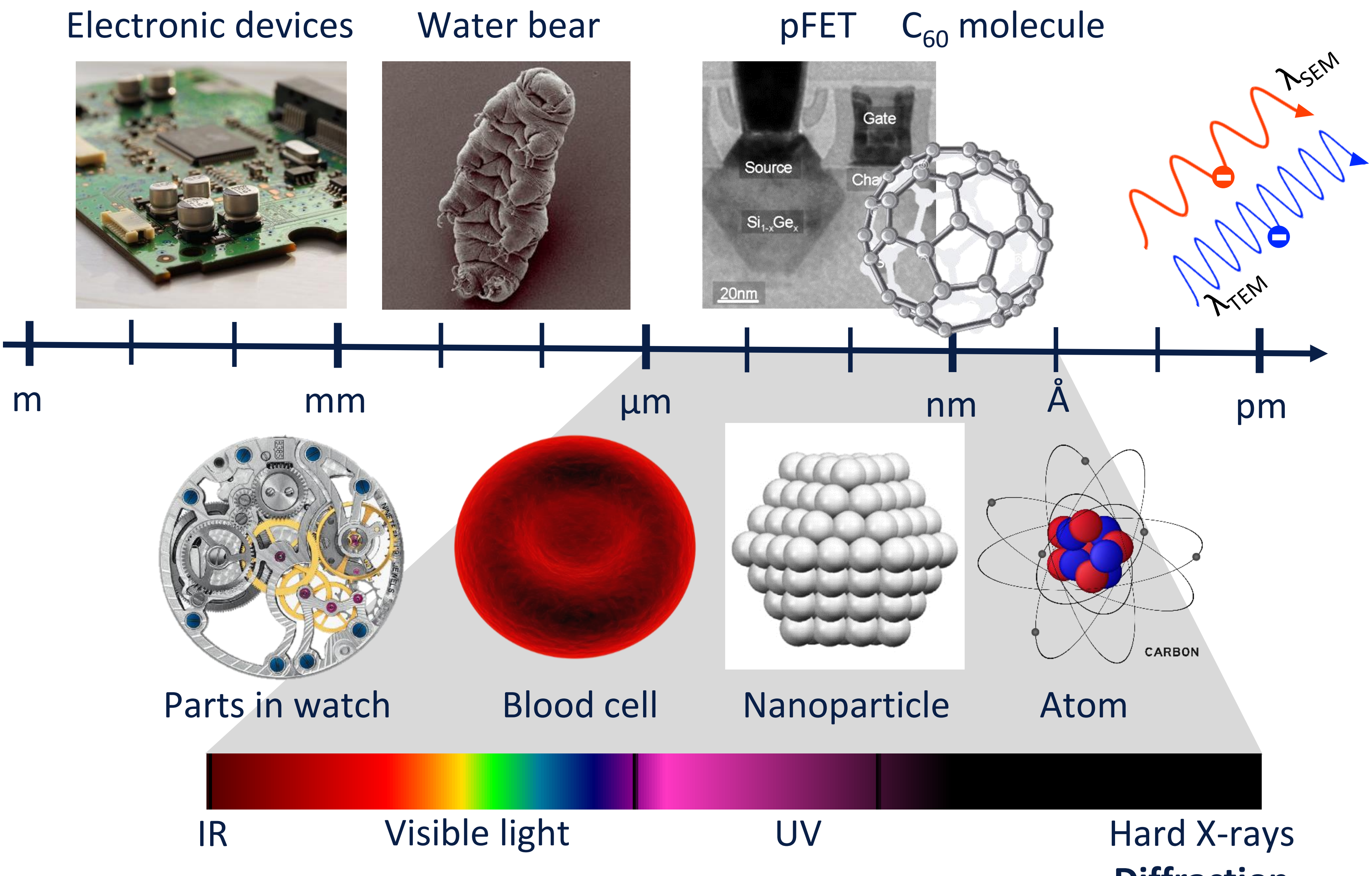
Local properties, morphology, structure and chemistry
of
Li dendrites, cell parts, interfaces

High-capacity batteries with pure-Li anode

Properties of reaction products of Li with O_2, N_2, H_2O, …

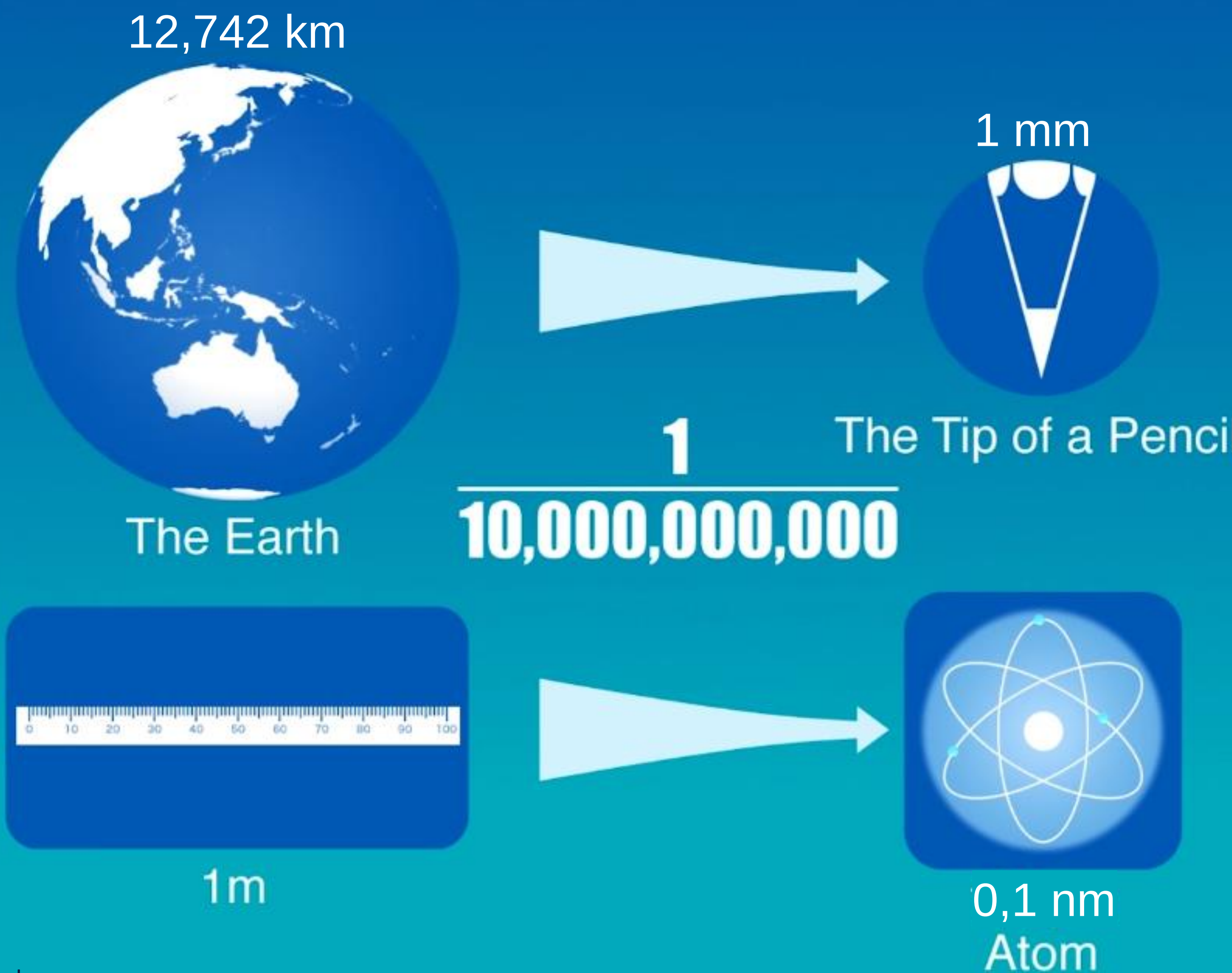
Characterization on very small length scales down to the nanometer and atomic scale

Size Scales — How small is a Nanometer?



Quian et al, PNAS 109 (2012) 696, wikipedia.com, piaget.de

How small is an Atom?



Hitachi/Youtube.com

How to Probe the nm-Level — LM vs. TEM

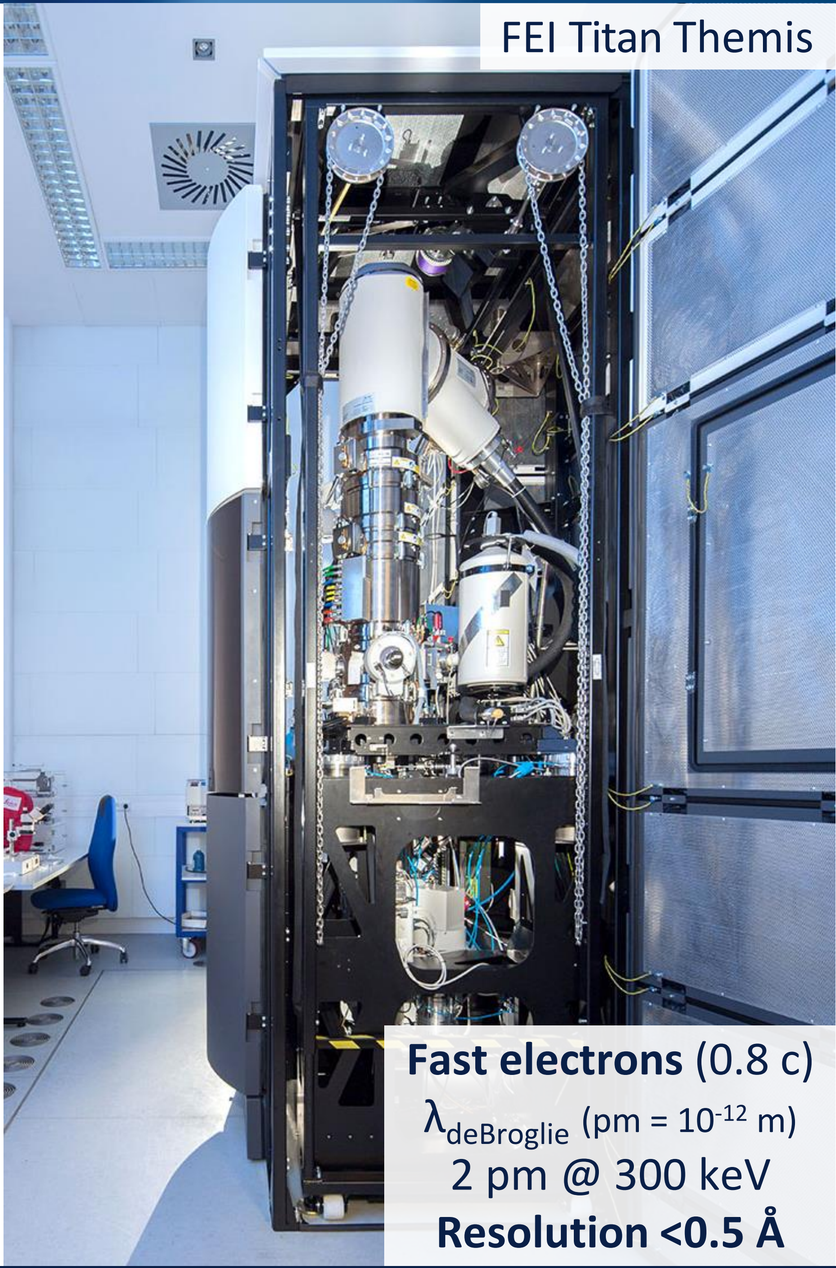
Resolution (Ernst Abbe) $d=\frac{\lambda}{2n\sin\alpha}$

λ=[400 nm, 800 nm]

Light Microscope

leica-microsystems.com

Transmission Electron Microscope



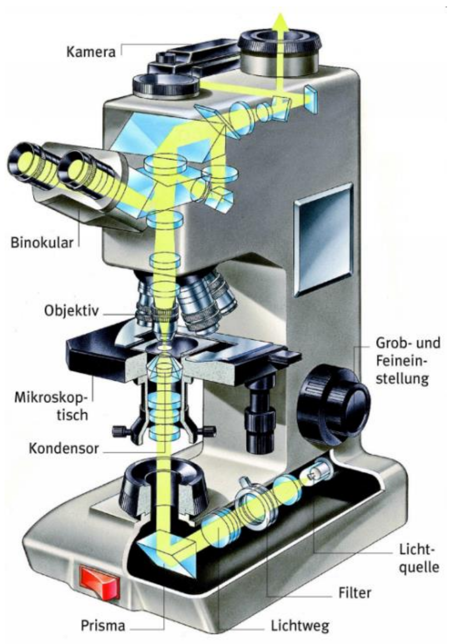
FEI Titan Themis

Fast electrons (0.8 c)

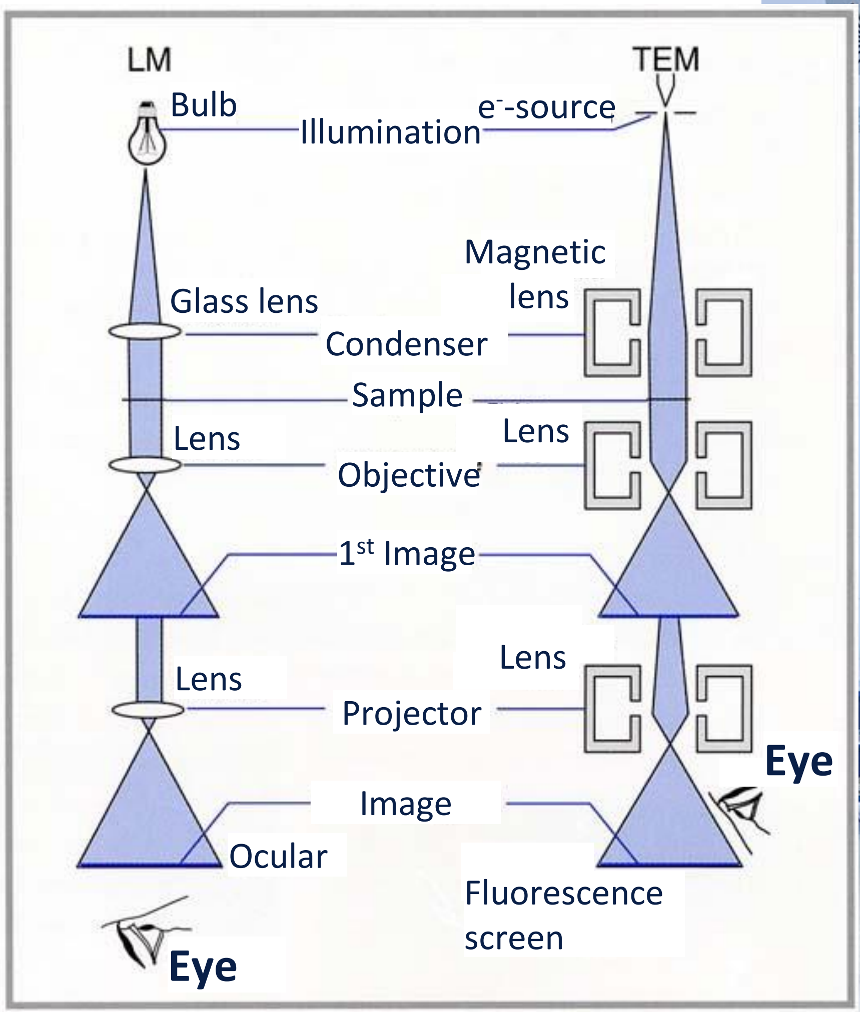
$\lambda_{deBroglie}$ (pm = 10^{-12} m)

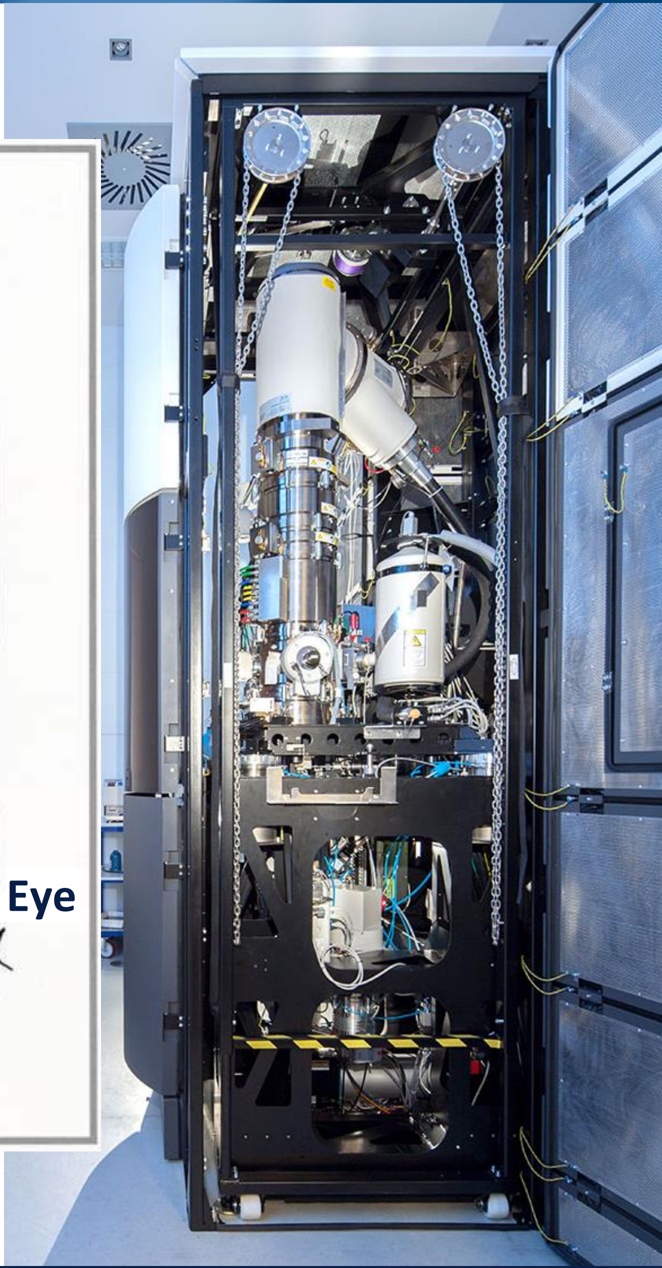
2 pm @ 300 keV

Resolution <0.5 Å

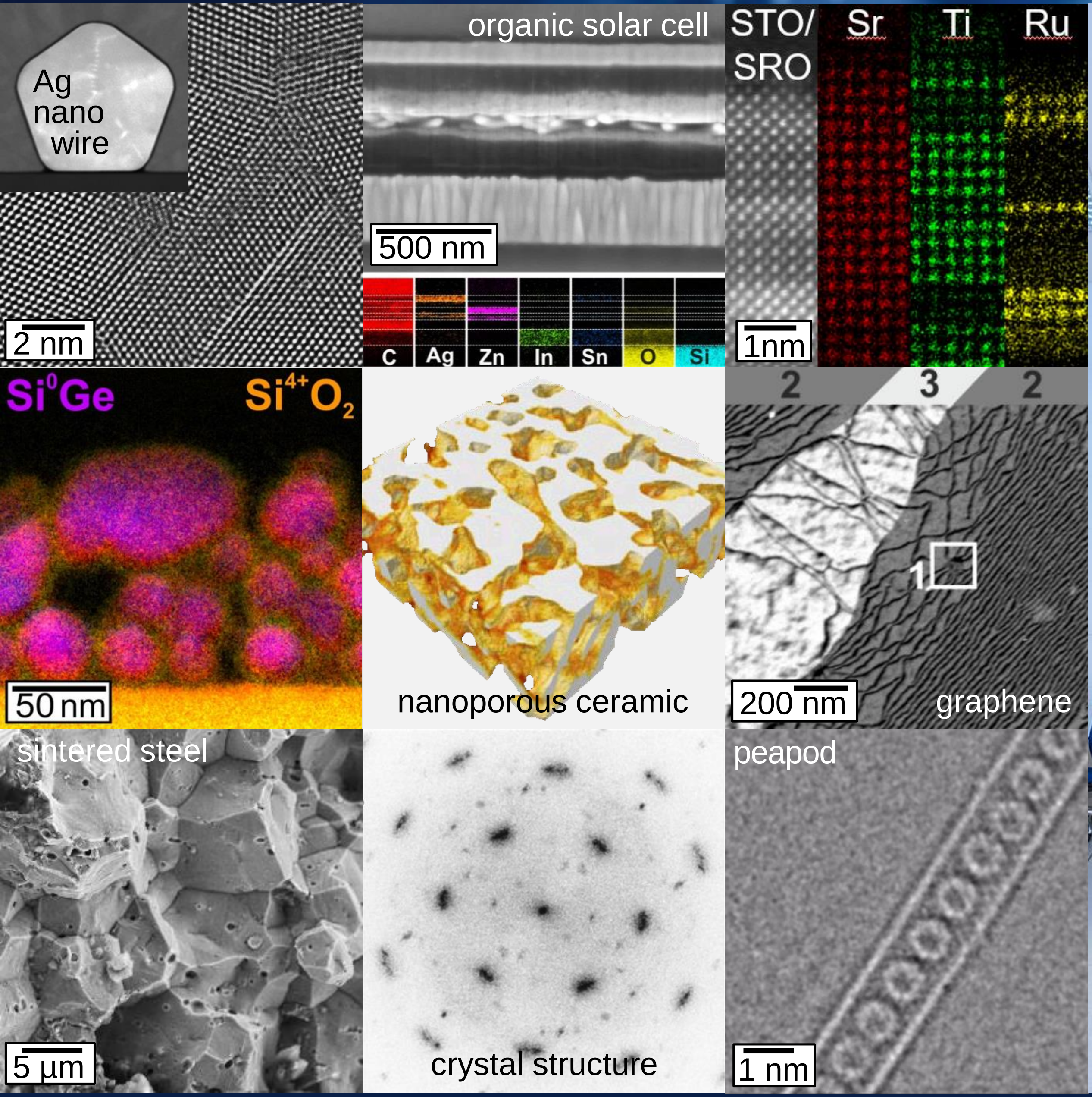


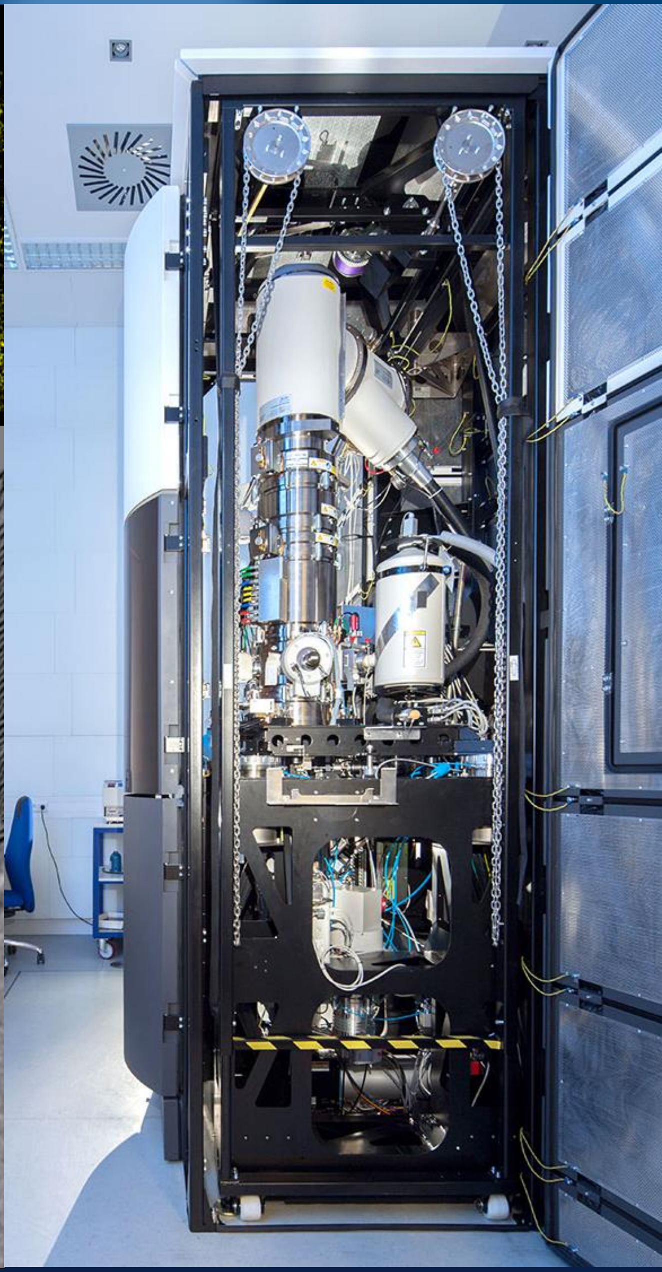
Functional principle





Probing Materials at the nm- and Atomic Level





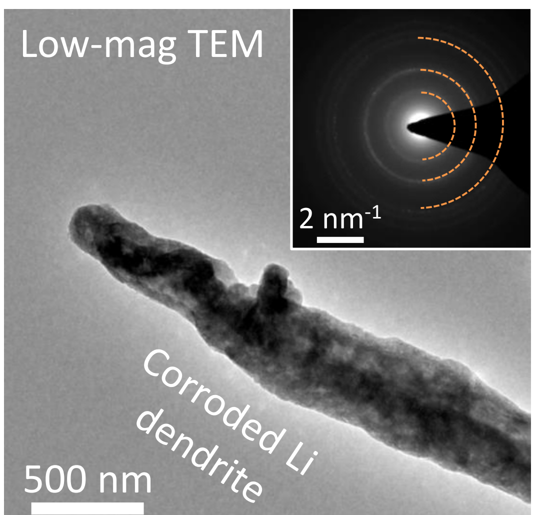
Probing Battery Materials at the nm-Level

1) Characterization of Li dendrites, cell parts, interfaces
2) Systematic study of reaction of Li with O_2, N_2, H_2O

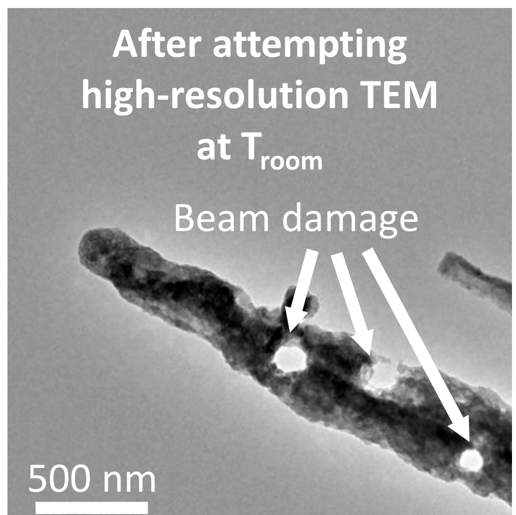
Regular TEM sample handling in air & TEM analyses in high vacuum

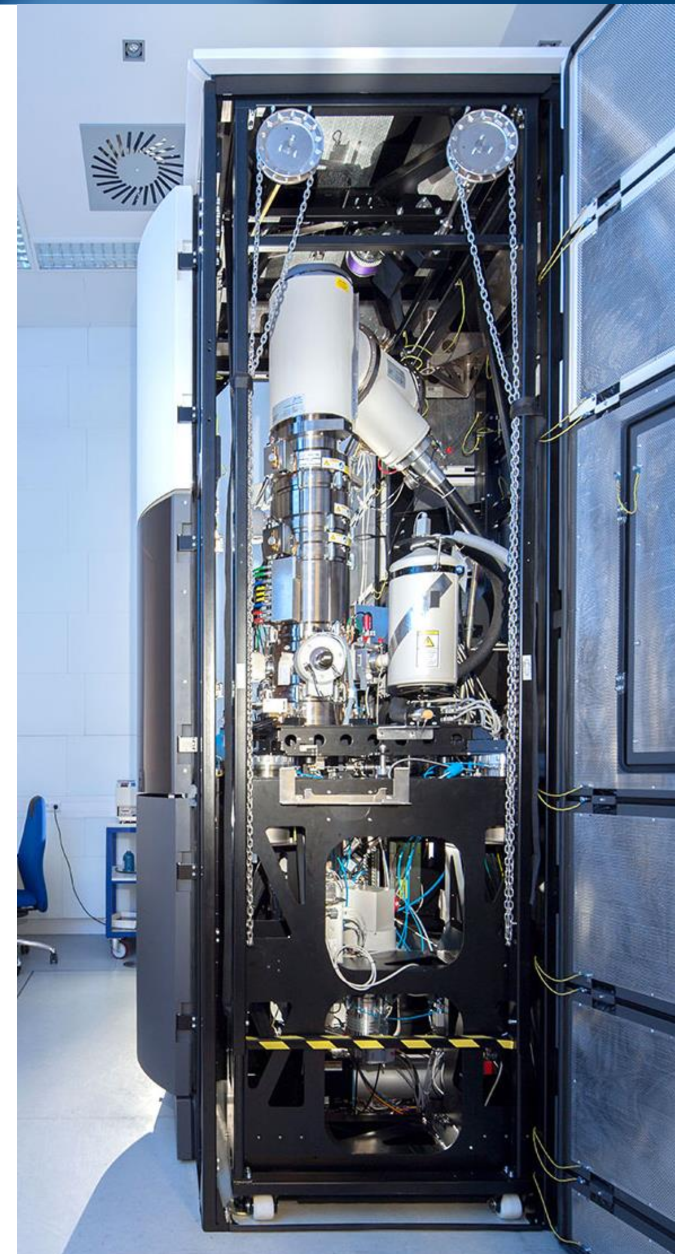
→ How to investigate reactive Li and battery parts?
→ How to study Li reactions (corrosion, passivation)

Transfer through air



Li electron-beam sensitive!





Probing Battery Materials at the nm-Level

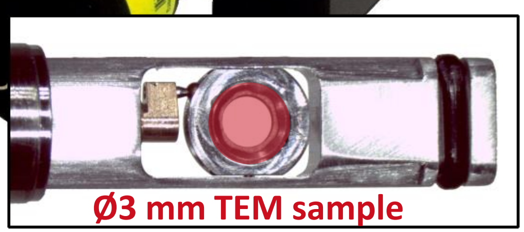
1) Battery disassembly
+ TEM sample preparation
in **Ar environment**

TEM characterization
at -196 °C (LN_2)
Reduced Li reactivity
& Li mobility
(+ enhanced vacuum)

Ø3 mm
TEM
sample

2) Cooling with LN_2

3) Transfer w/
cryo-holder

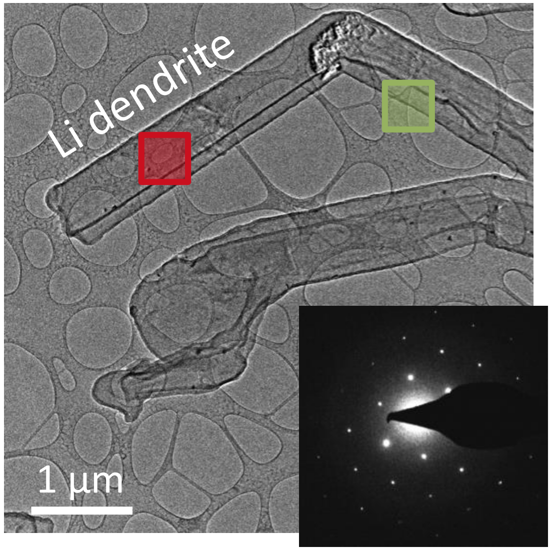


4) TEM characterization
under **cryo-conditions**

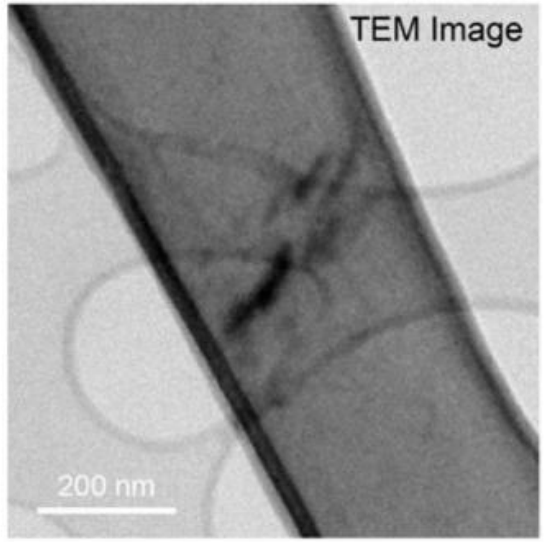
Li et al, Science 358 (2017) 506

Characteristics of Li-metal dendrites @ -196 °C

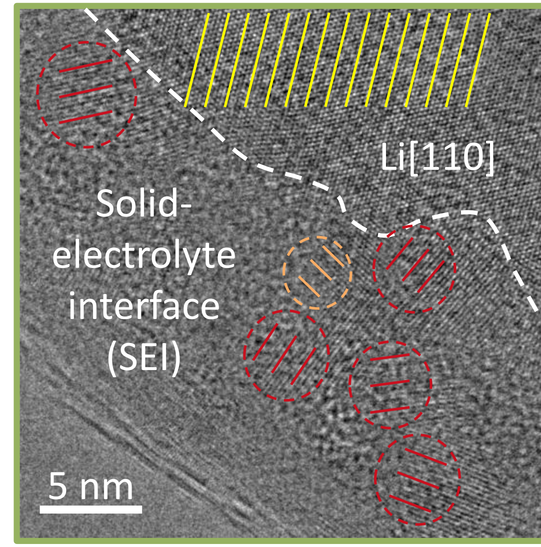
Single-crystalline dendrites

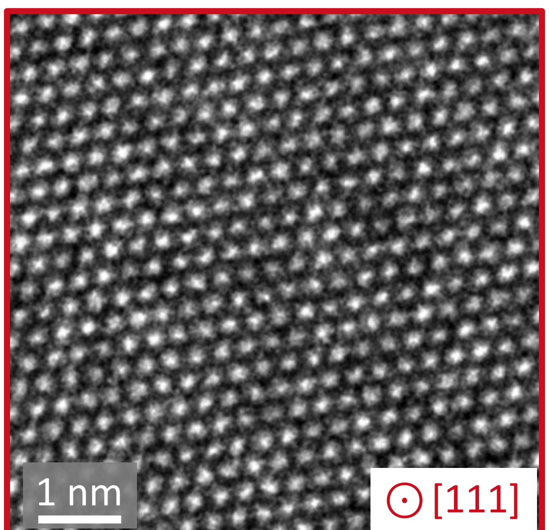


Pure Li core

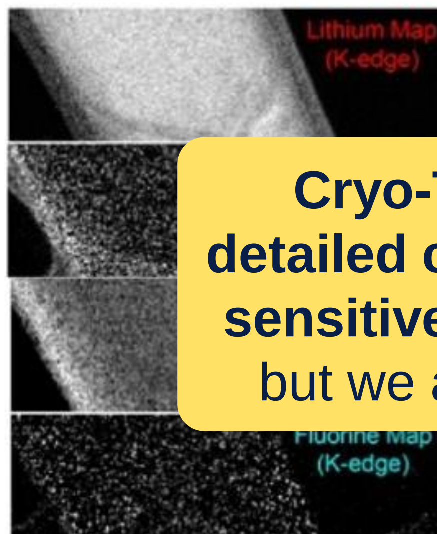


Complex multiphase SEI

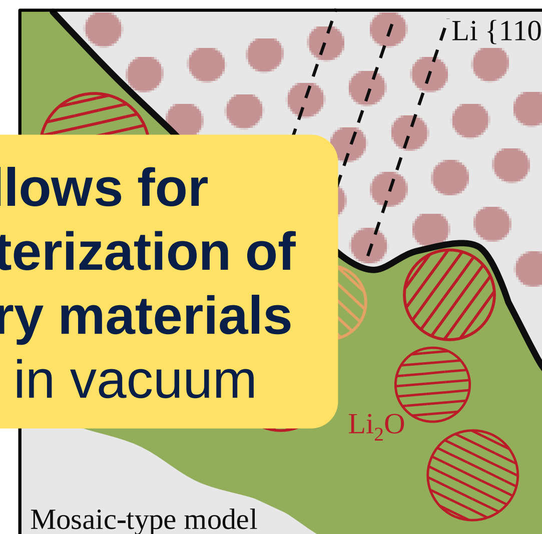




Atomic-resolution TEM



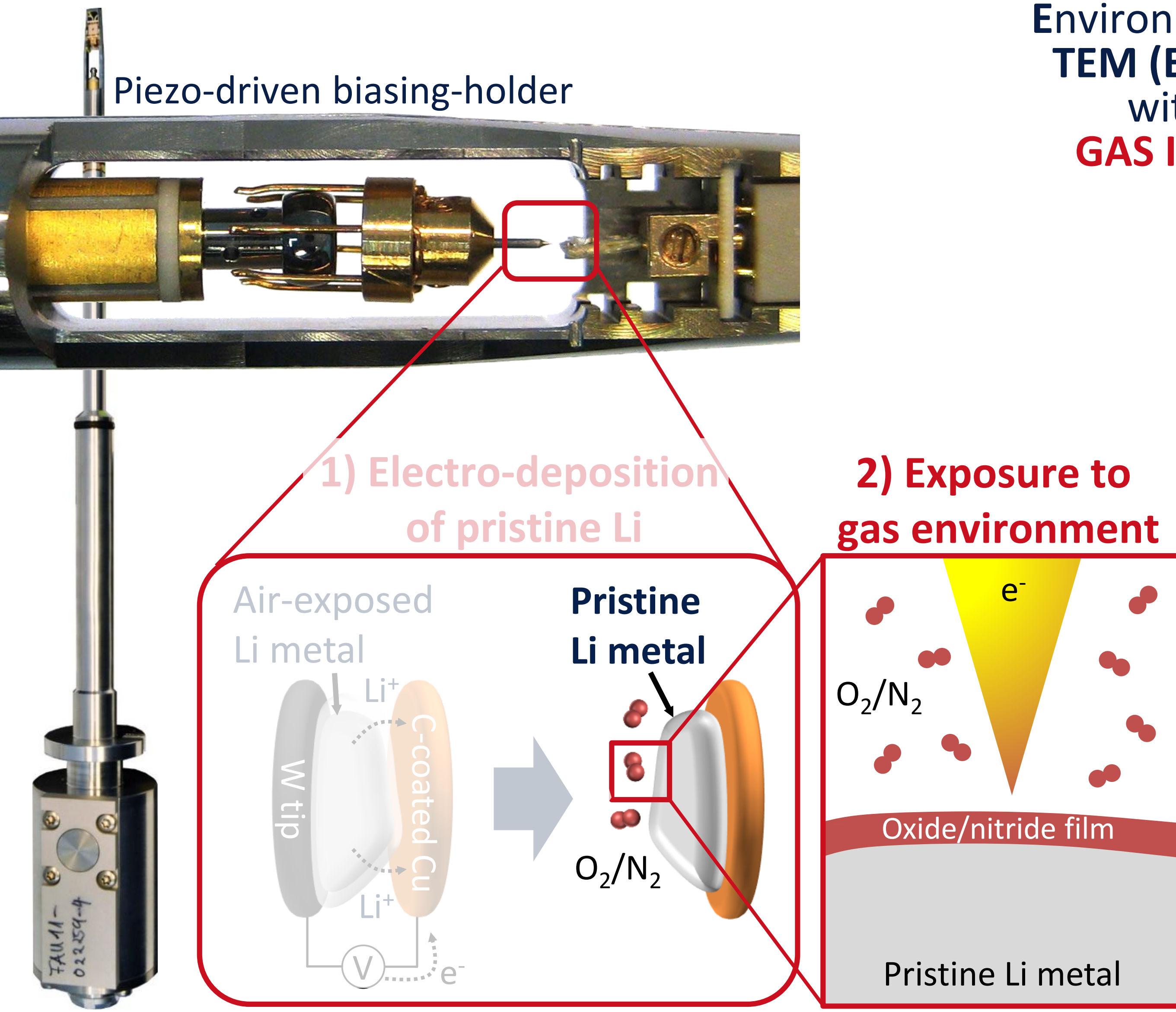
Energy-filtered TEM

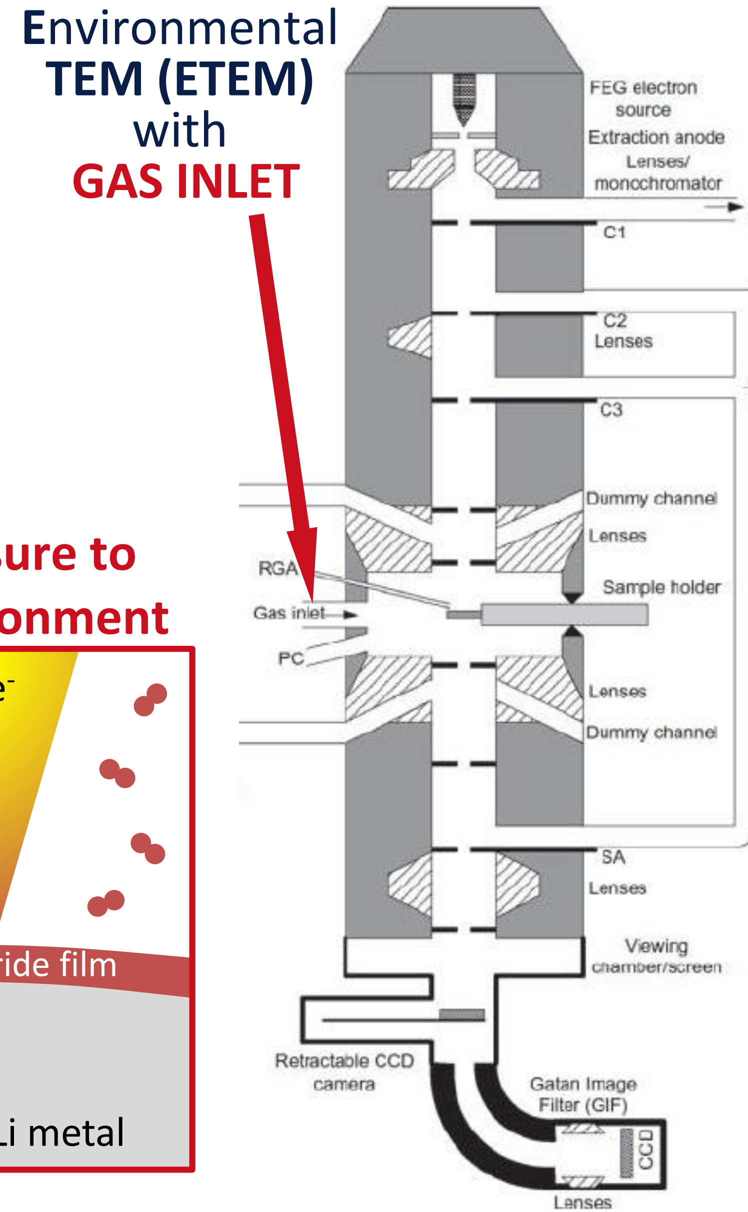


Cryo-TEM allows for detailed characterization of sensitive battery materials
but we are still in vacuum

Li et al, Science 358 (2017) 506

Reactions of Metallic Li by *in situ* TEM

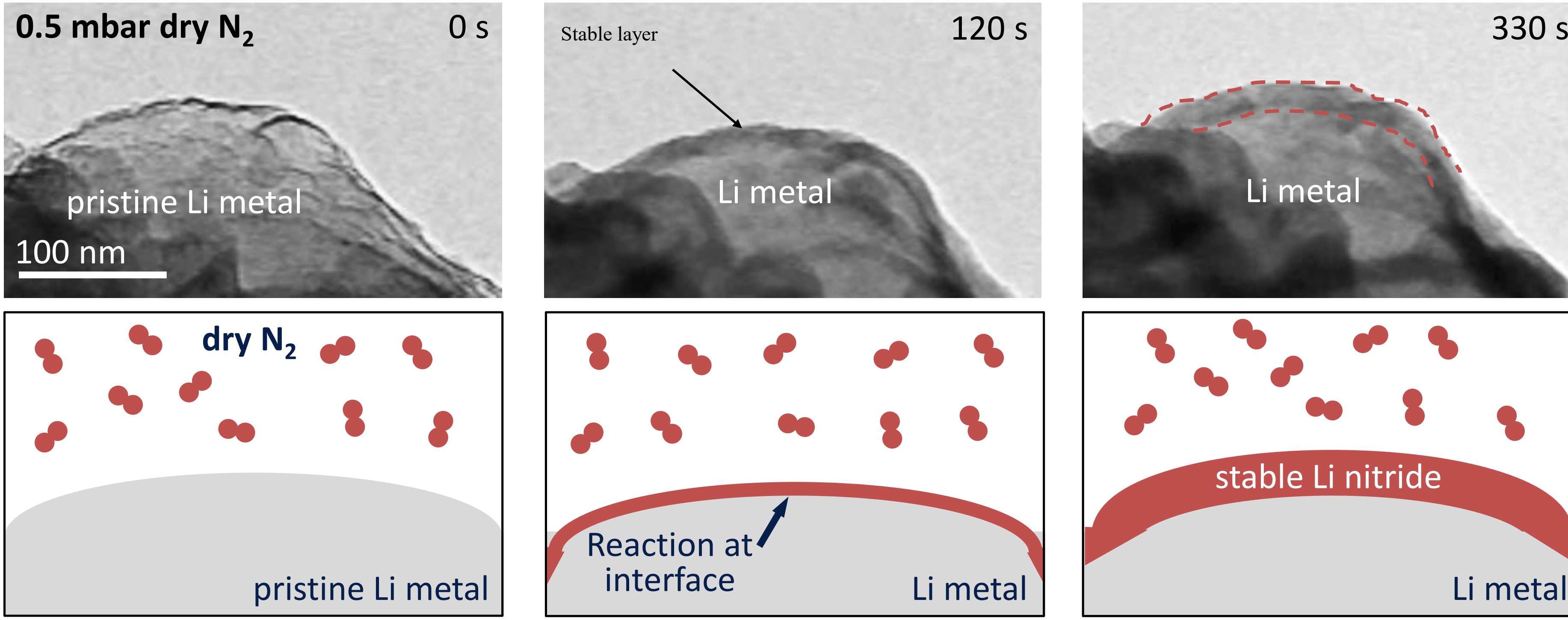




Li et al, Nano Lett. 17 (2017) 5171–5178

Passivation of Li in dry N_2

$6Li + N_2 \rightarrow 2Li_3N$ (at Li/Li_3N interface)

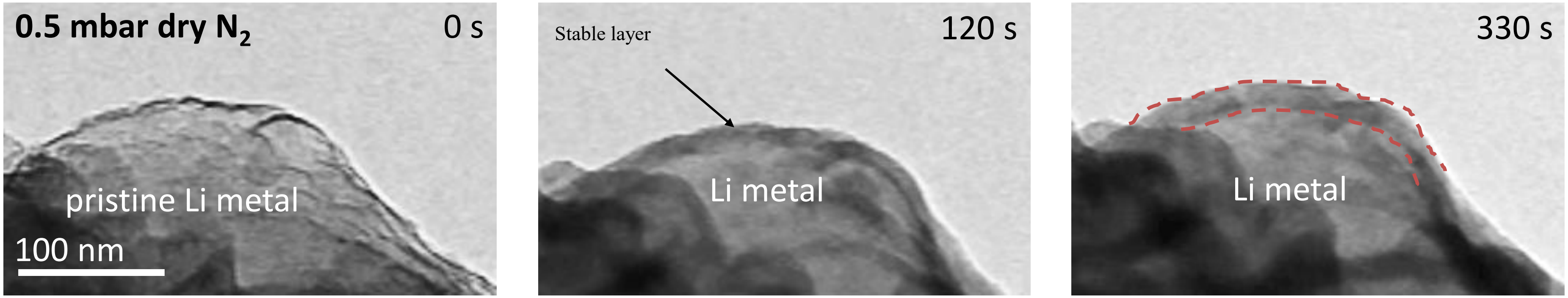


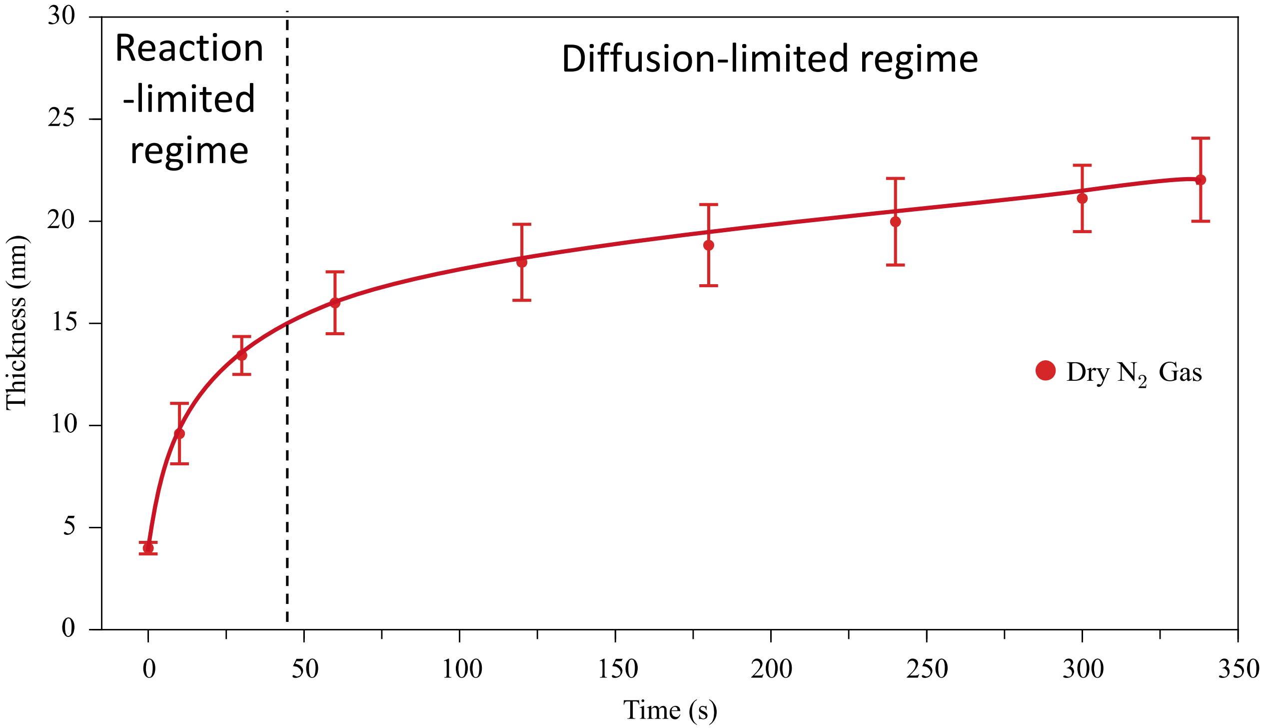
Reaction-limited regime

Diffusion-limited regime

Passivation of Li in dry N_2

6Li + N_2 → 2Li_3N (at Li/Li_3N interface)

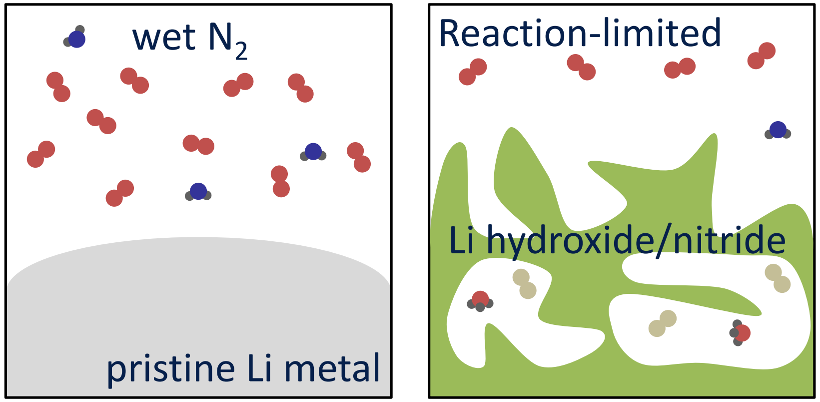




Passivation of Li in dry N_2

Video not available

Corrosion of Li in humid environment (air)

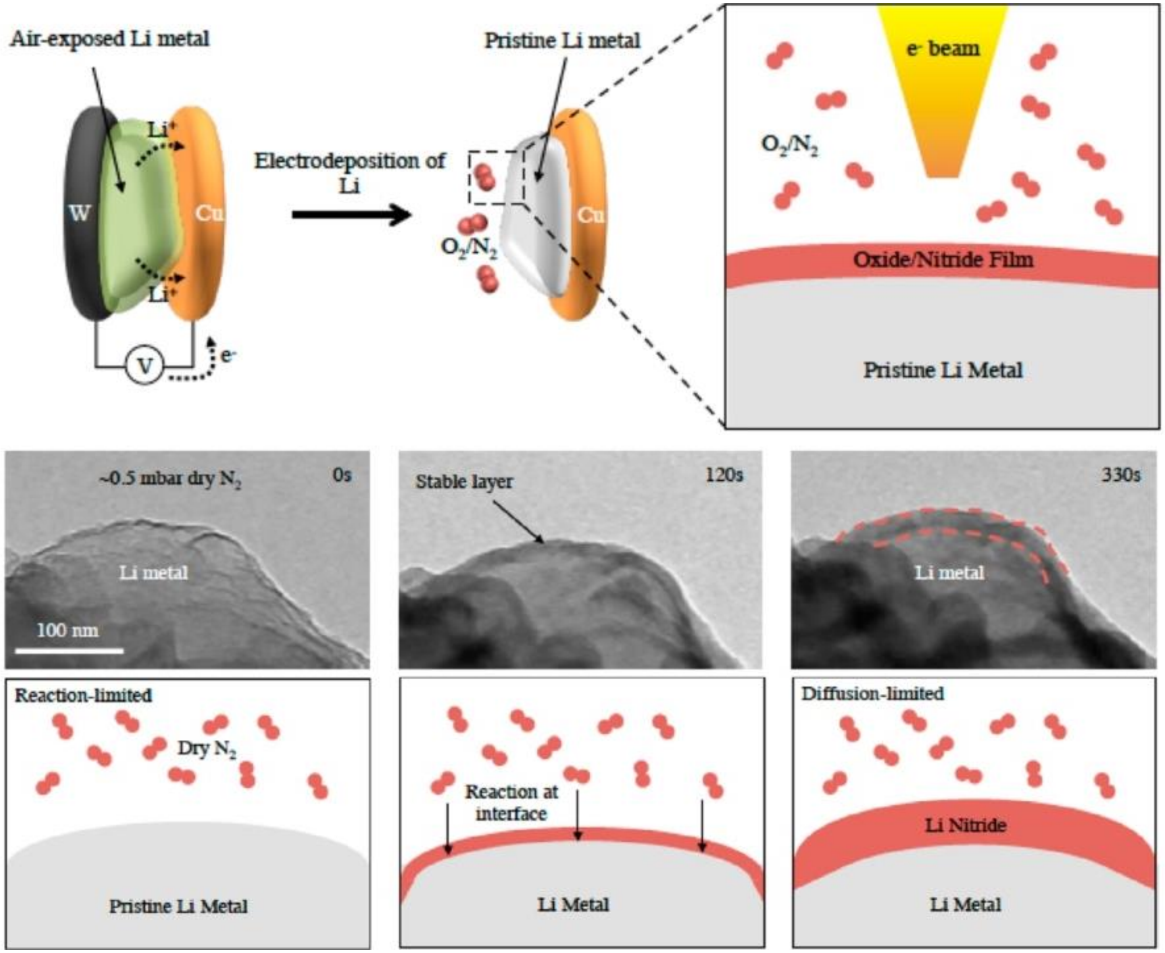


$$6Li + N_2 \rightarrow 2Li_3N$$
$$2Li + 2H_2O \rightarrow 2LiOH + H_2$$
$$Li_3N + 3H_2O \rightarrow 3LiOH + NH_3$$

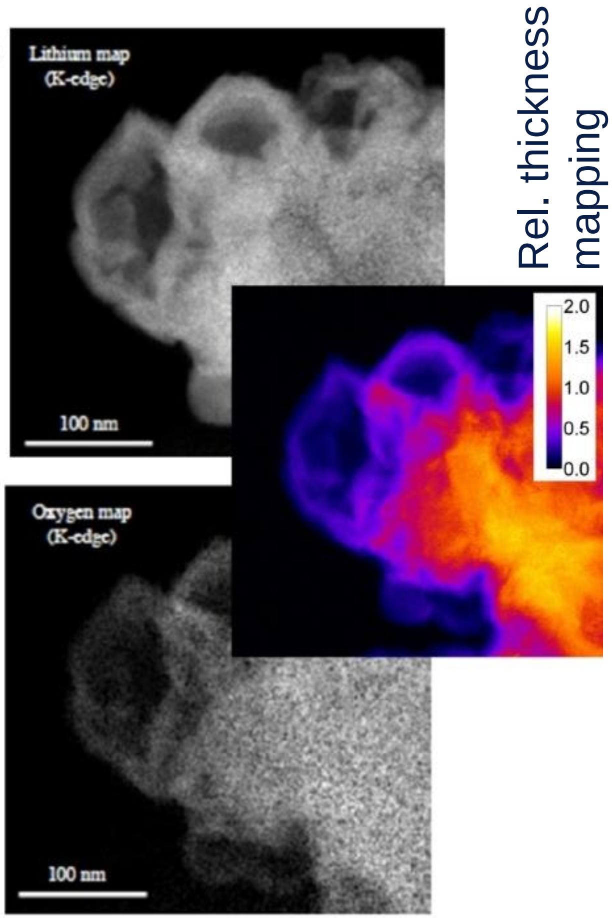
Gaseous reaction products → Pores

Video not available

Passivation in dry N_2



Corrosion in air



→ **Novel Li-ion batteries with Li-metal anode + passivation interlayer with high capacity and long-term cycling stability**

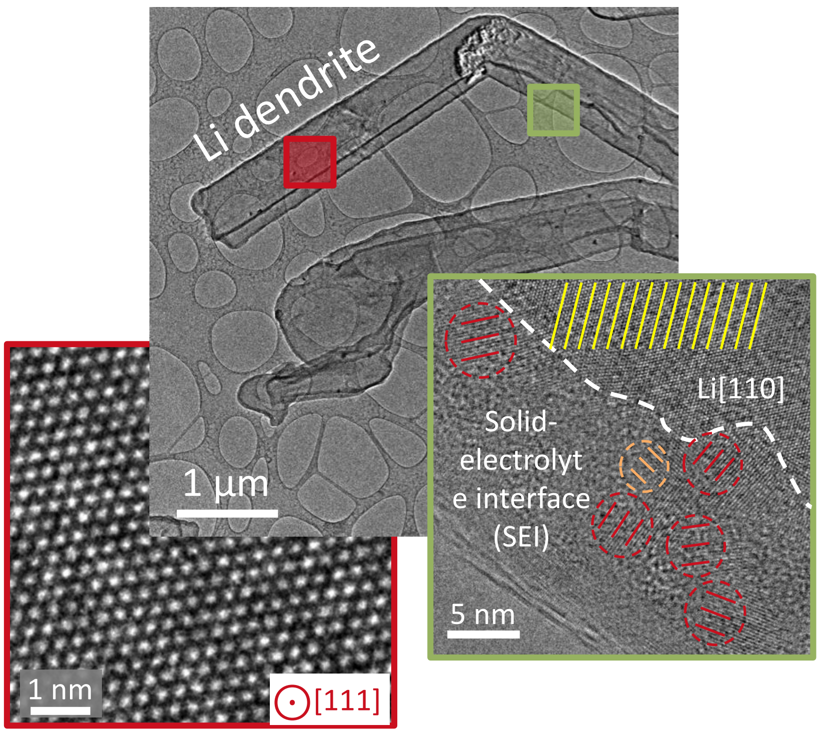
Lessons learned

TEM contributes to development of <u>safe</u>, <u>durable</u>, <u>light</u> batteries with <u>high capacity</u> & <u>fast charging</u>

Establishing low-dose microscopy for materials science

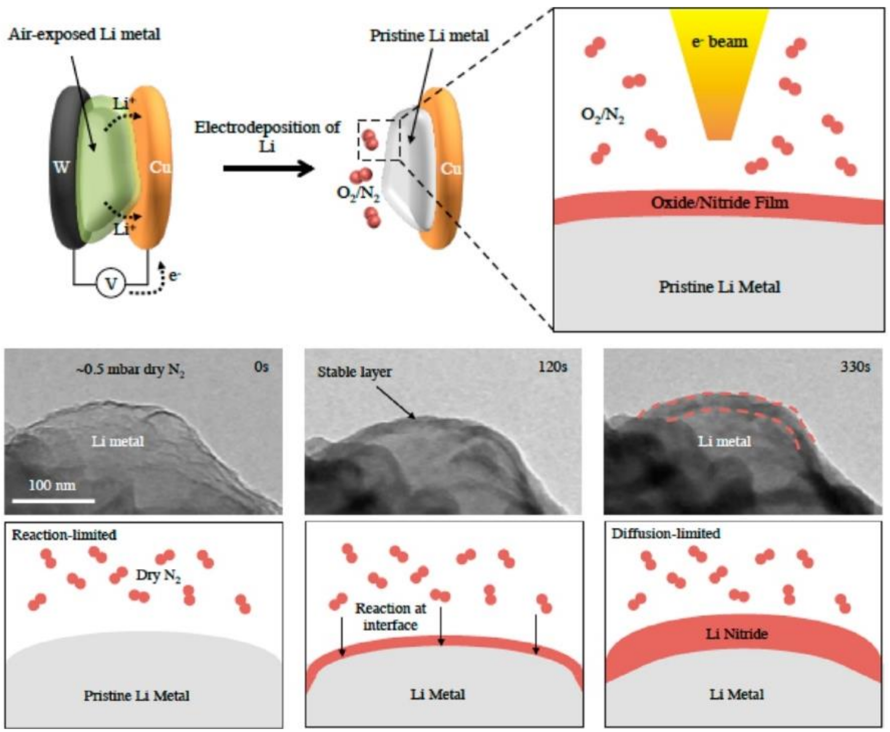
Cryo-TEM

Nanocharacterzation of sensitive battery materials



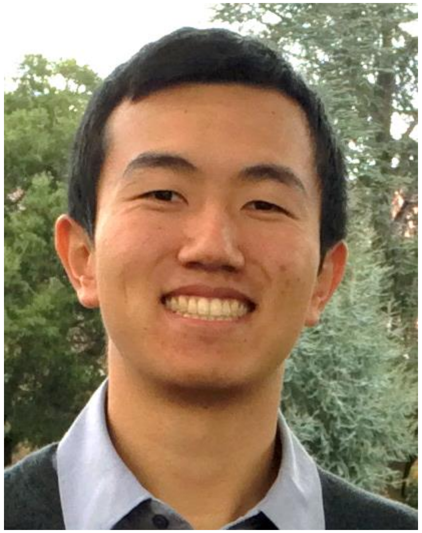
in situ & environmental TEM

Characterzation of reactions of sensitive battery materials



Acknowledgement

Stanford University


Yuzhang Li


Prof. Yi Cui


Dr. Ai Leen Koh


Prof. Bob Sinclair

Li, Li, Pei, Yan, Sun, Wu, Joubert, Chin, Koh, Yu, Perrino, <u>Butz</u>, Chu, Cui
Atomic structure of sensitive battery materials and interfaces revealed by cryo-electron microscopy
Science 358 (2017) 506

Li, Li, Sun, <u>Butz</u>, Yan, Koh, Zhao, Pei, Cui
Revealing Nanoscale Passivation and Corrosion Mechanisms of Reactive Battery Materials in Gas Environments
Nano Letters 17 (2017) 5171

DFG
Grant BU 2875/2