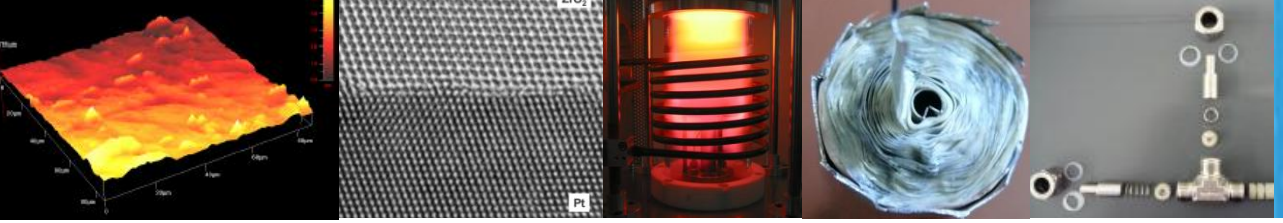


JUSTUS-LIEBIG-UNIVERSITÄT GIESSEN

Interface chemistry in lithium (ion) batteries

Grenzflächenchemie in der Lithium(ionen)batterie

Jürgen Janek

I. Interfaces in lithium batteries

a. „Reactive“ interfaces and interphases
b. „Non-reactive“ interfaces
c. The analytical problem

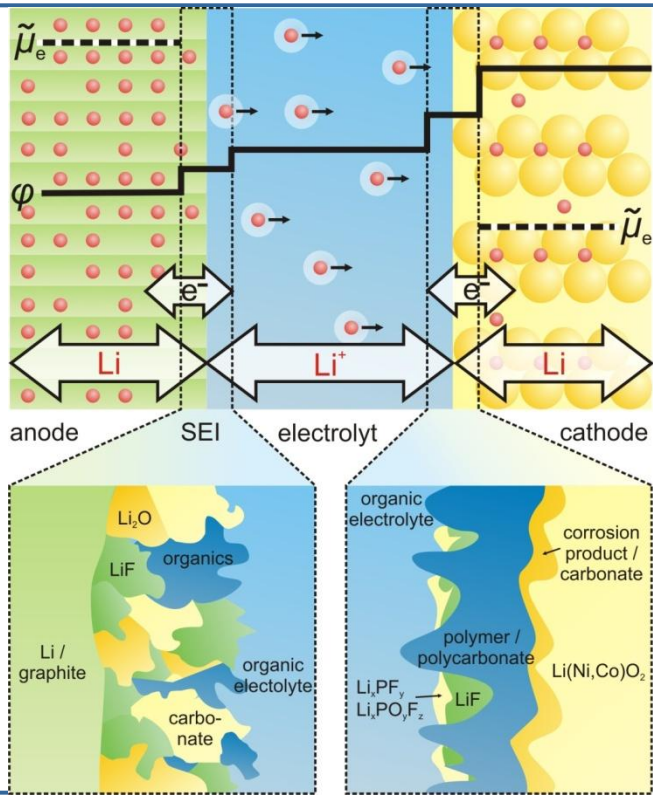
II. Electrodes and Interphases (SEI)

a. Example: ToF-SIMS on graphite anode
b. Example: ToF-SIMS on cathode

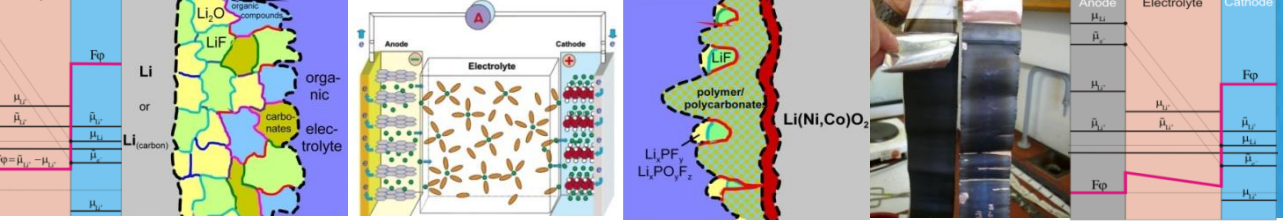
III. Electrolyte dispersions

a) Example: „Soggy sands“ – filled liquid electrolytes
b) Example: Filled Polymers

IV. Li-sulfur and Li-air cells



The (fundamental) physico-chemical view…



JUSTUS-LIEBIG-UNIVERSITÄT GIESSEN

Interface chemistry in lithium (ion) batteries

Grenzflächenchemie in der Lithium(ionen)batterie

Jürgen Janek

I. Interfaces in lithium batteries

a. „Reactive“ interfaces and interphases
b. „Non-reactive“ interfaces
c. The analytical problem

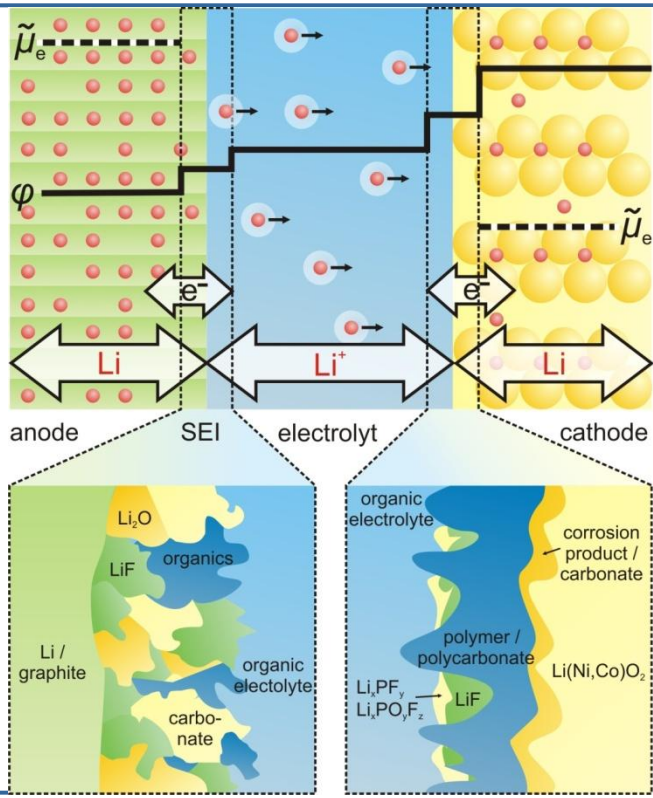
II. Electrodes and Interphases (SEI)

a. Example: ToF-SIMS on graphite anode
b. Example: ToF-SIMS on cathode

III. Electrolyte dispersions

a) Example: „Soggy sands“ – filled liquid electrolytes
b) Example: Filled Polymers

IV. Li-sulfur and Li-air cells



JLU Gießen	Laboratory for Materials Research
BMBF	Network „Electrochemistry“, HE-Lion, LiVe
DFG	SPP 1191, SPP 1415, PAK 77
FCI	Electrochemistry Initiative

TransMIT

TransMIT Center for Solid State Ionics and Electrochemistry

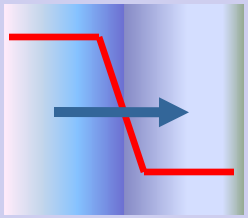
Profile: Solid State Ionics/Electrochemistry

A. Electroceramics, Defects, Nano-/Microstructure and Transport

Prof. Jürgen Janek, PD Dr. Korte

B. Materials and interfaces in electrochemical systems

Prof. Jürgen Janek
Dr. Philipp Adelhelm



C. In situ characterisation of electrochemical components and cells

Dr. Bjoern Luerßen

D. Plasmas, surface modifications and thin films

Dr. Marcus Rohnke

Science/Fundamentals

Lithium Cells/Batteries

Ionic Thermoelectrics

Solid Oxide Fuel Cells

Electrochemical Sensors

Application

Profile: Resources

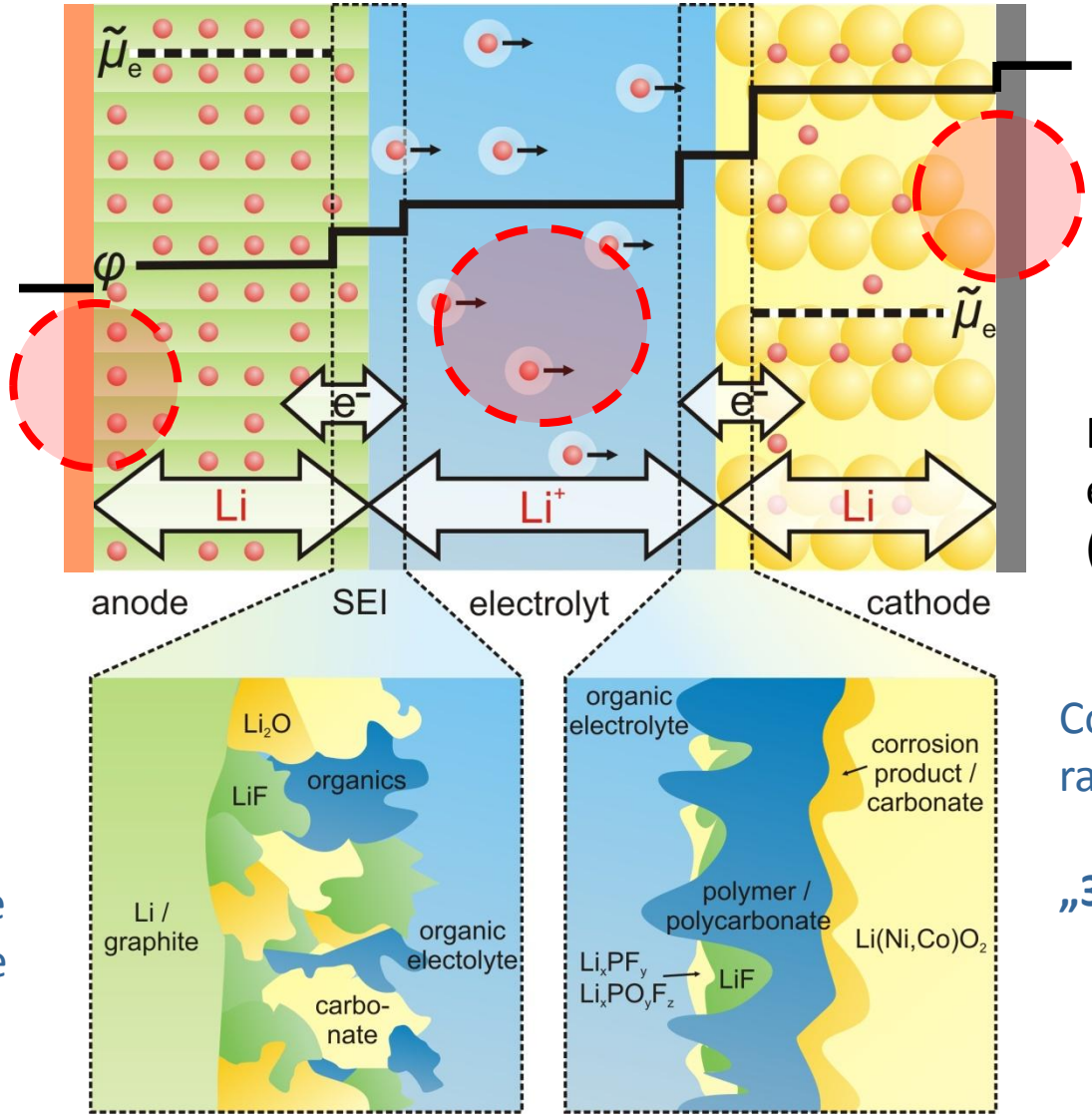
- **Characterisation/Analysis:**
  - **HREM**/EDX/EBSD/nm-prober
  - **TOF-SIMS (Ion-Tof) + *ESCA***
  - PEEM (**µ-ESCA** at ELETTRA/Trieste)
  - XRD, ***XR-Texturanalytik***, AFM (ex situ)
  - ***IR/Raman (AG Over)***
  - **EIS, CV, electrochemical techniques**
  - **microelectrode setups** (< 800 °C)
  - **(HT) contact angle measurement**
  - Catalytic reactor (Kelvin probe, QMS)
- **Lithium laboratory:**
  - **Gloveboxes (6 places -> 8)**
  - **Electrolyte characterisation** in glovebox (Karl-Fischer, Tensiometer, Viscosimeter)
  - **16-channel cycler (incl. Impedance) -> 90**
  - ***PLD deposition/glovebox combination***
- **Preparation/Chemistry:**
  - **High T laboratory** (< 1800 °C, controlled atmospheres)
  - **Pulsed Laser Deposition** (3 chambers, 4 planned), Dual beam
  - PVD, Sputtering (AG Meyer)
  - **Electrochemistry** (e. g. ceramic thin films from non-aqueous solvents)
  - **Plasma reactors** (rf, µw, dc)
  - **Nano-/Microlithography** (joint lab)

Group members:

2 permanent scientists
4 Post-Docs
13 Dr. rer. nat. candidates
1 technician
6 MSc students
8 BSc students

Interfaces in lithium (ion) batteries

Cu|electrolyte
|anode contact



Al|electrolyte
|cathode contact

(passivation of Al)

Interfaces in
electrolyte composites
(e.g. „soggy sands“)

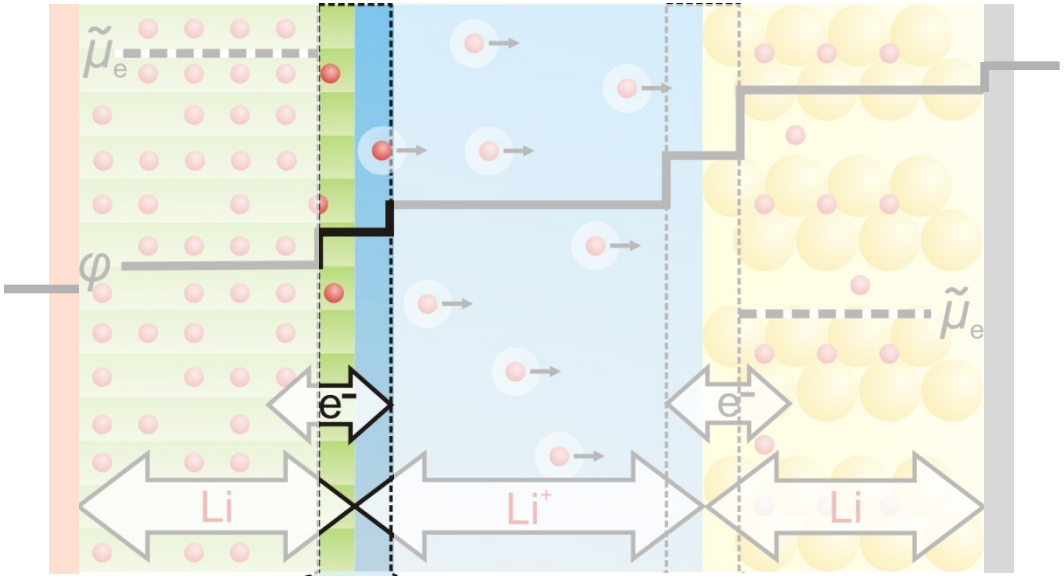
„SEI“

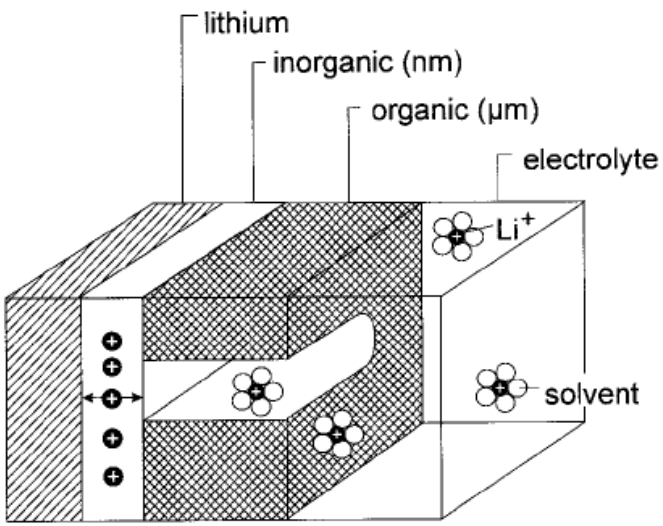
Solid
Electrolyte
Interphase

Complex „interphases“
rather than interfaces

„3D electrodes“

The anode SEI

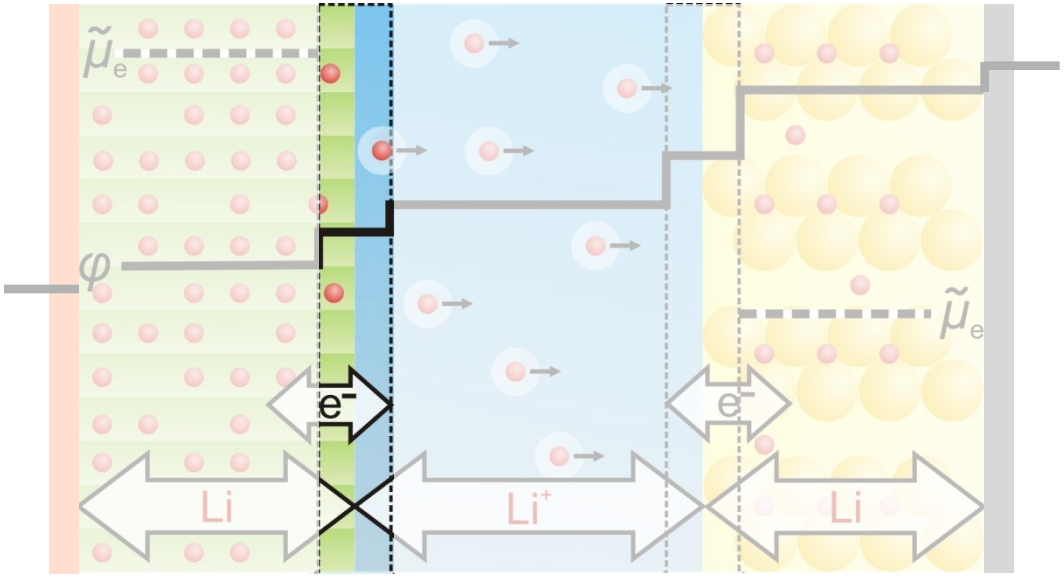


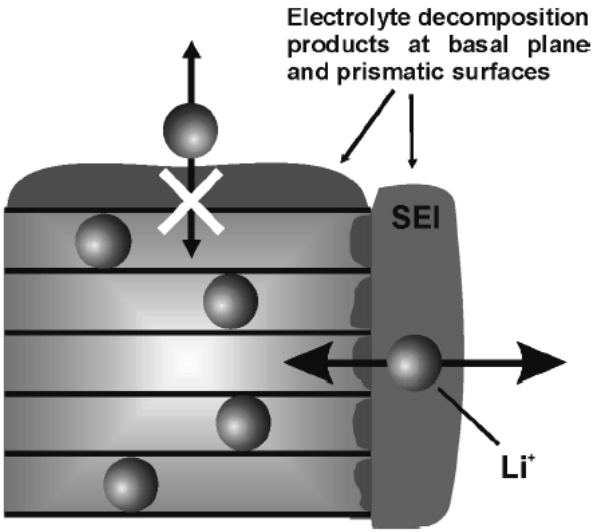


- Organic solvents are decomposed by Li
- Graded multiphase film (SEI)
- SEI acts as „electron filter“
- SEI acts as „gellified solid electrolyte“
- detailed composition still not fully known
- problem: in situ analysis

see e. g. E. Peled, D. Aurbach or M. Winter for more details

The anode SEI





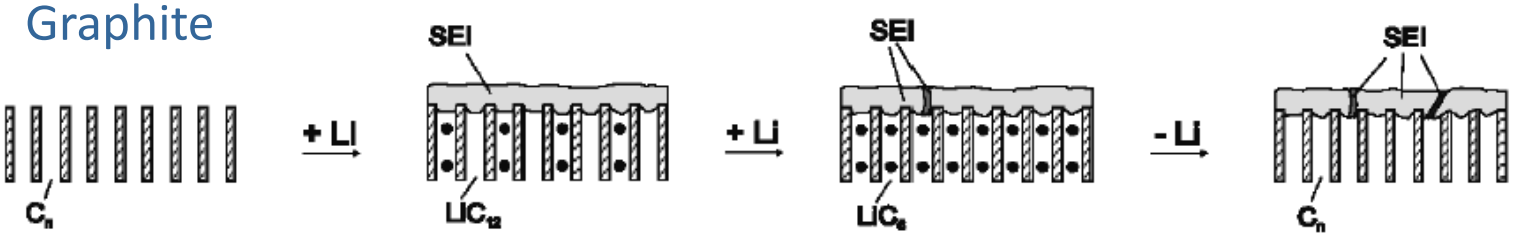
- SEI composition and properties depend on anode material and electrolyte components
- SEI participates in self-discharge, fast charge/dicharge, ageing
- SEI is one reason for poor cyclability of Li metal

see e. g. E. Peled, D. Aurbach or M. Winter for more details

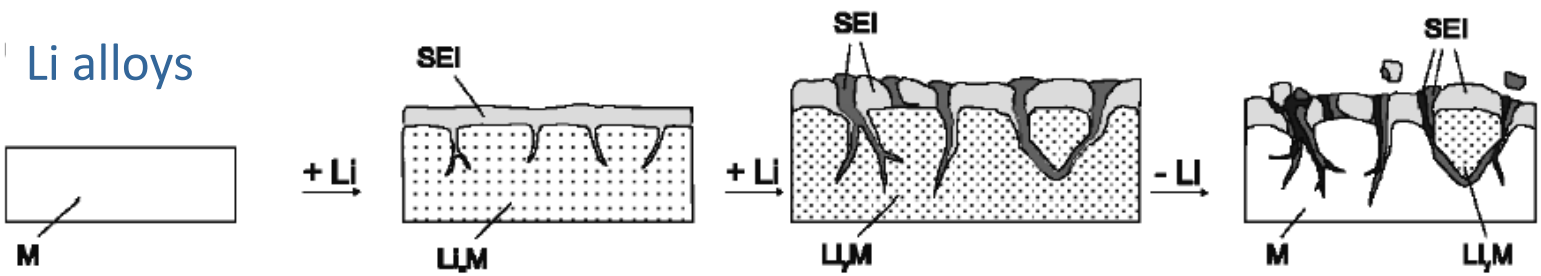
The anode SEI

Li metal

Graphite



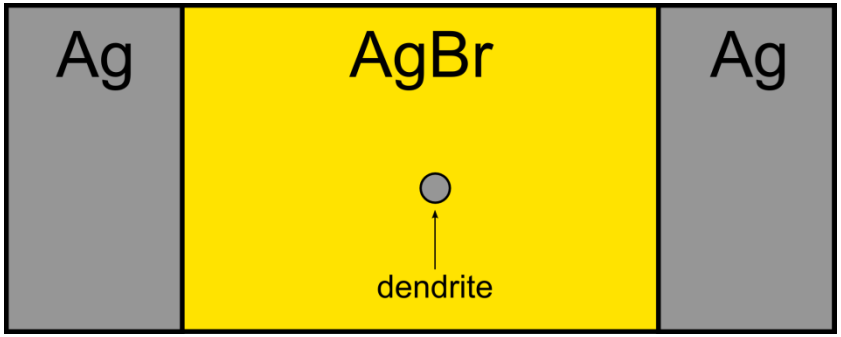
Li alloys



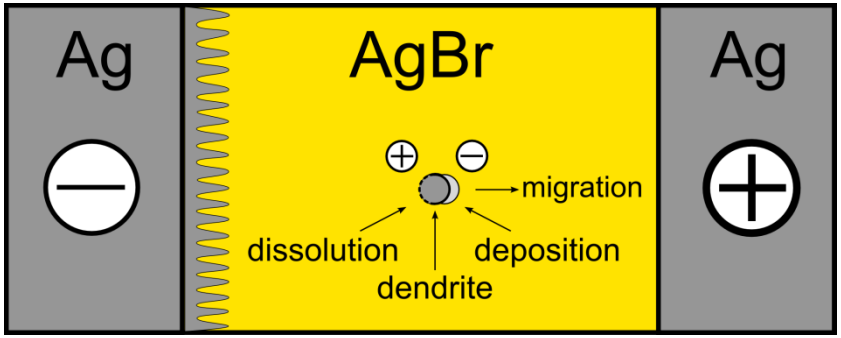
M. Winter, Z. Phys. Chemie **223** (2009) 1395

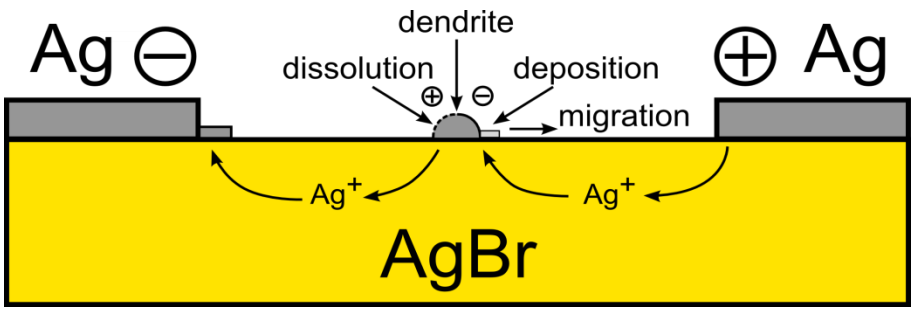
The solid electrolyte interphase – The most important and the least understood solid electrolyte in rechargeable Li batteries

Fast Transport along Metal/Electrolyte Interfaces



"Bipolar" electrodes:
Surface movement



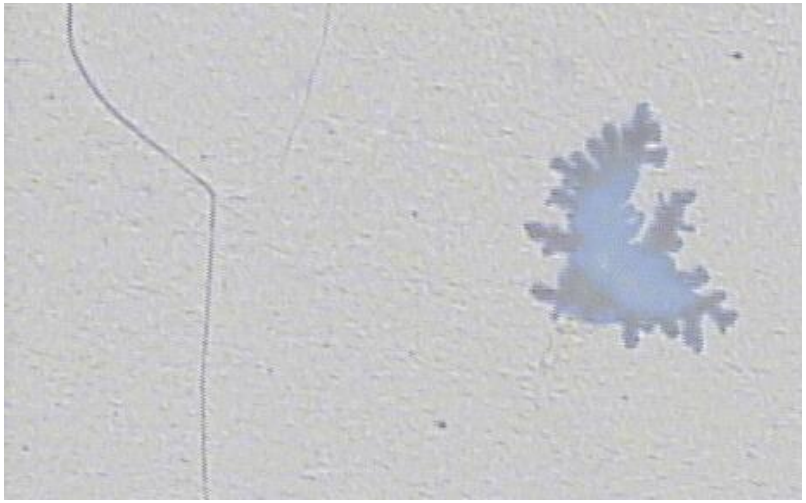


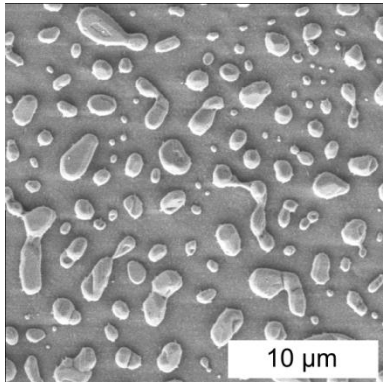
„free" metal/electrode pieces as a failure mechanism of Li batteries?

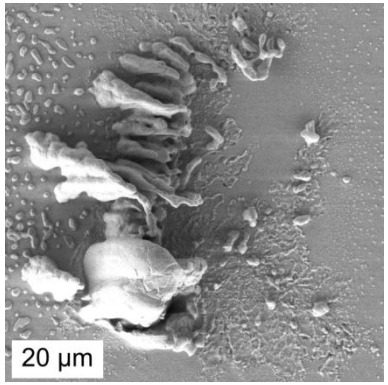
K. Peppler and J. Janek, APL **93** (2008) 074104

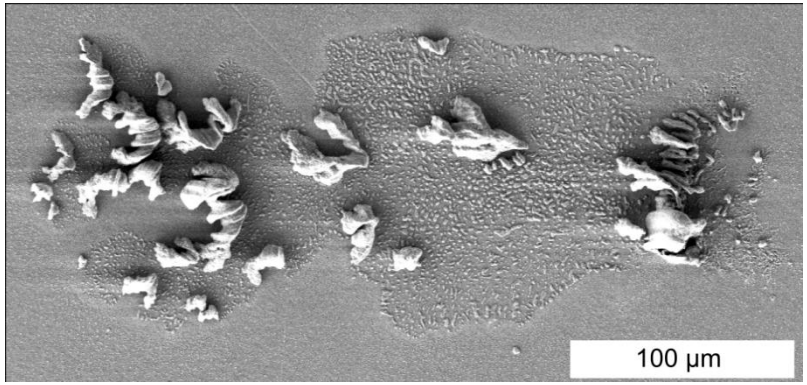
“Bipolar” electrodes: Surface movement

- accelerated animation
  t = 2370 s (≈ 40 min)
- T ≈ 200 °C
- U = 750 mV



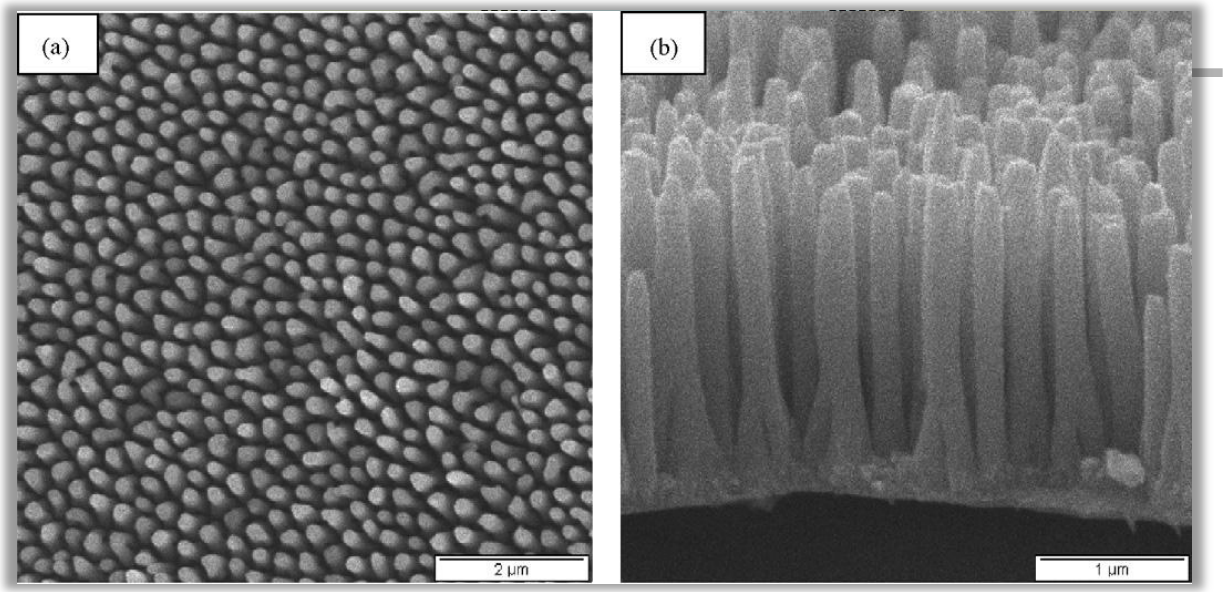


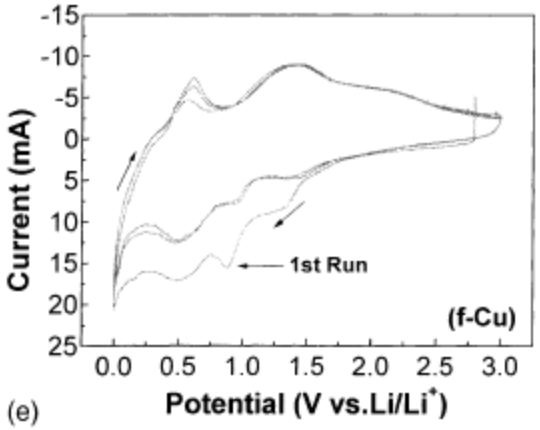




K. Peppler and J. Janek, APL **93** (2008) 074104

The anode/copper contact





C(Cu foil, 500 nm CuO) ≈ $5.2 \cdot 10^{-3}$ mAh/cm^2

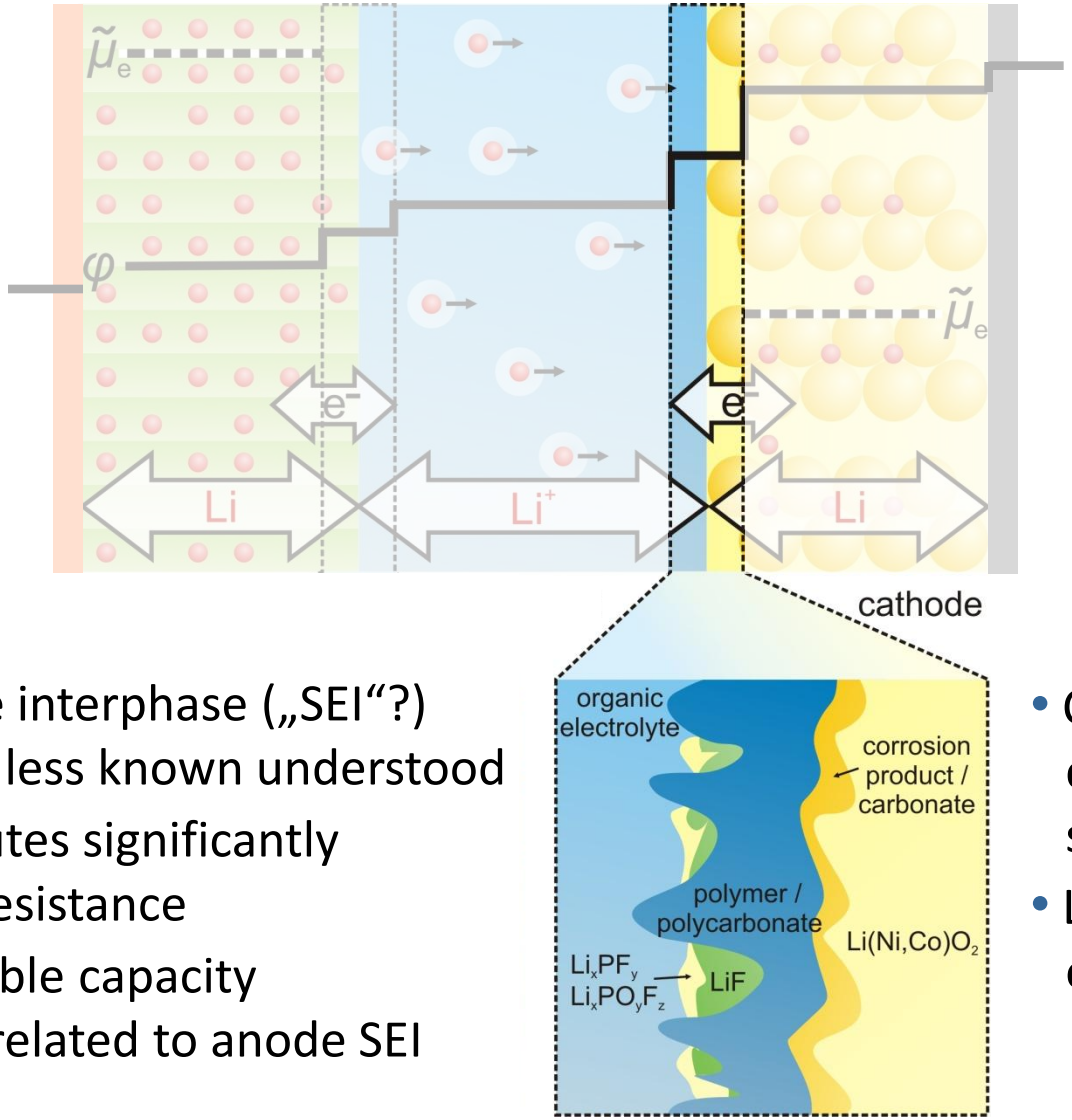
C(graphite, 10 mg/cm^2) ≈ 3.4 mAh/cm^2

Design of Cu surface
for improved anode characteristics?

H. Duan et al., J. Power Sources **185** (2008) 512
Fabrication and characterization of Fe_3O_4-based Cu nanostructured elecrode for Li-ion battery

J. Zhang et al., J. Power Sources **137** (2004) 88
Li insertion in naturally surface-oxidized copper

The cathode interface (interphase?)



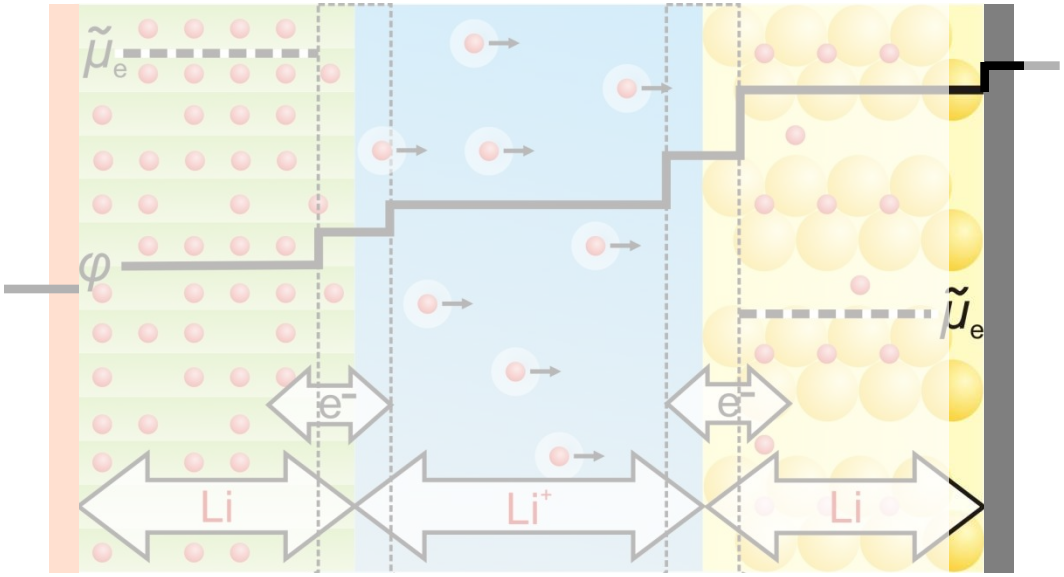
- Cathode interphase („SEI“?) is much less known understood
- contributes significantly to cell resistance
- irreversible capacity is more related to anode SEI

- Coating of high voltage cathodes with stable oxides
- $LiCoO_2$: e. g. ZrO_2 or $AlPO_4$

C. Li et al., Electrochim. Acta **51** (2006) 3872

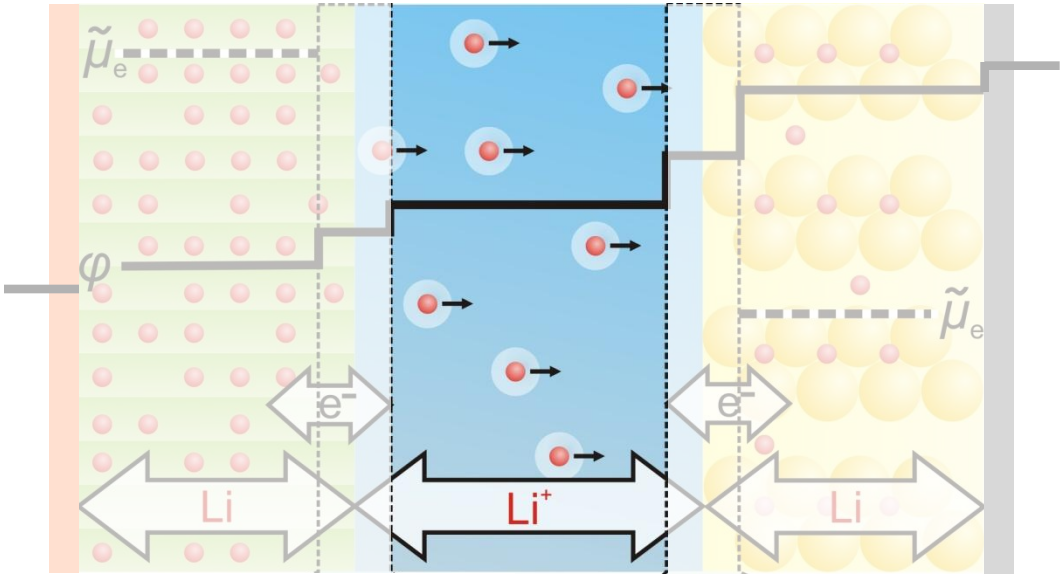
Cathode materials modified by surface coating for lithium ion batteries

The cathode/aluminium contact



- air-formed Al_2O_3 layer (a few nm)
- anodic formation of thin protecting AlF_3 film on top during charging
- AlF_3 is insoluble in typical Li electrolytes
- „duplex“ oxide/fluoride film prevents corrosion
- Al corrosion takes primarily place under the cathode oxides

Interfaces in composite electrolytes



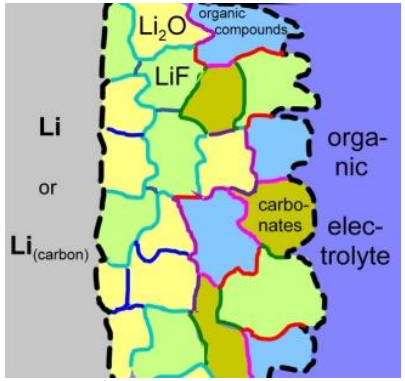
- Inorganic fillers
- e.g. in liquid electrolytes
- e.g. in polymers

The analytical problem: Spectroscopy/Microscopy/Diffraction

	Specific identification	In situ characterization	Non-destructive	High local resolution
FTIR	●	●	●	
Raman	●	●	(●)	(●)
SIMS	●			●
XPS	●			
EXAFS	●	●		
XRD	●	●	(●)	
EDX				●
REM, TEM				●
AFM, STM		●	(●)	●
NMR			●	

SIMS = Secondary Ion Mass Spectrometry
XPS = X-ray Photoelectron Spectroscopy
FTIR = Fourier-Transform IR
EXAFS = Extended X-ray Absorption Fine Structure

Electrodes and interphases

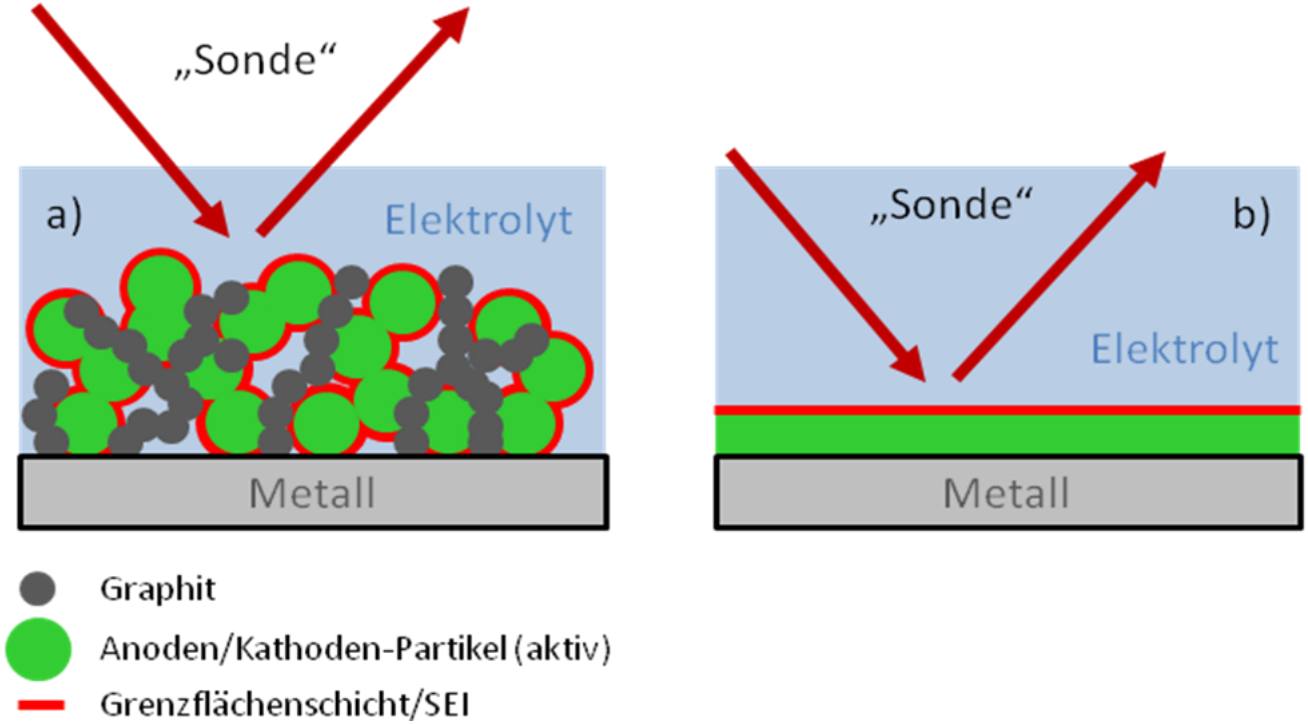


Own examples

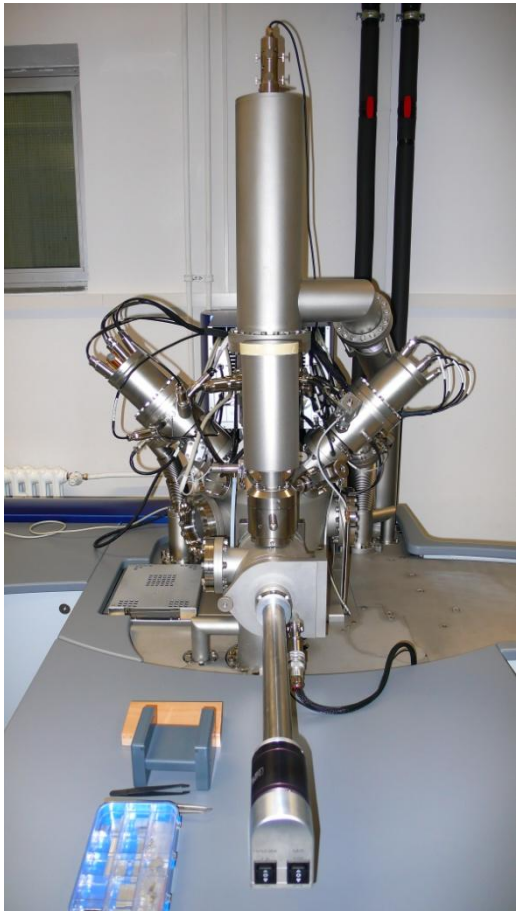
ToF-SIMS of SEI on graphite

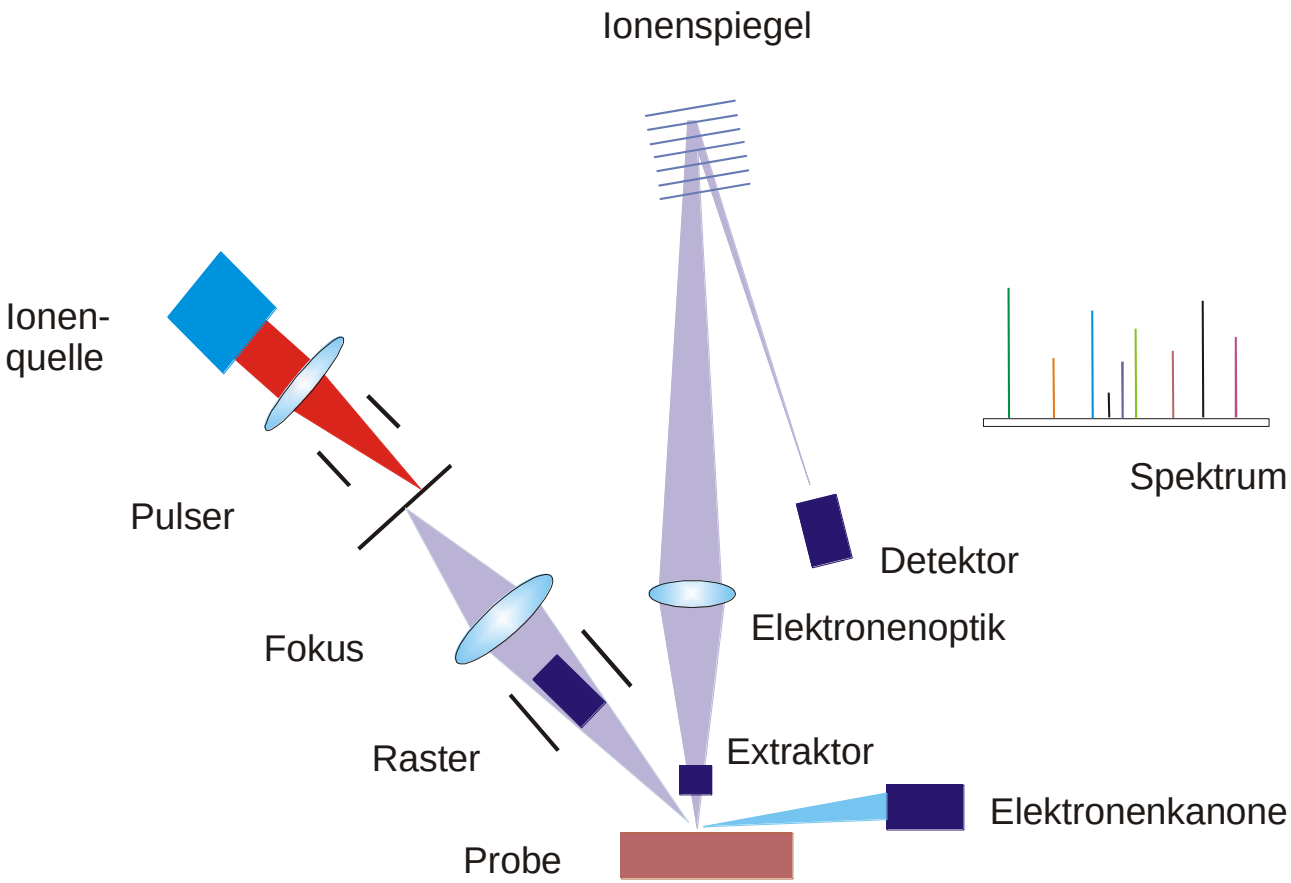
ToF-SIMS of cathode surface

The *materials gap*: Real electrodes vs. model-type electrodes



ToF-SIMS

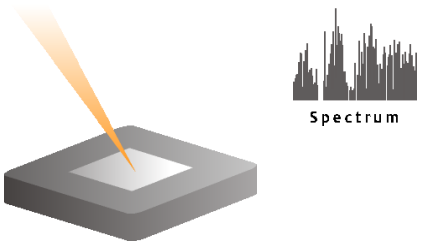



Ionenspiegel
Ionen-
quelle
Spektrum
Pulser
Detektor
Elektronenoptik
Fokus
Raster
Extraktor
Elektronenkanone
Probe

ToF-SIMS

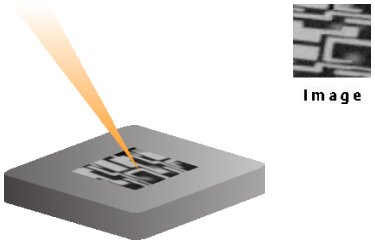
Surface spectroscopy

- Element and molecule information
- ppm sensitivity
- Masses > 10 000



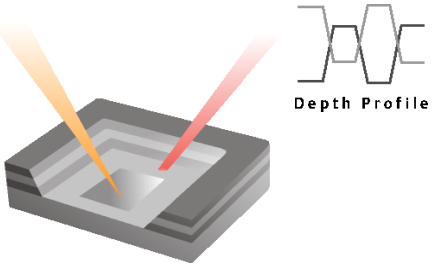
Surface imaging

- lateral resolution < 100 nm
- parallel mass counting



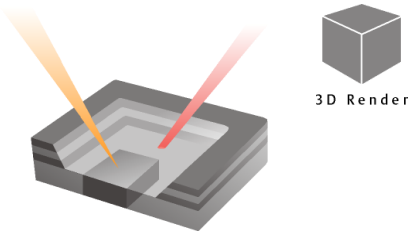
Depth profiling

- depth resolution < 1 nm
- thin film analysis from 1 nm to > 10 µm
- also for Insulators



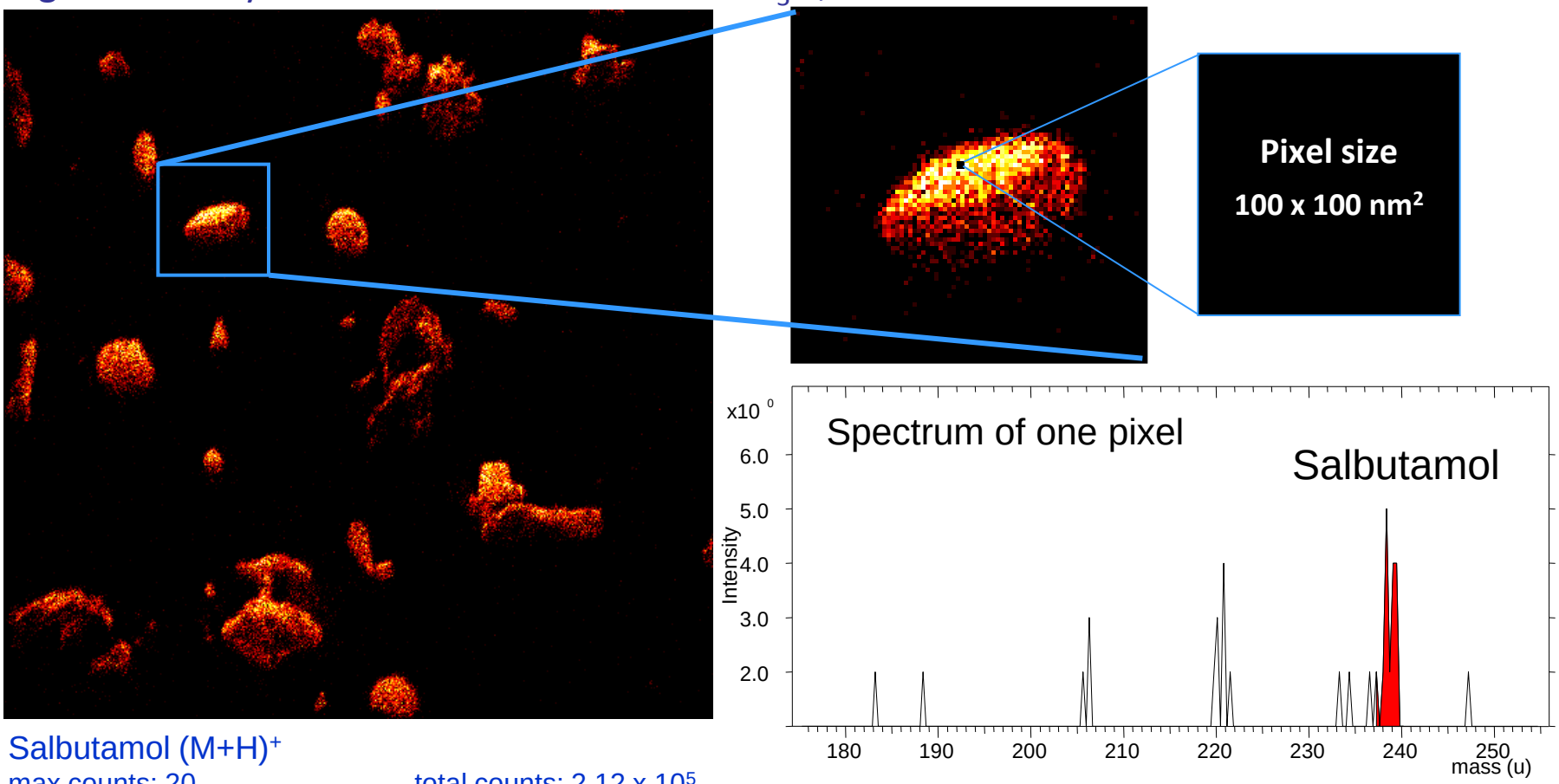
3D analysis

- parallel mass counting
- high depth resolution
- high lateral resolution



ToF-SIMS

High Sensitivity and Lateral Resolution with Bi_3^{++}; 50 keV



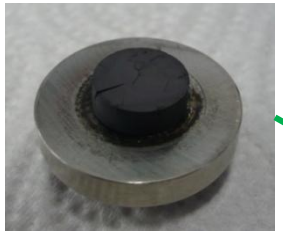
Salbutamol $(M+H)^+$

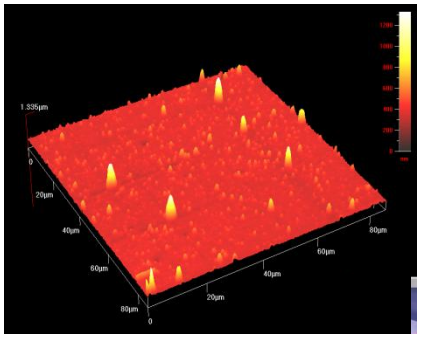
max counts: 20 total counts: 2.12×10^5

⇒ $2 \cdot 10^{-20}$ mol determined in 100 x 100 nm² area

Deposition of $LiNi_{0.5}Mn_{1.5}O_4$ cathode films (PLD)

Lithium excess of 15 mol%

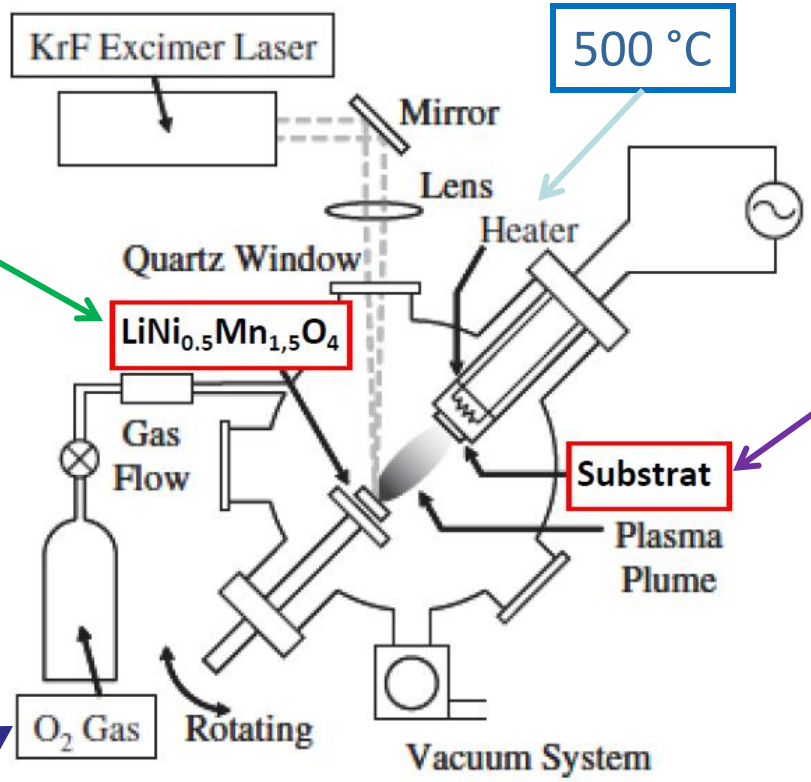




200 mJ, 10 Hz

500 °C

Gold foil
Si(100) wafer

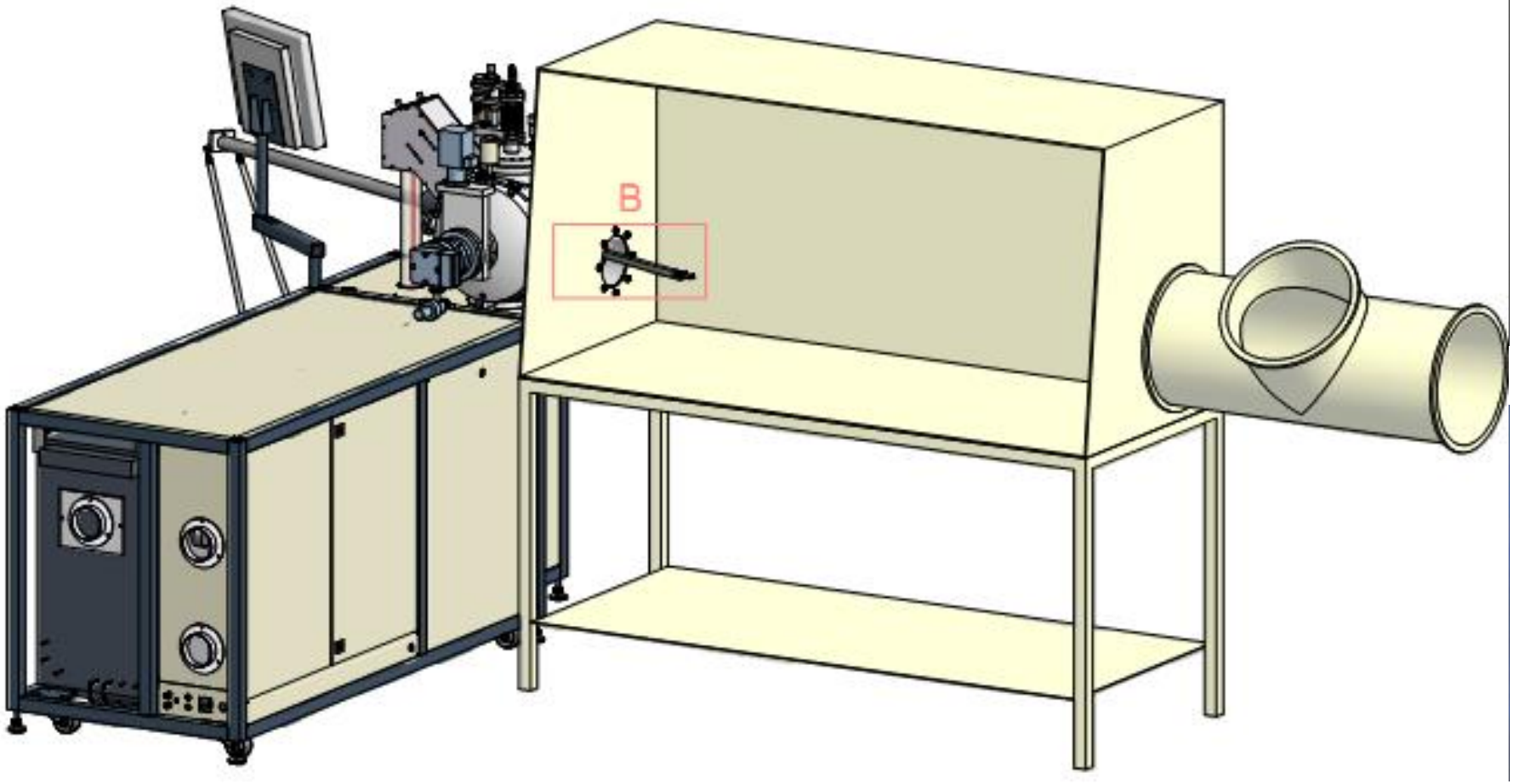


200 mTorr

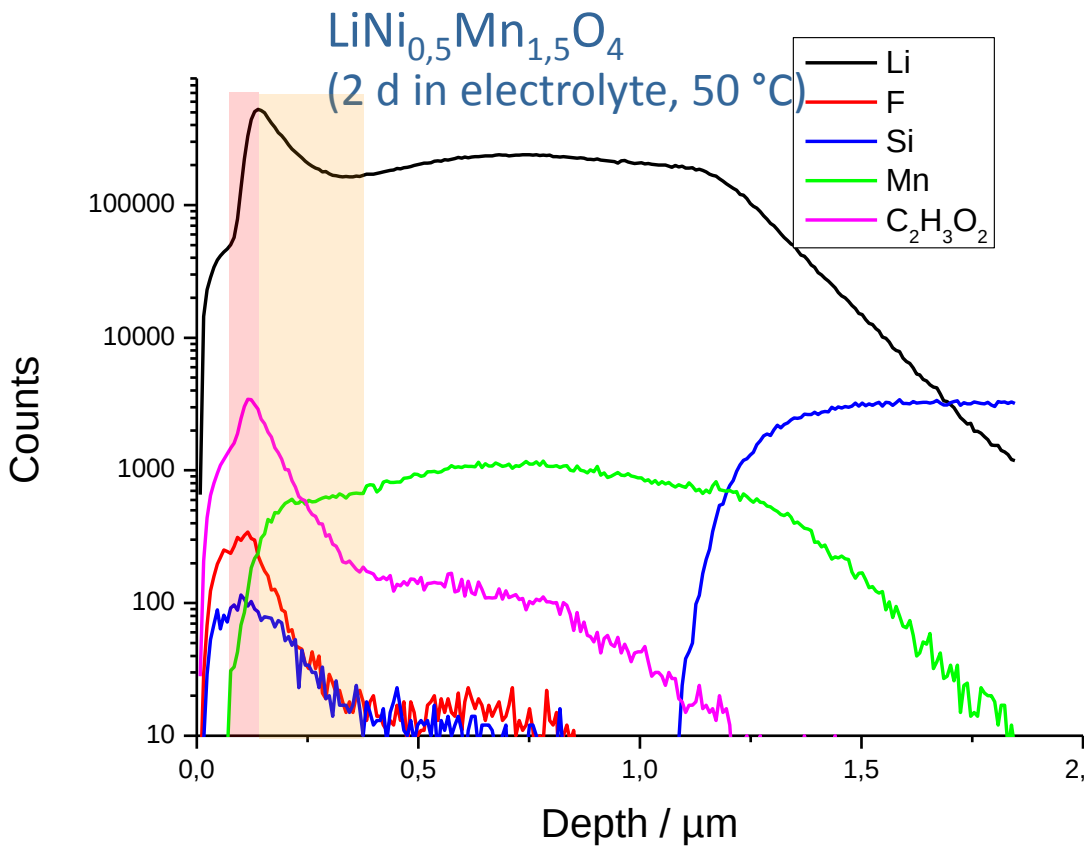
20.000 - 60.000 laser pulses

H. Xia, S. B. Tang, L. Lu et al., *Electrochimica Acta* **2007**
H. Xia, Y. S. Meng, L. Lu et al., *Journal of the Electrochemical Society* **2007**
H. Otsuji, K. Kawahara, T. Ikegami et al., *Thin Solid Films* **2006**

Pulsed Laser Deposition (PLD) / Glovebox combination

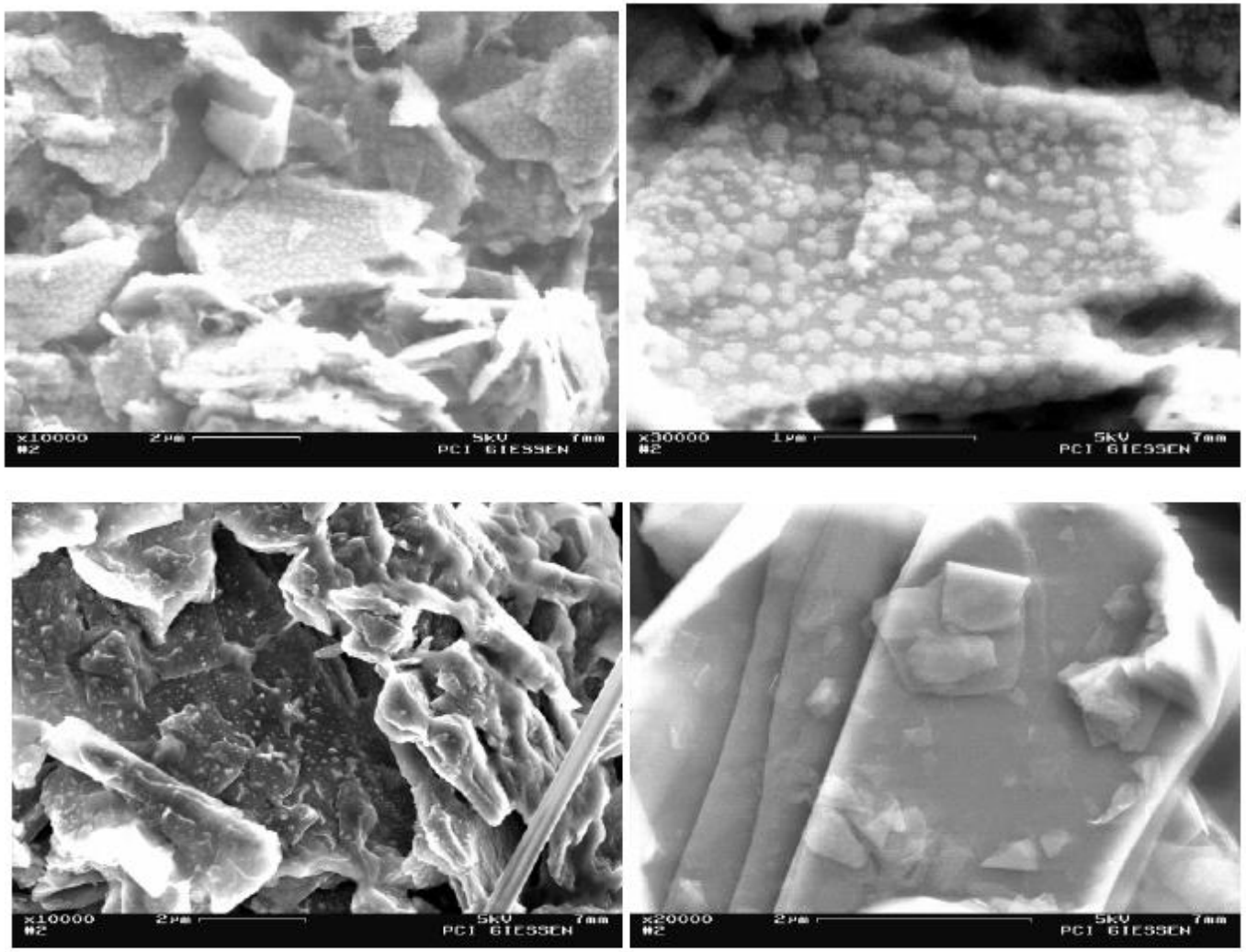


ToF-SIMS measurements of cathode surface films



- no Mn within first 150 nm (surface film or dissolution of Mn in electrolyte?)
- F and $C_2H_3O_2$ show maximum within surface film at 200 nm
- Li shows maximum even deeper
- Si impurity

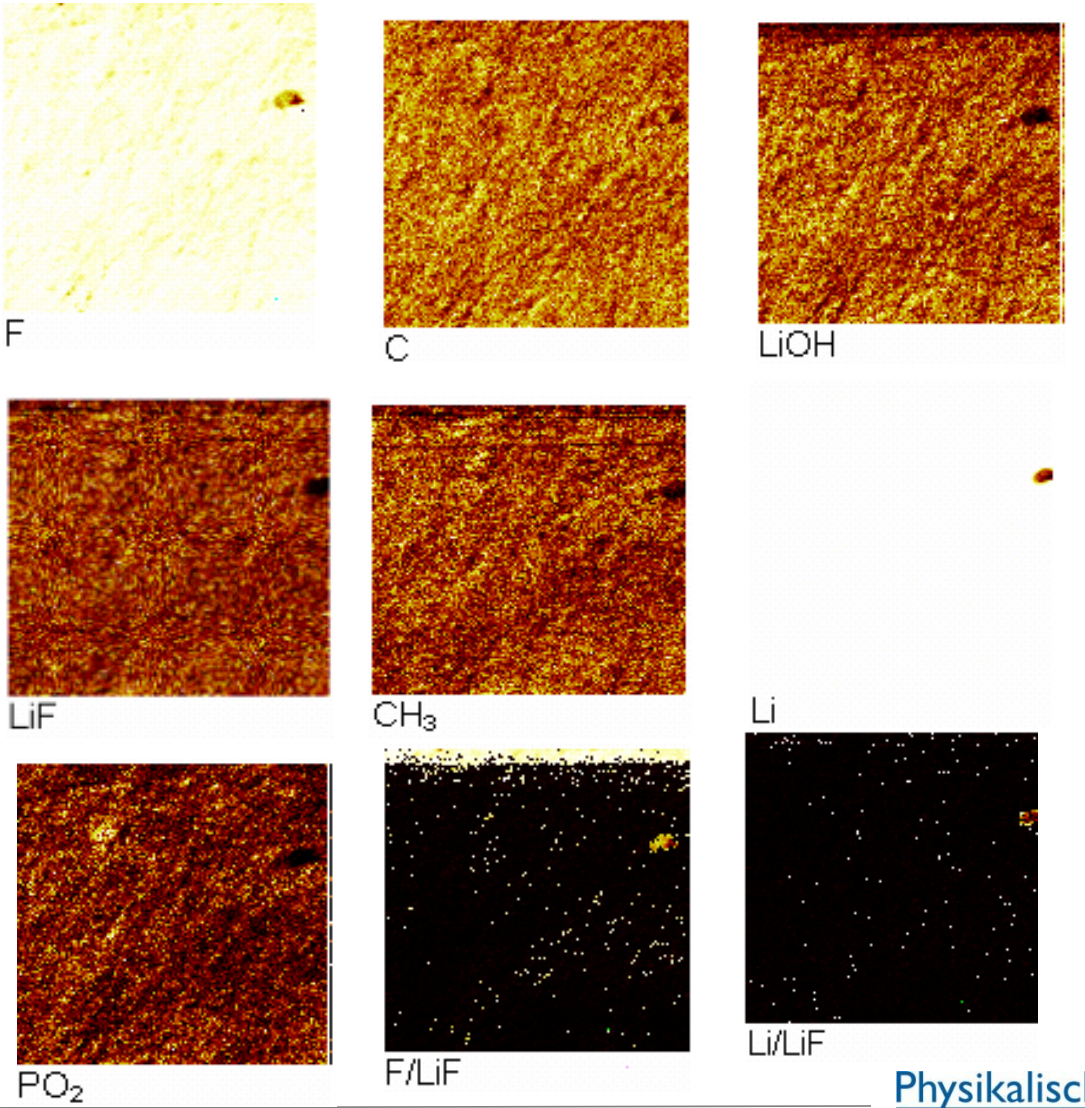
ToF-SIMS of graphite surfaces (SEI)



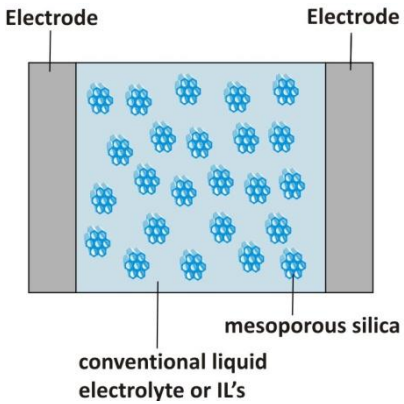
ToF-SIMS of graphite surfaces (SEI)

- SIMS images of graphite electrode (wothout binder) after cycling
  (Bildgröße 1000 µm x 1000 µm)

- Main constituents of SEI: F, Li, C, LiOH, carbon-hydrogen fragments (CH_3), LiF and phosphates (PO_2)



Electrolyte dispersions



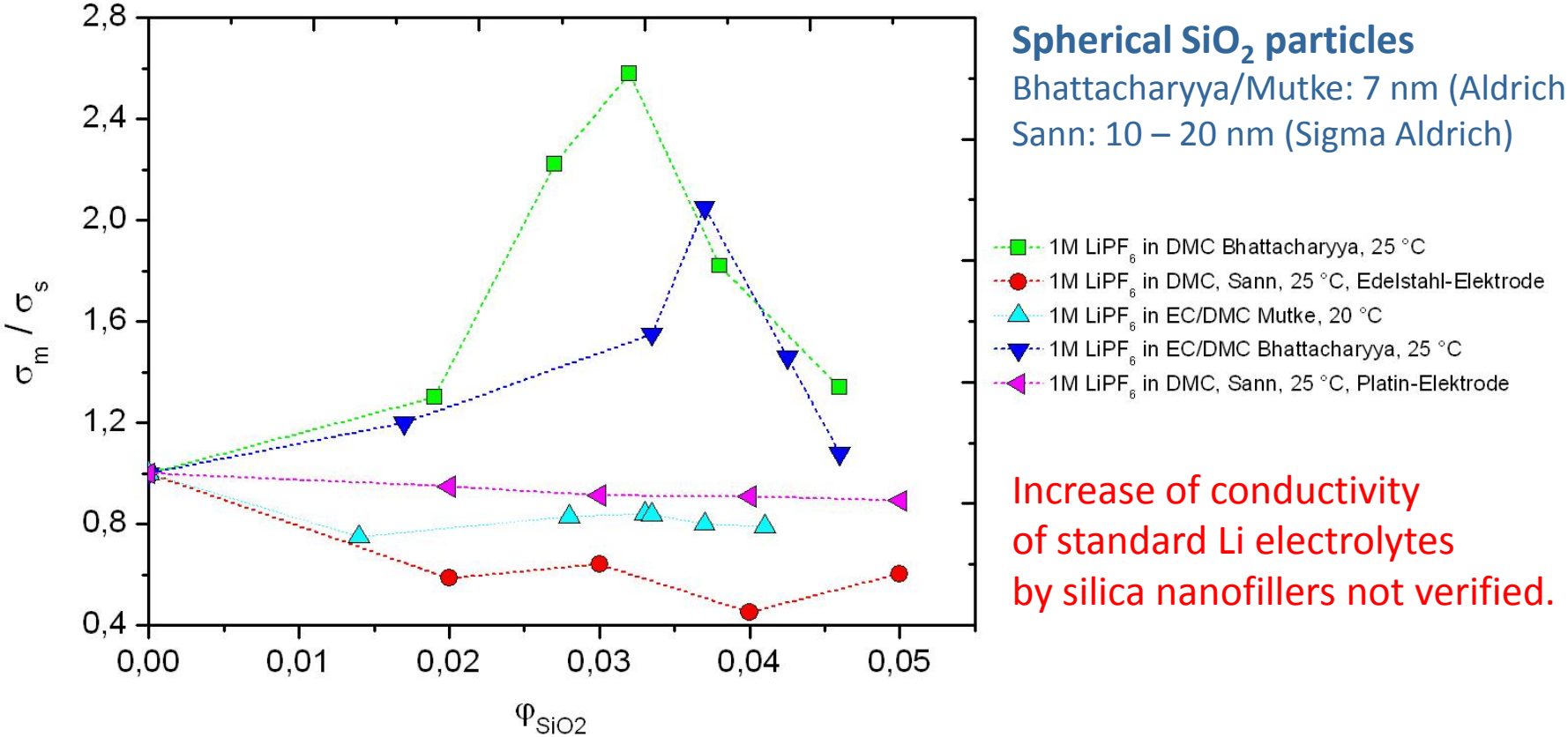
Mesoporous silica
in liquid electrolytes
and polymer electrolyte

Prof. M. Fröba (U Hamburg)

Prof. H. D. Wiemhöfer (U Münster)

K. Sann, JLU Gießen, Diploma thesis
H. Buschmann, JLU Gießen, Diploma thesis

Liquid electrolytes with SiO_2 nanofiller



Spherical SiO_2 particles

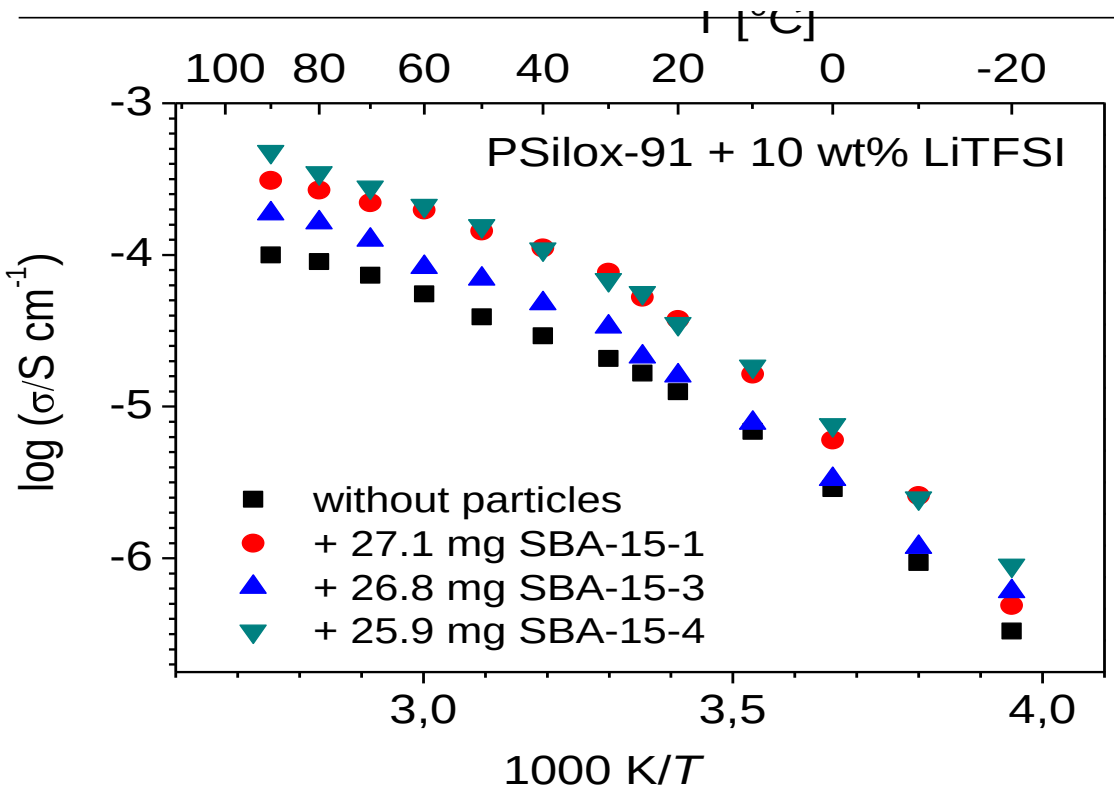
Bhattacharyya/Mutke: 7 nm (Aldrich)

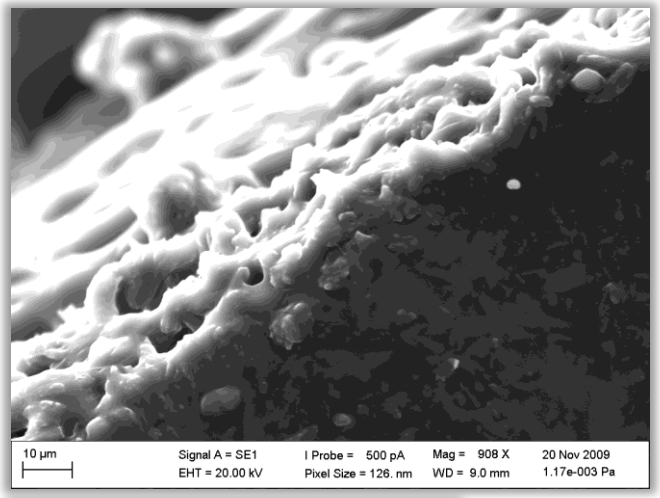
Sann: 10 – 20 nm (Sigma Aldrich)

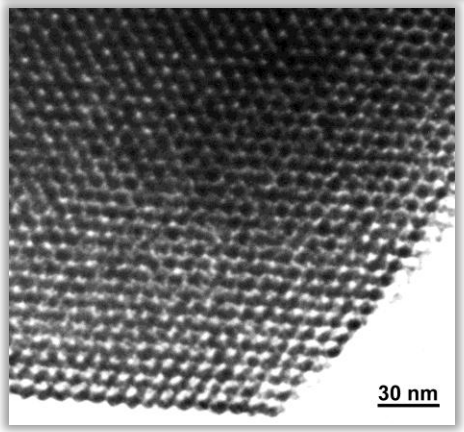
Increase of conductivity
of standard Li electrolytes
by silica nanofillers not verified.

K. Sann et al., JLU Gießen/U Hamburg, to be published

Polymer electrolytes with mesoporous SiO_2 nanofiller







SBA-15
9 nm pores

Increase of conductivity of polymer electrolytes by dispersed mp-SiO_2.

Westfälische Wilhelms-Universität Münster

Universität Hamburg

JUSTUS-LIEBIG-UNIVERSITÄT GIESSEN

Physikalisch-Chemisches Institut

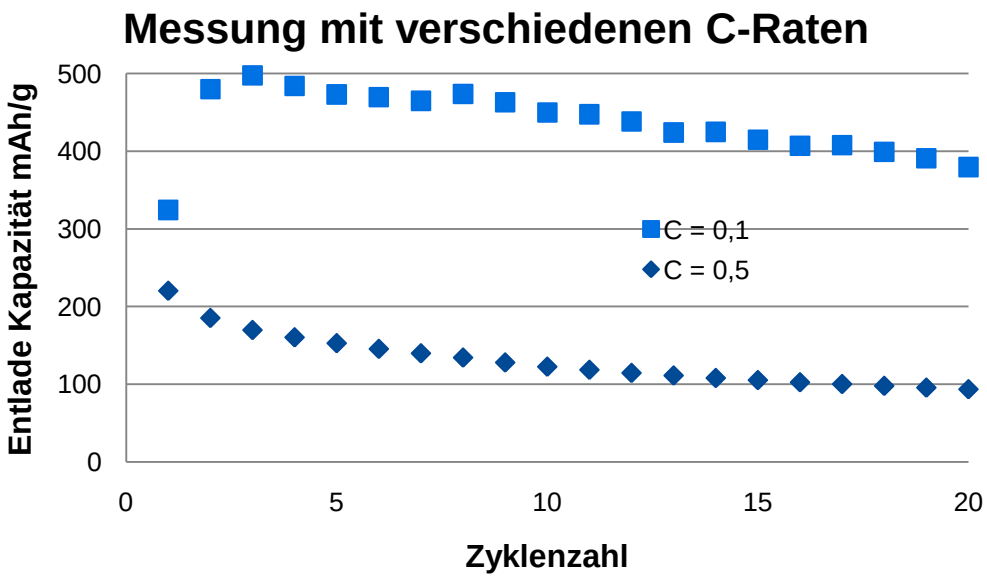
A. C. Gentschev et al., U Münster/JLU Gießen/U Hamburg, to be published
see also work by W. Wieczorek

Disperse electrolytes

Silica	Pore radius / nm	Specific surface area / $m^2\ g^{-1}$	Density / $g\ cm^{-3}$	Average particle size / µm
SBA-15	3,9	348	2,228	13,3
SBA-15	5,8	581	2,215	12,7
SBA-15	8,2	392	2,209	11,6
SBA-15	12,4	301	2,223	12,0
MCM-41	2,9	867	2,278	12,7

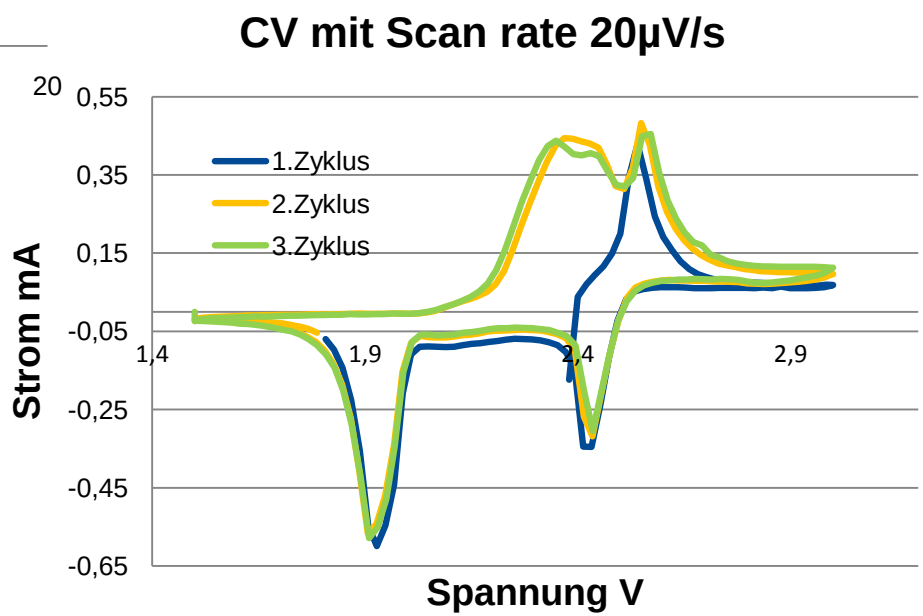
- Electrolyte/silica-dispersions with silica mass fractions between 2,5 % and 10 % (if possible)
- Standard (commercially available) electrolyte 1m $LiPF_6$ in EC/DEC 3:7 water content < 5 ppm
- Determination of the conductivities via Impedance spectroscopy between 1 kHz and 1 Hz

Lithium-sulfur battery

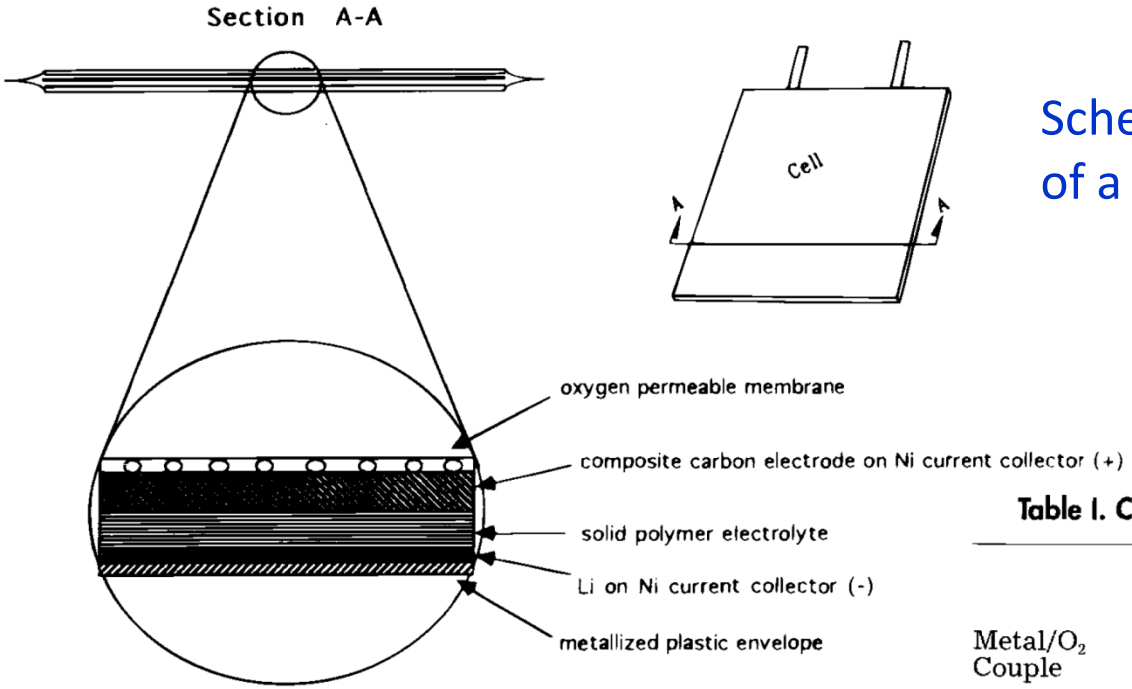


- **Zusammensetzung:**
  - 70% Schwefel
  - 10% SFG6
  - 10% SuperPLi
  - 10% PVdF

- **Elektrolyt:**
  - 1M $LiCF_3SO_3$ in TEGDME



Lithium-O_2 battery



Schematic representation of a Li/O_2 plastic battery

- thin Li metal foil anode
- Polyacrylonitrile-based plasticized polymer electrolyte
- Lithium salt: $LiPF_6$
- thin carbon composite electrode

Table I. Characteristics of some metal/oxygen battery couples.

Metal/O_2 Couple	Idealized cell reaction[a]	Calculated open-circuit voltage (V)	Theoretical specific energy[b] (Wh/kg) Including O_2	Theoretical specific energy[b] (Wh/kg) Excluding O_2
Li/O_2	$4Li + O_2 \rightarrow 2Li_2O$	2.91	5,200	11,140
Al/O_2	$4Al + 3\ O_2 \rightarrow 2Al_2O_3$	2.73	4,300	8,130
Ca/O_2	$2Ca + O_2 \rightarrow 2CaO$	3.12	2,990	4,180
Zn/O_2	$2Zn + O_2 \rightarrow 2ZnO$	1.65	1,090	1,350

[a] The reduction of O_2 to O^{2-} usually occurs only in the presence of a catalyst; often the product is the peroxide, O_2^{2-}.
[b] Includes only the active materials. Since O_2 does not have to be carried in the battery, values are given for the cases of including and excluding O_2. The battery weight will increase once the discharge begins.

K.M. Abraham and Z. Jiang., J. Electrochem. Soc., *143* (1), **1996**, 1

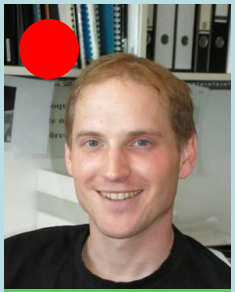
Summary

- Study of **interfaces** as a key to understand cell **kinetics** and **stability**
- Detailed information requires **combination** of several techniques
  - similar strategy as in heterogeneous catalysis!
  - bridging the „pressure gap“ and the „materials gap“
- **Design of interfaces** as a key target for improved cells
  - SEI relatively well understood for standard anodes
  - cathode interface by far less studied (-> high voltage cathodes)

Dr. P. Adelhelm

Materials, synthesis and characterisation, carbon electrodes

Synthesis, structure



Dr. M. Rohnke

Plasma chemistry, diffusion, hybrid materials

ToF-SIMS

Dr. B. Luerssen

In situ surface /interface analysis

Project leader PAK Lithium

µ-ESCA, PEEM

Dr. K. Peppler

Li/O_2 batteries

Education & Teaching

Post-Doc

Dr. J. Sann

Project leader BMBF KVS

Project leader LiVe

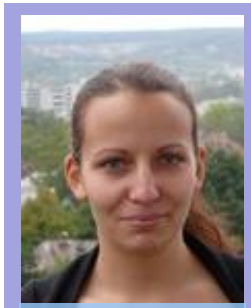
PLD and spectroscopy

Dr. M. Vracar

Li/O_2 batteries

Project leader HE-Lion

Cell design Data acquis.



S. Diegelmann

Cathodes, Li/S batteries,

electrode preparation

K. Sann

Disperse electrolytes

electrolyte characterisation

H. Buschmann

Artificial SEI, solid Li electrolytes

PLD, PLD/Glovebox

R. Dippel

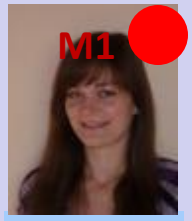
Li metal anodes, Li/O_2 batteries

Micro-electrodes, HRSEM

Dr. rer. nat.

M1

J. Dölle



M1

B. Michalak

M2

N. Ariai

M2

T. Jäger

+ B3: C. E. Bender, B. Jache, S. Wenzel, J. Schultheis

+ BSc M. Falk

M2

J. Reinacher

The lithium team @ AG Janek


Justus v. Liebig