HZB Helmholtz Zentrum Berlin

HOW TO AND NOT TO DESIGN ELECTROCHEMICAL SAMPLE ENVIRONMENTS

Helmholtz-Zentrum Berlin

Elmar Kataev

PROBING BURIED ELECTROCHEMICAL INTERFACES

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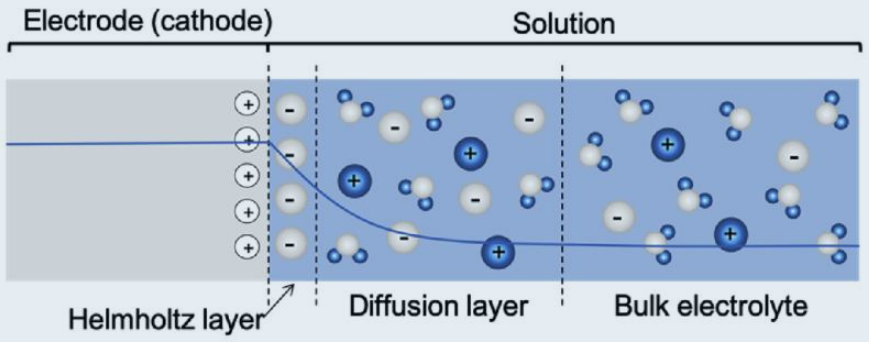
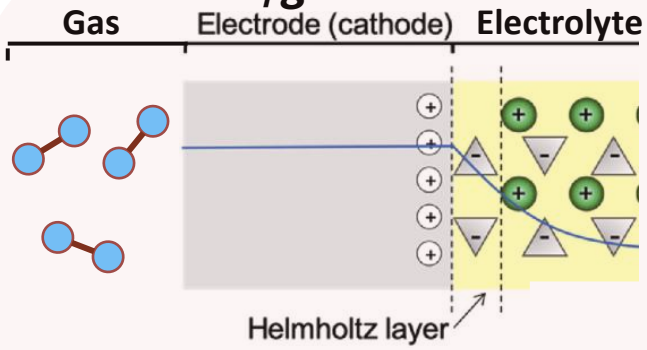
Electrochemical processes start the Helmholtz layer and continue in diffusion layer and bulk electrolyte, motivating us to study its interfaces and bulk with surface and bulk-sensitive methods at operating conditions

Solid/liquid interfaces



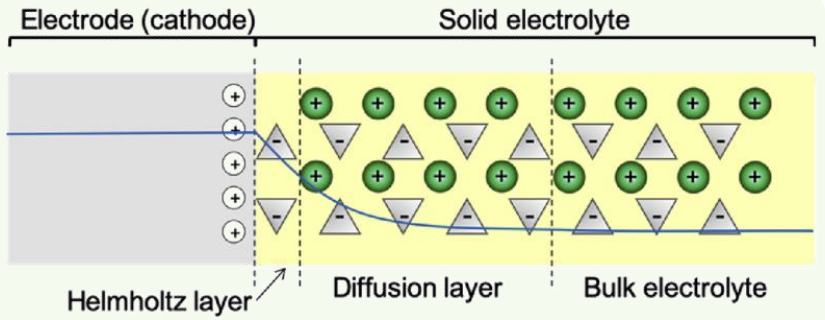
Aqueous and non-aqeous Me-ion cells with liquid electrolyte
Me-MeH batteries (KOH)
Redox-flow batteries
Supercapacitors
Fuel cells (alkaline, phosphoric acid, direct methanol, molten carbonate)

Solid/gas interfaces



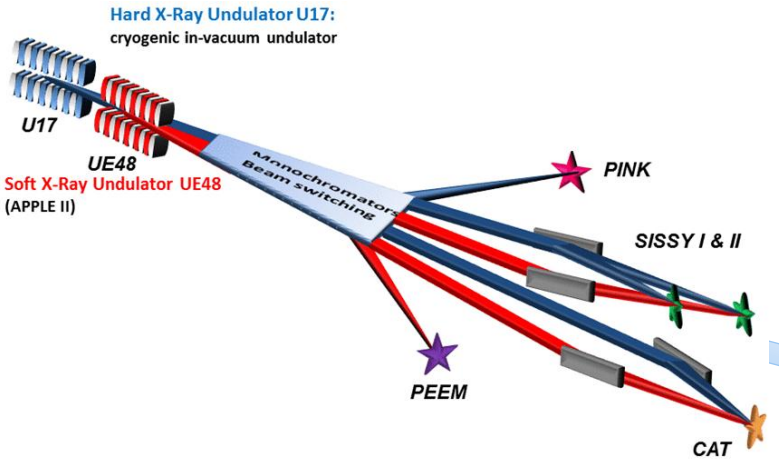
Me-air/O_2 batteries (Zn-air, Li-O_2)
Solid oxide fuel cells
Alkaline and proton-exchange membrane fuel cells
Gas electrochemical sensors
CO_2/N_2 electroreduction cells

Solid/solid interfaces



All-solid-state batteries
Batteries with polymer electrolyte
Solid oxide fuel cells
Thin-film batteries

EMIL — ENERGY-MATERIALS IN-SITU LABORATORY BERLIN



EMIL — ENERGY-MATERIALS IN-SITU LABORATORY BERLIN

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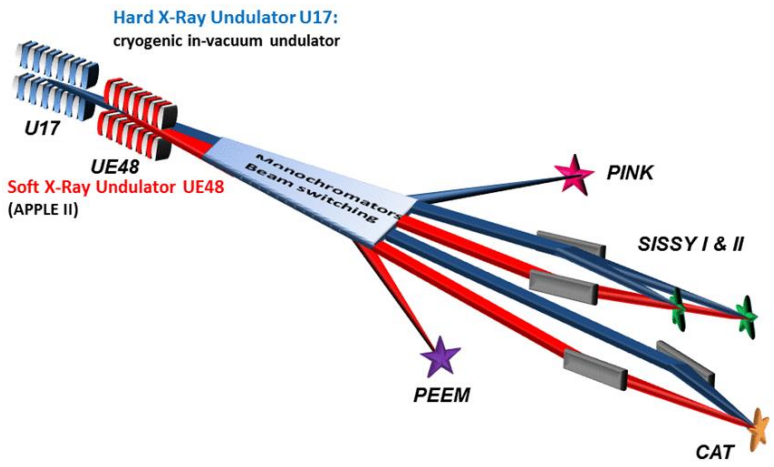
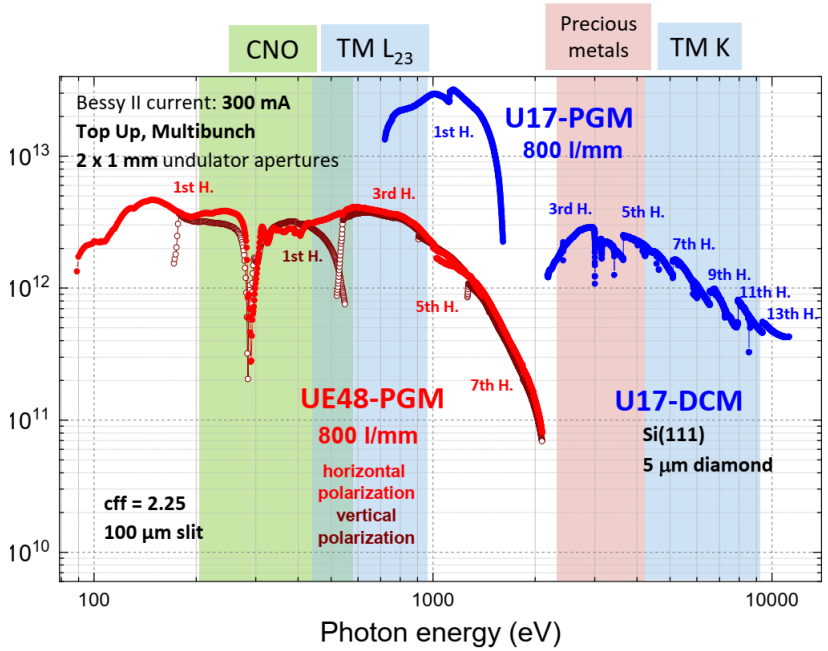
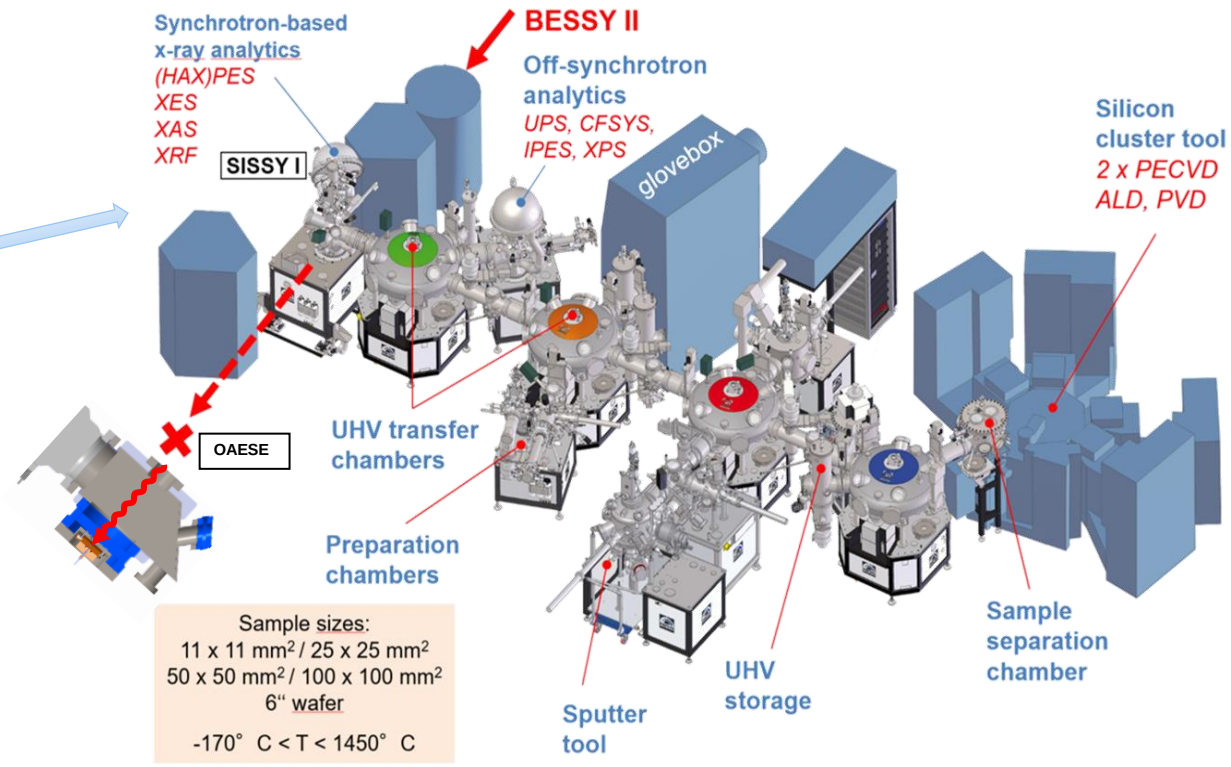






- **2 combined radiation sources (Soft + Hard X-rays) covering energy range 80-10000 eV**
- **Sample environments for *in situ* and *operando* XAS of liquids and gases and HAXPES/XAS of solids**

SYNCHROTRON-SPECIFIC PROBLEMS

Does my *operando* cell reflect processes in the real cell?

Is my area of analysis representative to all material and responds similarly to applied EC conditions?

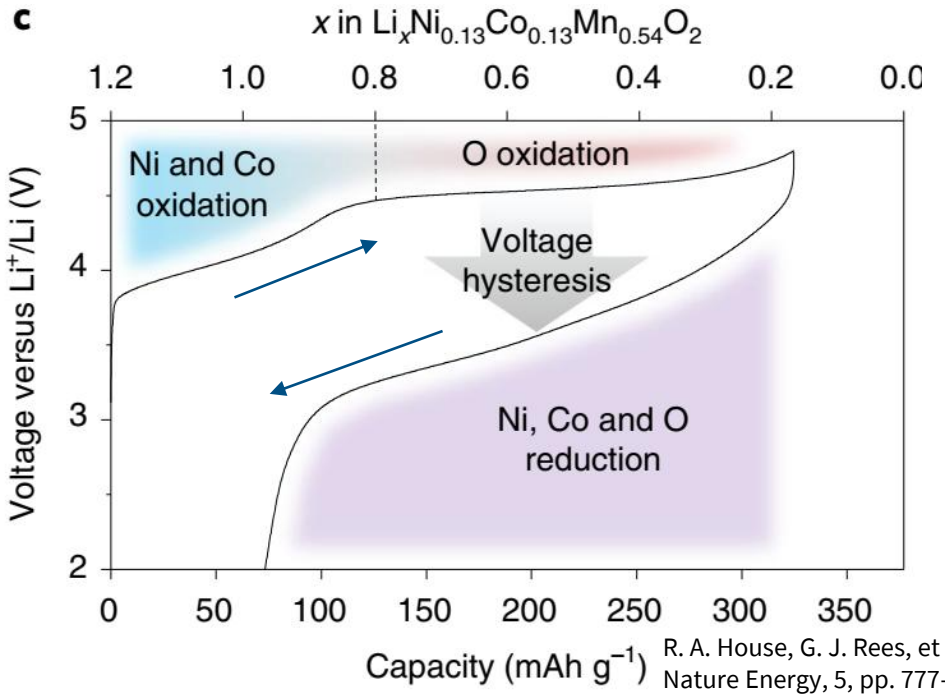
Synchrotron sources – pinhole or window (1mm ⌀) and the beam (100 um ⌀) is smaller than the cell area (10 mm ⌀)

$$\Delta V_{max} \sim f\,\Delta\eta$$

Global potential change

Fraction of area (hole vs whole electrode)

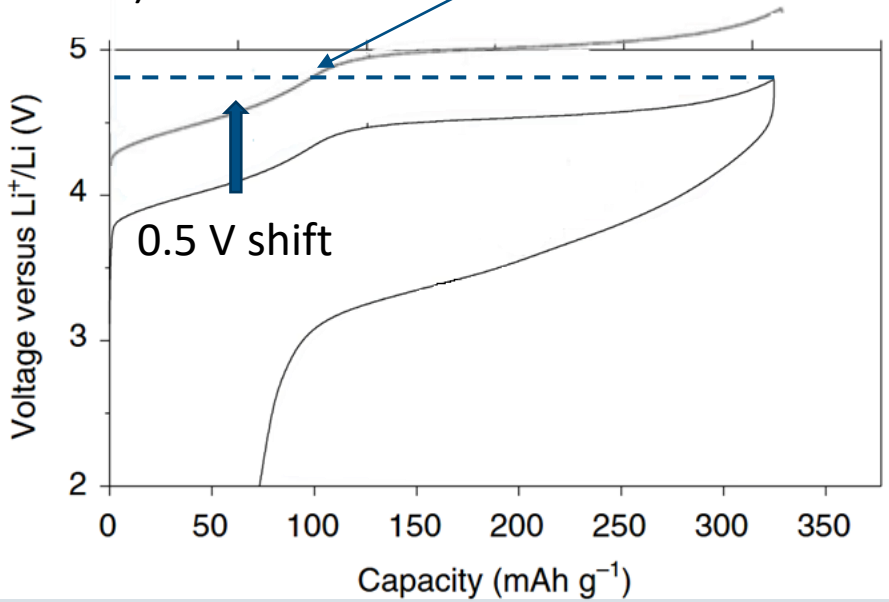
Local overpotential



R. A. House, G. J. Rees, et al. Nature Energy, 5, pp. 777–785 (2020)

Local impedance increase

At the end of operando experiment local spot is still in simple Ni,Co oxidation mode



Beam and sample environment local electrochemical fails can be invisible globally - Local overpotential of 0.5 V will shift global curve only by 50 µV and 5 mV for beam and window area!

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NEUTRON SOURCE SPECIFIC PROBLEM

Does my *operando* cell reflect processes in the real cell?
Is my area of analysis representative to all material and responds similarly to applied EC conditions?

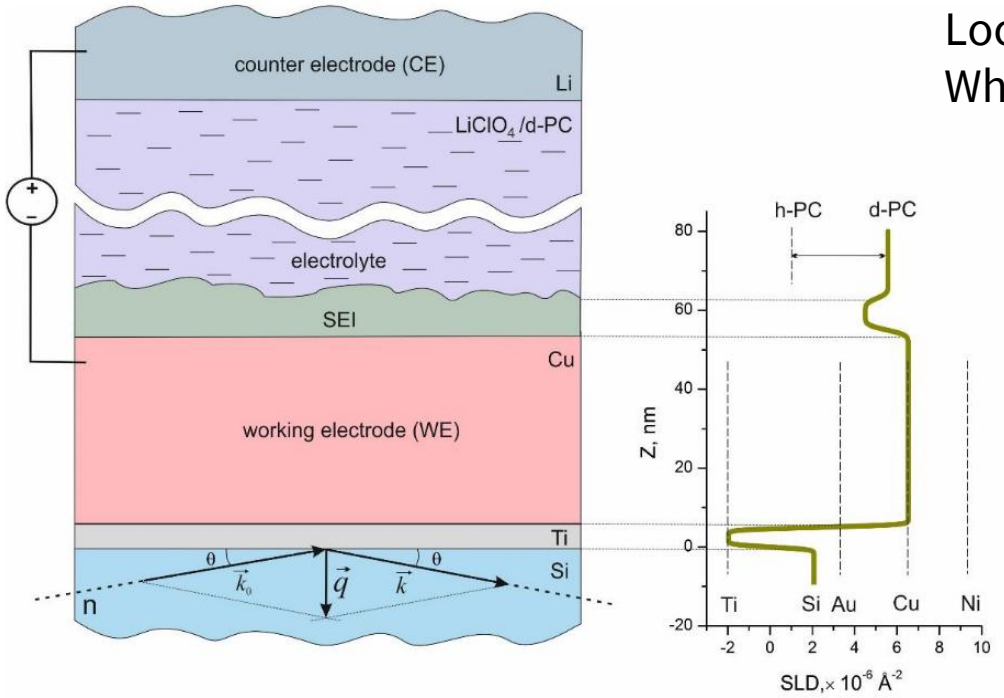
Neutron sources – large beam ≠ safe averaging!
Fully lithiated and partially lithiated co-existing phases will be interpreted as effective 1 phase with different properties => extremely large uniformity is needed, i.e. small roughnesses

roughness

$$q_z \, \sigma \leq 1$$

Normal momentum transfer

Li and SEI growth neutron reflectometry experiment



https://doi.org/10.1016/j.apsusc.2017.01.290

Local resistance ∝ thickness => thin spots carry more current
When local current doubles, measurement usually doesn't make sense:

$$\frac{j_{max}}{j_{avg}} \approx \frac{t_{avg}}{t_{avg} - 2\sigma}$$

$$\frac{j_{max}}{j_{avg}} \sim 2 \Rightarrow \frac{t_{avg}}{t_{avg} - 2\sigma} = 2 \Rightarrow \sigma \sim \frac{t_{avg}}{4}$$

j_{max} – local current, j_{avg} –average current through the cell, t_{avg} – average thickness, σ – roughness

For the uniformity roughness should be 4 times smaller than average thickness

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NEUTRON SOURCE SPECIFIC PROBLEM

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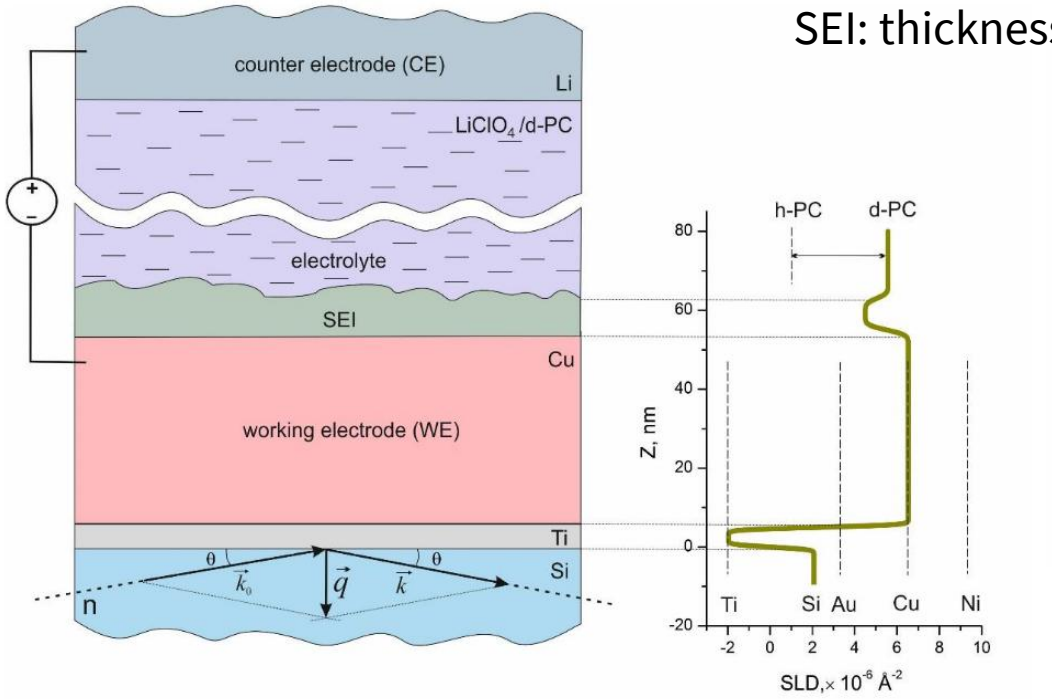
Fully lithiated and partially lithiated co-existing phases will be interpreted as effective 1 phase with different properties => extremely large uniformness is needed, i.e. small roughnesses

85x50mm Si crystal block (42.5 cm^2 area), roughness 0.5 nm, after Ti/Cu deposition (55 nm thick overall) roughness is 1.7nm

SEI: thickness 5 nm, with diffusive roughness 3.5 nm



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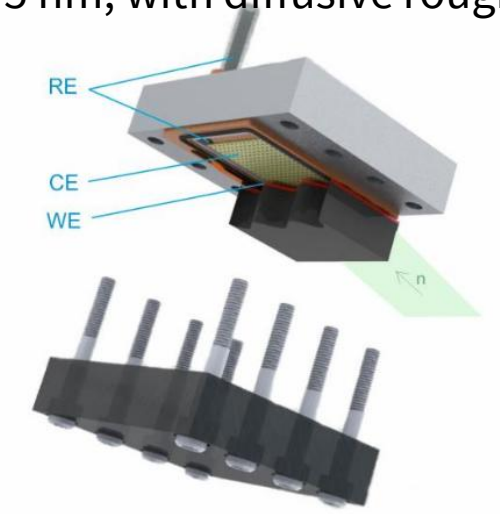

$$\sigma \sim \frac{t_{avg}}{4}$$

For Ti/Cu ✓

For SEI ✗

Li plating proceeds non-uniform

For the uniformity roughness should be 4 times smaller than average thickness

PROBING BURIED ELECTROCHEMICAL INTERFACES

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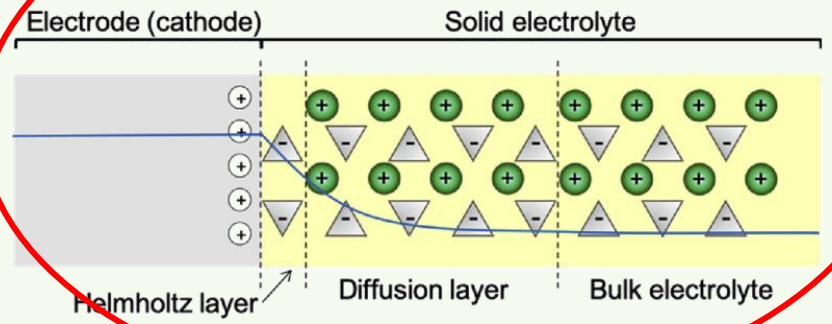
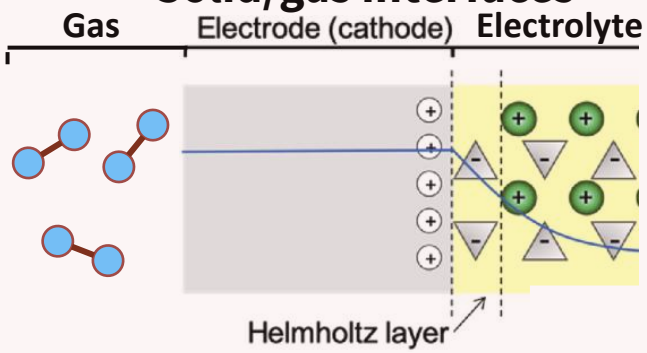
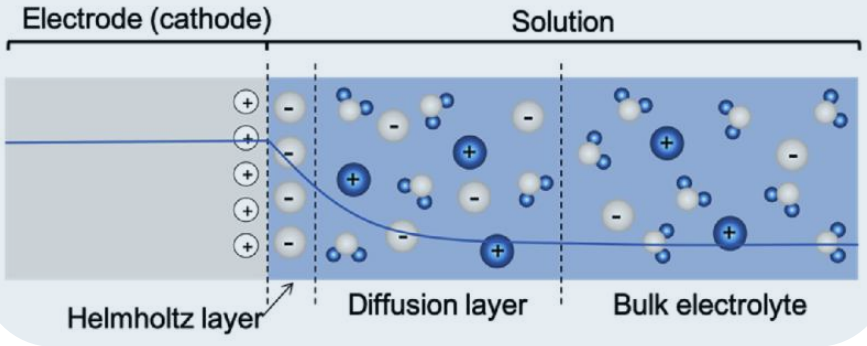
Solid/solid interfaces



Solid/gas interfaces



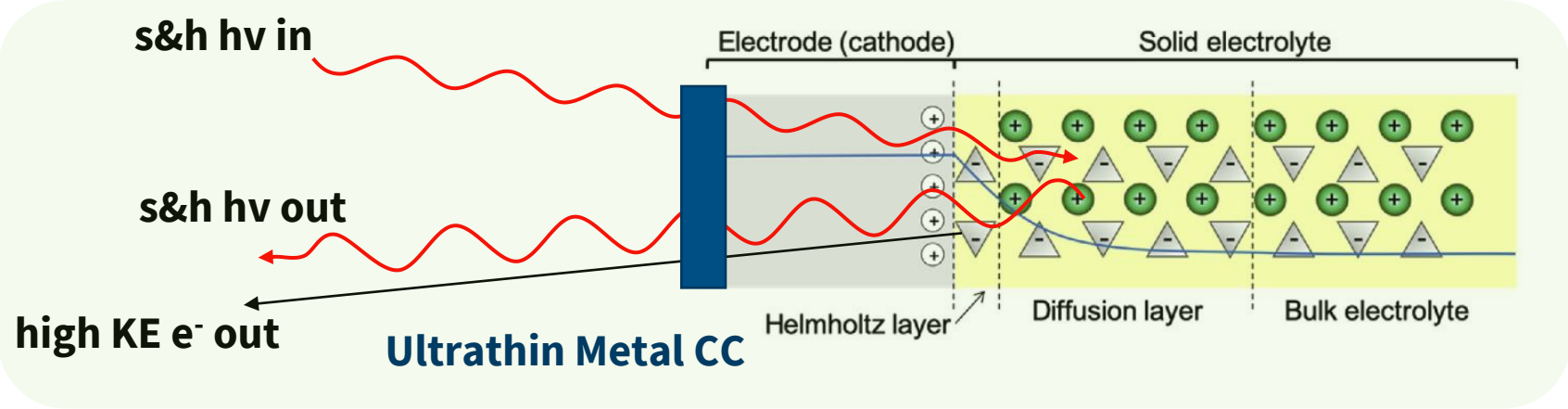
Solid/liquid interfaces



PROBING THE SOLID/SOLID INTERFACES: WINDOW APPROACH

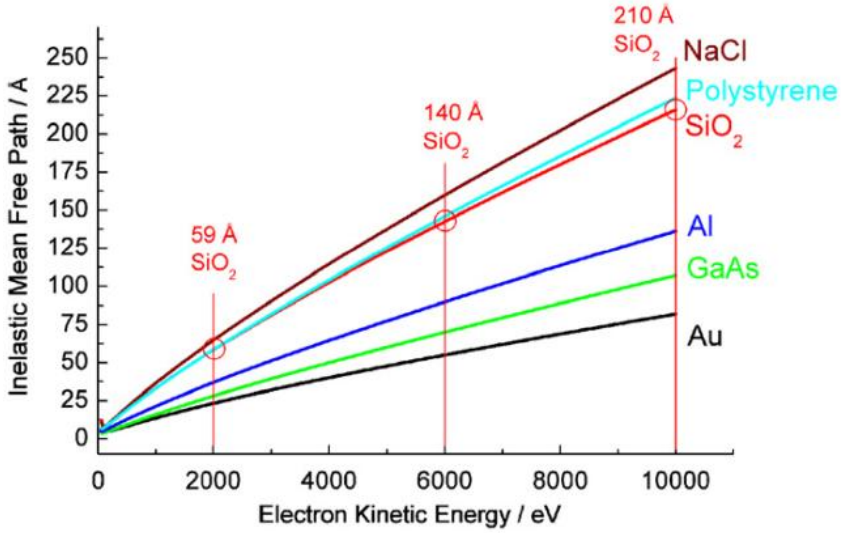
Features

1. Usually HV and UHV-compatible
2. High stacking pressure is required to operate the battery
3. Slow kinetics of solid-state reactions sometimes require higher temperatures

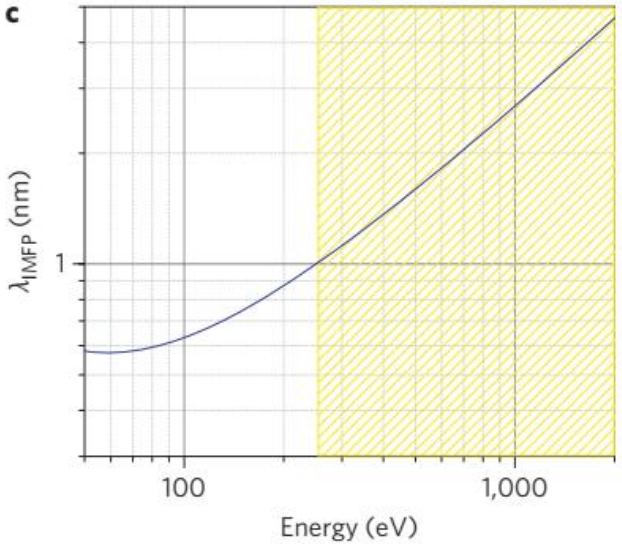


Window material:
Ultrathin metal film (6-10 nm)
Graphene (2L)

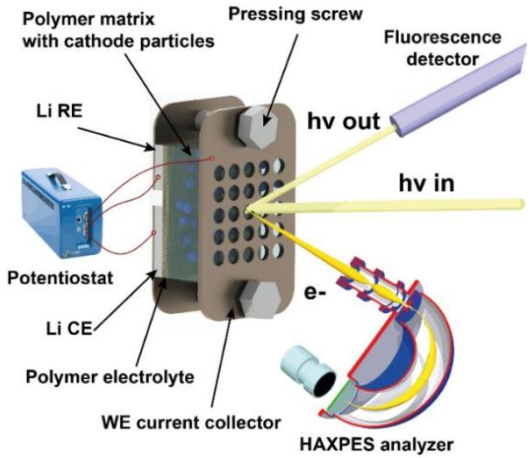
Inelastic mean free path for different materials



Inelastic mean free path for graphene

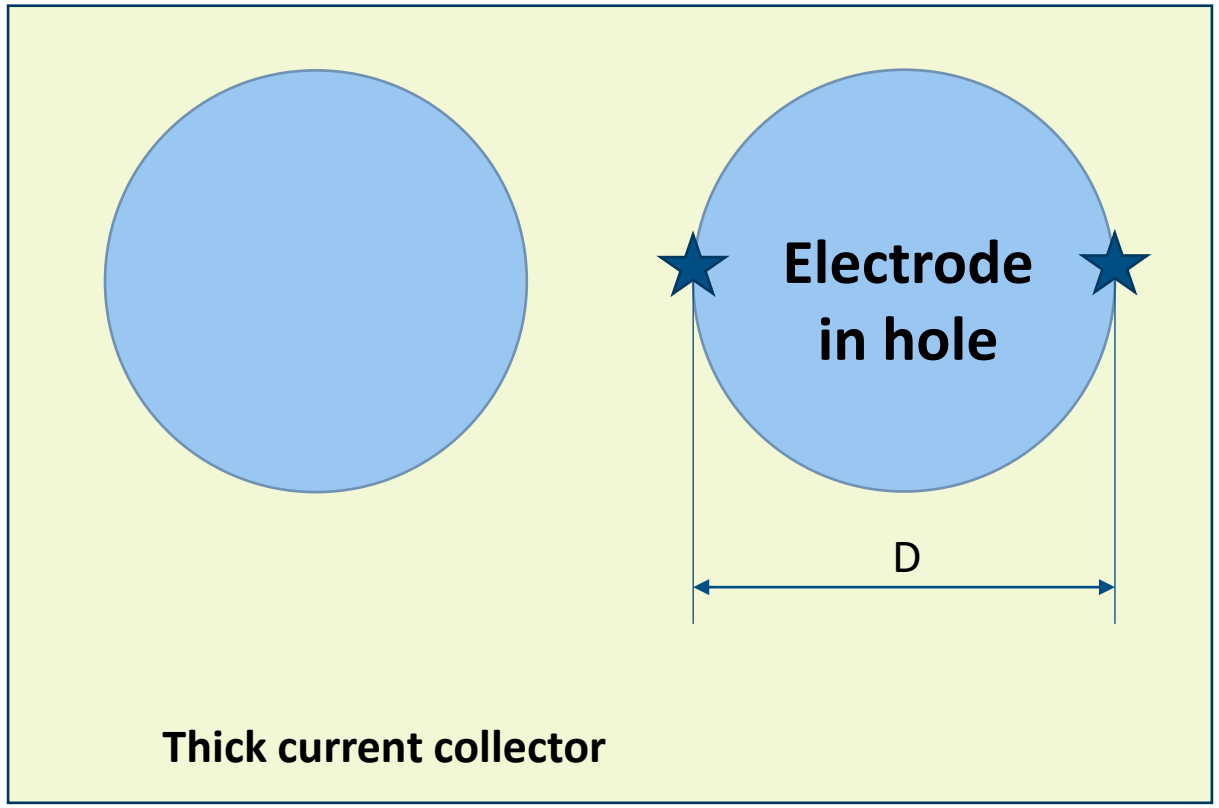


PROBING THE SOLID/SOLID INTERFACES: WINDOWLESS APPROACH



Requirements

- good electrical conductivity of the electrode, **stable over cycling**. Overpotential should be no more than 0.1 – 0.2 V, acceptable resistance is calculated using distance between holes and operating currents



Overpotential (aim at max 0.1 V)

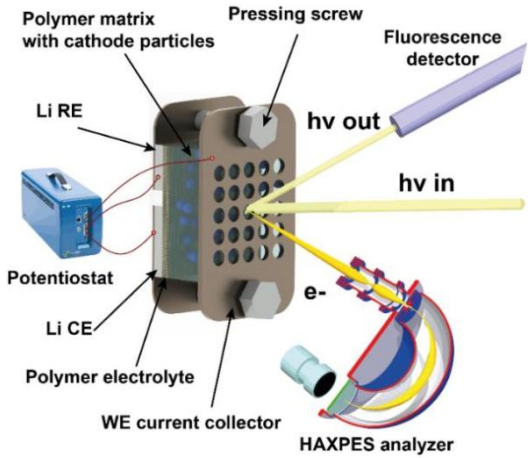
$\Delta U = R \cdot I_{op}$

Two-point resistance (radius of the hole)

Operating current of the cell

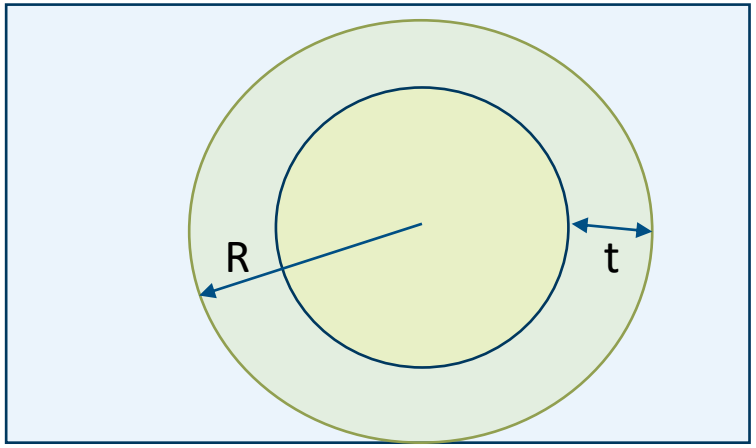
If calculated ΔU is too high, reduce D or I_{op}

PROBING THE SOLID/SOLID INTERFACES WINDOWLESS APPROACH



Requirements

- good electrical conductivity of the electrode, **stable over cycling**. Overpotential should be no more than 0.1 – 0.2 V, acceptable resistance is calculated using distance between holes and operating currents
- Smaller particles for better interfacial contribution (for 50% interfacial contribution one needs particles with diameter not more than 10 times higher compared to expected interfacial thickness).



$$f = \frac{V_{interface}}{V_{total}} = \frac{R^3 - (R-t)^3}{R^3}$$

$$f = 1 - \left(1 - \frac{t}{R}\right)^3$$

t – interfacial thickness
R – full particle radius
f – interfacial contribution

- Lower C-rates (operating currents) to ensure that material in hole is at the same state as material under CC

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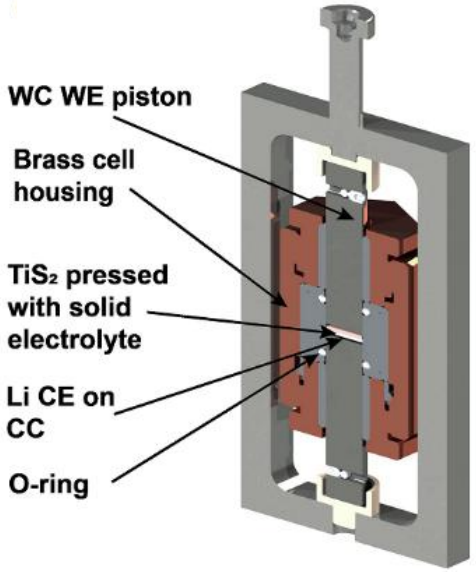
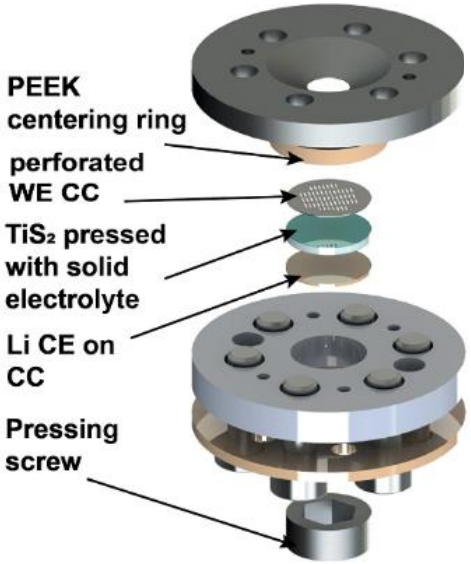
PROBING THE SOLID/SOLID INTERFACE

Achieving high static pressure in the cell

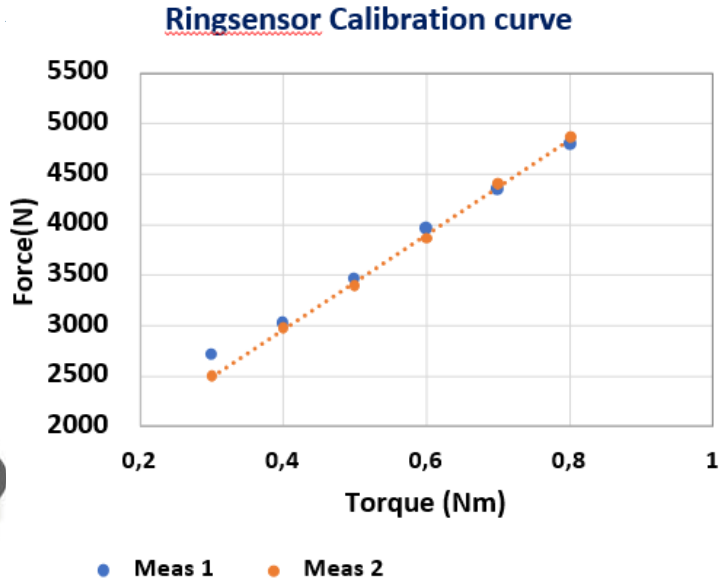
Typical laboratory all-solid-state cell

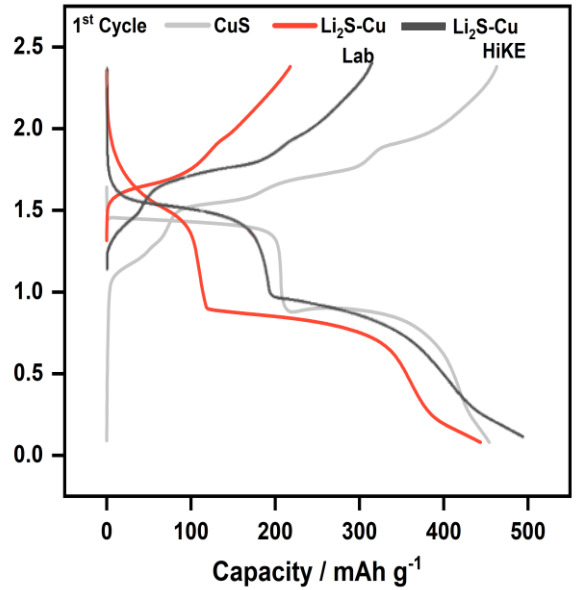


Operando cell



Same electrode diameters (10mm), much different pressing systems





$CuS + 2Li \rightarrow Li_2S + Cu$

$Li_2S + Cu \rightarrow CuS + 2Li$

CuS or Li_2S/Cu electrode, Li metal anode, Li_6PS_5Cl electrolyte

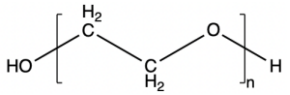
- To achieve reasonable electrochemical performance, pre-pressing of the cell stack in the standard laboratory cell is needed
- The stacking pressure of the cell should be measured, ideally during operation as well

P. Adelhelm group

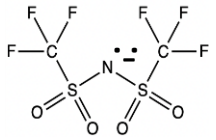
PROBING SOLID/SOLID INTERFACES
CELL VERIFICATION

For anode-free studies: growing of metallic alkali should be confirmed beforehand electrochemically and microscopically

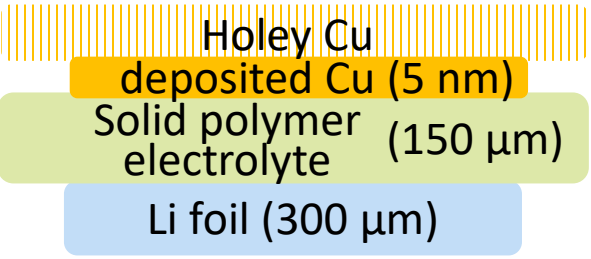
PEO+LiTFSI



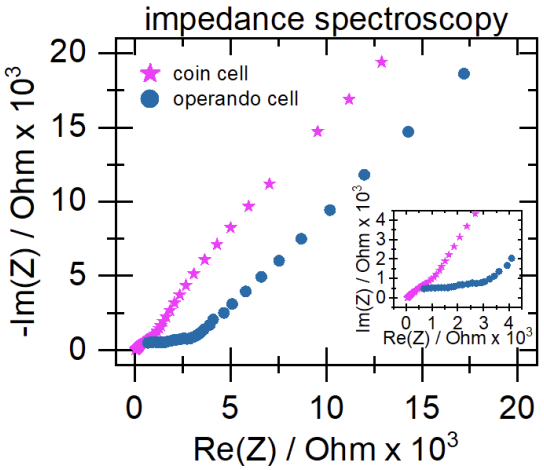
PEO

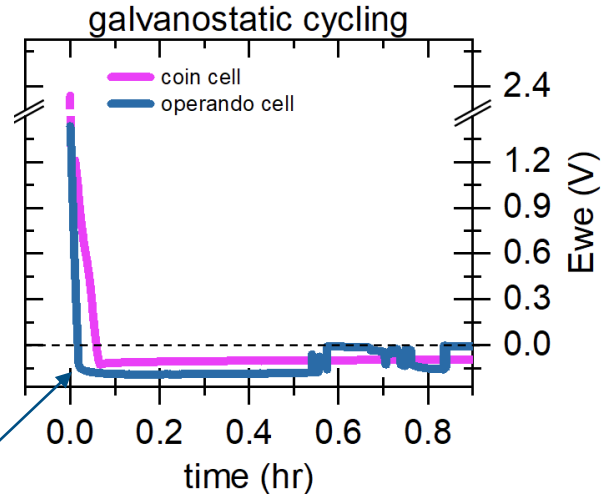


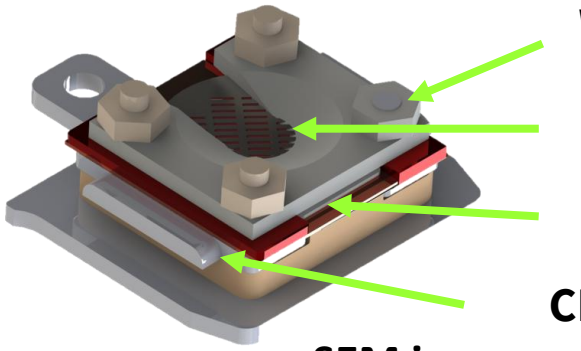
TFSI



Nucleation potential

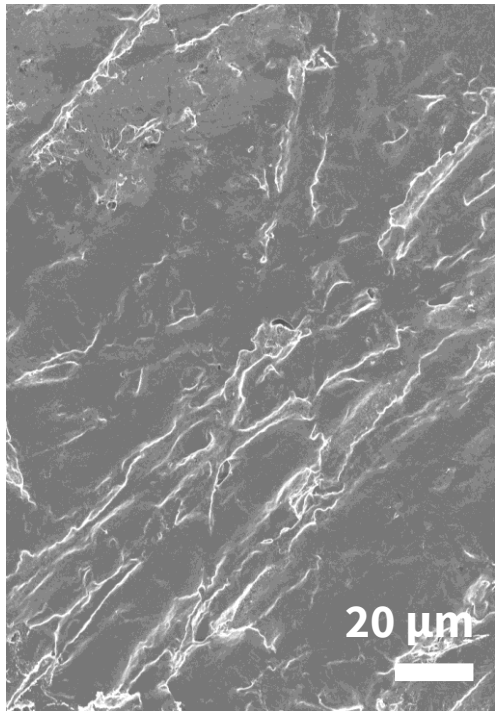




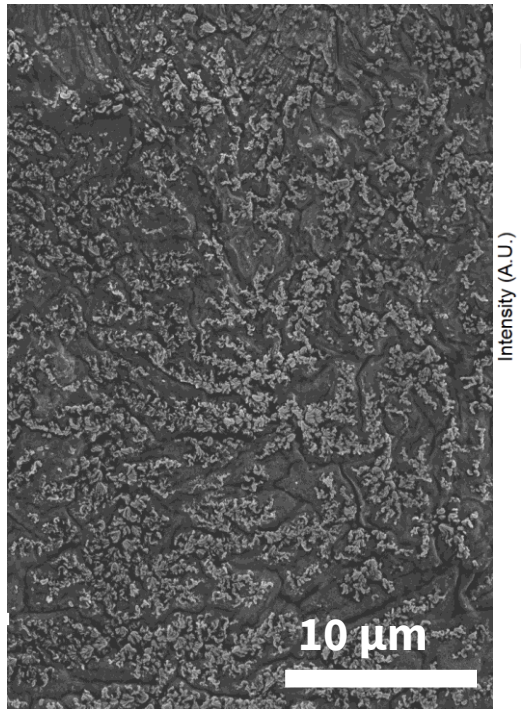


SEM images

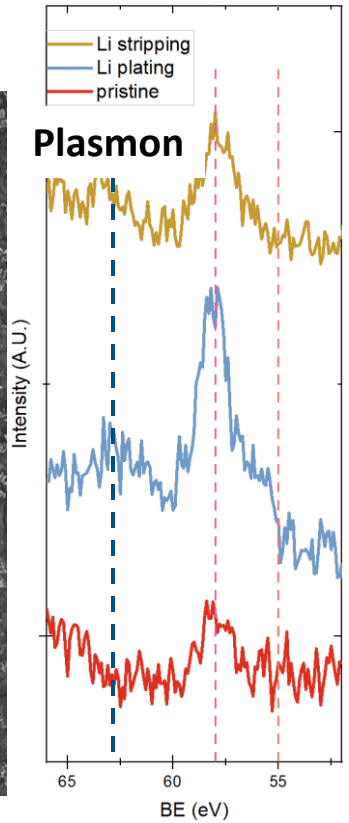
Pristine



After cycling

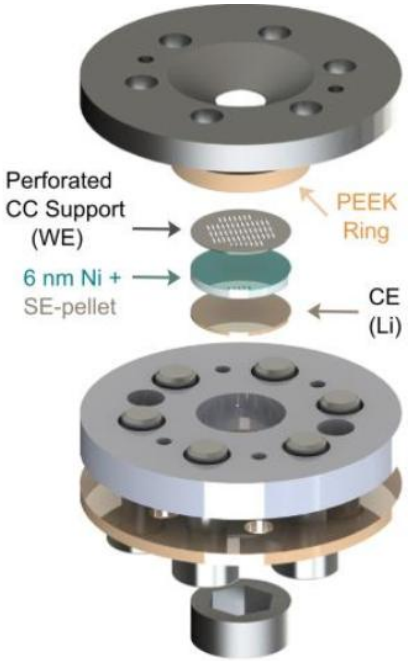


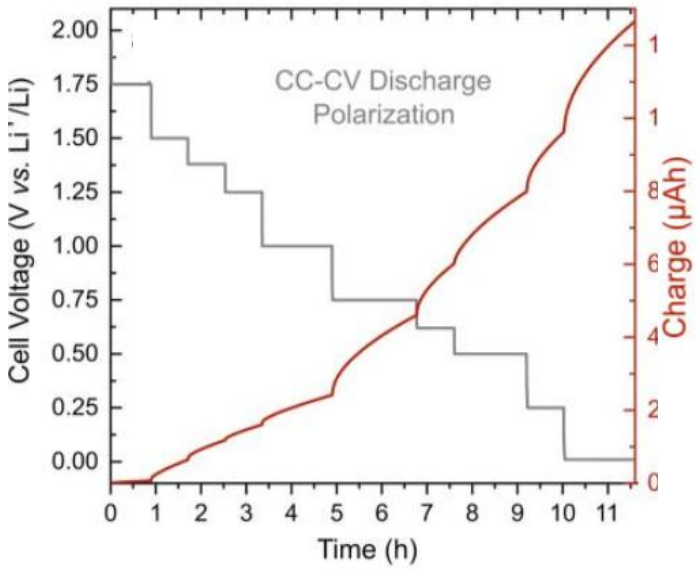
Li 1s hv=2100 eV



PROBING SOLID/SOLID INTERFACES

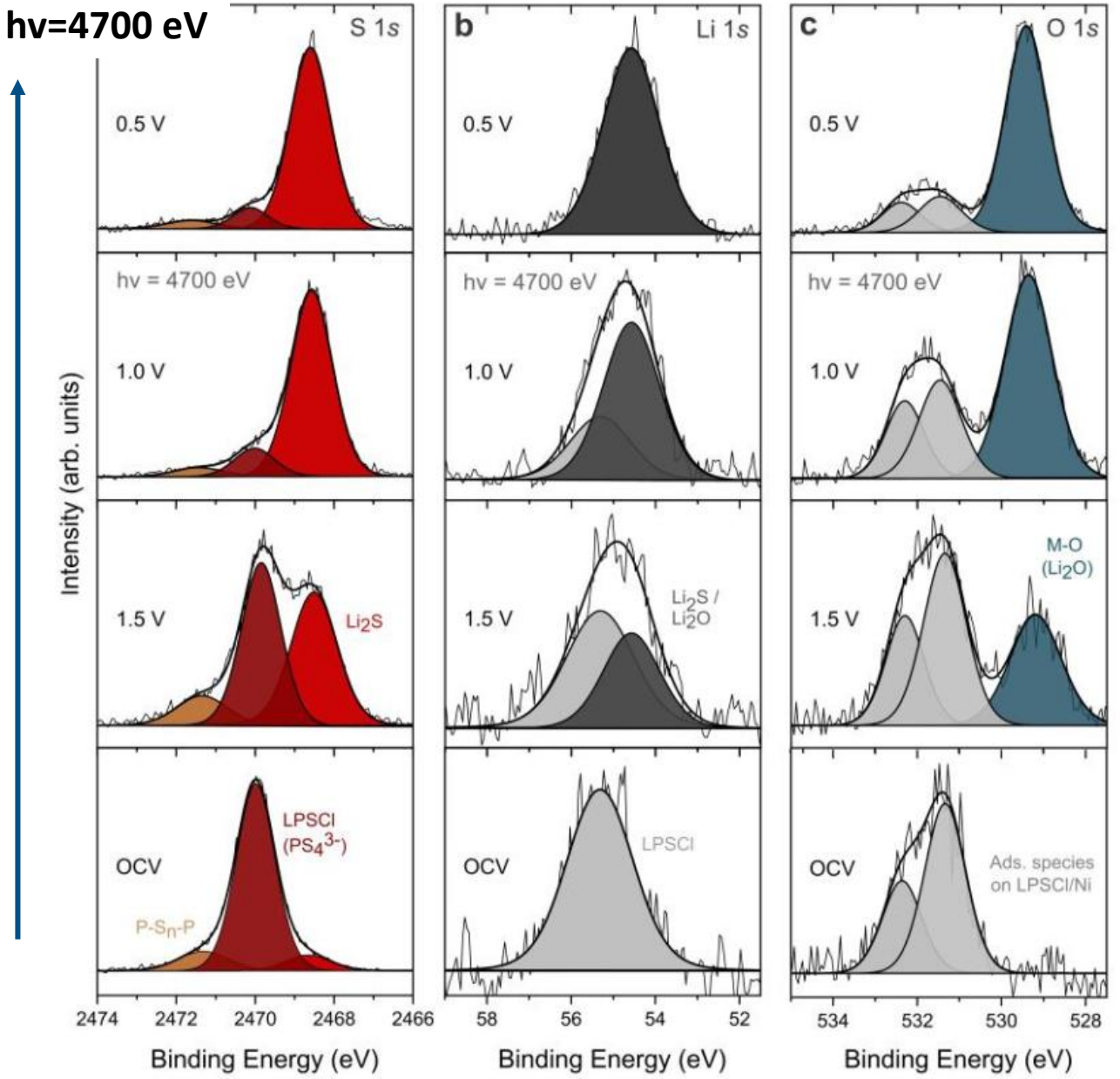
Separating pure electrochemical from pure chemical reaction





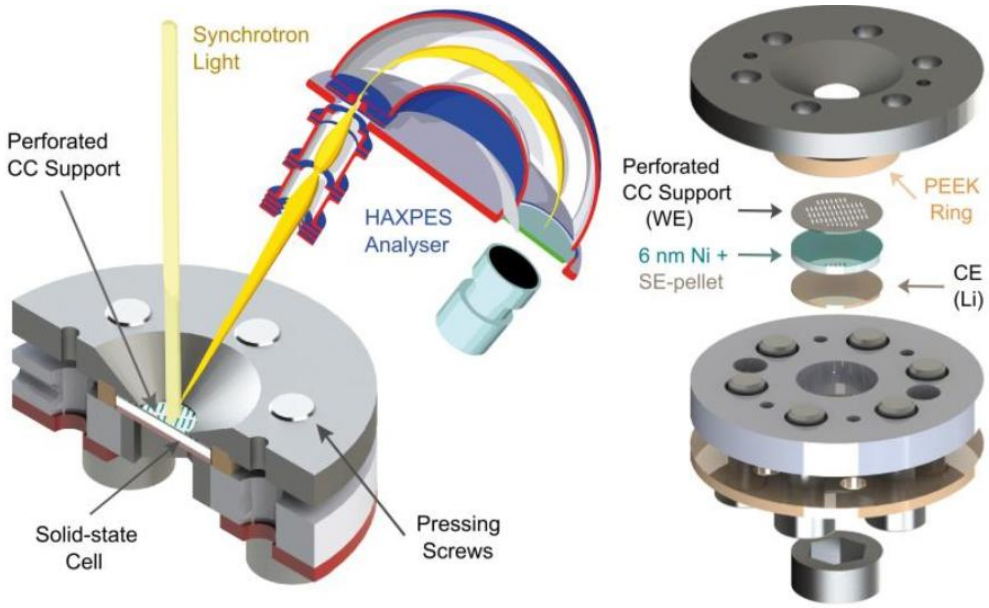
Li_6PS_5Cl electrolyte, Li metal CE, 6nm of Ni WE CC

B. Aktekin, E. Kataev et al//
doi.org/10.26434/chemrxiv-2024-g4wkt

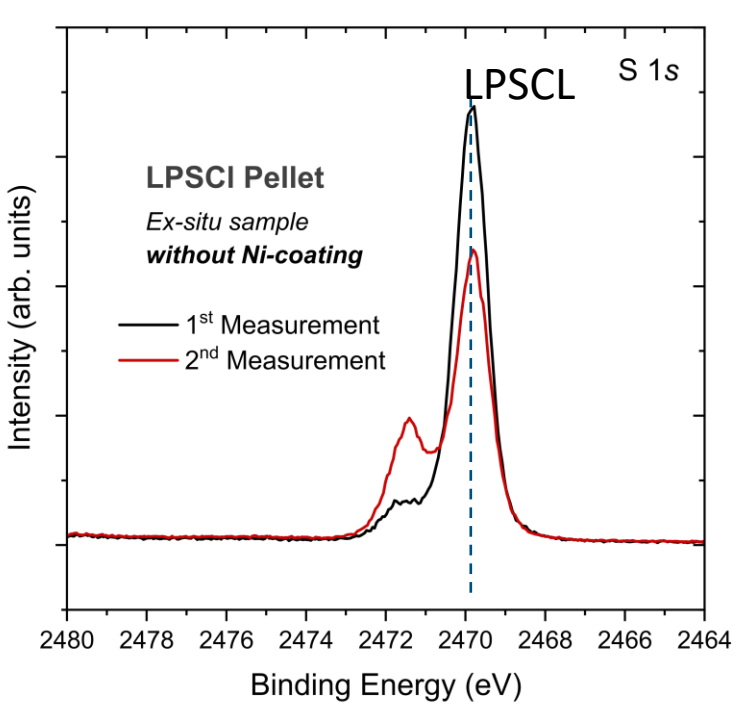


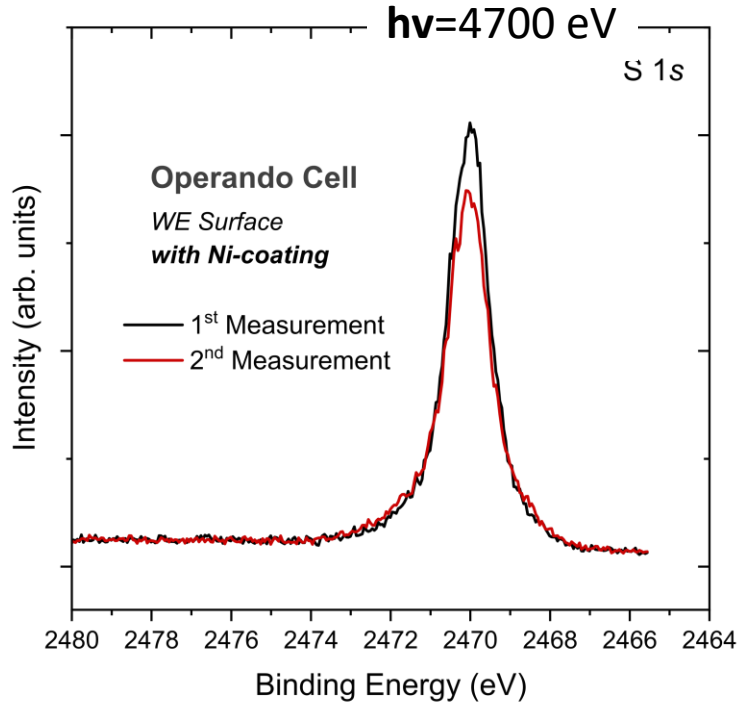
For probing stability of electrolytes, it is important to separate its electrochemical reduction or oxidation from pure reaction a) with Li metal b) evolved O2 on the cathode: **stepwise control of potential is important**

BEAM DAMAGE MITIGATION IN UHV



LPSCl – Li_6PS_5Cl electrolyte pellet





- Ultrathin current collector approach helps to drain electrons and mitigate beam damage
- For this, grounding of WE to spectrometer is needed

B. Aktekin, E. Kataev et al// doi.org/10.26434/chemrxiv-2024-g4wkt

PROBING BURIED ELECTROCHEMICAL INTERFACES

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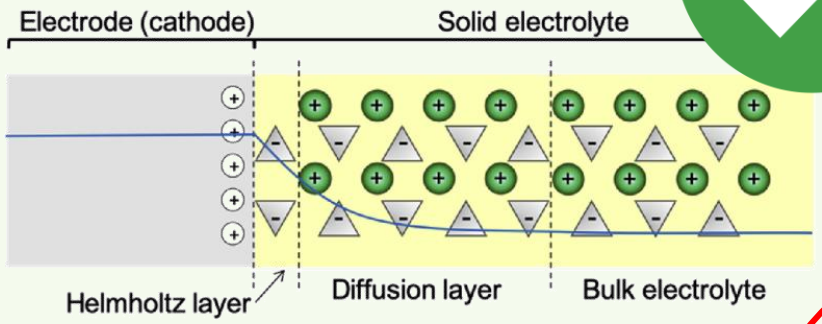
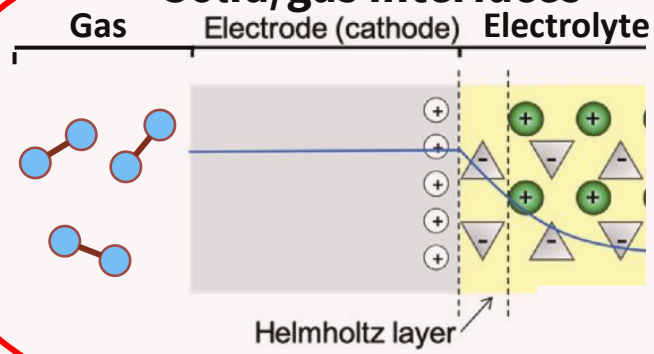
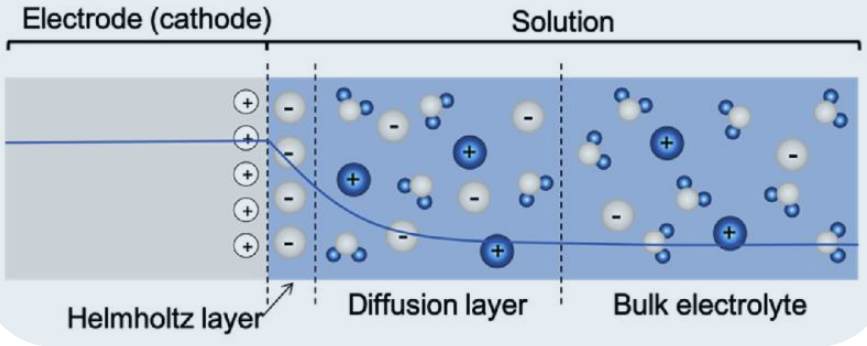
Solid/solid interfaces



Solid/gas interfaces

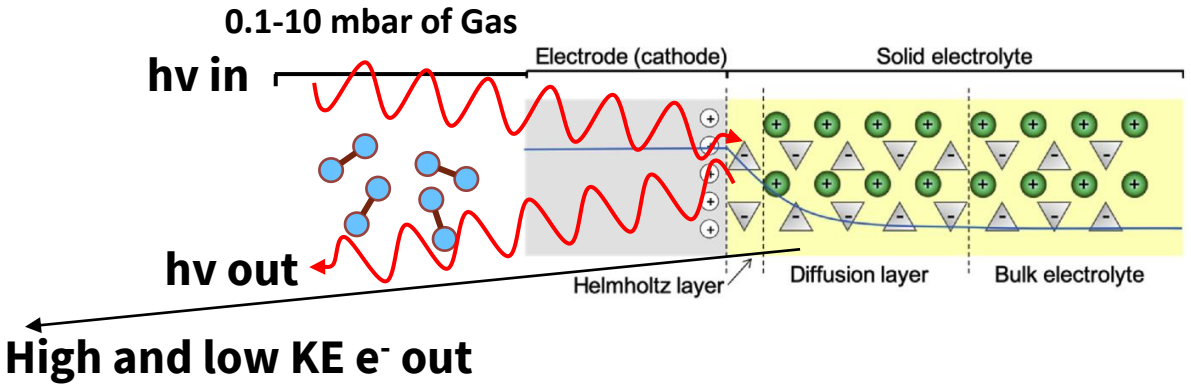


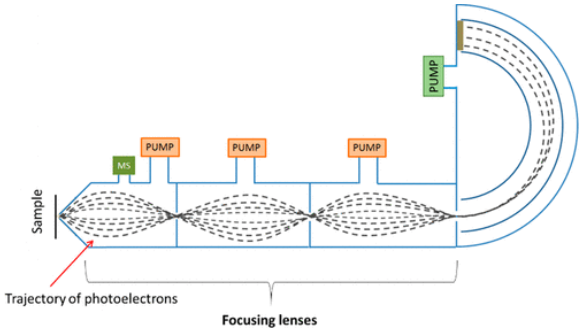
Solid/liquid interfaces



PROBING SOLID/GAS INTERFACES

Windowless approach

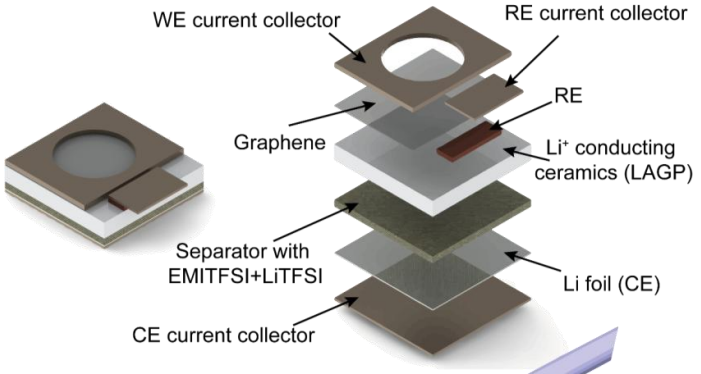


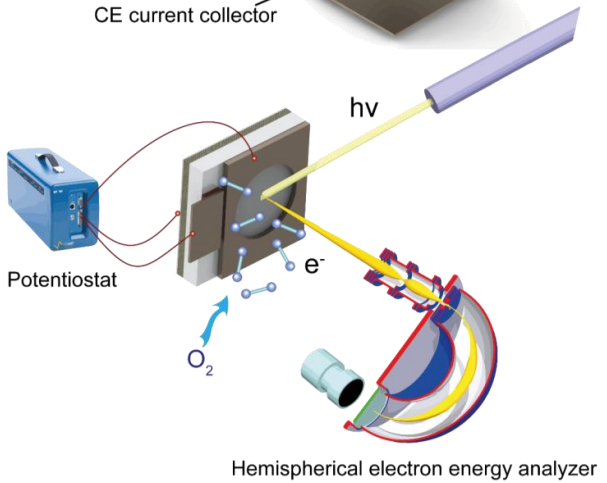


L. Nguyen, et al, Chem. Rev. 119(12) (2019) 6822-6905.

APXPS Li-O_2 electrochemical cell

Anode $Li \rightarrow Li^+ + e^-$
Cathode $O_2 + 2Li^+ + 2e^- \rightarrow Li_2O_2$



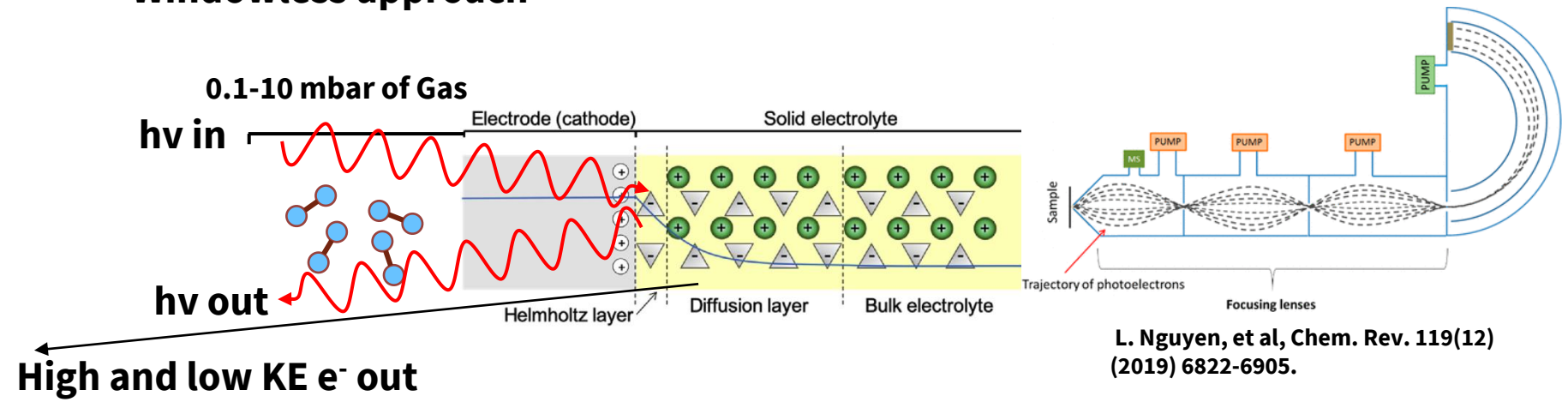


Requirements

- As for solid\solid: sufficient interfacial contribution, low electrode impedance
- Detectors and photon sources should be at reasonable pressure, using differential pumping stages and beamline windows
- High porosity for creating three-dimensional border electrode/electrolyte/gas

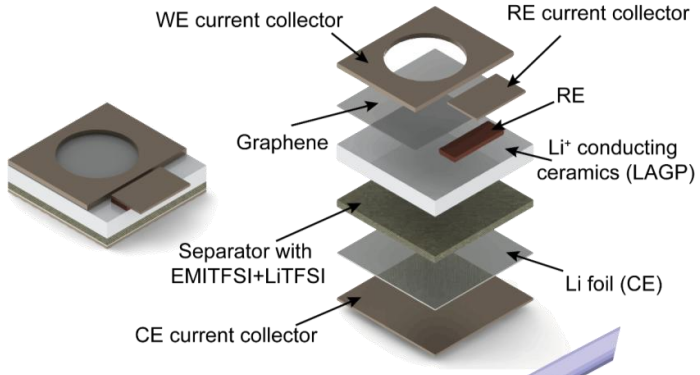
PROBING SOLID/GAS INTERFACES

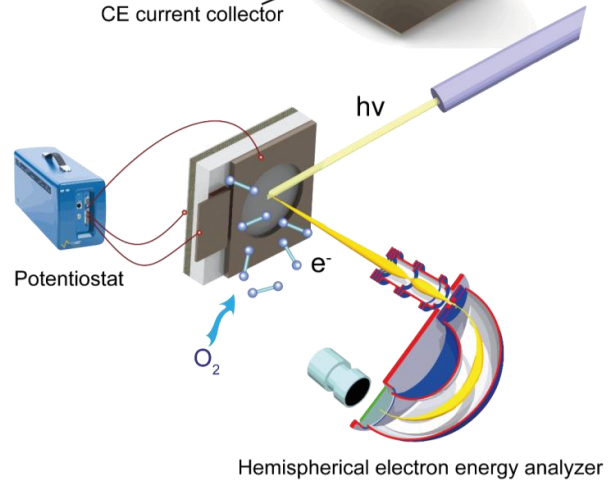
Windowless approach



L. Nguyen, et al, Chem. Rev. 119(12) (2019) 6822-6905.

APXPS Li-O_2 electrochemical ce





What is reasonable pressure?

General case

$$\Delta G = -nFE$$

$$\Delta G_{gas} = RT \ln\left(\frac{p_{gas}}{p^0}\right)$$

$$\Delta E_{gas} = -\frac{RT}{nF}\nu \ln\left(\frac{p_{gas}}{p^0}\right)$$

Moles of gas

Anode Li → $Li^+ + e^-$
Cathode $O_2 + 2Li^+ + 2e^- \rightarrow Li_2O_2$

n=2, RT

13 mV

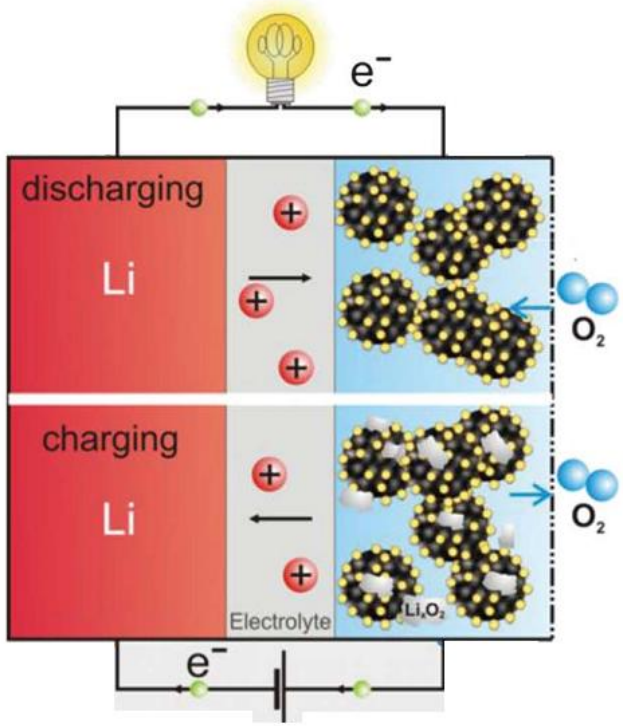
For 10 mbar: 60 mV difference
For 1 mbar: 90 mV difference
For 0.1 mbar: 112 mV difference
For e-4 mbar: 200 mV difference

PROBING SOLID/GAS INTERFACES REVEALING REACTION PATHWAYS

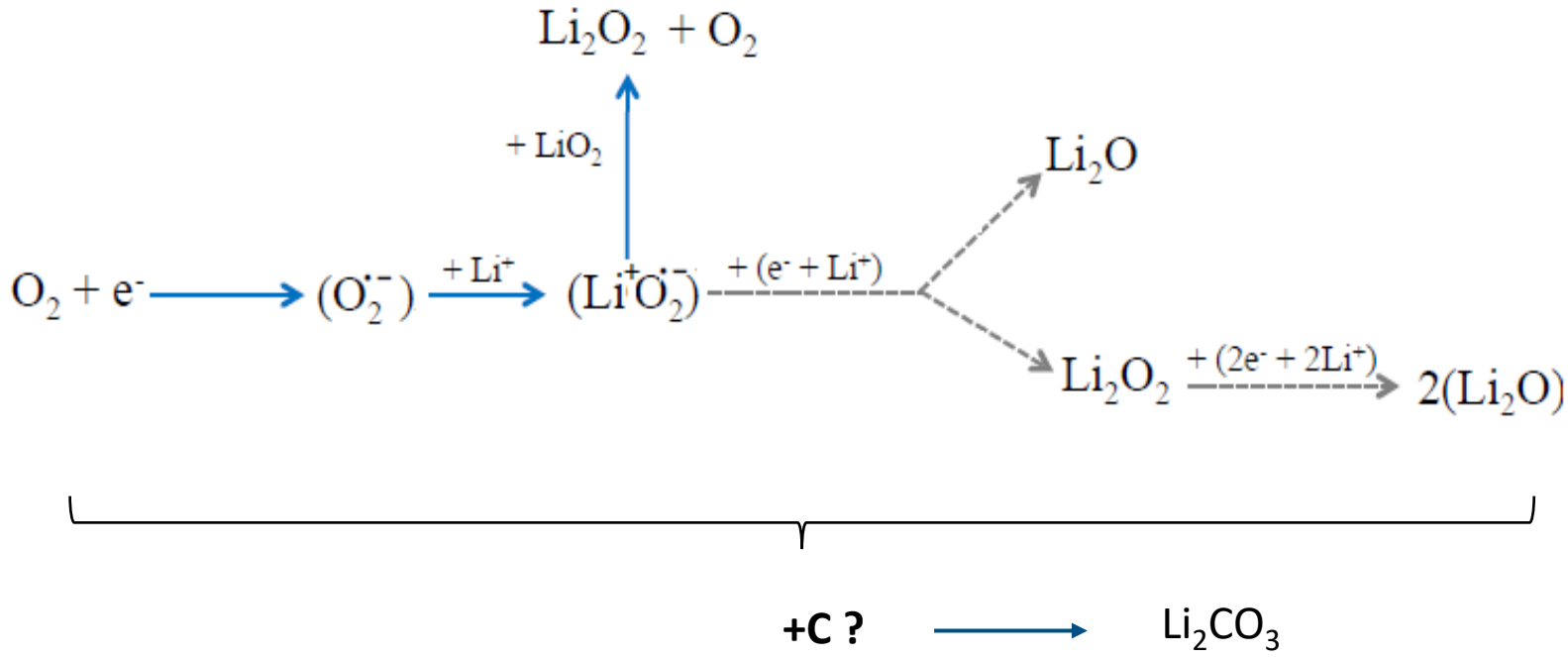
EMIL HZB Helmholtz Zentrum Berlin

Separating pure electrochemical from pure chemical reaction

Lithium-air battery



Anode(lithium) $Li \rightarrow Li^+ + e^-$
Cathode (carbon) $O_2 + 2Li^+ + 2e^- \rightarrow Li_2O_2$

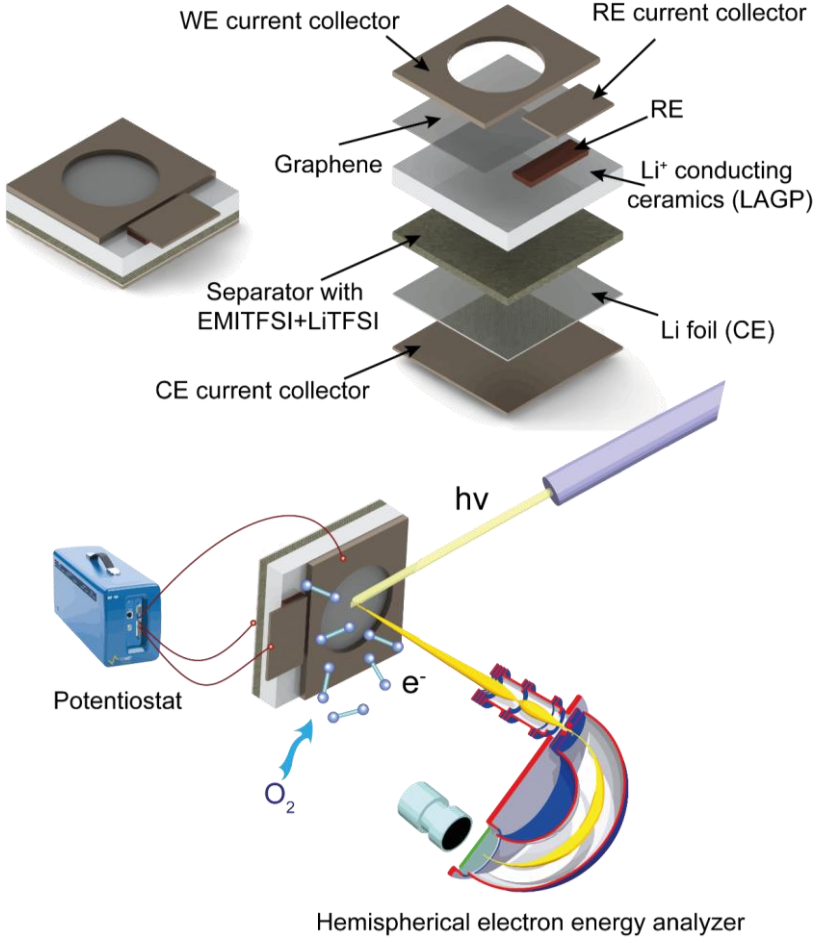


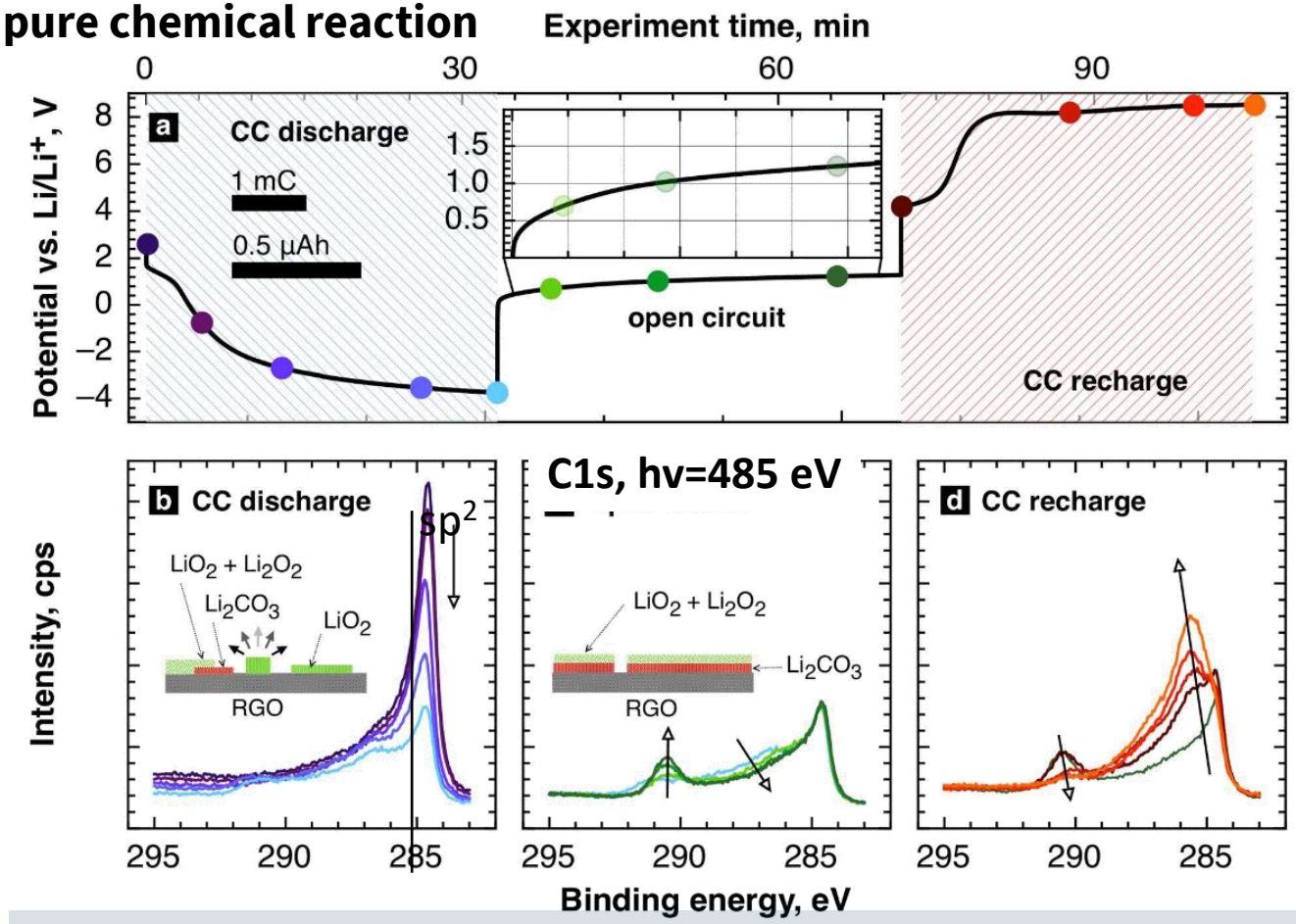
Electrochemical reaction often result in reactive intermediates, that can purely chemically interact with electrode and electrolyte materials

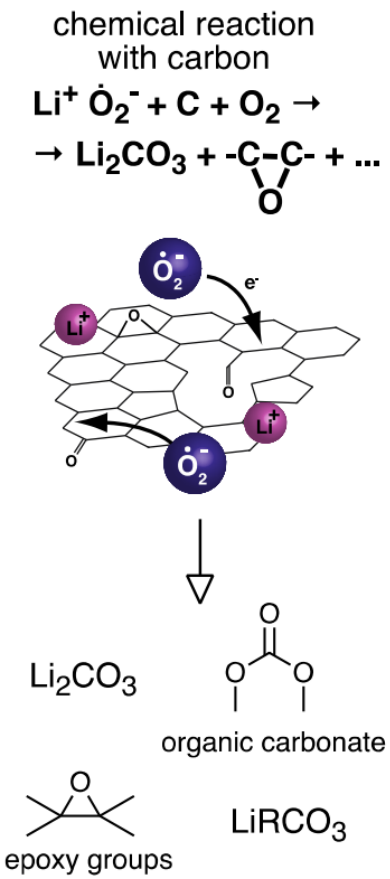
Y.-C. Lu et al. **Energy Environ. Sci.**, 2013

PROBING SOLID/GAS INTERFACES REVEALING REACTION PATHWAYS

Separating pure electrochemical from pure chemical reaction

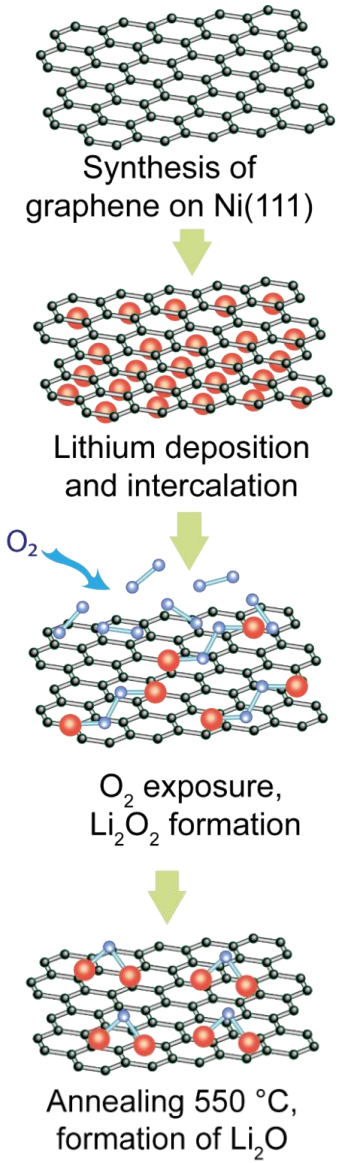




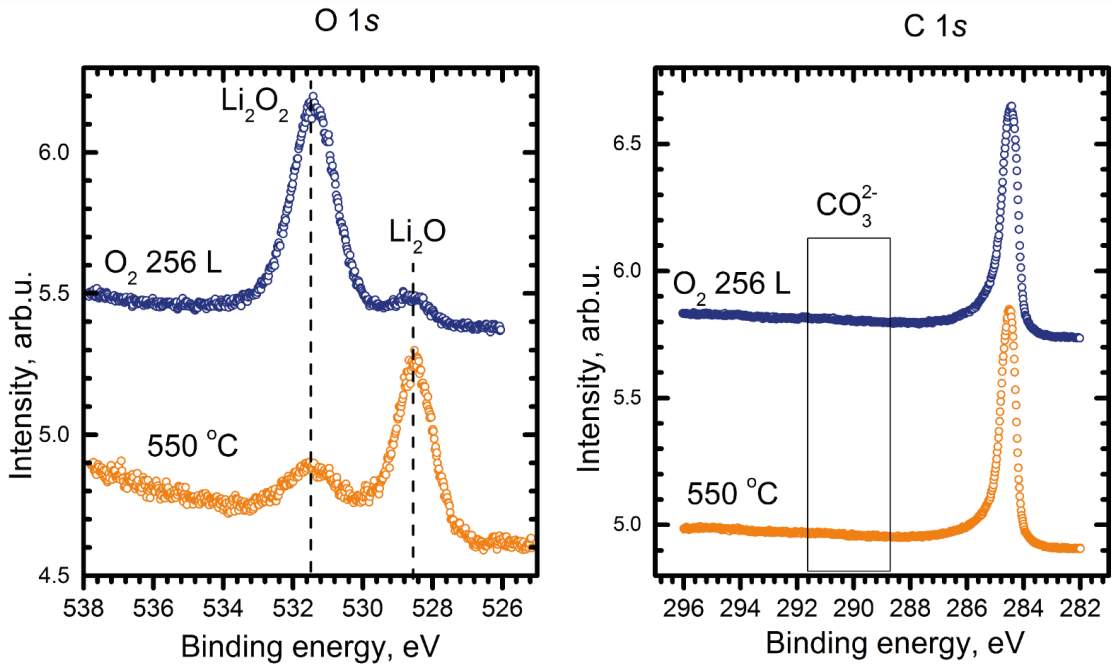


- Pure chemical interaction of intermediates can be isolated by setting system to OCV state for periods of time
- The presence of O2 in this or that reaction pathway can be figured out by reducing gas pressure

SUPPORTING OPERANDO RESEARCH
CHEMICAL MODELLING



KE=200 for all spectra



$$Li_2O + C \not\rightarrow Li_2CO_3$$

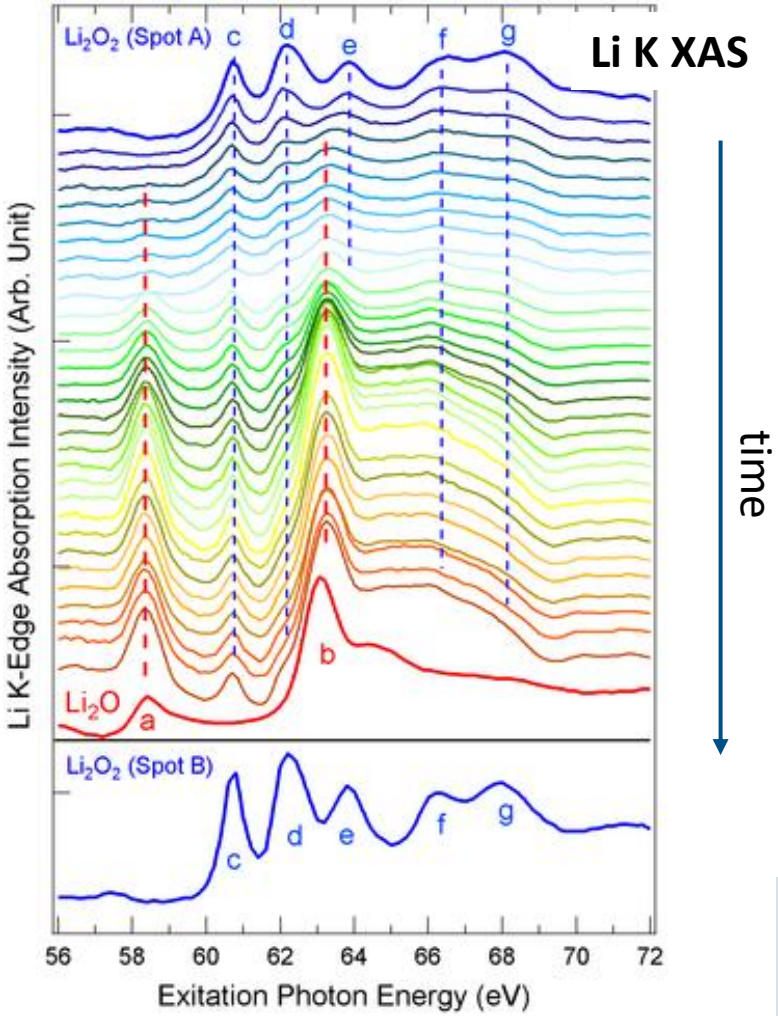
$$Li_2O_2 + C \not\rightarrow Li_2CO_3$$

Kataev, et al. // ACS Nano 2015

PROBING SOLID/GAS INTERFACES
BEAM IRRADIATION EFFECTS

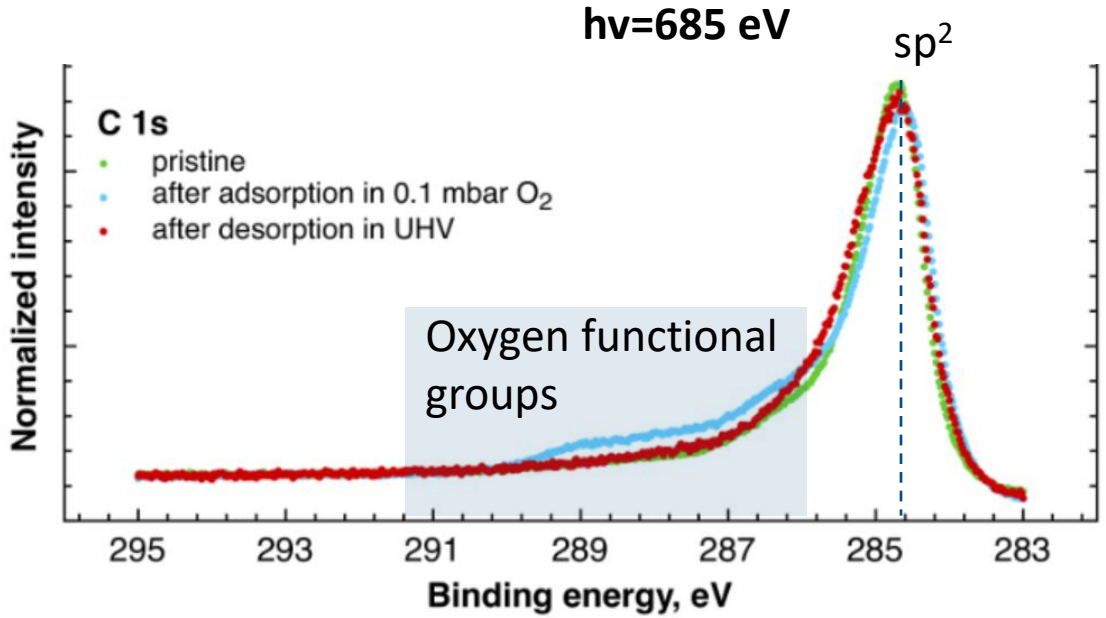
EMIL HZB Helmholtz Zentrum Berlin

Classical beam irradiation effects – reduction by secondary electrons



https://doi.org/10.1371/journal.pone.0049182

Operando beam irradiation effects – oxidation by decomposed gas and electrolyte products



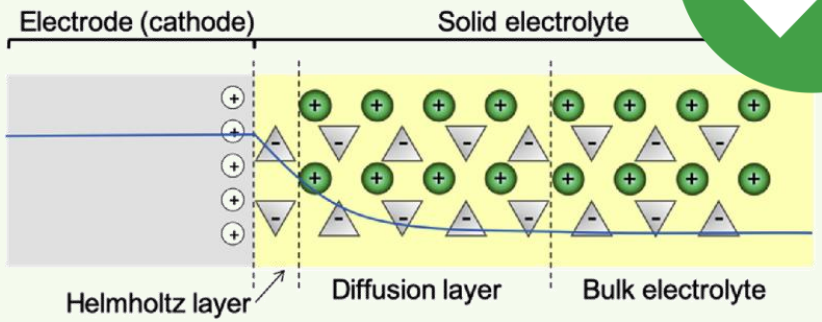
Li-O_2 cell with reduced graphene oxide cathode, Li anode and LAGP electrolyte, 1 h exposure time

- Beam exposure results in generation of radicals that tend to chemically react with material, which might lead to oxidation as compared to classical ex situ UHV reduction
- Solution: setting excitation energy below ionization of gas/liquid, adjusting flux **and** pressure, electrolyte composition

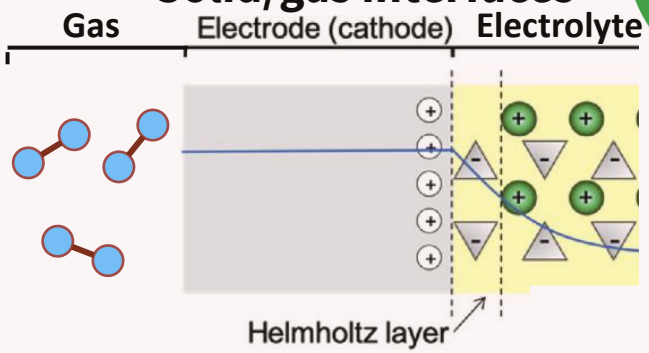
PROBING BURIED ELECTROCHEMICAL INTERFACES

EMIL HZB Helmholtz Zentrum Berlin

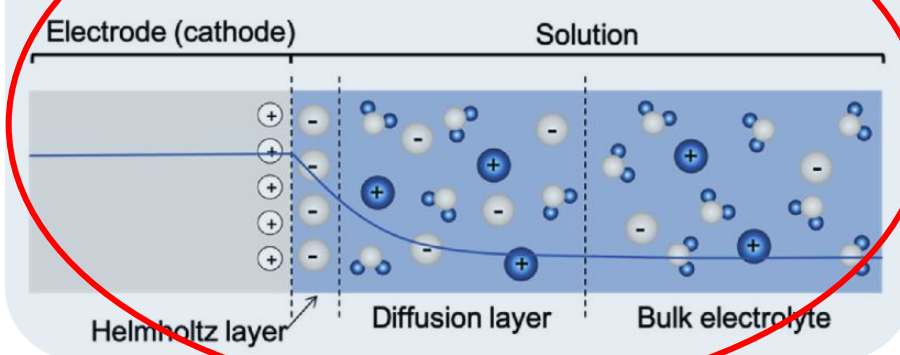
Solid/solid interfaces



Solid/gas interfaces

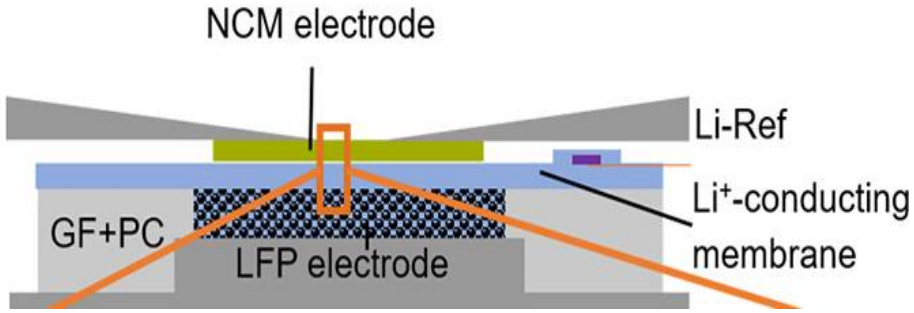


Solid/liquid interfaces



SOLID/LIQUID INTERFACES–WINDOWLESS APPROACH

Material-on-membrane approach



Requirements

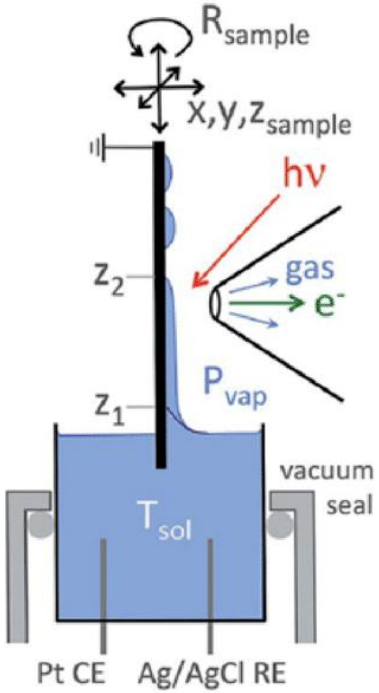
- Electrolyte wetting membrane
- Electrolyte evaporation is compensated by dosing solvent (PC) in the chamber

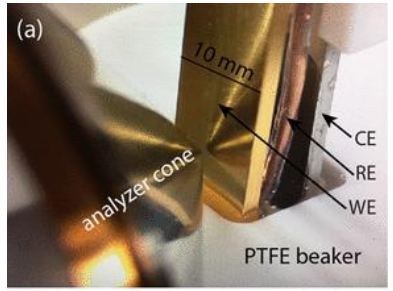
PC vapor pressure at RT is 0.04 mbar

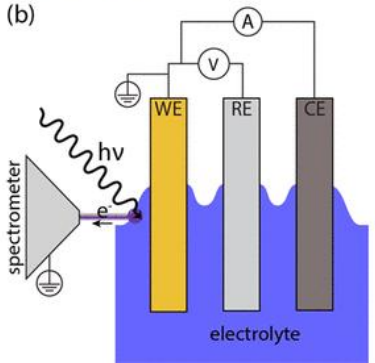
GF – glass fiber, LFP – $LiFePO_4$, PC – propylene carbonate, NCM – NiCoMnOxide, Membrane chemically-exchanged NAFION

Dip and pull approach

ACS Appl. Mater. Interfaces 2023, 15, 4743−4754







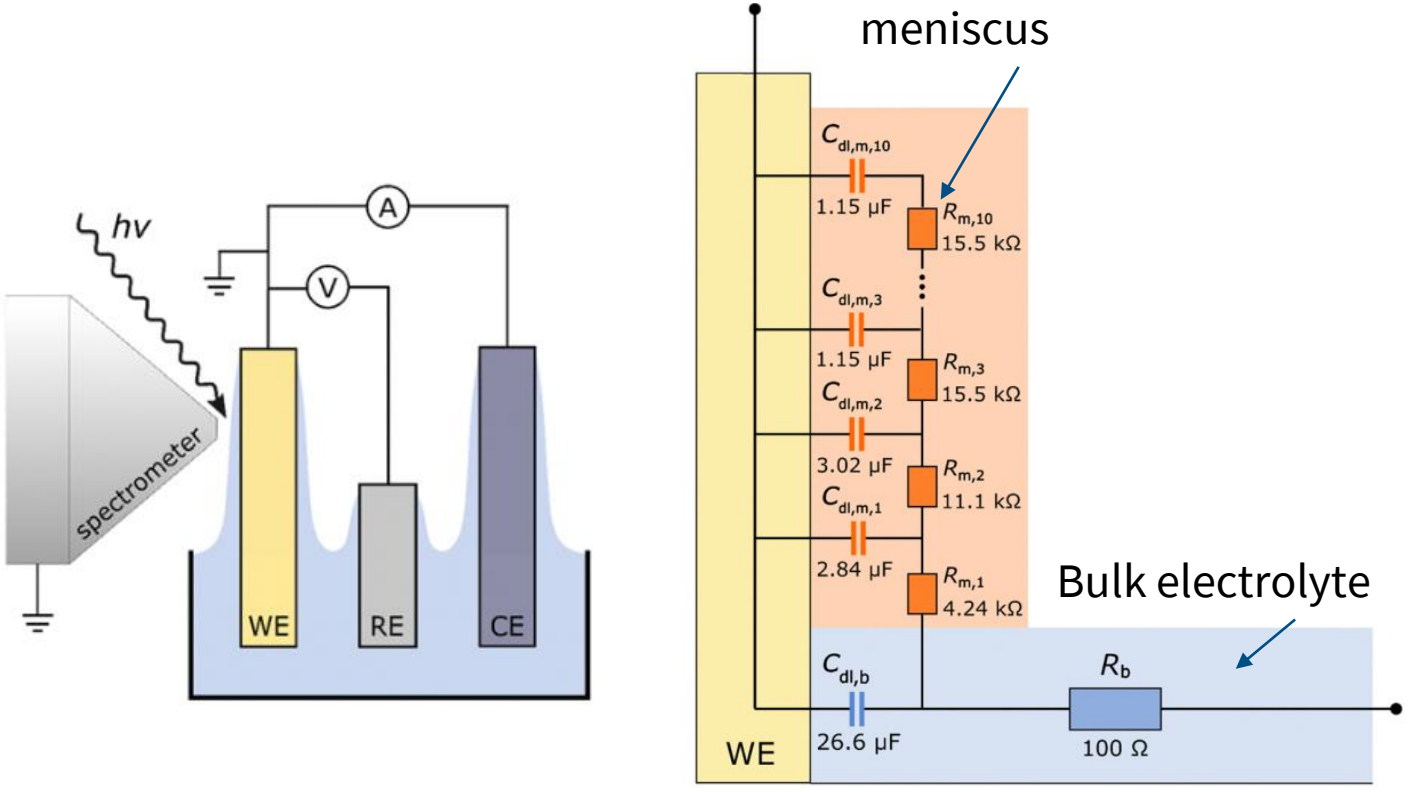
Requirements

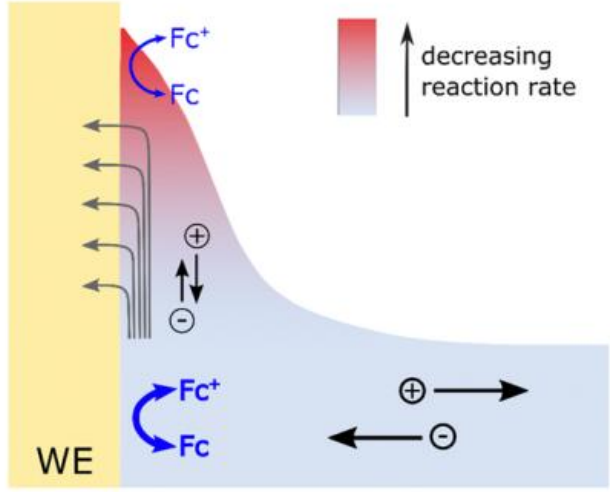
- Small contact angle of liquid on WE to produce meniscus and avoid droplets
- Electrolyte with low enough vapor pressure (or dozing electrolyte solvent in chamber simultaneously)

https://doi.org/10.1021/acsami.1c07424

SOLID/LIQUID INTERFACES– WINDOWLESS APPROACH

Dip and pull method – ionic resistance in the meniscus





Au WE, 1M $LiClO_4$ in propylene carbonate, Fc/Fc^+ (ferrocene)

Phys. Chem. Chem. Phys., 2025, 27, 7456–7466

The **electrolyte meniscus has extremely poor mass transport** compared to the bulk (iR drop is ca 1000 times larger) => faradaic processes **are 2-3 times order of magnitude slower**

- Applicable to capacitive/pseudocapactive processes, with current decaying to zero (equilibrium conditions)
- For studying faradaic processes consider in situ as the possible experiment scenario (dipping => EC => OCV => pulling => spectroscopy => dipping etc)

EMIL HZB Helmholtz Zentrum Berlin

SOLID/LIQUID INTERFACES WINDOW APPROACH

How to separate environment of my analytical probe (UHV, RT) from the cell environment (higher gas and static pressures, elevated temperatures, corrosive liquids)?

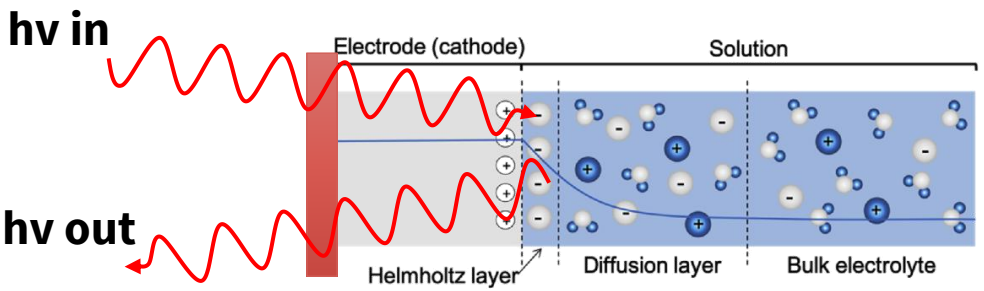
CHANGE FONTS IN EXCEL

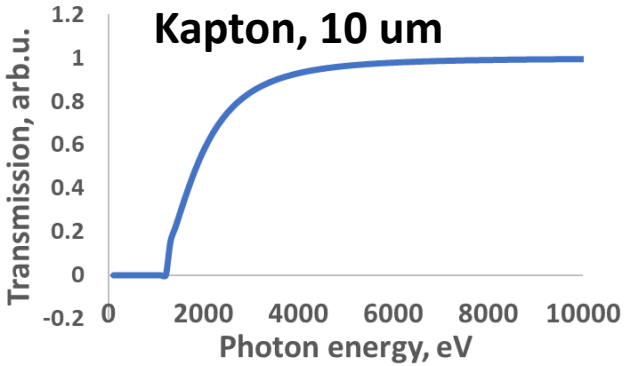
Windows

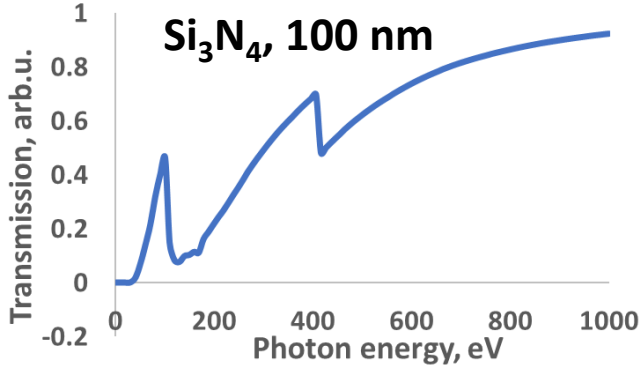
Soft X-rays out – 50-200 nm SiN_x

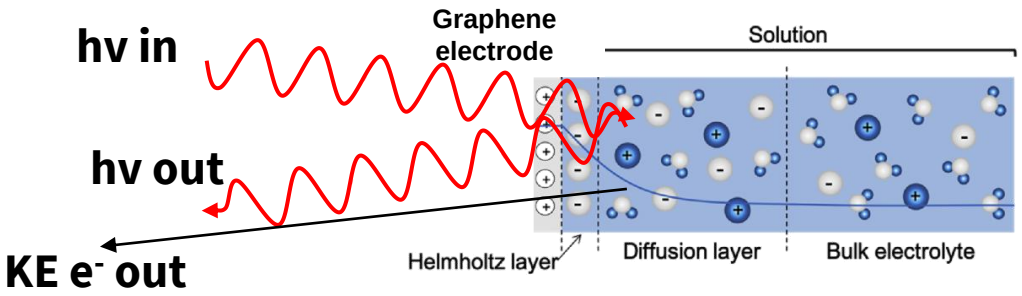
Hard X-rays out – several microns of polyimide

Photoelectrons out – several nm of metal or graphene

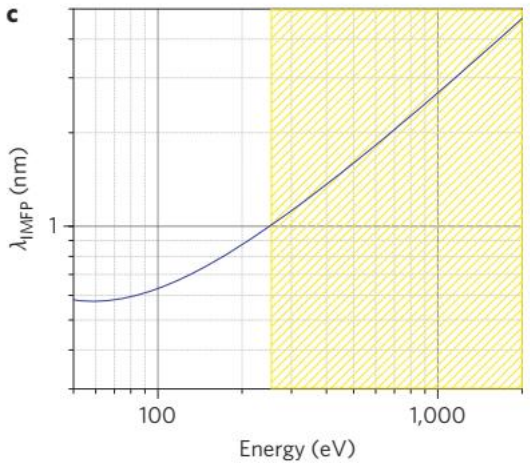








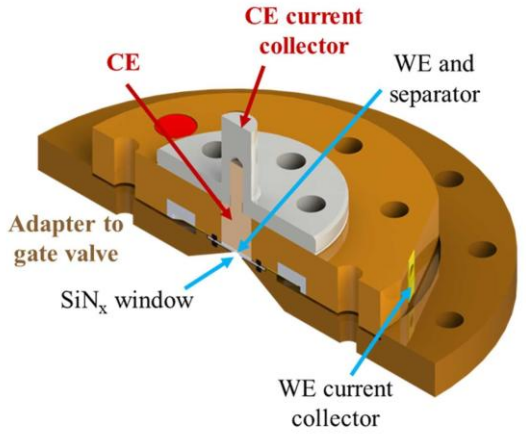
Inelastic mean free path for graphene



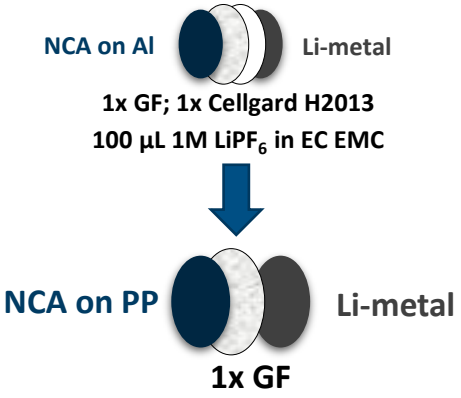
SOLID/LIQUID INTERFACES
CELL VERIFICATION PARAMETERS

To verify: capacity, C-rate performance, dQ/dV curves, reaction onset potentials (incl nucleation potentials)

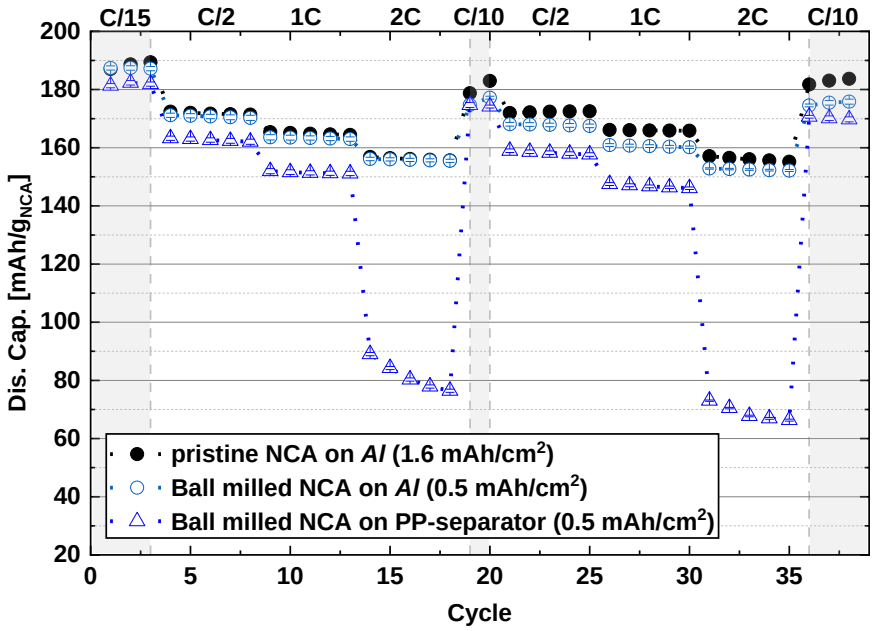
If electrode preparation technology is adjusted, first studies should be conducted in the coin cells

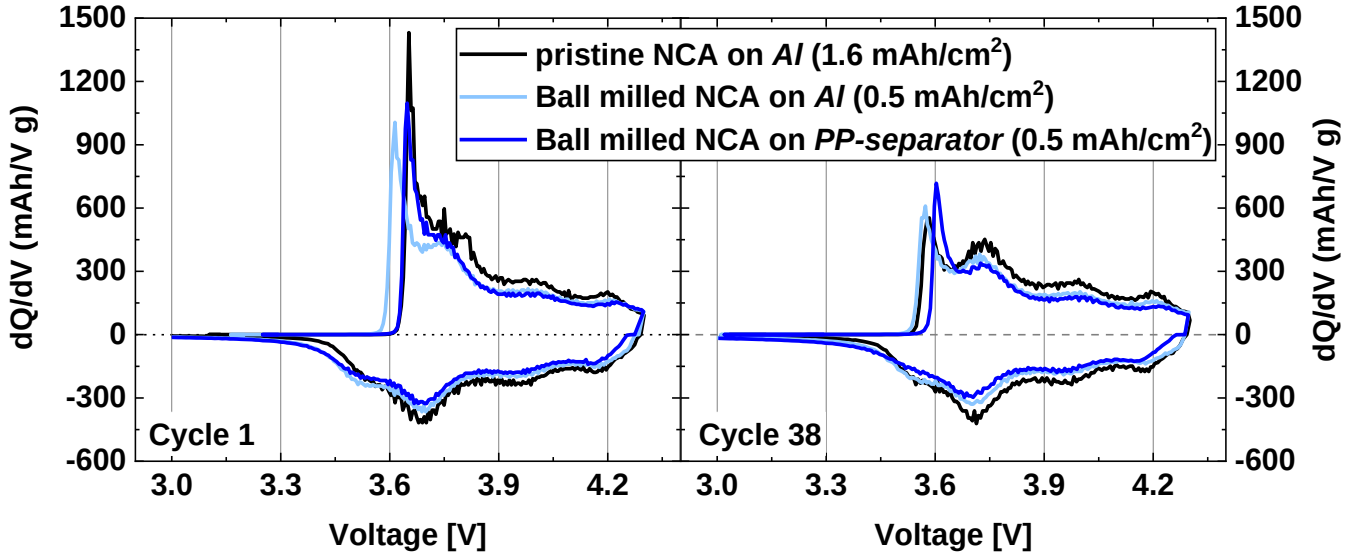


NCA - $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$



Electrochemical performance of the coin cells





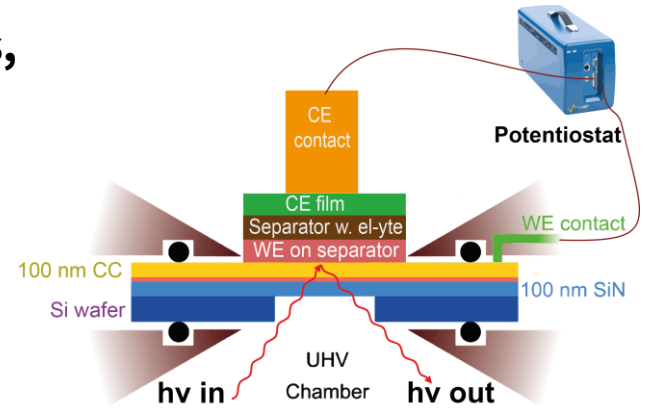
- Slight decrease in Q_{dis} of separator coated electrodes
- ✓ Rate capability sufficient for aimed op. conditions (*C/10*)

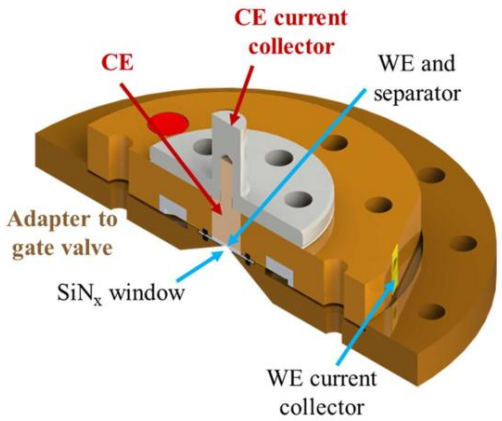
SOLID/LIQUID INTERFACES
CELL VERIFICATION PARAMETERS

EMIL HZB Helmholtz Zentrum Berlin

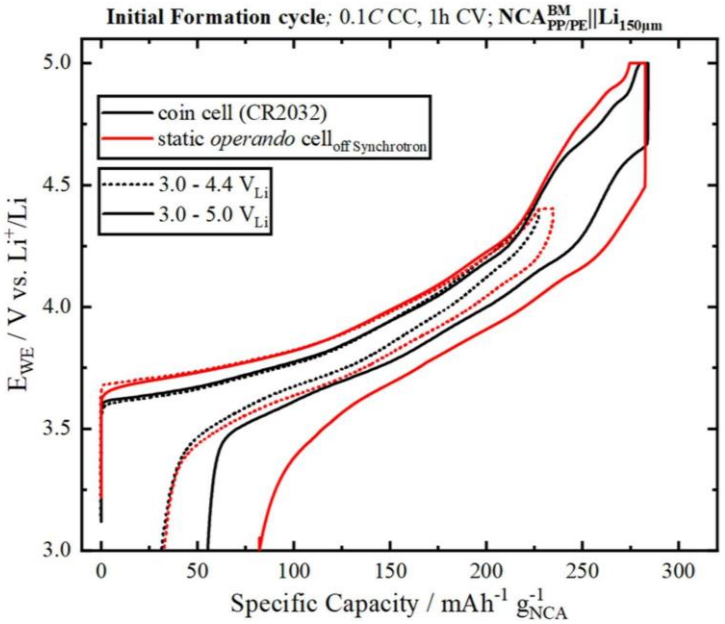
To verify: capacity, C-rate performance, dQ/dV curves, reaction onset potentials (incl nucleation potentials)

Operando cell performance should be similar to coin/pouch cells at the same C-rate and electrochemical window!





Electrochemical performance of the operando cells



LP57 = 1.0 M $LiPF_6$ in EC/EMC 3:7

NCA - $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$

Tricks to achieve reasonable performance

- No drop-casting - pressing of electrode material on the separator or window, calendaring if needed
- Increasing amount of conductive additive (carbon) in the electrode
- Using carbon paper as conductive matrix/current collector
- Increasing static pressure by introducing thicker separators, fine adjustment of the cell parts size

SOLID/LIQUID INTERFACES BEAM IRRADIATION EFFECTS

Nernst equation

$$E = E^0 + \frac{RT}{nF} \ln \frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$

Reaction kinetics

Current density

$$j = j_0 f(\eta)$$

Exchange current density

Kinetic law

$$j_0 \propto a_{Li+}^{\gamma} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

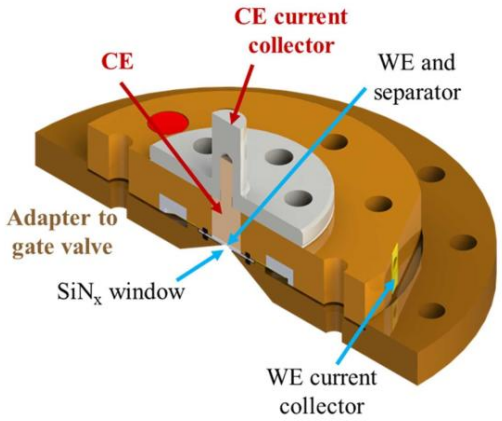
Activity of Li+ at the interface

Activation energy for the charge transfer

Simple water radiolysis leads to

$$H_2O \xrightarrow{\text{Ionizing radiation}} e_{aq}^-, HO\cdot, H\cdot, HO_2\cdot, H_3O^+, OH^-, H_2O_2, H_2$$

More complicated EC solvents and salts will create massive side reaction pathways



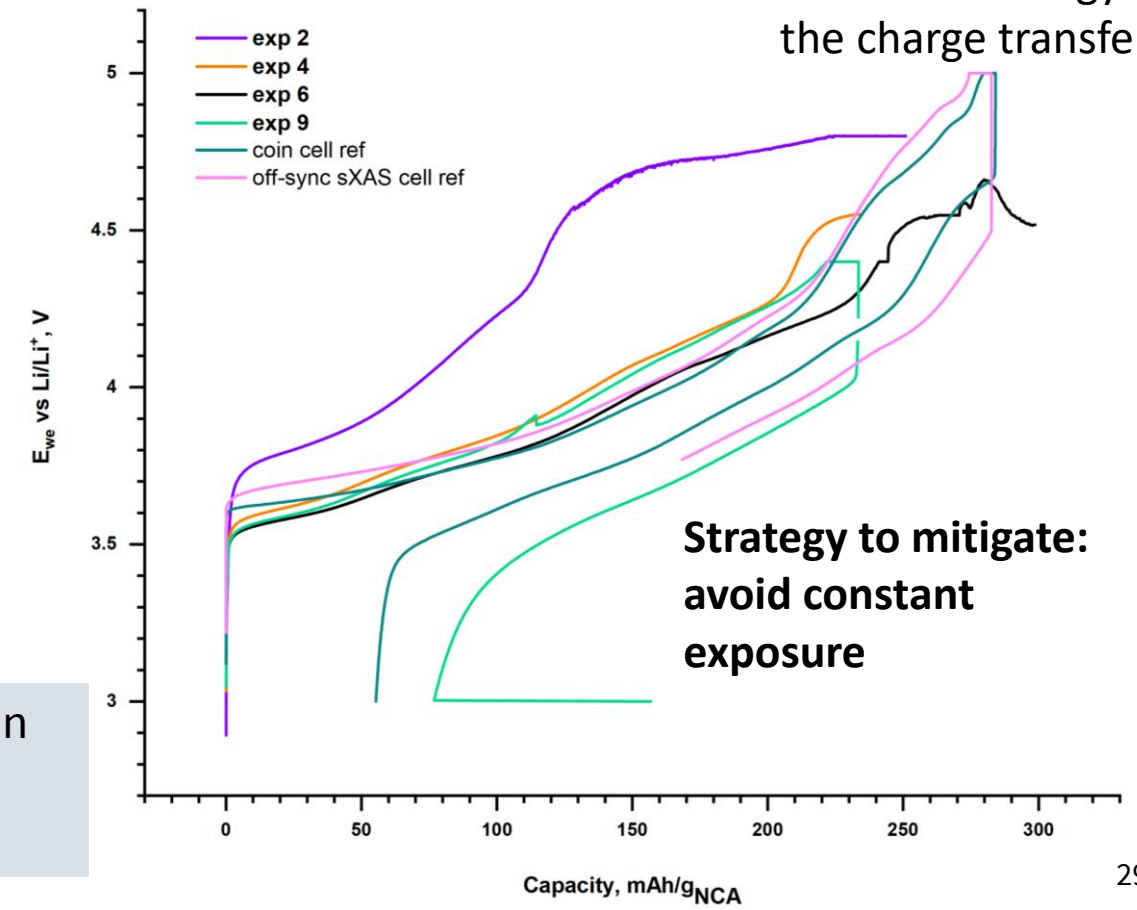
Radiolysis products

H_2, CH_4, CO, CO_2 from EC, EMC

HF, PF_5, POF_3 from $LiPF_6$

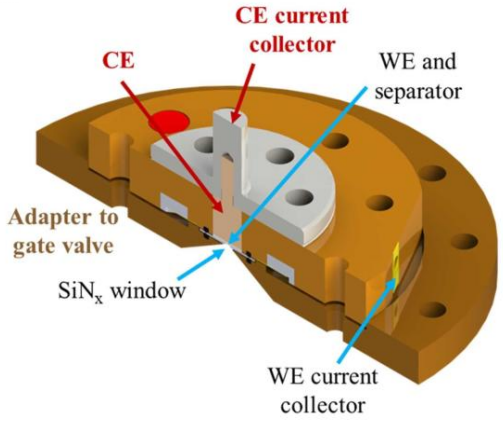
NiCoAl oxide cathode, Li metal anode, 1.0 M $LiPF_6$ in EC/EMC 3:7

Continuous X-ray beam exposure can jeopardize whole electrochemical charge/discharge curves



Strategy to mitigate: avoid constant exposure

SOLID/LIQUID INTERFACES BEAM IRRADIATION EFFECTS

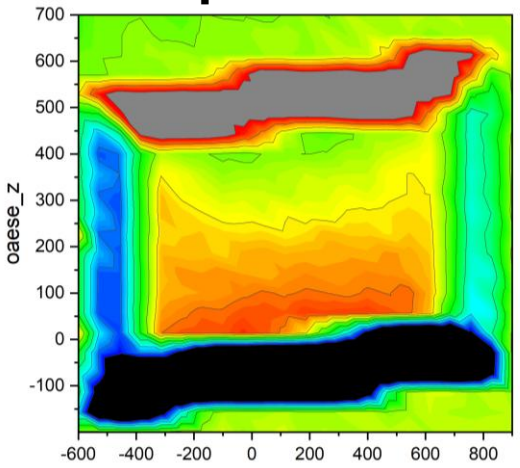


NiCoAl oxide cathode, Li metal anode, 1.0 M $LiPF_6$ in EC/EMC 3:7

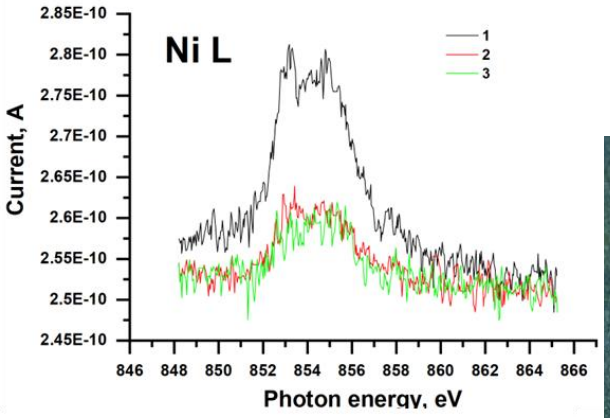
- Beam damage polymerizes electrolyte affects signal intensity, but doesn't change chemistry of cathode material
- Mass transport in polymerized electrolyte might be reduced

hv=855 eV mapping, OCV measurement

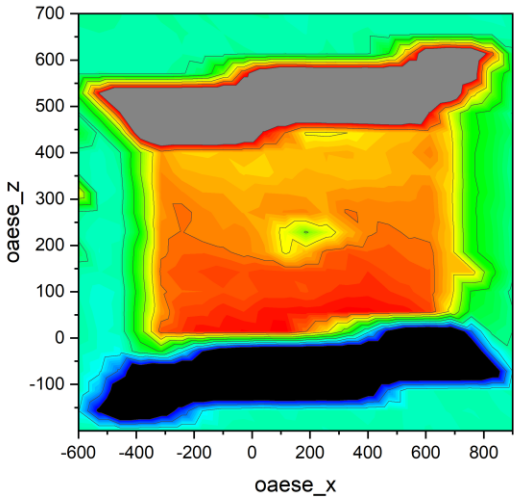
pristine



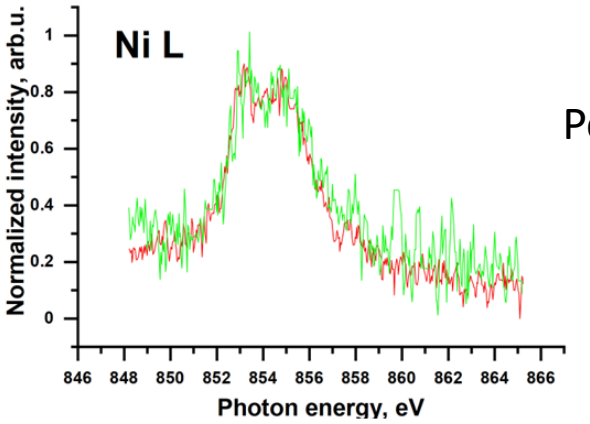
3 consecutive sweeps



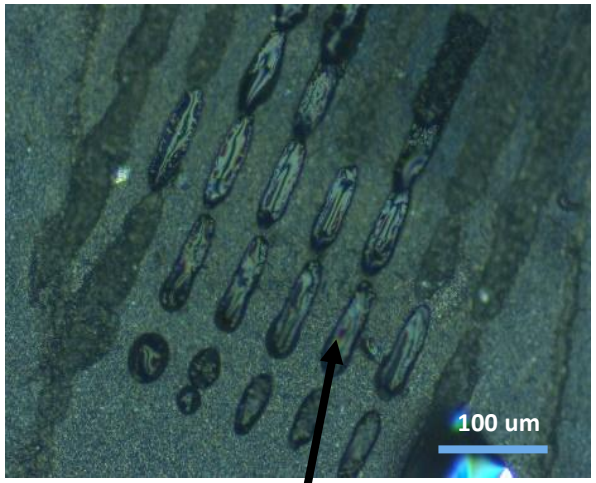
After 1 measurement



after normalization



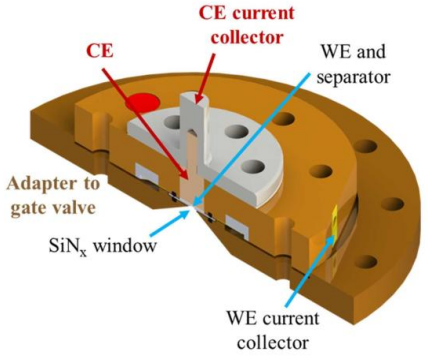
***Ex situ post mortem* optical image of electrode**

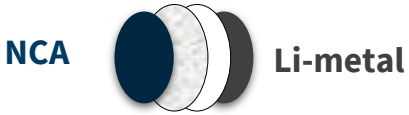


Polymerized area

Strategy to mitigate: change spot for each acquistion

SOLID/LIQUID INTERFACES
CELL VERIFICATION PARAMETERS
SPECTROSCOPIC FEATURES

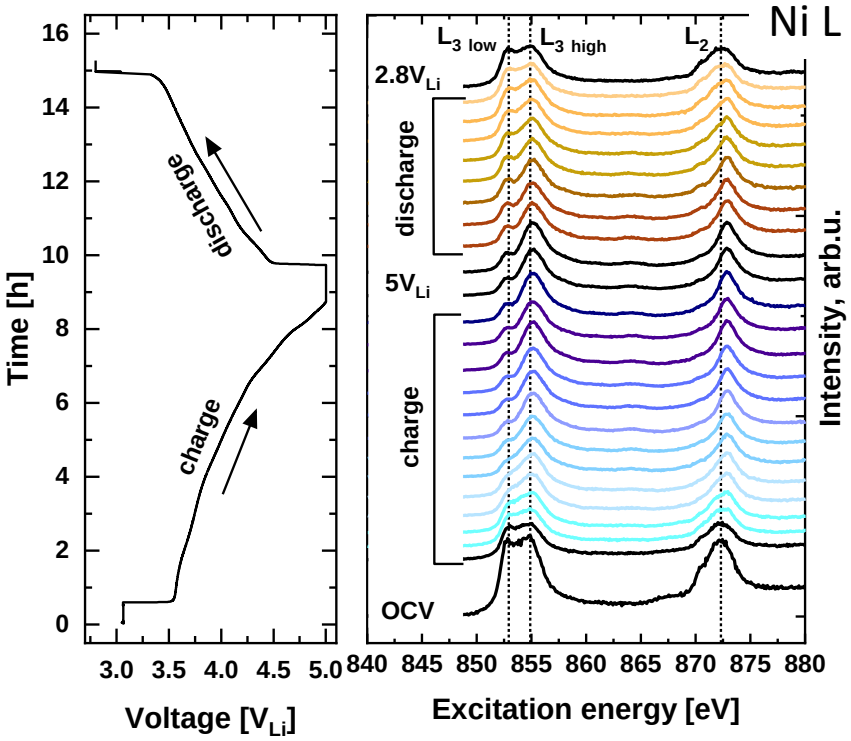


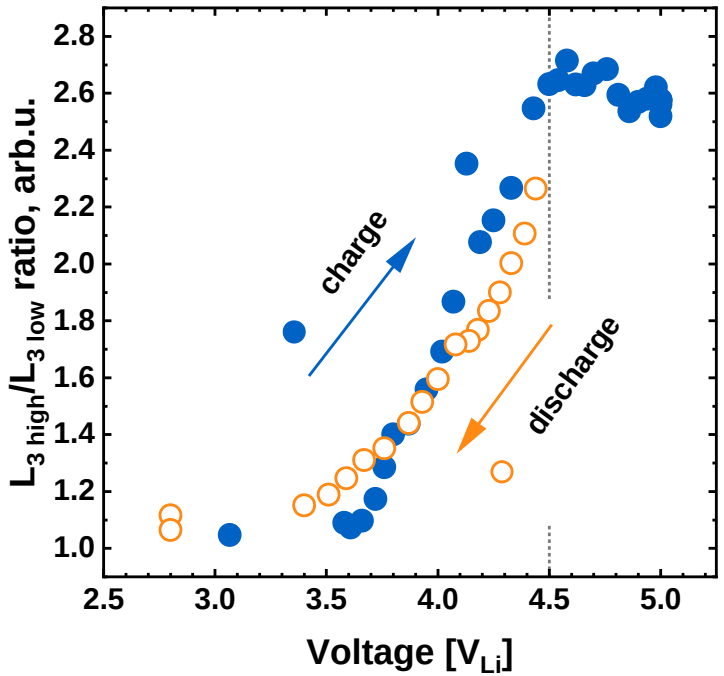


1x GF; 8 µL LP57

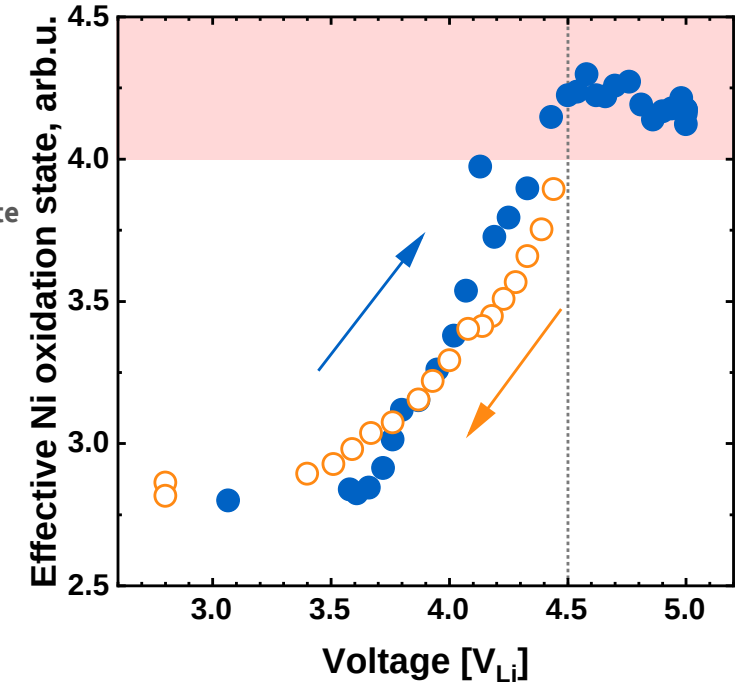
LP57 = 1.0 M $LiPF_6$ in EC/EMC 3:7

NCA - $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$





Oxidation state extraction



$Li_1Ni_{0.8}Co_{0.15}Al_{0.05}O_2 \rightleftharpoons Li_{1-n}Ni_{0.8}Co_{0.15}Al_{0.05}O_2 + nLi^+ + ne^-$

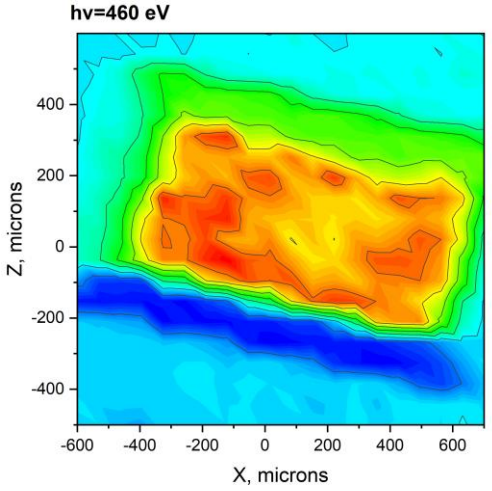
Conversion of Ni^{3+} and Co^{3+} to Ni^{4+} and Co^{4+} on charge

- Ni oxidation state was calculated from L_{3high}-L_{3low} ratio of Ni L-edge sXAS (assuming linear dependence)
- For constant load, NCA reaches Ni^{4+} state at ca. 4.5V_{Li} on charge, at higher voltages no further Ni oxidation (indicating O anion redox)
- For lithiation/delithiation - amount of extracted/inserted Li etc

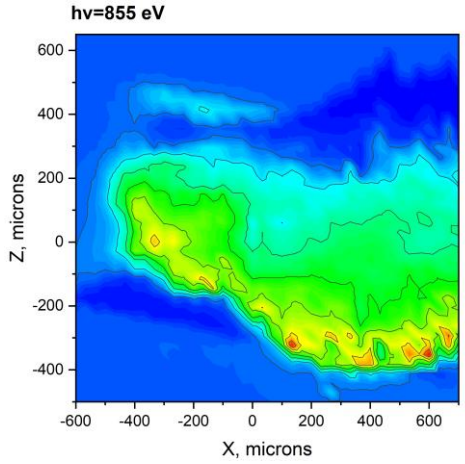
SOLID/LIQUID INTERFACES RELATED PROBLEMS

Liquids: bubble formation, leaking

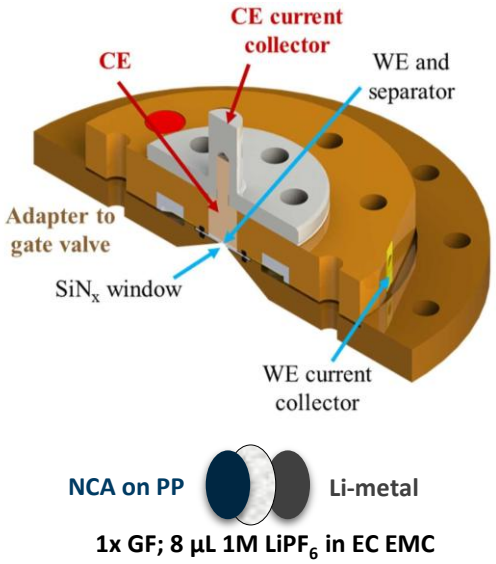
SiN_x window in the beginning of the experiment



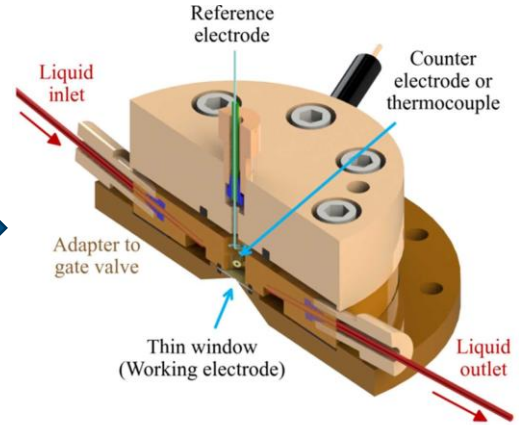
SiN_x window in the end, Ni contrast



Static cell



Flow cell



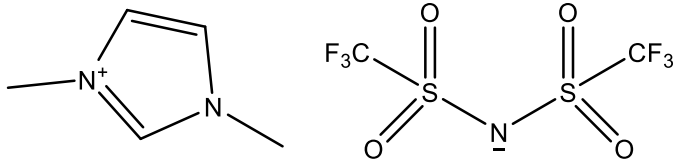
Electrocatalysis, fuel cells ✓

Batteries ✗

Using flow cell can help with bubbles in liquids, high static liquid pressure and beam irradiation effects, but

- Harder to control temperature (if necessary)
- Impurities from electrolyte are constantly flowing to the cell –for batteries accumulated HF ruins performance
- Doesn't model real cell conditions well for batteries – e.g. dissolved metal are washed away

SOLID/LIQUID INTERFACES RELATED PROBLEMS



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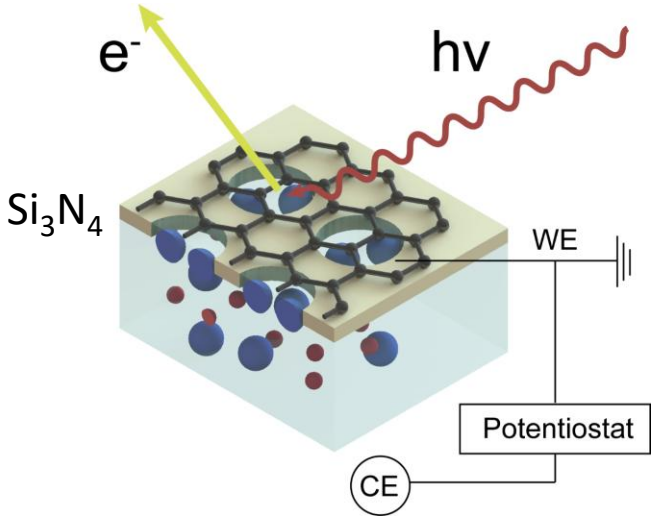
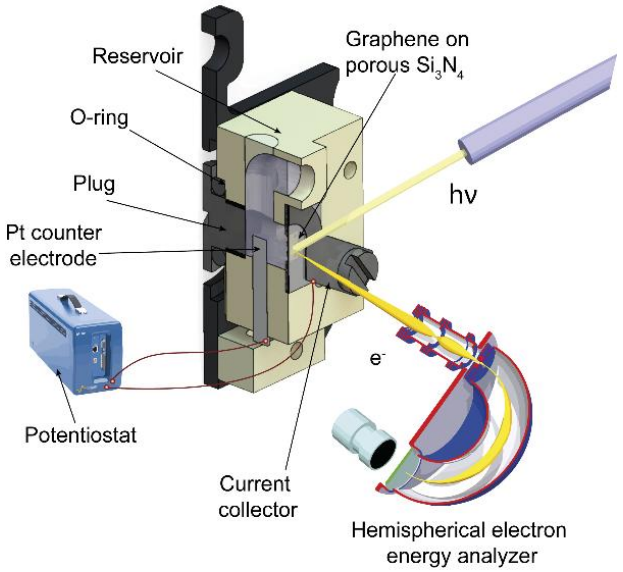
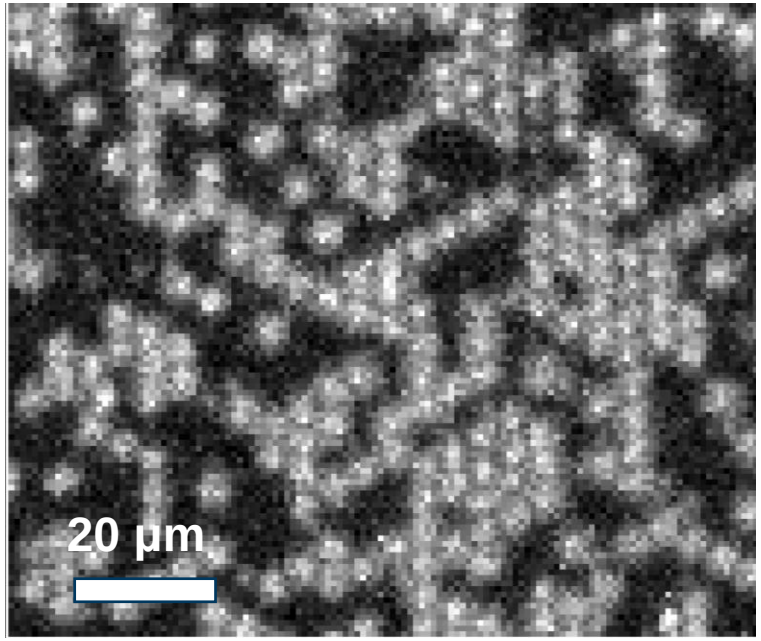
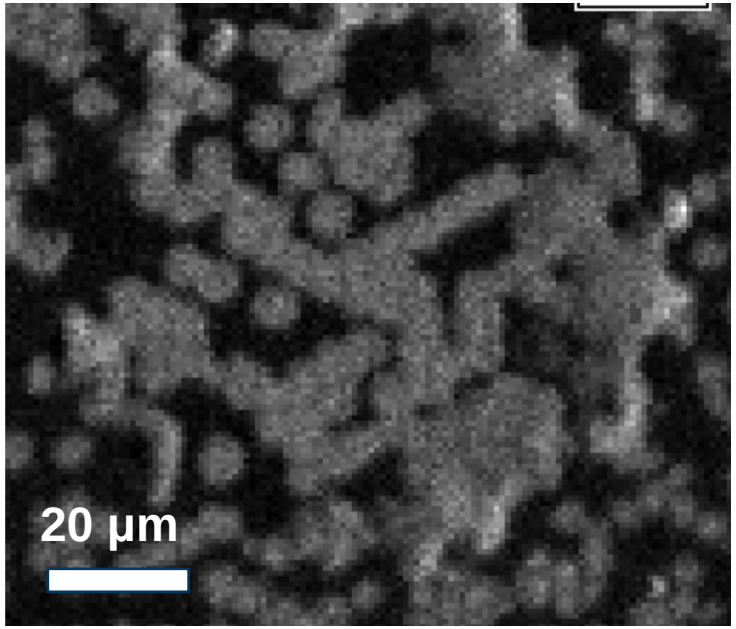


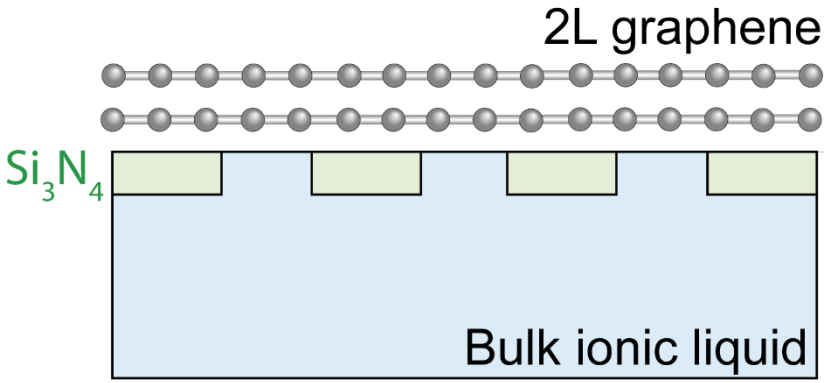


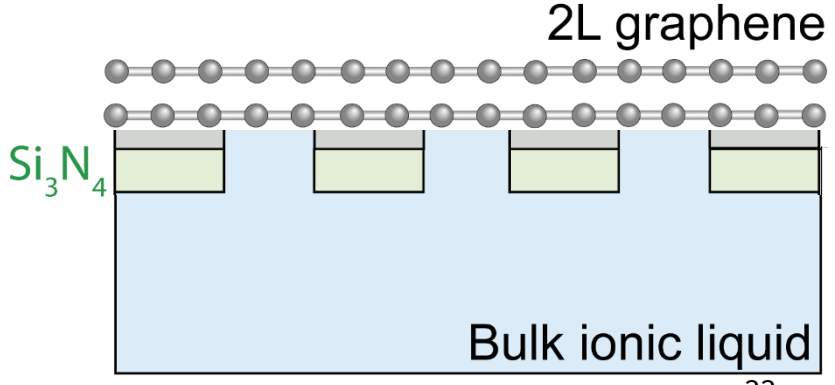
S 2p map hv=750 eV, KE~600 eV



time







ELETTRA, ESCAmicroscopy

TAKE-AWAY MESSAGES

- **Local X-ray sensitivity does not guarantee electrochemical relevance.**
  Representativity must be engineered, not assumed.
- **Beam size and electrode uniformity set the meaning of operando data.**
  Small beams probe extremes; large beams average assumptions.
- **Interfacial roughness governs local kinetics, not necessarily cell voltage.**
  Significant heterogeneity can remain electrochemically silent.
- **X-ray irradiation is an active perturbation.**
  Radiolysis and beam–electrolyte interactions can modify interfaces and kinetics during measurement.
- **Cell design defines electrochemistry.**
  Static, flow, and meniscus cells each impose distinct transport and history artefacts.
- **An operando cell is successful only if its electrochemistry is credible.**
  Signal quality without electrochemical fidelity is misleading.
- **Interpretation requires triangulation.**
  Combine operando probes, electrochemistry, isolated in situ studies and DFT modelling to avoid false causality.

MINIMUM REQUIREMENTS FOR RELIEABLE OPERANDO ELECTROCHEMISTRY

Defined electrochemical representativity
off-the-beam: CV (dQ/dV), EIS, current rates, capacities, performance stability over supposed time of the measurement per 1 cell
Ex situ post mortem off-the beam studies of the cells
SEM, optical imaging, chemical information (EDX or XPS)
Verified electrode structure at the probed scale
Thickness, roughness, wetting, compression must be homogeneous over the illuminated region and in the whole cell area.
Quantified transport limitations
Ionic resistance, concentration gradients, and iR drops must be estimated for the chosen geometry.
Assessed beam–matter interaction
Radiolysis, heating, and beam-induced chemistry must be considered as active perturbations – use short experimental time opportunieis to check it before hand
Key observables (OCV, polarization, impedance, dQ/dV) must be reproducible with and without the probe.
Stated interpretational limits
The experiment must declare what can and cannot be inferred from the operando signal.
Include chemical modelling of the isolated reactions to decipher full reaction scheme
Consider DFT for extracting fingerprints and information of the unstable species

Prof. Dr.-Ing. Marcus Bär, Dr. Regan Wilks. Dr. Raul Garcia-Diez, Dr. Mihaela Gorgoi, Dr. Roberto Felix-Duarte, Dr. Anna Efimenko, Alexander Steigert, Enggar Wibowo, Marianne van der Merwe, Zora Chalkley

Prof. Dr. Hubert Gasteiger, Leon Reinschlüssel, Gülen Ceren Tok

Prof. Dr. Caterina Cocchi, Dr. Daniel Duarte-Ruiz, Timo Reents

Prof. Dr. Jürgen Janek, Dr. Anja Henß, Dr. Burak Aktekin, Luise Riegger

Prof. Dr. Philipp Adelhelm, Dr. Katherine Ann Mazzio, Dr. Nazia Nazer

Prof. Dr. Stefano Nannarone, Dr. Angelo Giglia

Dr Lada Yashina, Dr. Daniil Itkis, Dr. Olesya Kapitanova, Dr. Vera Neudachina, Dr. Alina Belova, Dr. Anna Kozmenkova

Dr. Axel Knop-Gericke, Dr. Juan Velasco-Velez

Dr. Carlos Escudero, Dr. Virginia Perez

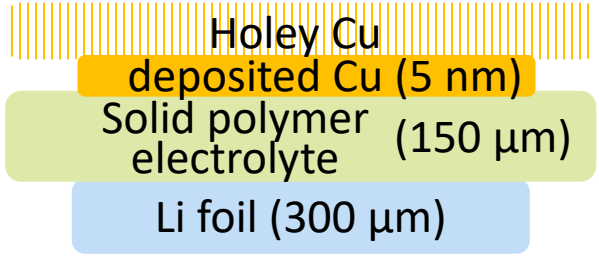
Prof. Denis Vyalikh

Prof. Yang Shao-Horn, Dr. David Kwabi, Dr. Hao-Hsun Chang

ADDITIONAL SLIDES

REVEALING REACTION PATHWAYS

Separating pure electrochemical from pure chemical reaction



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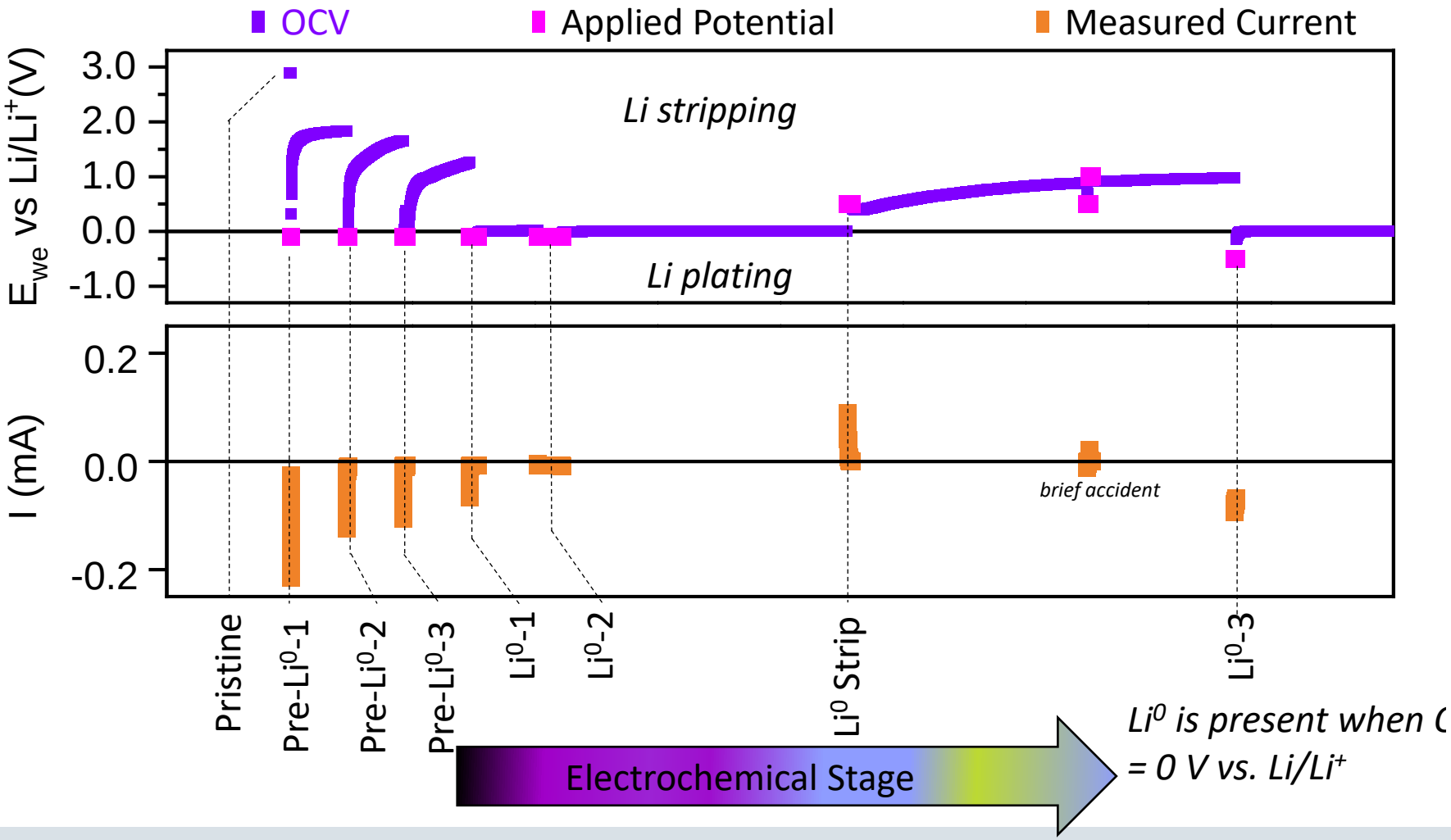
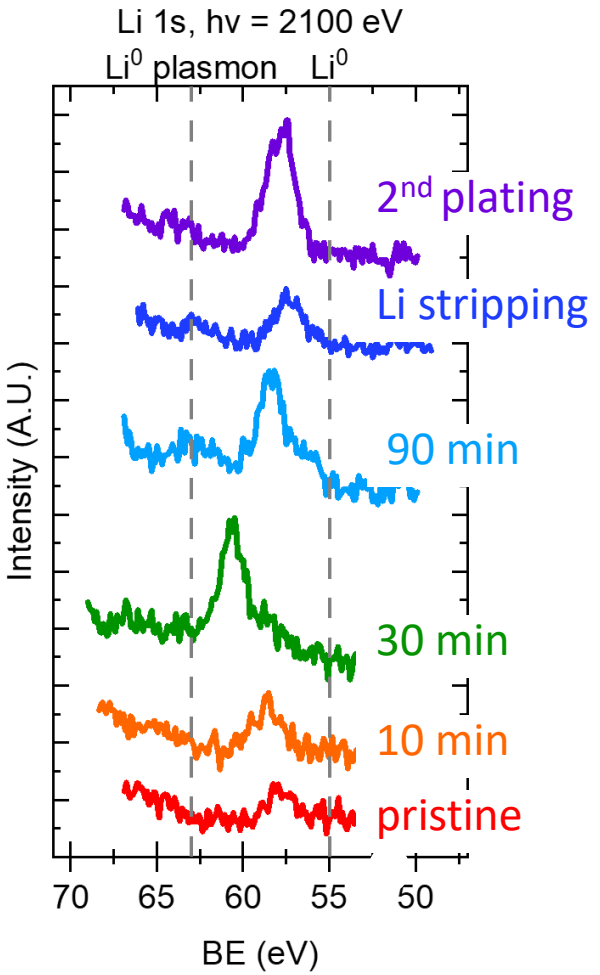
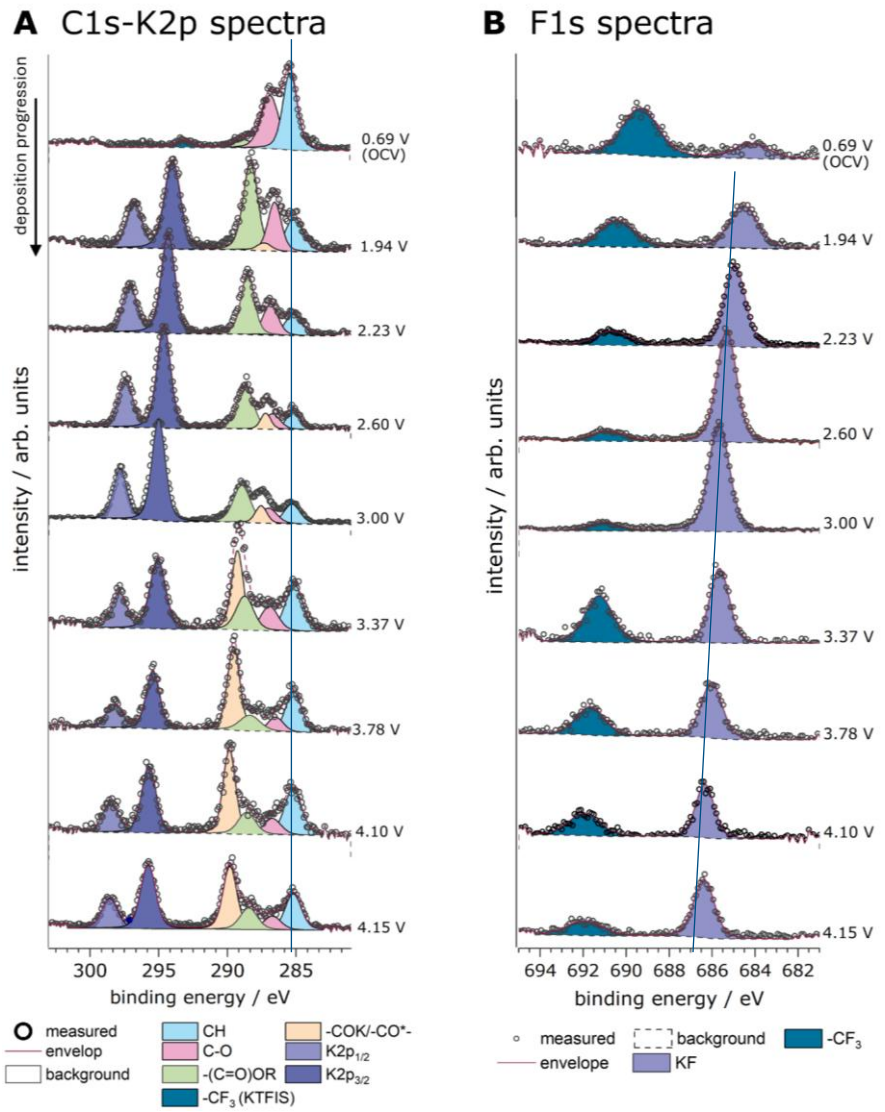
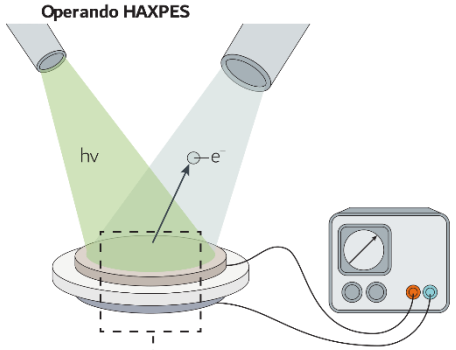


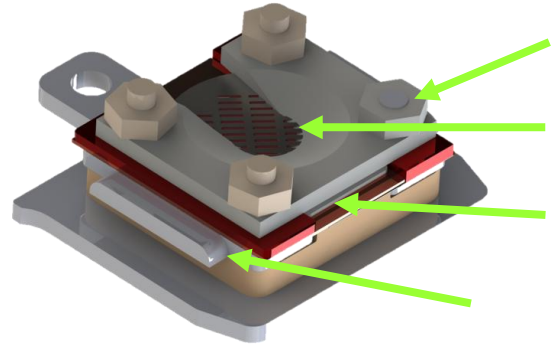


For generating large amount of chemical species, potential steps at extreme conditions might be useful

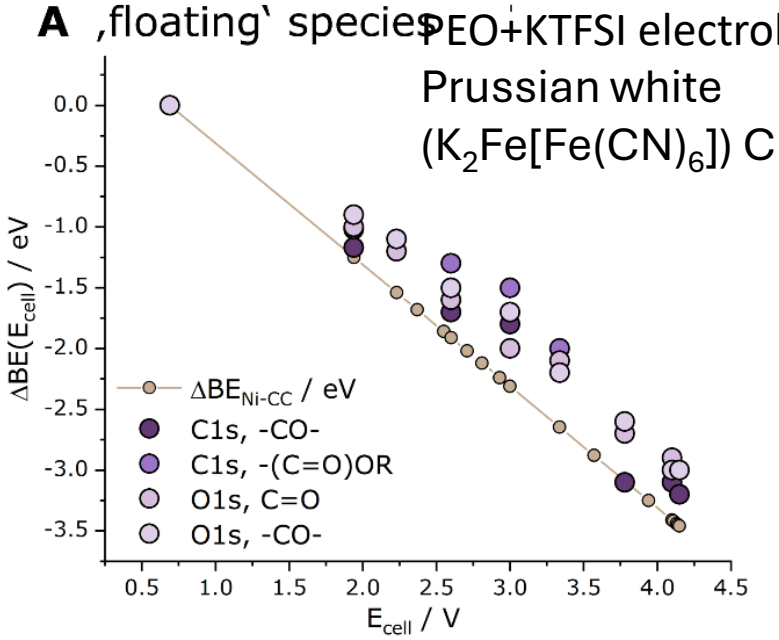
SEPARATING OF CHARGED VS UNCHARGED SPECIES

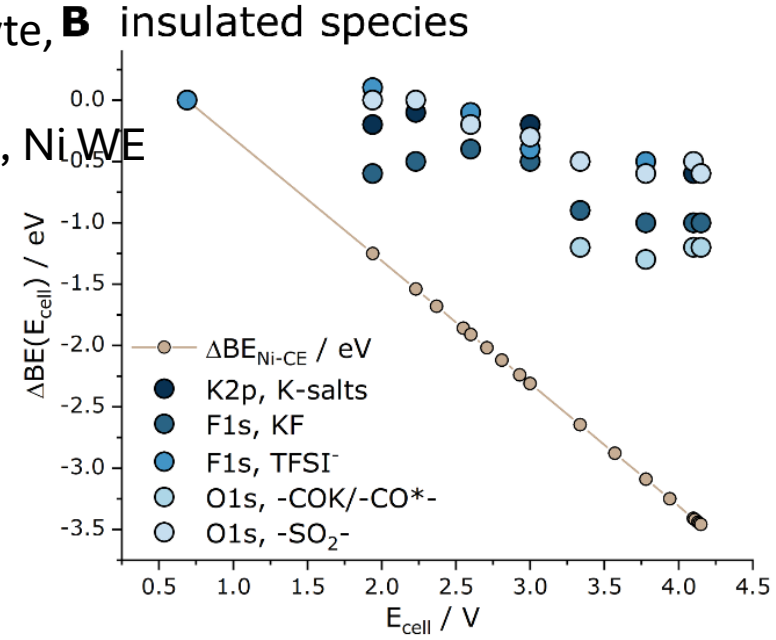






PEO+KTFSI electrolyte, Prussian white ($K_2Fe[Fe(CN)_6]$) CE, Ni WE





Creating of SEI and insulating species during operando XPS experiment might cause line shift with potential

- This line shift is purely electrostatic and should be separated from newly evolved species
- The separation is possible by plotting ΔBE vs Ecell lines, where ΔBE is difference between line of interest at OCV and given potential
- Pure electrostatic shifted species will then lie on the straight x=y line

ELECTROCHEMICAL CELL DESIGN – MATERIALS

Materials requirements: electrochemical stability, chemical resistance, temperature stability (for high T experiments), absence of impurities, UHV compatibility (when applicable), compatibility with detectors (non-magnetic for electron detectors)

Cell body&other electrical isolation connections: polyestheretherketone (PEEK), will oxidize above 2.0 V vs SHE (5.0 V vs Li^+/Li), will react with hot acid/bases upon prolonged exposure

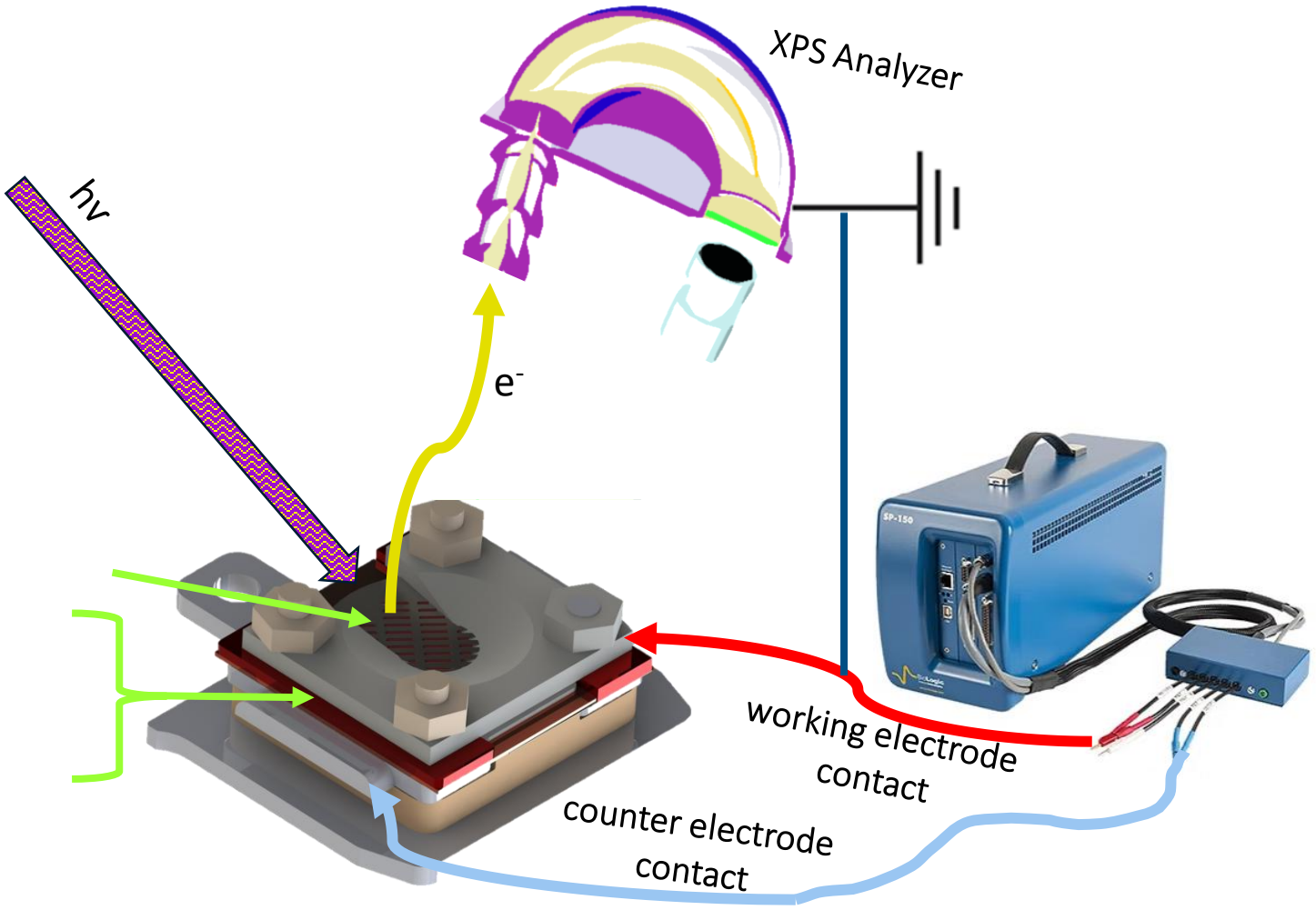
Current collector: standard for the systems of study (Al for cathode, Cu for anode in classical LIBs). If not possible, consider stainless steel or pure metals, check for ESW. Can be also produced by magnetron deposition of desired material on stainless steel pieces.

Plastic gasket: PTFE – the best stability, very firm; fluorinated carbons – lower stability, swelling, but softer (FFKM)

Glue: no glue, even outside cell working area, exception: ceramic glues on the parts not exposed to electrolyte are fine (Al_2O_3/MgO mixtures)

Reference electrodes: for liquid – standard choice for the system of study; for solid and gas for batteries lithiated Au or magnetron-sputtered LFP

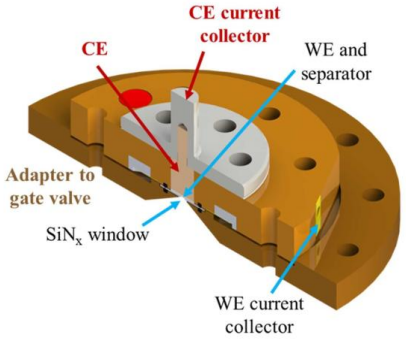
GROUNDING ISSUES

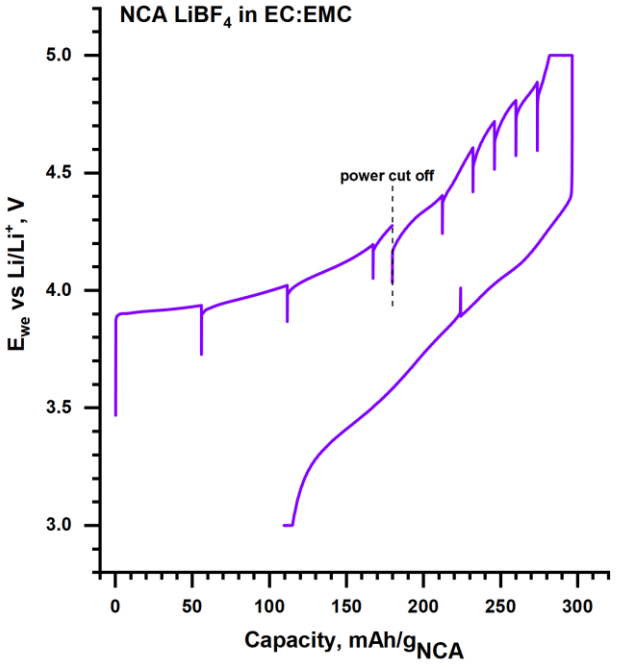


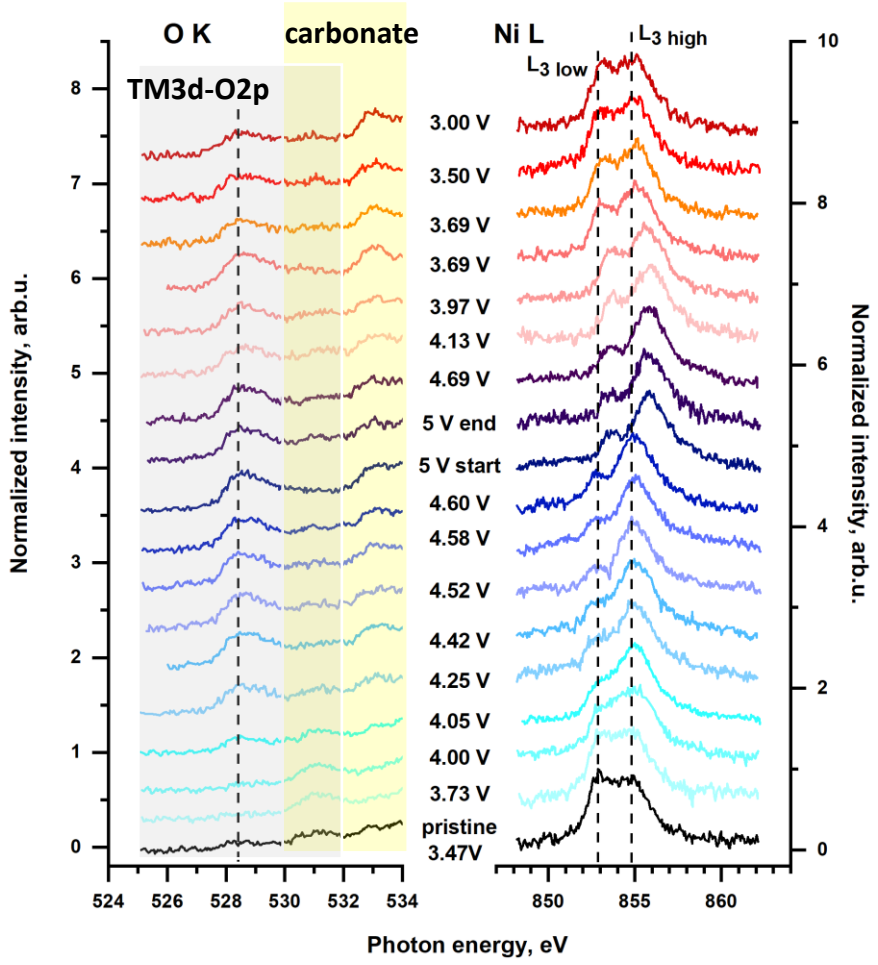
Working electrode which is not grounded to analyzer can

- Collect noise from the ground of the whole large machines
- Introduce ground loops => WE oscillation
- Separate peaks in XPS by amount of applied potential or less, making analysis and measurement harder
- Inhibit hole compensation which increases differential charging and leads to stronger beam damage

CONTRAST PROBLEMS

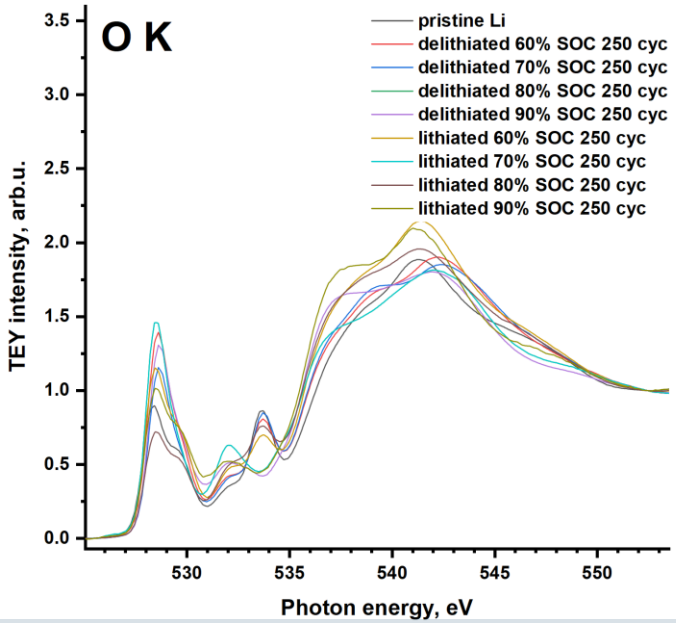






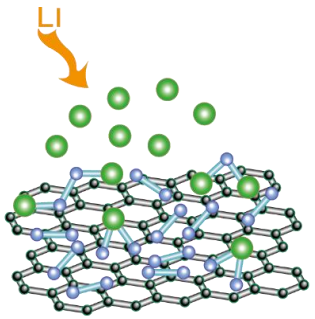
Ball-milled NCA ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$)on PP behind 100nm Al/100nm SiN, 1M $LiBF_4$ in 3:7 EC/DMC, lithium metal anode.

Ex situ analysis is required

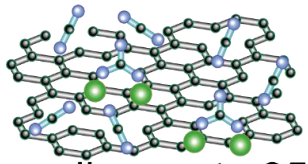


- **Electrolytes often contain the same elements as electrodes**, making operando analysis not feasible (O in carbonates, SiN window and TMO, S in sulfides and Li_6PS_5Cl etc)
- For achieving contrast and separating reactions, different solvents should be used (carbonates replaced by acetonitrile, Li_6PS_5Cl by Li_3YCl_6)
- If replacement is not possible, supporting ex situ study is required

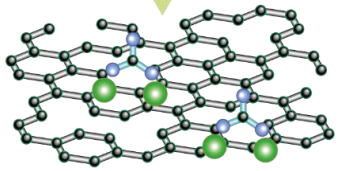
SUPPORTING OPERANDO RESEARCH
CHEMICAL MODELLING



Li deposition on solid O_2,
LiO_2 formation

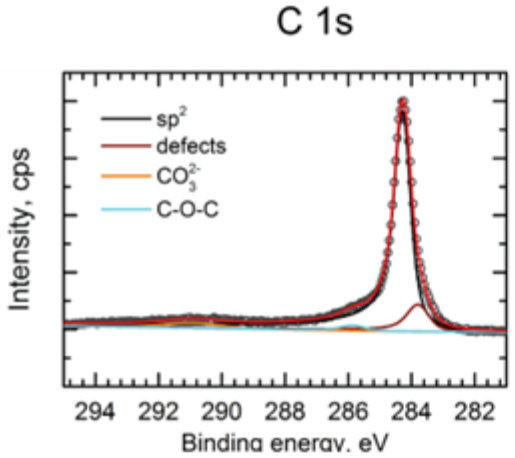


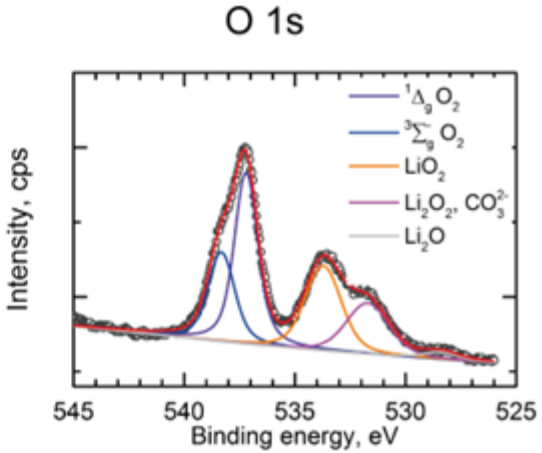
Annealing up to 35K,
Li_2CO_3 and CO_2 formation



Annealing up to 220 K,
CO_2 desorption

KE=200 for all spectra

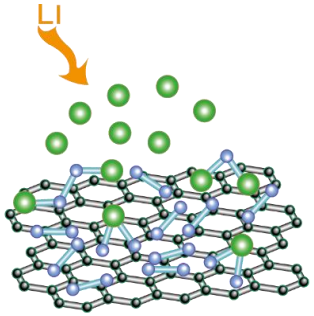




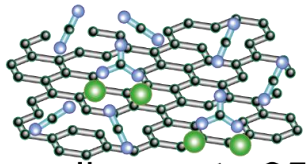
Li deposition on solid O_2

$$Li + O_2 \rightarrow LiO_2$$
$$2Li + O_2 \rightarrow Li_2O_2$$

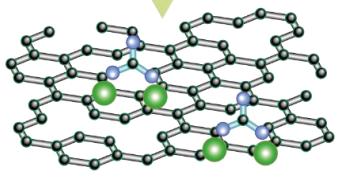
SUPPORTING OPERANDO RESEARCH
CHEMICAL MODELLING



Li deposition on solid O_2,
LiO_2 formation

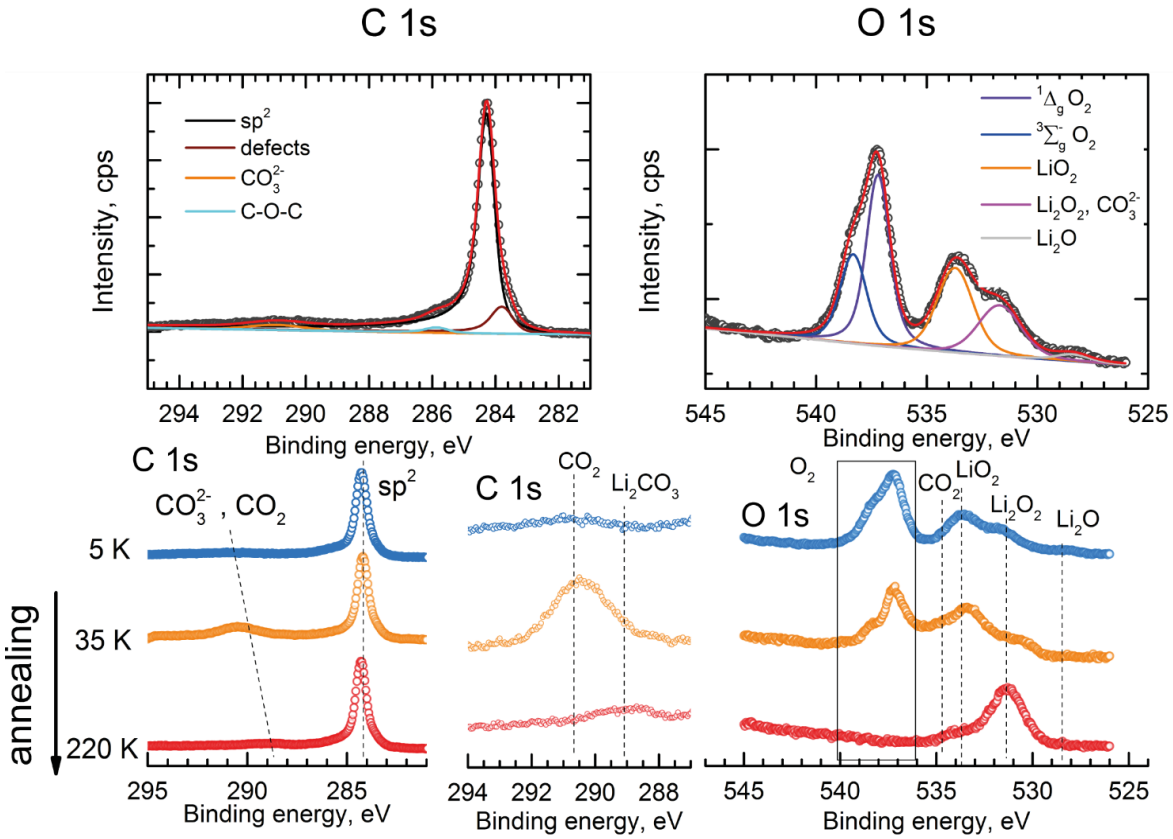


Annealing up to 35K,
Li_2CO_3 and CO_2 formation



Annealing up to 220 K,
CO_2 desorption

KE=200 for all spectra



Li deposition on solid O_2

$$Li + O_2 \rightarrow LiO_2$$
$$2Li + O_2 \rightarrow Li_2O_2$$

Annealing up to 220 K

$$4LiO_2 + 2C \rightarrow 2Li_2CO_3 + O_2$$
$$2LiO_2 + C \rightarrow Li_2O_2 + CO_2$$