

SURFACE-SENSITIVE AND COHERENT X-RAY METHODS TO STUDY BATTERY MATERIALS

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11/13/2025

**“TIME AND LENGTH-SCALE OPERANDO BRIDGING TECHNIQUES TO STUDY BATTERY
INTERFACES” – WEBINAR SERIES**

Part 1 – tutorial / theory

- Coherent X-ray methods
- Surface-sensitive X-ray methods
- X-ray Coulomb counting
- Q&A

Part 2 – scientific examples

- Coherent X-ray methods
- Surface-sensitive X-ray methods
- X-ray Coulomb counting
- Q&A

X-rays and a generic (synchrotron) X-ray experiment

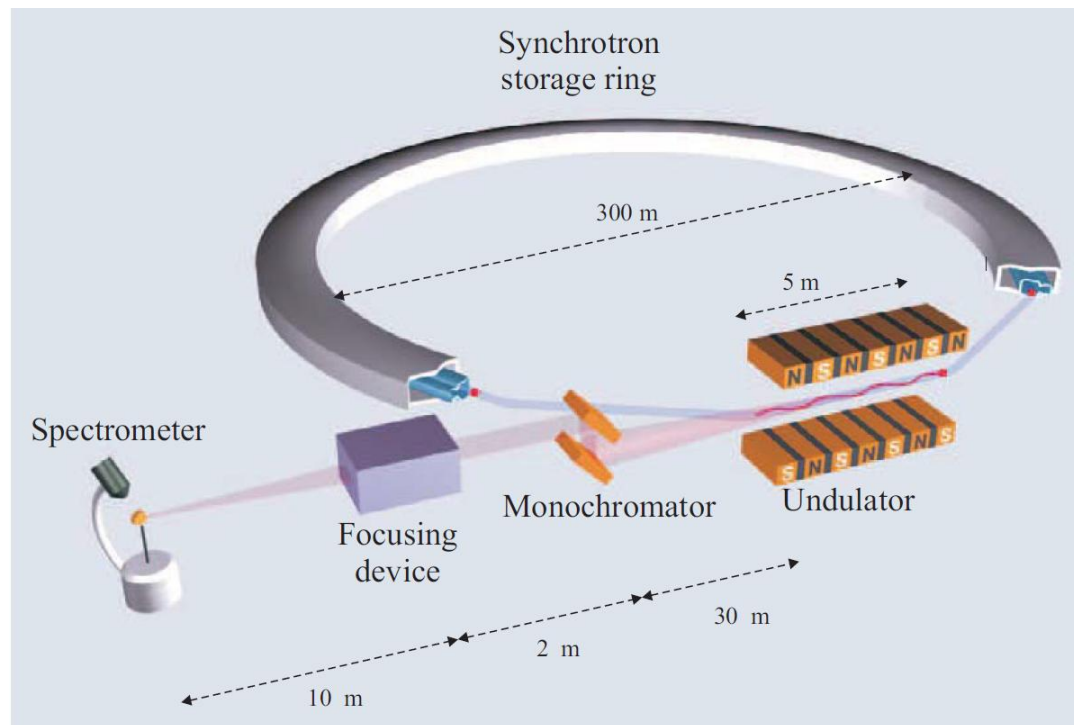
*To probe something,
it is best to use a probe of similar scale (size and energy)!*
(after Giorgio Margaritondo)

X-ray wavelength ($\text{\AA}$) $\approx$ length of chemical bonds

$\rightarrow$ *atomic structure*

X-ray energy (keV) $\approx$ energy of core electrons

$\rightarrow$ *chemical bonds*



Als-Nielsen, McMorrow; Elements of modern X-ray physics.

Coherent X-ray methods

X-ray speckle

LETTERS TO NATURE

Observation of speckle by diffraction with coherent X-rays

M. Sutton*, **S. G. J. Mochrie†**, **T. Greytak‡**,
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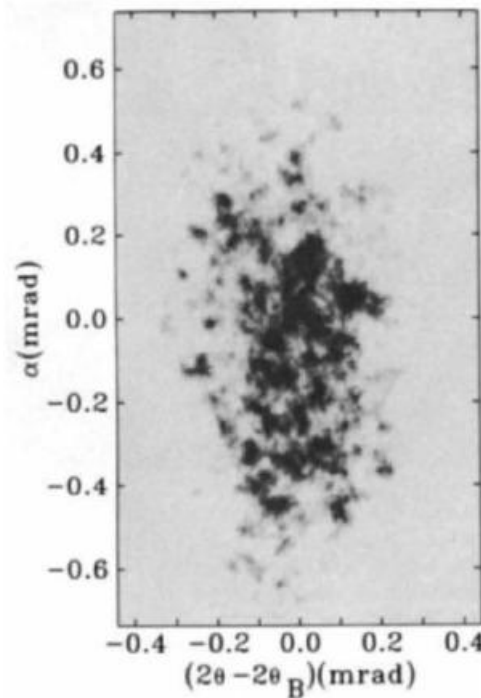
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REFLECTED light from a coherent light source such as a laser shows a graininess known as speckle. In general, a speckle pattern is produced whenever randomly distributed regions of a material introduce different phase shifts into the scattering of coherent incident light. If the arrangement of the regions evolves with time, the speckle pattern will also change. Observation of the intensity



Stringent conditions to observe speckle pattern:

- Difference in the path lengths of rays scattered by different parts of the sample < longitudinal coherence length of the incident beam
- Incident beam size < transverse coherence length

→ Coherent light

Incoherent (chaotic, spontaneous emission) light sources (laboratory x-ray source and synchrotron) can be made coherent by monochromatizing and collimation at the expense of photon flux

Coherent scattering

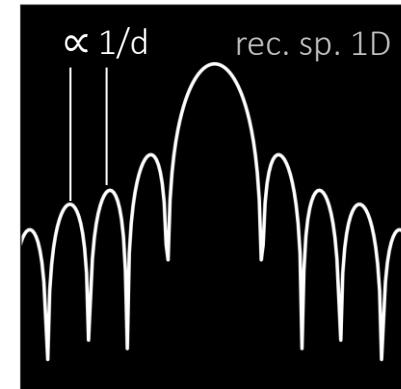
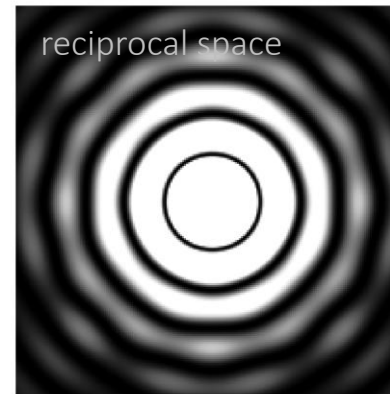
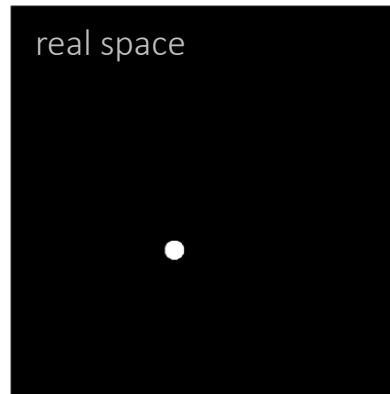
X-ray scattering intensity is $\propto$ to the Fourier transformation $\hat{F}$ of (continuous) electron density ρ_r

$$I(\vec{q}) \propto \left| \int_V \rho_r e^{-i\vec{q}\vec{r}} d\vec{r} \right|^2 = \hat{F}(\rho_r) \\ = |F(\vec{q})|^2 = F(\vec{q})F^*(\vec{q})$$

$F(\vec{q})$: Structure factor

Single particle (of size d):

e.g.: Single particle @ **A**: $|F(\vec{q})|^2 = f_p^2(\vec{q})(e^{-i\vec{q}\mathbf{A}}e^{i\vec{q}\mathbf{A}}) = f_p^2(\vec{q})$



For particles

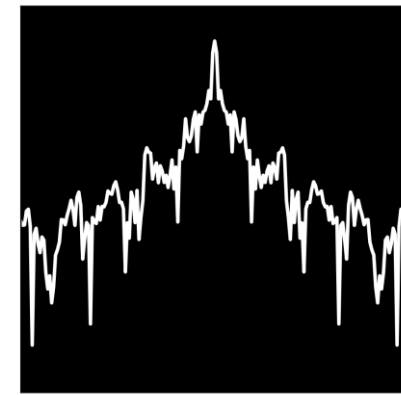
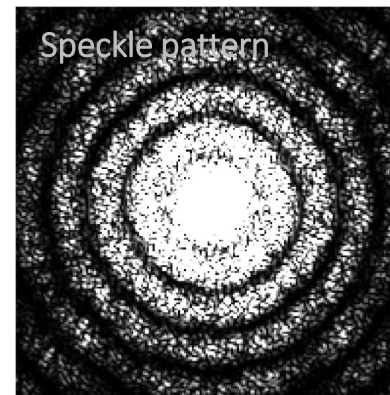
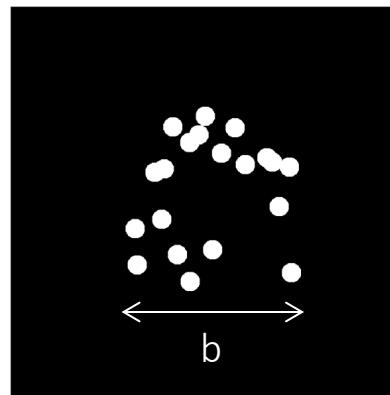
$$F(\vec{q}) = f_p(\vec{q}) \sum_n e^{-i\vec{q}\vec{r}_n}$$

$f_p(\vec{q})$: Form factor

Spheres: sinc-function

Finite number of particles

Two particles @ **A** and **B**: $|F(\vec{q})|^2 = f_p^2(\vec{q})(2 + e^{-i\vec{q}(\mathbf{A}-\mathbf{B})} + e^{-i\vec{q}(\mathbf{B}-\mathbf{A})})$

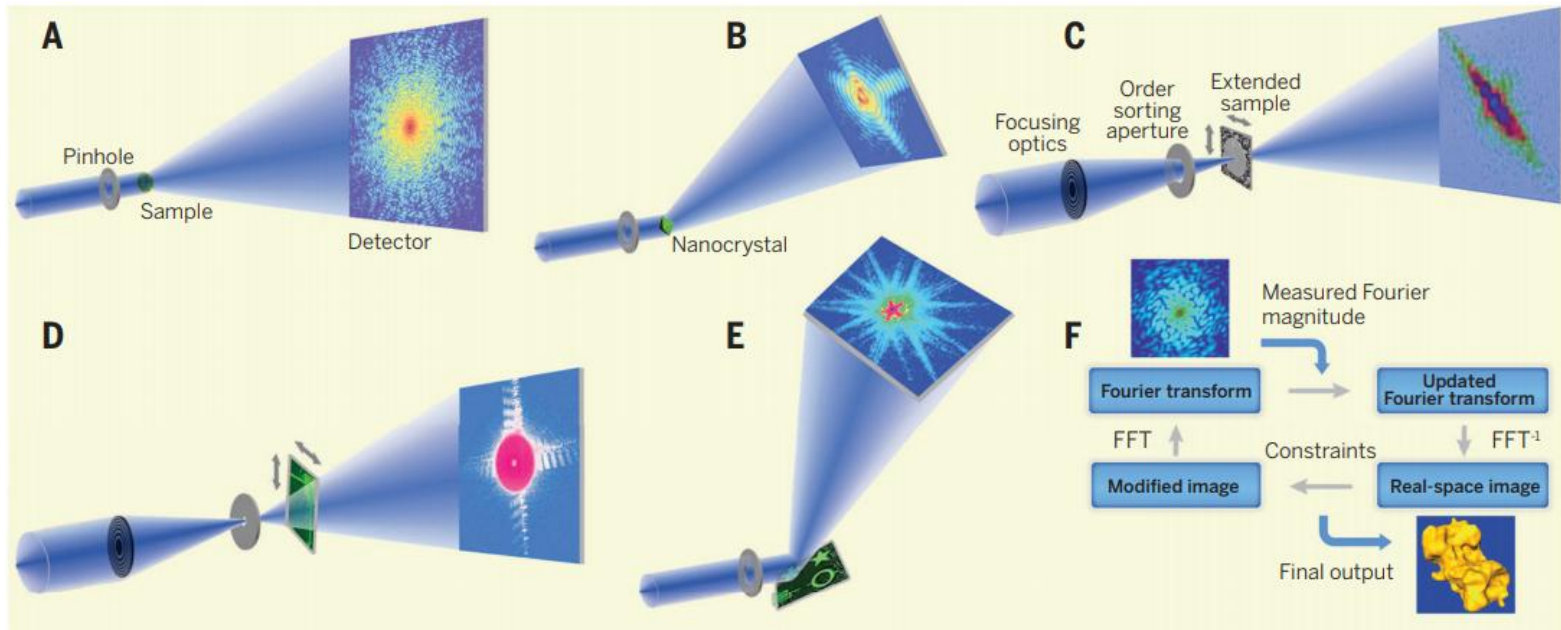


Speckle size: $\propto 1/b$

Coherent scattering – use case

Lenseless imaging

Coherent diffractive imaging (in principle resolution is limited by wavelength)



Iterative phase retrieval algorithms $\leftrightarrow$ several different methods

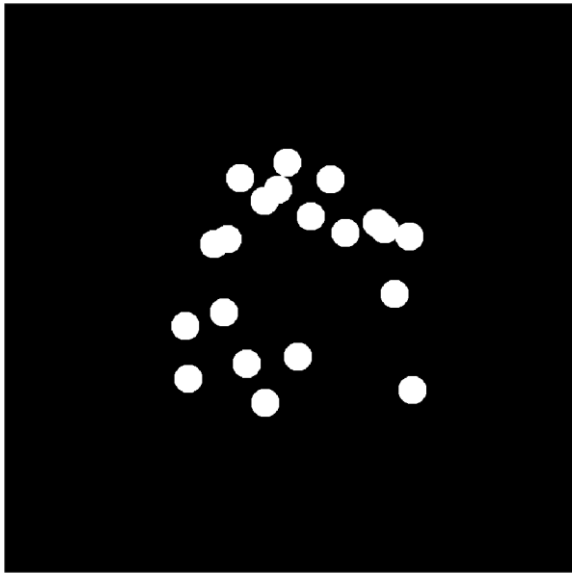
- Bragg CDI
- Ptychography

Dynamics: X-ray photon correlation spectroscopy

X-ray photon correlation spectroscopy

T = 0 K

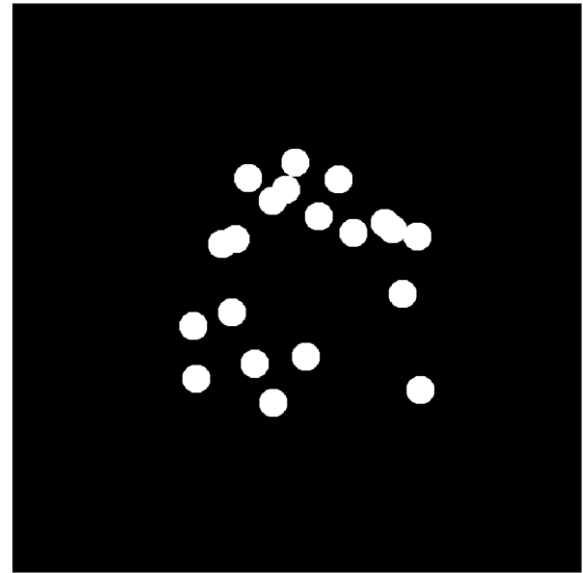
Static, $\vec{r}_n$'s are frozen



$$F(\vec{q}) = f_p(\vec{q}) \sum_n e^{-i\vec{q}\vec{r}_n}$$

T = 330 K

$\vec{r}_n \rightarrow \vec{r}_n(t)$

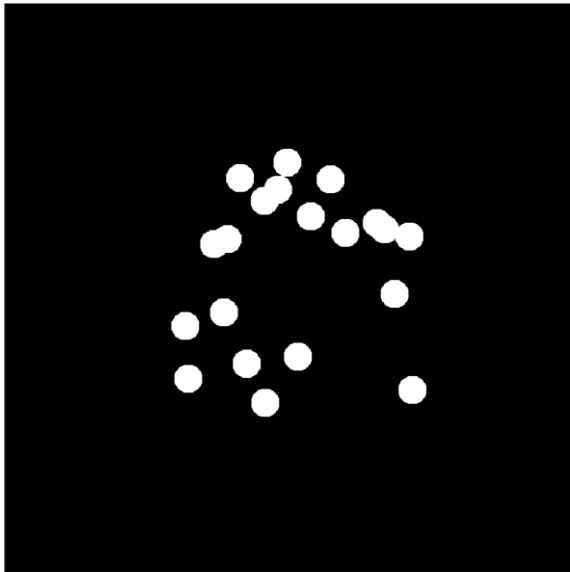


$$F(\vec{q}, t) = f_p(\vec{q}) \sum_n e^{-i\vec{q}\vec{r}_n(t)}$$

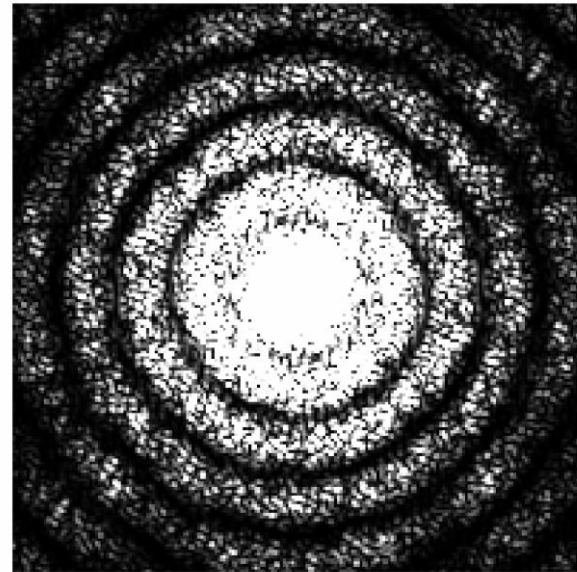
X-ray photon correlation spectroscopy

$$F(\vec{q}, t) = f_p(\vec{q}) \sum_n e^{-i\vec{q}\vec{r}_n(t)}$$

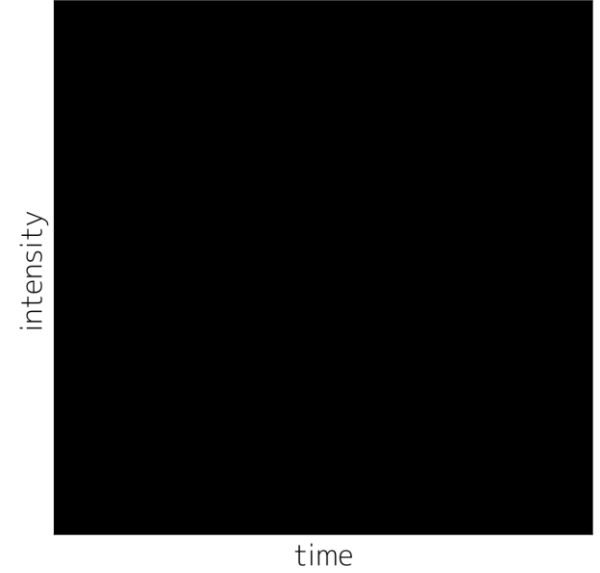
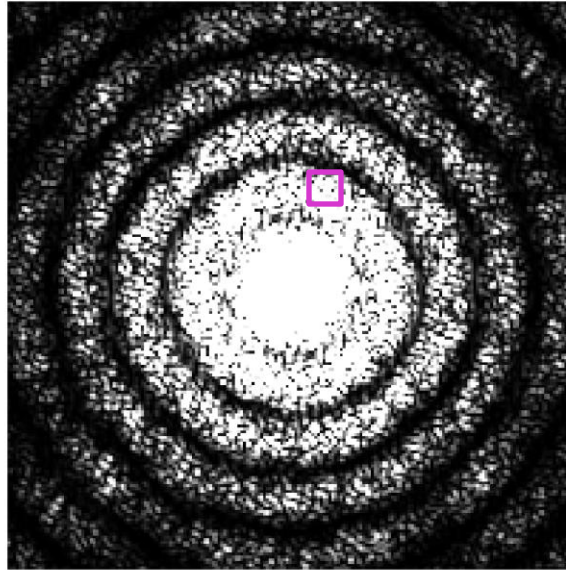
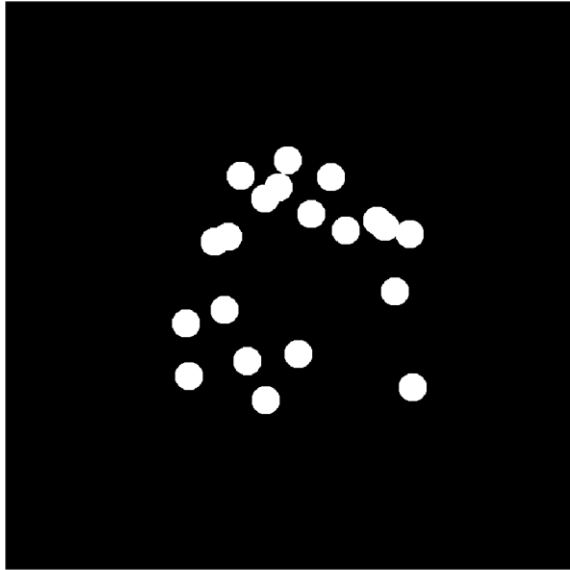
Real space



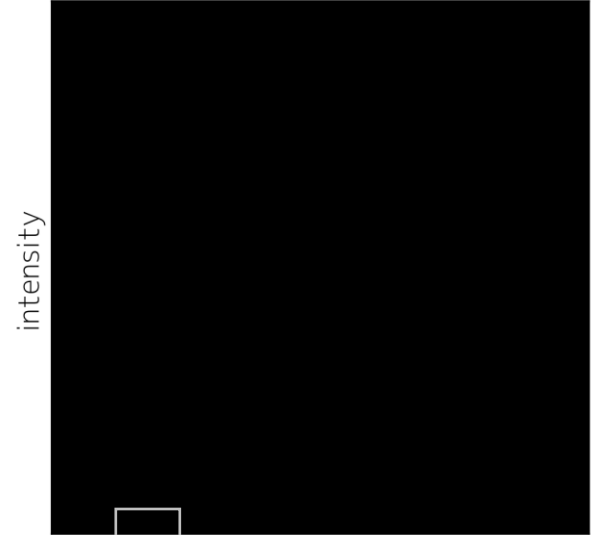
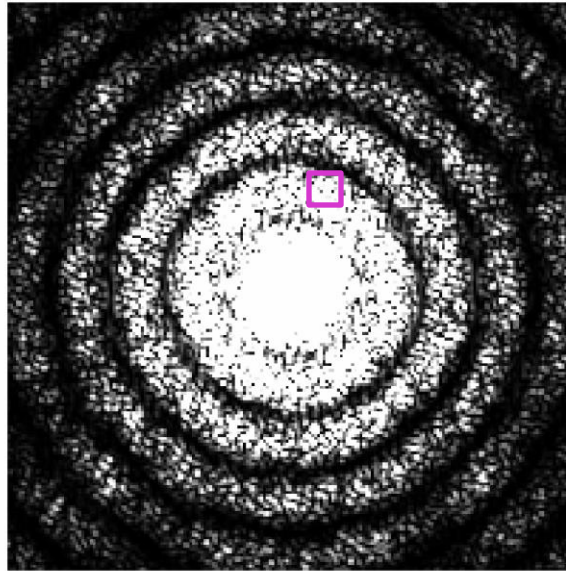
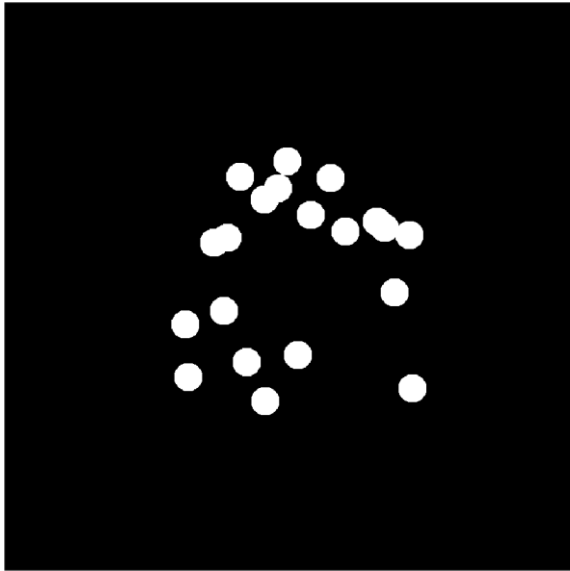
Reciprocal space



X-ray photon correlation spectroscopy



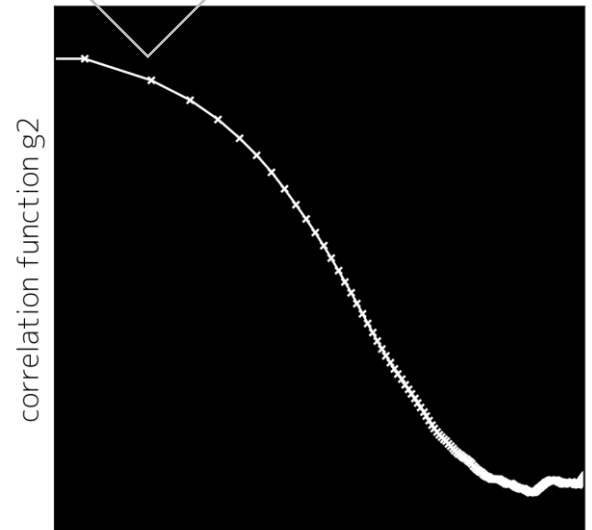
X-ray photon correlation spectroscopy



intensity

time

$$g^2(\vec{q}, \tau) = \frac{\langle I(\vec{q}, t) I(\vec{q}, t + \tau) \rangle}{\langle I(\vec{q}, t) \rangle^2}$$



correlation function g2

log(time delay τ)

Quantification of temporal correlations:

Normalized second order (time averaged) intensity correlation function

$$g^2(\vec{q}, \tau) = \frac{\langle I(\vec{q}, t) I(\vec{q}, t + \tau) \rangle}{\langle I(\vec{q}, t) \rangle^2}$$

Expressed in terms of intermediate scattering function:

$$g^2(\vec{q}, \tau) = 1 + |g^1(\vec{q}, \tau)|^2$$

$$g^1(\vec{q}, \tau) = \frac{F(\vec{q}, t + \tau)}{F(\vec{q}, t)}$$

X-ray photon correlation spectroscopy

How can we relate the measurement to the physics of the sample?

$$g^2(\vec{q}, \tau) = 1 + |g^1(\vec{q}, \tau)|^2 = \left| \frac{F(\vec{q}, t + \tau)}{F(\vec{q}, t)} \right|^2$$

$$F(\vec{q}, t + \tau) \propto \sum_{k,l} \langle e^{-i\vec{q} \cdot (\vec{r}_k(t+\tau) - \vec{r}_l(t))} \rangle$$

$$\vec{r}(t + \tau) - \vec{r}(t)$$

Diffusion

$$\langle [\vec{r}(t + \tau) - \vec{r}(t)]^2 \rangle = 6D_0\tau$$

$$g^1(\vec{q}, \tau) = e^{-\frac{\tau}{\tau_0}}$$

$$g^2(\vec{q}, \tau) = 1 + e^{-\frac{2\tau}{\tau_0}} \quad \tau_0 = 1/D_0q^2$$

Flow with uniform velocity

$$\vec{r}(t + \tau) - \vec{r}(t) = \vec{v}_0\tau$$

$$g^1(\vec{q}, \tau) = e^{-i\vec{q}\vec{v}_0\tau}$$

$$g^2(\vec{q}, \tau) = 1 + |e^{-i\vec{q}\vec{v}_0\tau}|^2 = 2$$

X-ray photon correlation spectroscopy

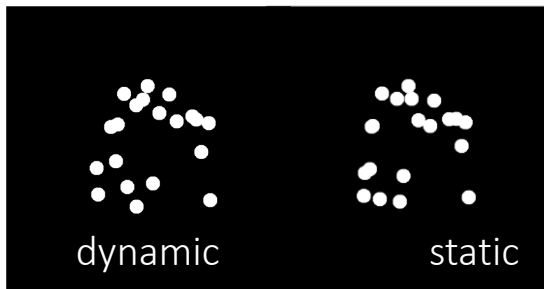
So far, we only considered the case of scattering solely from the dynamic sample

This is called *homodyne detection*

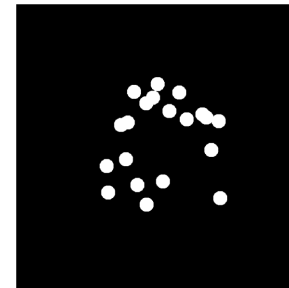
However, we can also mix the dynamic scattering with static scattering from a reference sample

This is called *heterodyne detection*

heterodyne detection



homodyne detection



$$g_{\text{heterodyne}}^2(\vec{q}, \tau) = 1 + |g_{\text{heterodyne}}^1(\vec{q}, \tau)|^2$$

$$g_{\text{heterodyne}}^1(\vec{q}, \tau) = h g_{\text{dynamic}}^1(\vec{q}, \tau) + (1 - h) g_{\text{static}}^1(\vec{q}, \tau) \quad h = \frac{I(q)_{\text{dynamic}}}{I(q)_{\text{dynamic}} + I(q)_{\text{static}}}$$

$$g_{\text{heterodyne}}^2(\vec{q}, \tau) = 1 + h^2 |g_{\text{dynamic}}^1|^2 + 2h(1 - h) \text{Re} \left(g_{\text{dynamic}}^{1,*} g_{\text{static}}^1 \right) + (1 - h)^2 |g_{\text{static}}^1|^2 \quad g_{\text{static}}^1 = 1$$

Sample physics $g_{\text{dynamic}}^1(\vec{q}, \tau) = e^{-i\vec{q}\vec{v}_0\tau} e^{-\left(\frac{\tau}{\tau_0}\right)^\gamma}$ Uniform velocity superimposed on Brownian motion

$$g_{\text{heterodyne}}^2(\vec{q}, \tau) = 1 + (1 - h)^2 + h^2 e^{-2\left(\frac{\tau}{\tau_0(q)}\right)^\gamma} + 2h(1 - h) \cos \omega\tau e^{-\left(\frac{\tau}{\tau_0(q)}\right)^\gamma} \quad \omega = \vec{q} \cdot \vec{v}_0 = qv_0 \cos \chi$$

Speckle visibility

Shutter-time

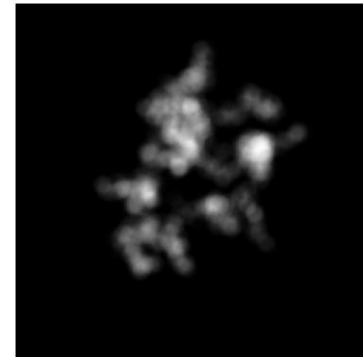
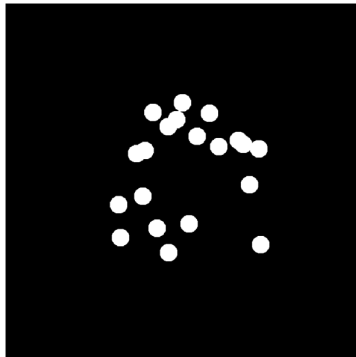
$$\Delta t = 0$$

$$\Delta t = a$$

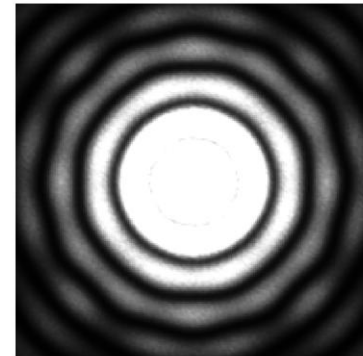
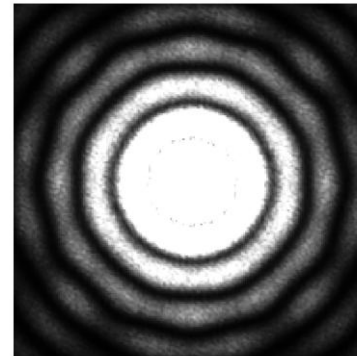
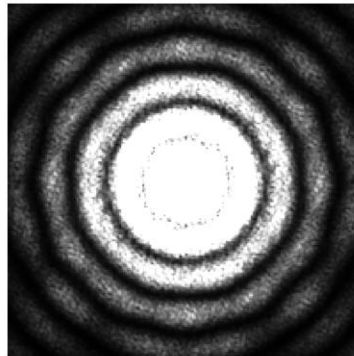
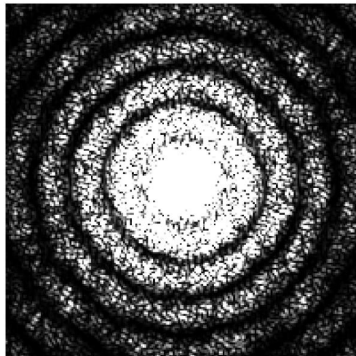
$$\Delta t = 4 \times a$$

$$\Delta t = 25 \times a$$

Real space
“photograph”



Reciprocal
space
pattern



Speckle visibility spectroscopy:

- Speckle contrast is calculated via statistical analysis of images
- Good for fast processes
- Good for low intensity

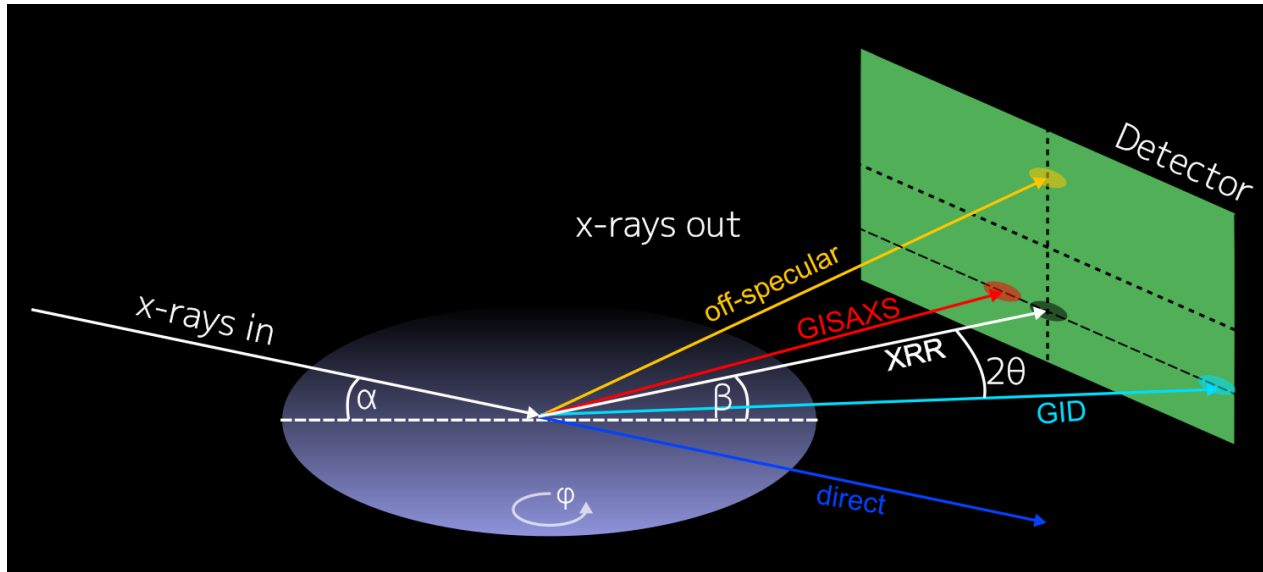
$$\Delta t \rightarrow \infty$$

→ incoherent pattern

→ $g(r)$

Surface-sensitive X-ray methods

Overview



1. X-rays impinge sample under grazing angle α (below critical angle $\rightarrow$ evanescent wave)
2. Interact with the sample
3. Exit sample according to sample structure under β and 2θ

$$\rightarrow I(\alpha, \beta, 2\theta) \leftrightarrow \text{structure}$$

X-ray reflectivity (XRR): Surface normal electron density profile

Off-specular diffuse: Surface roughness, lateral information, correlation-length, jaggedness

GISAXS: Surface and particle morphology, nano- macro-scale density correlations

GIWAXS, GID: Atomic order, crystallinity, unit cell, crystal size, molecular orientation of adlayers

Crystal truncation rods (CTR): Surface crystallography

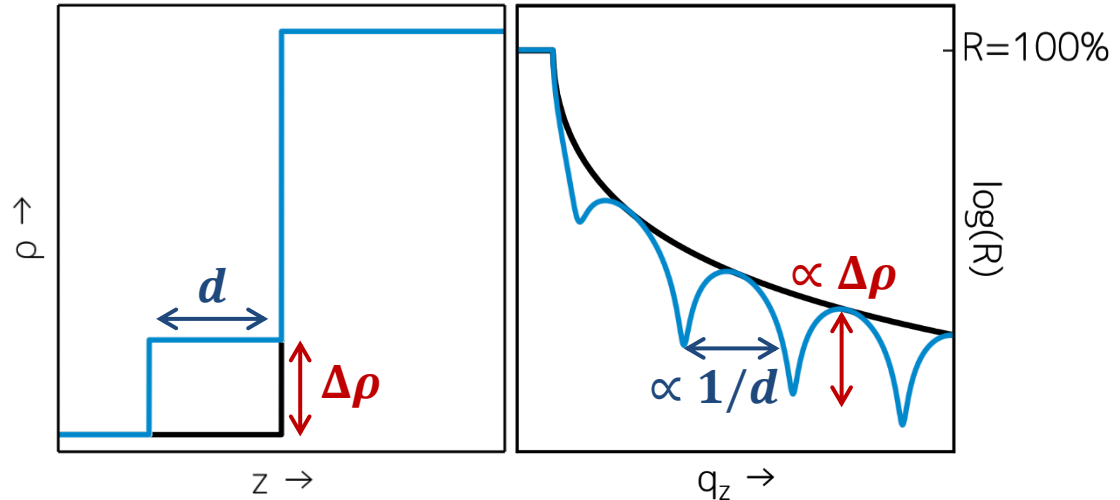
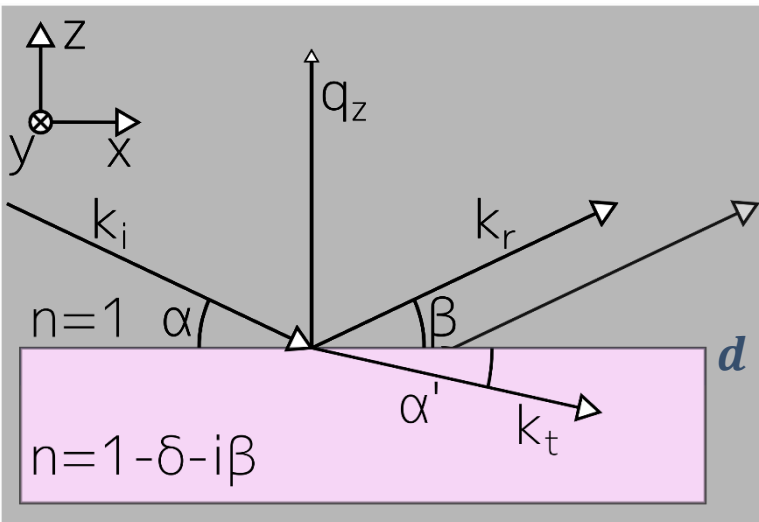
X-ray Reflectivity

Measures $R(\alpha) = \frac{I(\alpha)}{I_0}$

at $\alpha = \beta$

$$q_z = k_r - k_i = \frac{4\pi}{\lambda} \sin \alpha$$

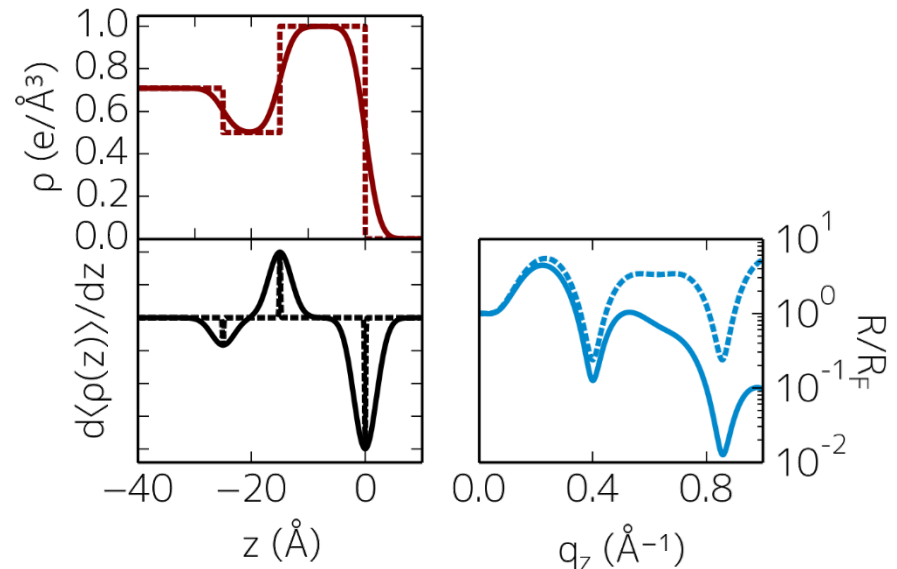
$$R(q_z) = \frac{I(q_z)}{I_0}$$



Arbitrary density profile:

- Slice into slabs
- Calculate via Master formula

$$\frac{R(q_z)}{R_F(q_z)} \approx \left| \frac{1}{\rho_\infty} \int_{-\infty}^{\infty} dz \frac{\partial \langle \rho(z) \rangle}{\partial z} e^{-iq_z z} \right|^2$$



Challenges

- Trade-off between accuracy and precision of experimental method and level of model system character of sample
- Both coherent and surface-sensitive X-ray methods typically require model systems (special cells, thin films, single crystals etc.)
- Challenges lies in interpreting (*operando*) results in context of materials and device performance
- If achieved, the respective knowledge can be used for rational improvements of and/or new concepts for materials and processes

X-ray Coulomb counting

Particular usefulness of X-ray (& neutron) methods

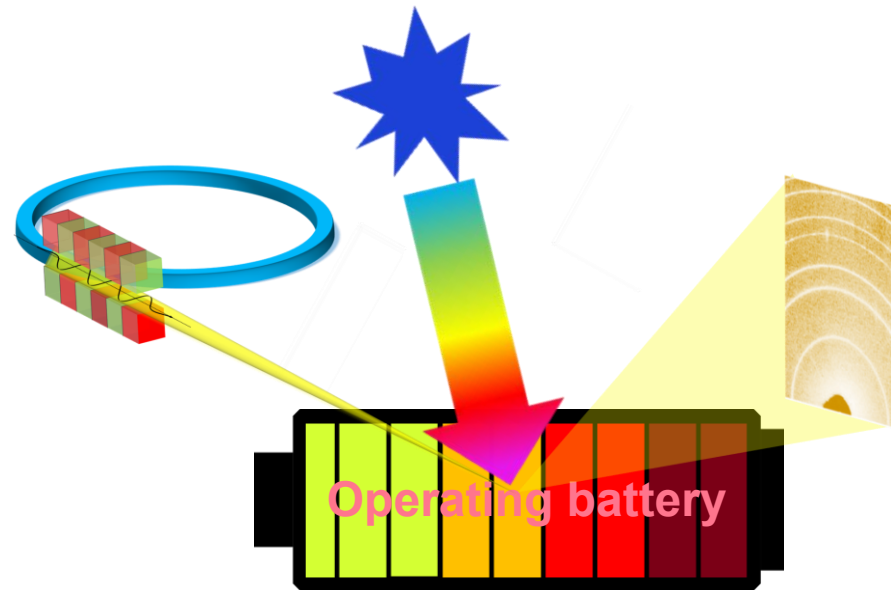
- *Operando* (and *in-situ*) modality across scales
- Quantitative on absolute scale
=
X-ray Coulomb counting

Bone, HGS, Toney, Joule 4, 1637 (2020)

Cao, HGS, Encyclopedia of Solid-Liquid Interfaces, Elsevier, 2024, Pages 391-416

Operando modality

Across scales



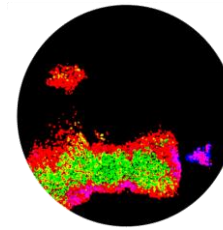
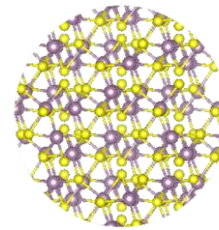
Desalination battery with 80 % capacity

Performance known

BUT explanation unknown

Structure and morphology

Arrangement of atoms/molecules and particles



Chemistry

Charge of atoms/molecules



Time resolution:

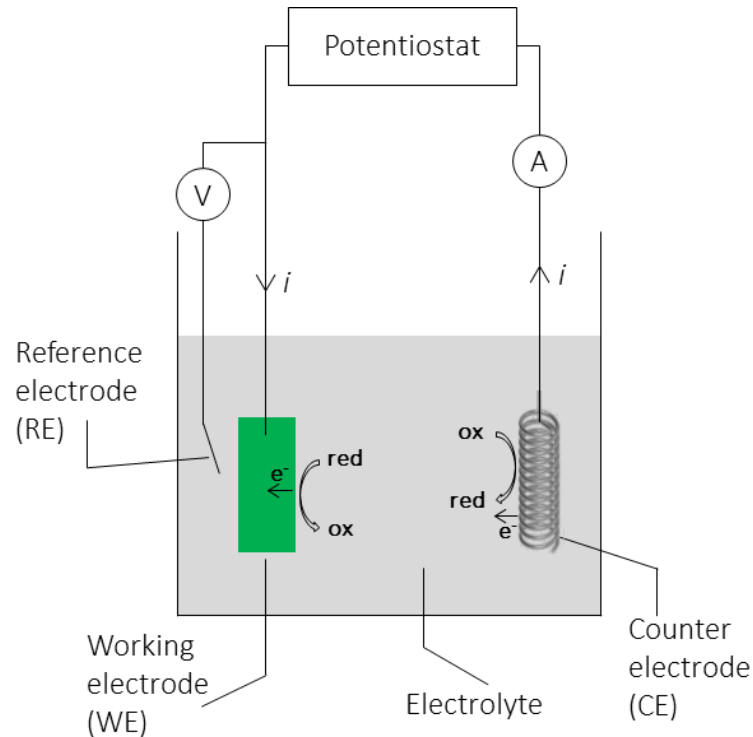
down to femtosecond

Spatial resolution:

sub-Ångström to meters

→ Explanation known → Foundational understanding

Electrochemistry – high-level research questions



Which reaction(s) occur(s)?

How much of this reaction occurs?

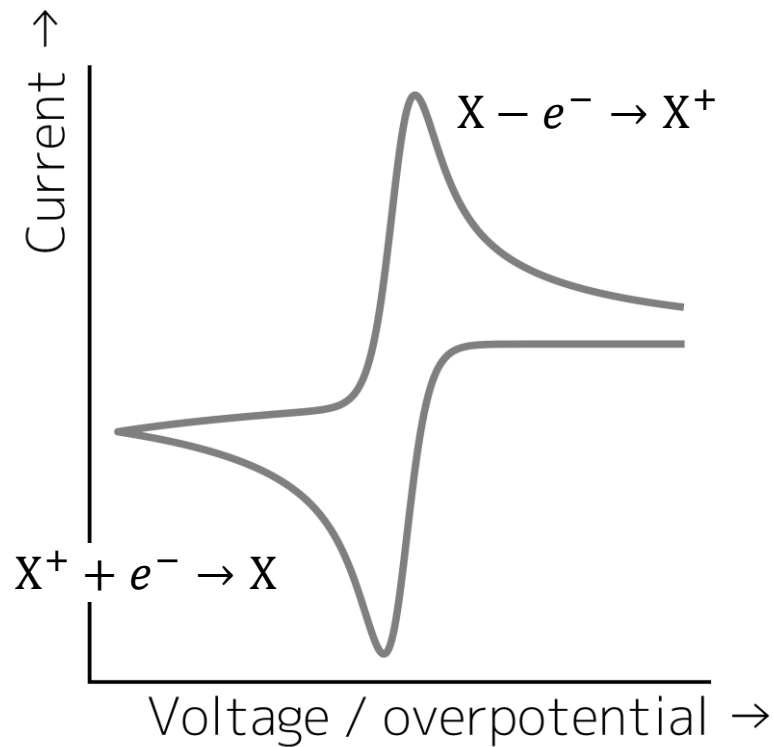
What happens to the WE/catalyst?

Why? Mechanism?

as a function of stimulus
(voltage, current, time, temperature, etc.)

How do we investigate these phenomena?

Electrochemistry

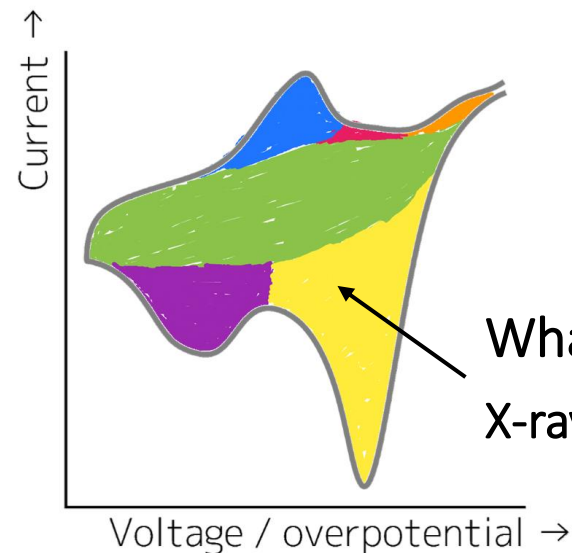


Which reaction(s) occur(s)?

How much of this reaction occurs?

$$Q^{\text{total}} = v^{-1} \int_{\text{Peak}} \text{Current}$$

Electrochemistry



What are the partial reactions?
X-ray Coulomb counting

Which reaction(s) occur(s)?

How much of this reaction occurs?

What happens to the WE/catalyst?
Why? Mechanism?

X-ray diffraction:

$$I_{hkl} = I_0 \frac{r_e^2 \lambda^3}{16\pi R} \times \text{LP} \frac{m_{hkl} |F_{hkl}|^2}{(v_{\text{unitCell}})^2} \times V$$

F_{hkl} and V encode
reaction and amount

X-ray reflectivity:

$$\frac{R(q_z)}{R_F(q_z)} \approx \left| \frac{1}{\rho_\infty} \int_{-\infty}^{\infty} dz \frac{\partial \langle \rho(z) \rangle}{\partial z} e^{-iq_z z} \right|^2$$

$\rho(z)$ encodes reaction
and amount

X-ray absorption:

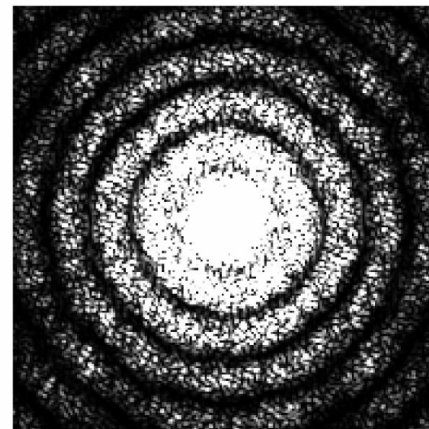
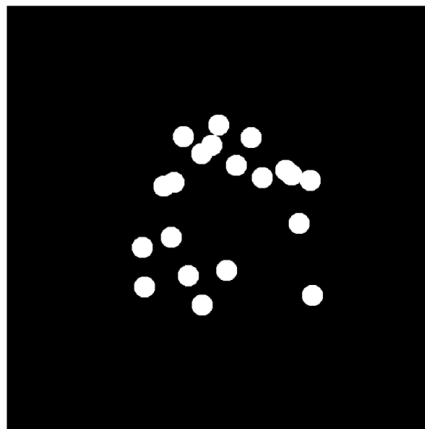
$$I_T = I_0 e^{-\mu(c,E)d}$$

$\mu(c,E)$ encodes
reaction and amount

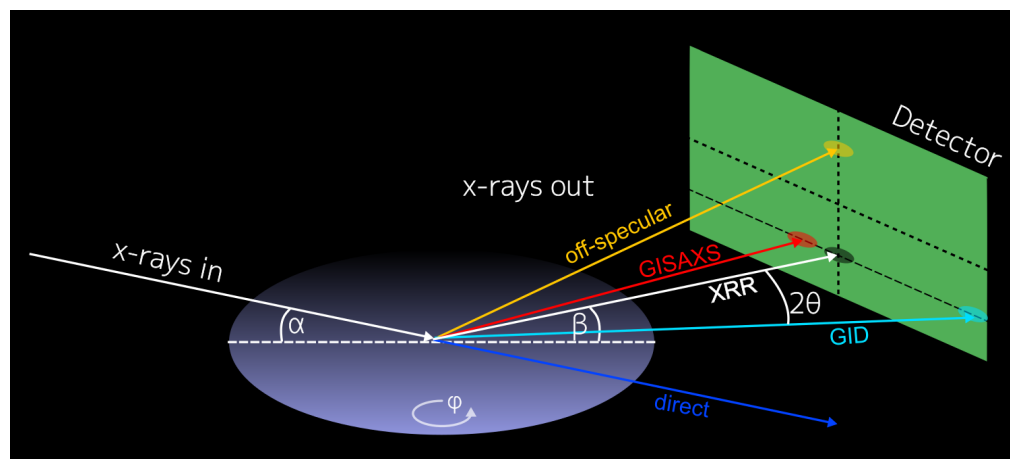
Neutrons/X-rays: *In situ/operando* absolute quantification of partial reactions & microscopy mode
→ Quantitative microscopy at the atomic scale and surface sensitivity

Q & A

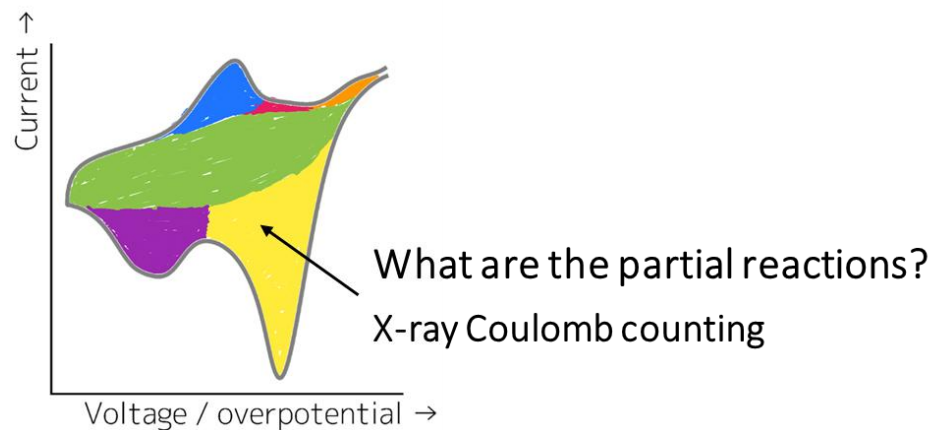
Coherent X-ray
scattering



Surface-sensitive
X-ray scattering



X-ray Coulomb
counting



Part 1 – tutorial / theory

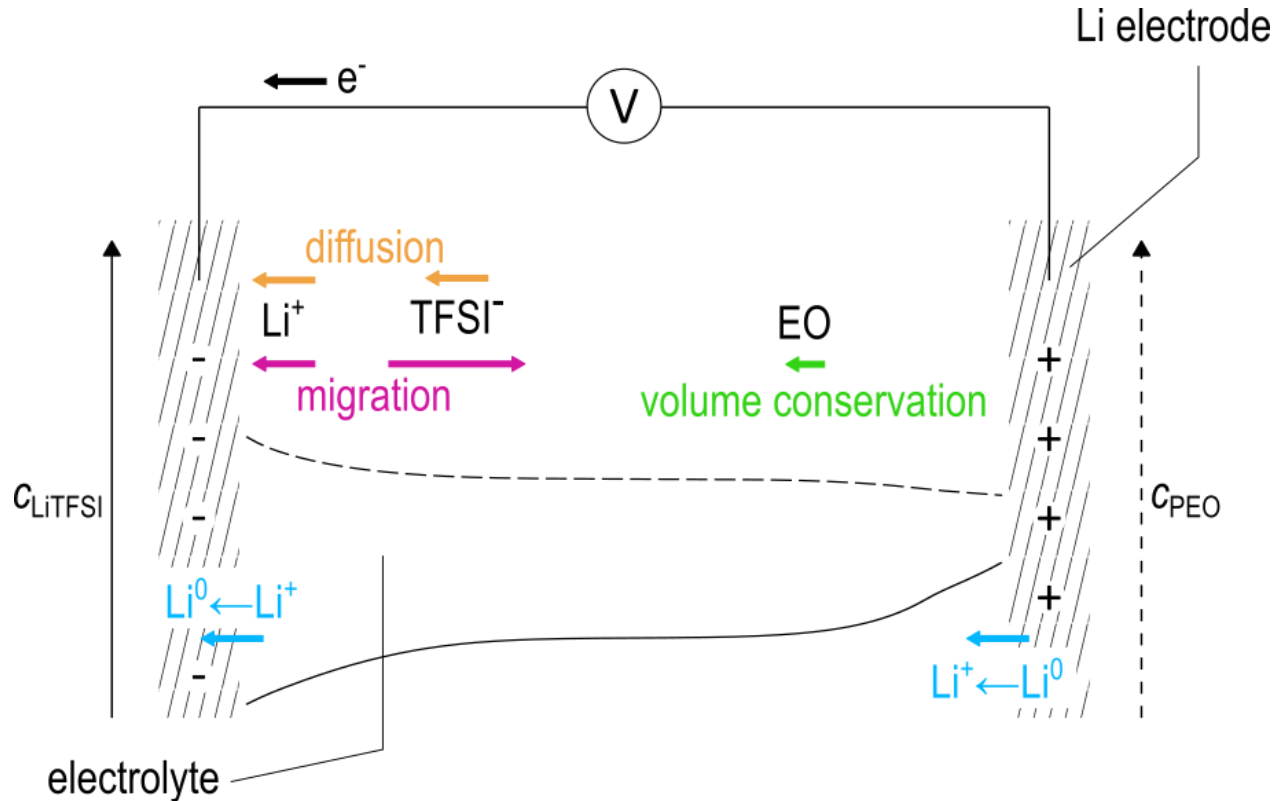
- Coherent X-ray methods
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Part 2 – scientific examples

- Coherent X-ray methods
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Coherent X-ray scattering

Ion Transport in Polymer Electrolytes



Transport parameters: Conductivity, diffusivity, **transference number**

Imperative information towards predictive cell modelling (DFN model)
→ Concentration gradient limits power density

Transference Number

- “Number of faradays of charge carried by the cations across a reference plane when a total of one faraday of charge passes across the plane”
- Fraction of ion conductivity that is useful to cell chemistry (charge transport efficiency)

THE IMPORTANCE OF THE LITHIUM ION TRANSFERENCE NUMBER IN LITHIUM/POLYMER CELLS

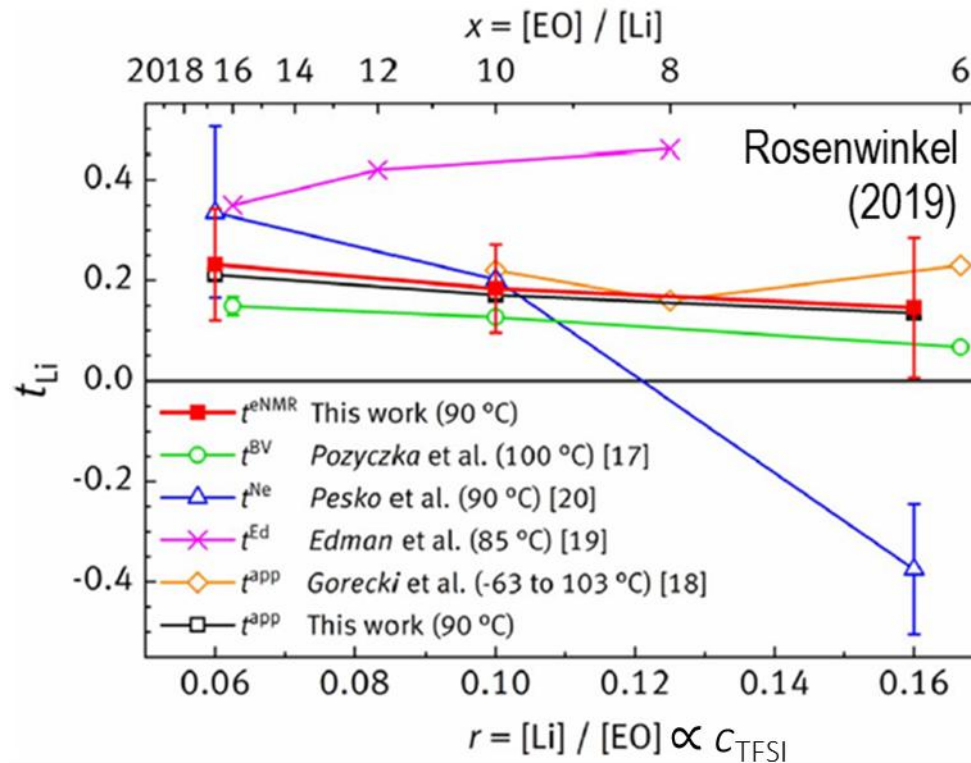
MARC DOYLE, THOMAS F. FULLER* and JOHN NEWMAN

Department of Chemical Engineering, University of California and Materials Sciences Division,
Lawrence Berkeley Laboratory, Berkeley, CA 94720, U.S.A.

(Received 23 July 1993; in revised form 23 November 1993)

Abstract—Simulation results are presented for a lithium negative electrode, solid polymer separator, manganese dioxide composite positive electrode cell. In particular, we assess the effect of conductivity and transference number on cell performance, establishing criteria for situations when a trade-off between these two properties is expected. We show that polymer-electrolyte systems with a unity transference number have improved performance over systems with $t_+^0 = 0.2$, even when the conductivity is decreased by an order of magnitude. The improvements are primarily at higher rates of discharge, where the latter cell would be depleted of electrolyte due to large concentration gradients that develop. Cells with a unity transference number have larger energy densities and can attain higher peak-power densities.

Transference Number - LiTFSI/PEO



Our approach [Mistry, Srinivasan, HGS, *Adv. Energy Mater.* 13, 2203690 (2023)]:

Not to measure coefficients
but **electrolyte concentration and velocity profiles**
and compare to DFN model

Rosenwinkel, Schönhoff, *JES* 166, A1977 (2019)

Methods

Ion concentration profiles

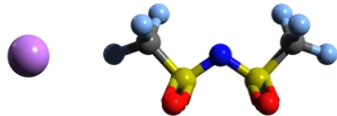
X-ray microscopy

$$I_T = I_0 e^{-\mu(c_{\text{TFSI}})t}$$

Strong absorption

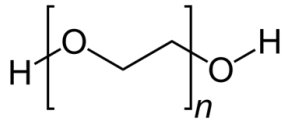
Cation:
Lithium

Anion:
TFSI



Weak absorption

Poly(ethylene oxide)

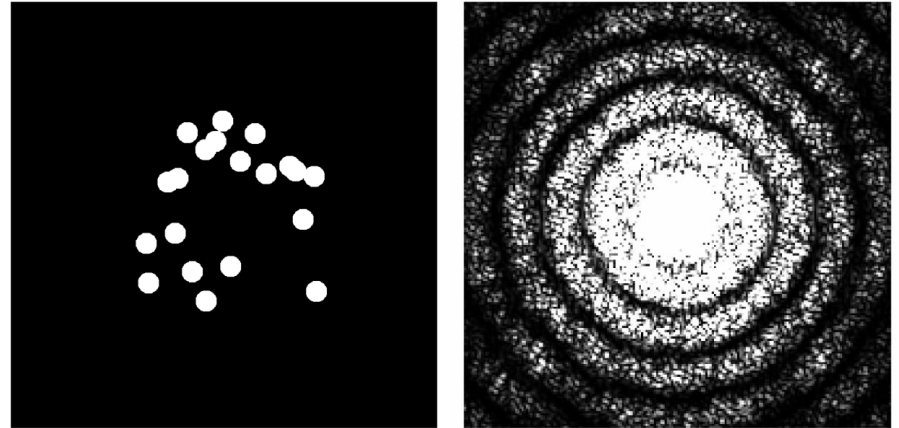


Exact solution:

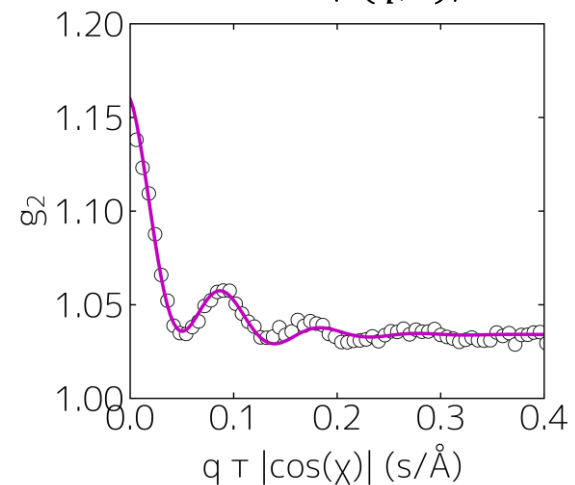
HGS, AIP Adv. 11, 115119 (2021)

Electrolyte velocity profiles

X-ray photon correlation spectroscopy

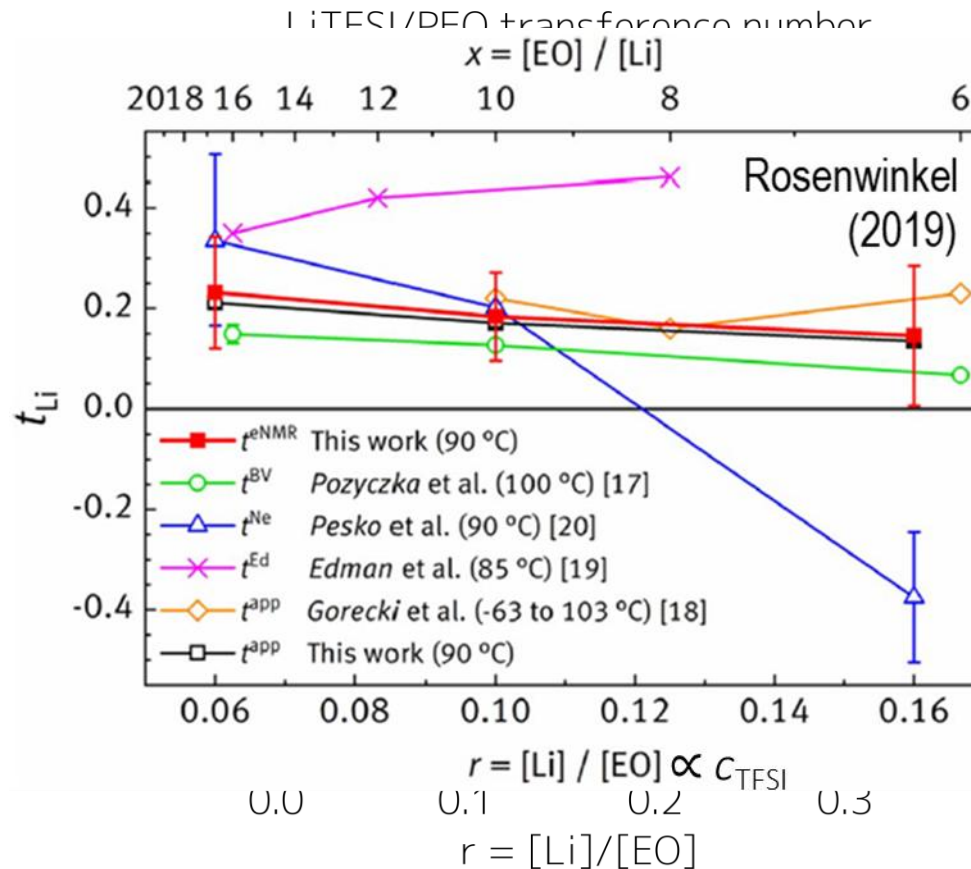


$$g^2(\vec{q}, \tau) = \frac{\langle I(\vec{q}, t) I(\vec{q}, t + \tau) \rangle}{\langle I(\vec{q}, t) \rangle^2}$$



Parameter Sets at 90° C

Transference number $t^+(r)$



Despite only a single starting concentration, a large concentration range is probed

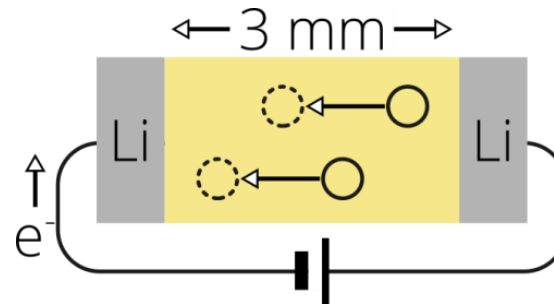
PNB: Pesko, Timachova, Bhattacharya, Smith, Villaluenga, Newman, Balsara, JES 164, E3569 (2017)

RS: Rosenwinkel, Schönhoff, JES 166, A1977 (2019)

Experiment

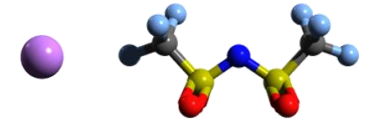
Sample:

- LiTFSI in 600 k Poly(ethylene oxide)
- Li:O = 0.1
- Li|LiTFSI|Li symmetric cell



Cation:
Lithium

Anion:
TFSI

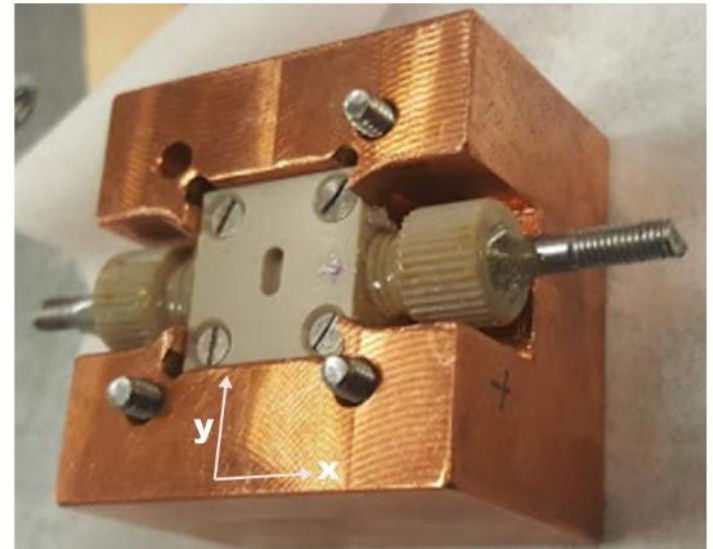
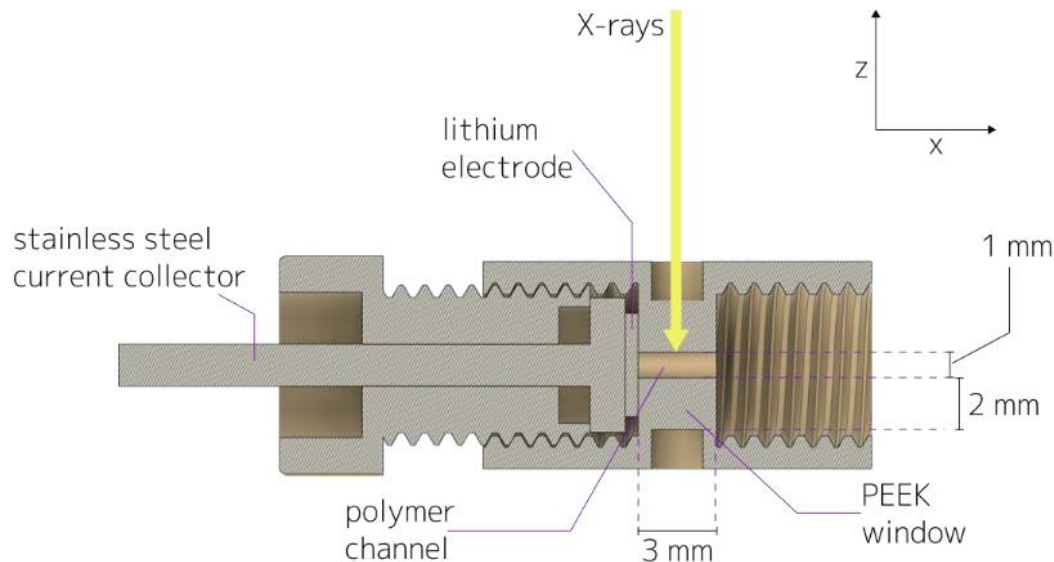


Electrochemistry:

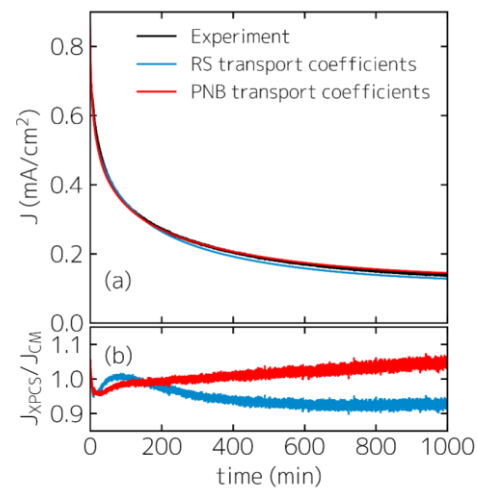
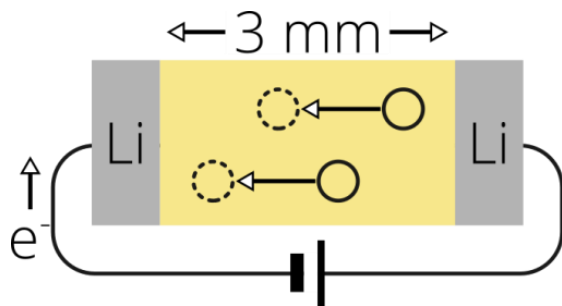
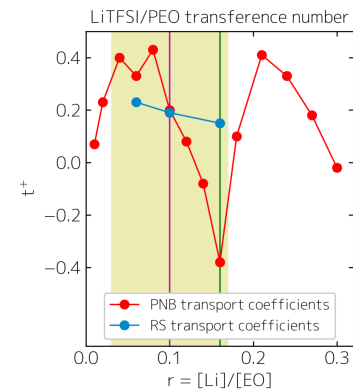
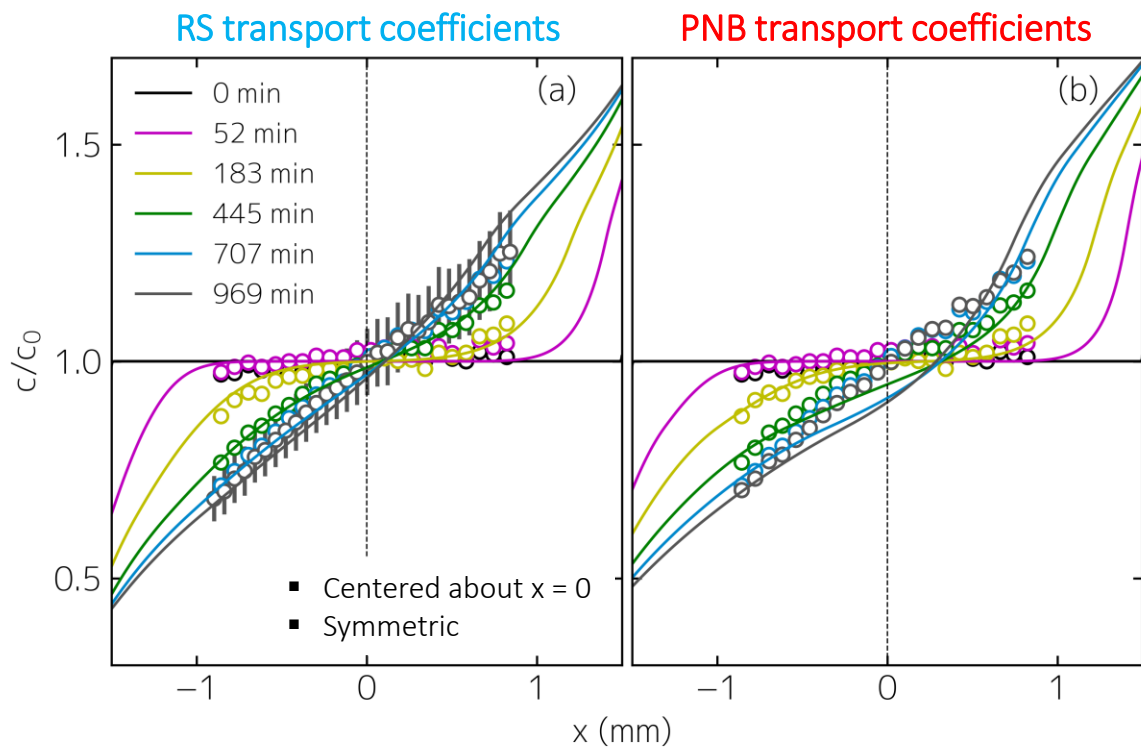
- Constant potential
- Typically 0.3 V
- 90° C

Dimension:

- Channel length: 3 mm
- Channel diameter: 1 mm
- Area: 0.8 mm²

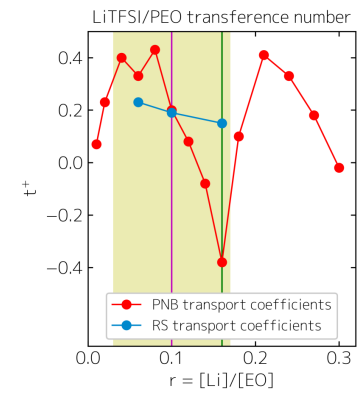
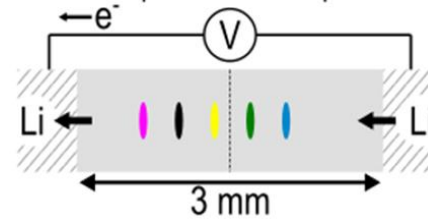
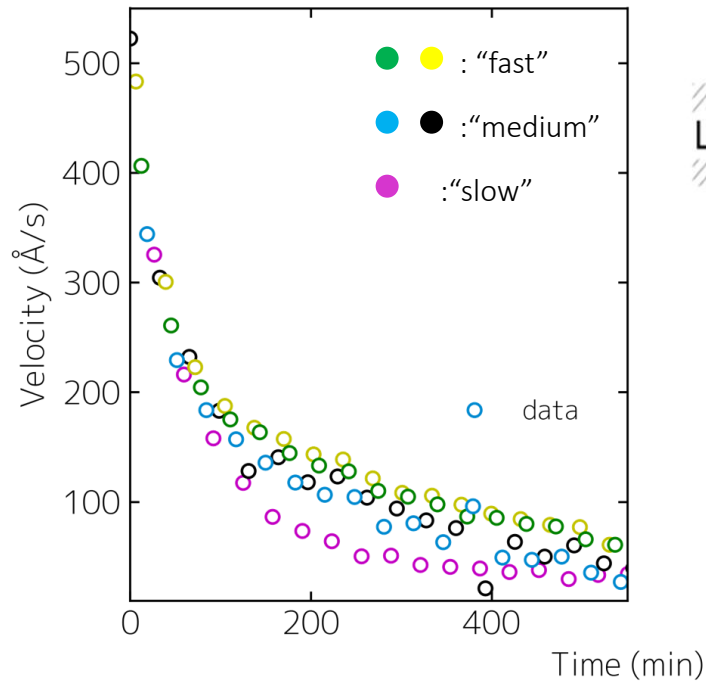


Concentration



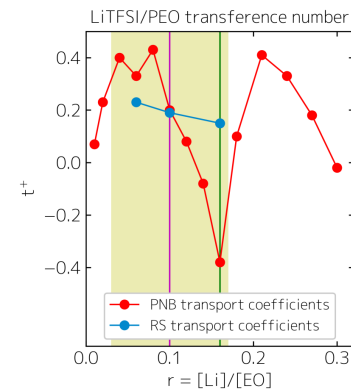
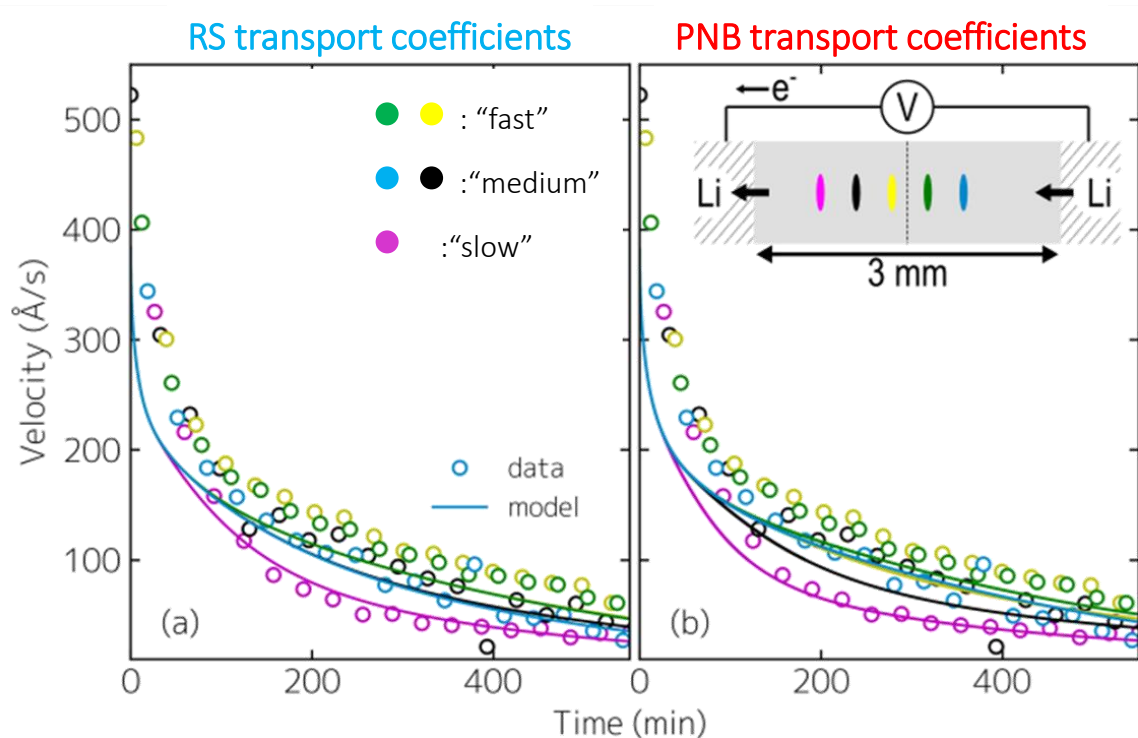
TFSI Velocities

Conversion from XPCS measured EO ensemble average velocity to TFSI velocity



TFSI Velocities

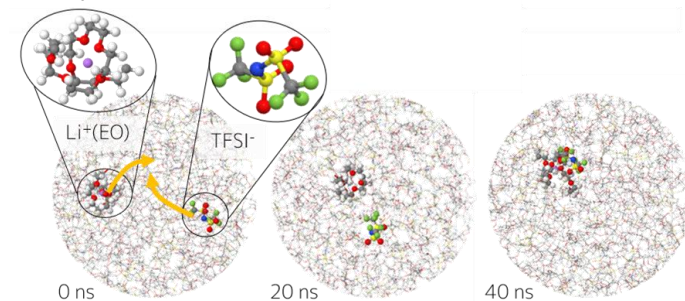
Conversion from XPCS measured EO ensemble average velocity to TFSI velocity



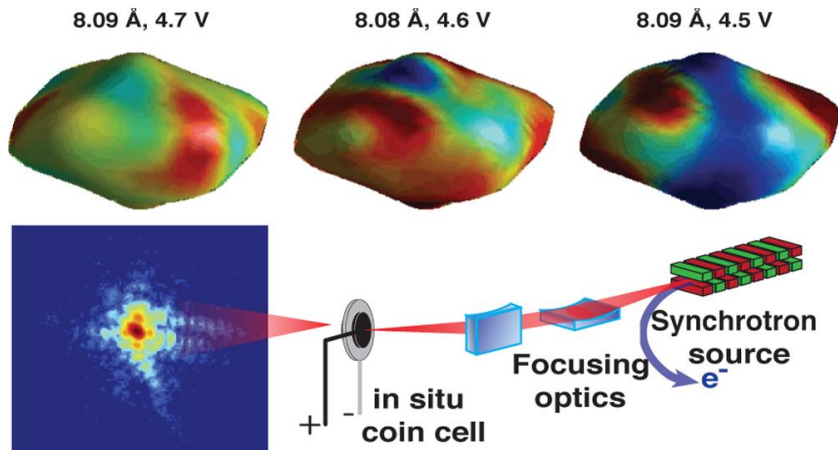
Relative distributions of velocities match RS transport coefficients

Together with concentration profiles and MD,
velocity measurements support RS transport coefficients

$$t^+(\text{LiTFSI}|\text{PEO}) \approx 0.2 \neq f(r)$$

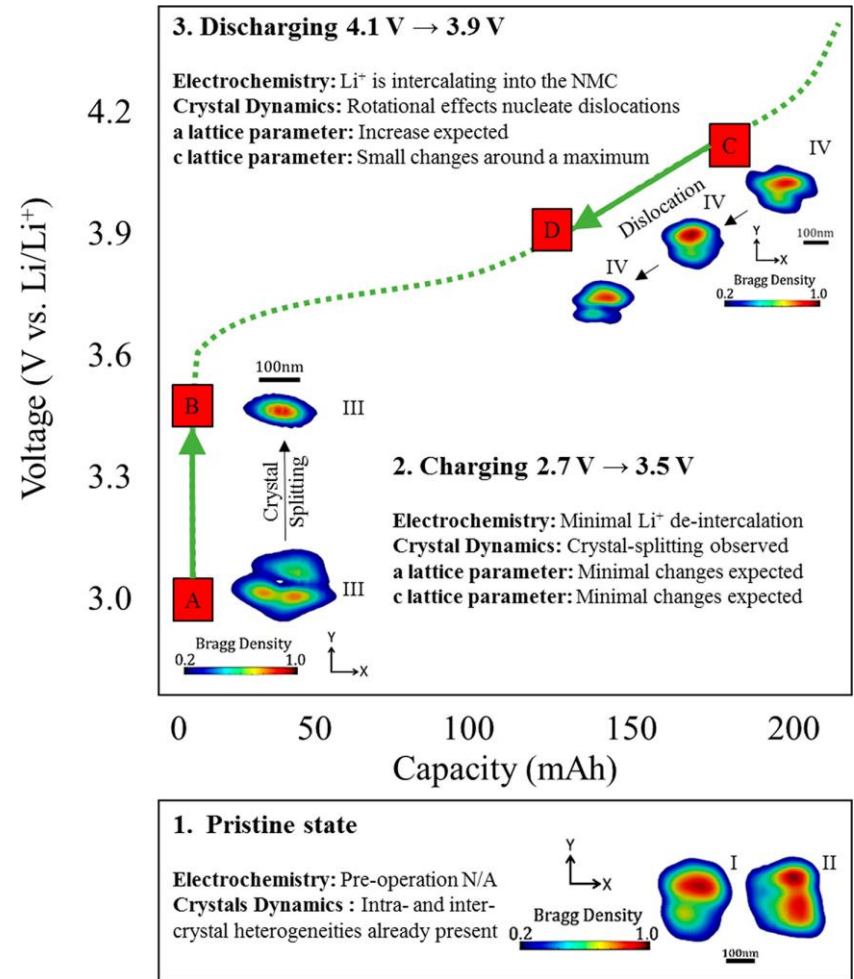


Coherent diffraction imaging



- 3D strain evolution of single $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ nanoparticle
- Stripe morphologies and coherency strain at the nanoscale
- Elastic energy landscape with femtojoule precision
- Hysteresis at the single particle level

Ulvestad et al., Nano Lett. 14, 5123 (2014)

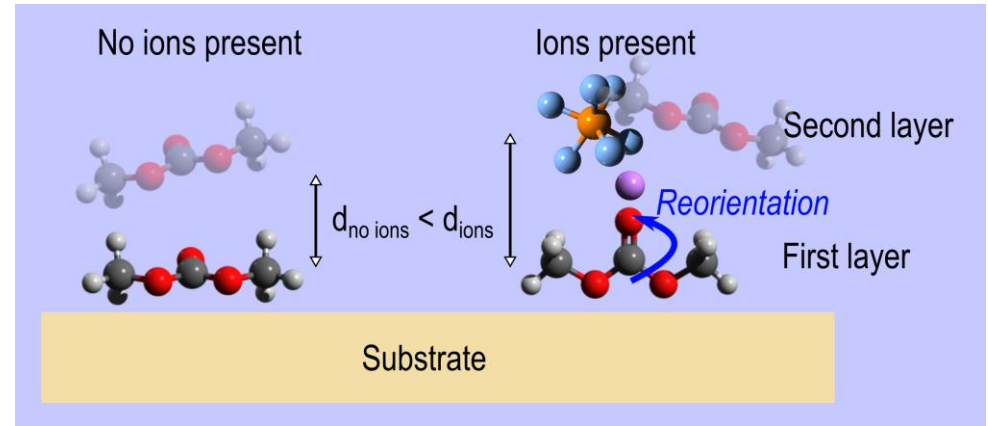
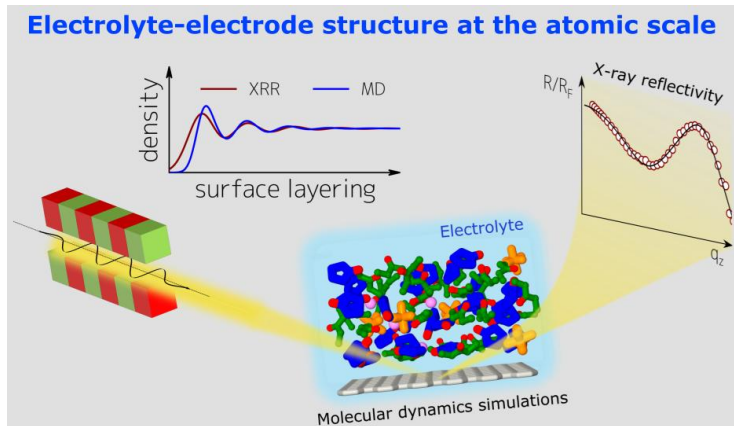


Estandarte et al., ACS Nano 15, 1321 (2021)

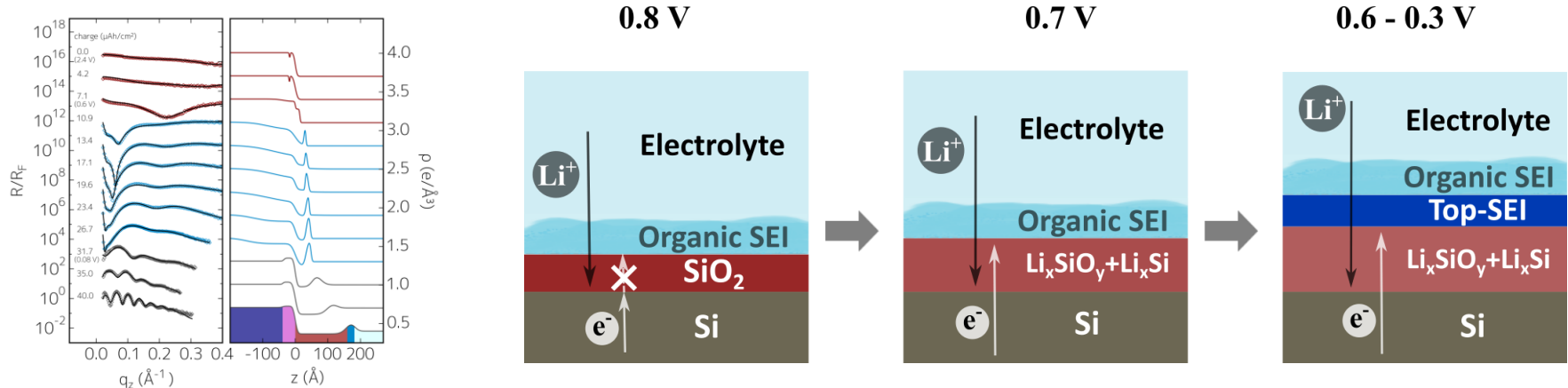
Surface-sensitive X-ray scattering

Surface and interface electrochemistry

Electric double layer structure and speciation in LIB electrolytes



Surface electrochemistry of Si anodes



HGS et al., *Energy Environ. Sci.*, 11, 594 (2018); Horowitz et al., *Nano Lett.* 18, 2105 (2018); HGS et al., *J. Chem. Phys.* 152, 084702 (2020); Cao et al., *Acc. Chem. Res.* 52, 2673 (2019); Cao et al., *Joule* 3, 762 (2019); Cao et al., *Adv. Mater. Interfaces* 4, 1700771 (2017); Cao et al., *Nano Lett.* 16, 7394 (2016).

Solid Electrolyte Interphase

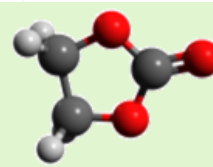
Solid Electrolyte Interphase

charging

reduction (+e⁻)

Carbon
electrode

Electrolyte



EC



Li⁺



PF₆⁻

or aqueous

Energetically more favorable to reduce electrolyte than carbon

$$E_{\text{reduction}}^{\text{carbon}} (\text{C} + \text{e}^- + \text{Li}^+ \rightarrow \text{LiC}_6) \approx 0.1 \text{ V versus Li/Li}^+$$

$$E_{\text{reduction}}^{\text{electrolyte}} (\text{EC} + \text{e}^- \rightarrow \text{oEC}^-) \approx 0.6 \text{ V versus Li/Li}^+$$



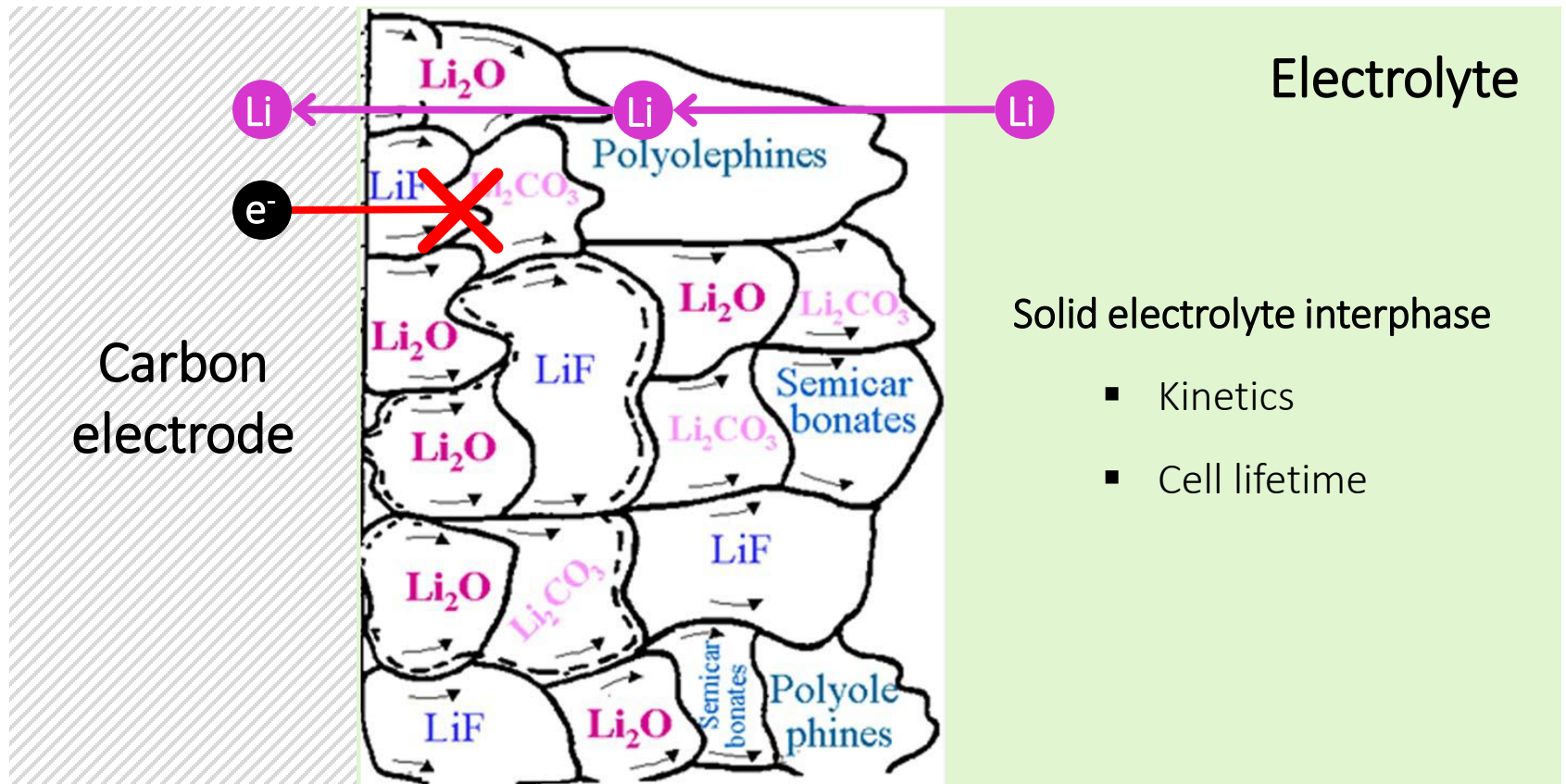
Solid insoluble products

Ionically conductive, electron blocking

→ passivating

(H₂ for aqueous)

Solid Electrolyte Interphase



“Growing Appreciation for the Role of LiF in the Solid Electrolyte Interphase”

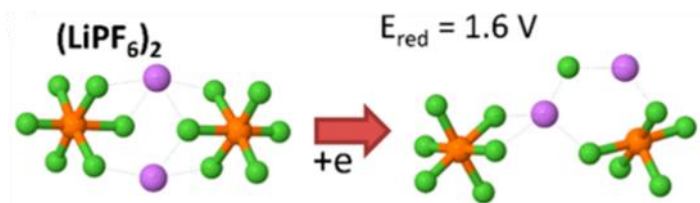
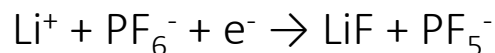
Tan et al., Adv. Energy Mater. 2100046 (2021).

*Peled, Golodnitsky, Penciner, Anode/electrolyte interface,
in Handbook of Battery Materials, ed Besenhard, Verlag Chemie (VCH), 410 (1998).*

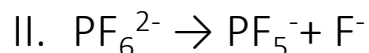
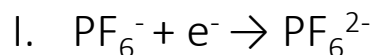
Origin of LiF in the Solid Electrolyte Interphase

Electrochemically

Direct anion reduction of LiPF_6 ($c_{\text{LiPF}_6} \approx 1 \text{ M}$)
reaction 1



“Sub-reactions”:

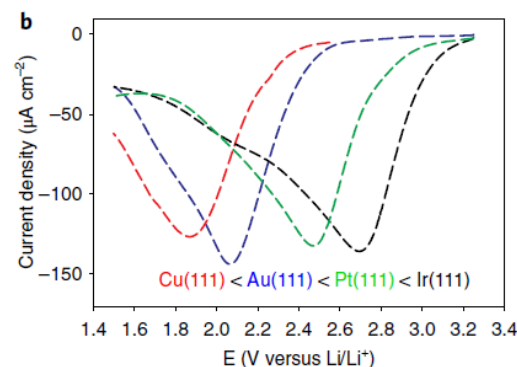
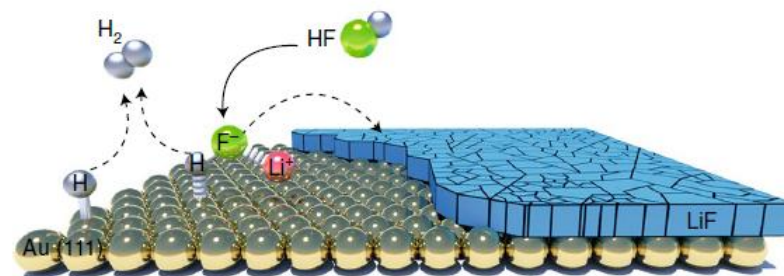
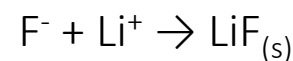
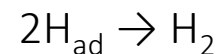
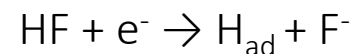


Reduction potential:

- 1.6 V (Borodin)
- 1.46 V (Leung)

Electrocatalytically

HF splitting ($c_{\text{HF}} \approx 0.002 \text{ M}$)
reaction 2



Reduction potential: Depends on electrode

Strmcnik et al., Nat. Catal. 1, 255 (2018)

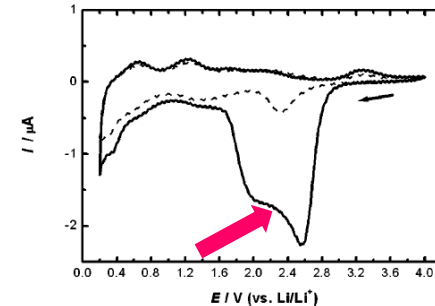
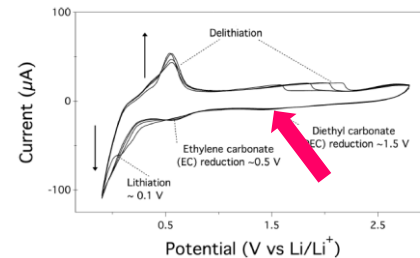
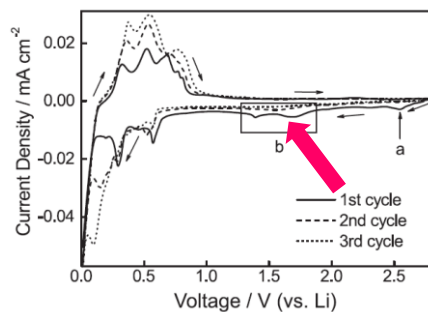
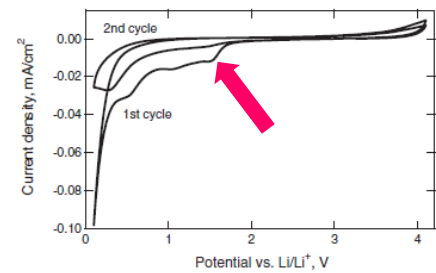
Aurbach et al., J. Electroanal. Chem. 297, 225 (1991)
Borodin et al., Acc. Chem. Res. 50, 2886 (2017)
Leung, PCCP 17, 1637 (2015)

Tang, Newman, JES, 159, A1775 (2012)

Kawaguchi et al., JPS 271, 431 (2014)

Horowitz et al., JACS 138, 726 (2016)

Lee et al., JES 152, A1193 (2005)

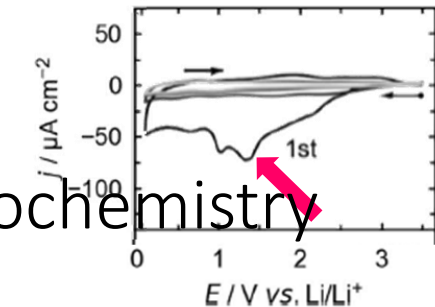
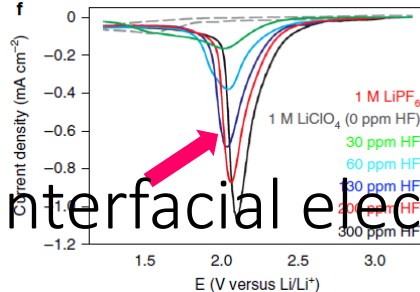
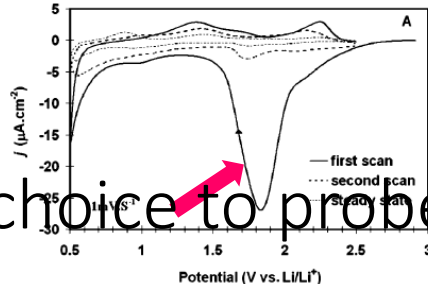
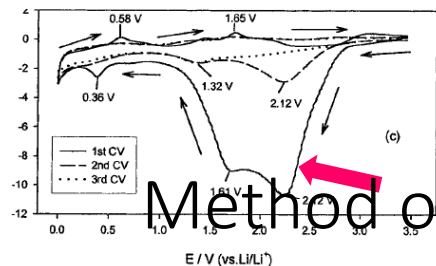


Gnanara et al., JES 150, A445 (2003)

Zhuang et al., JPCB 109, 17567 (2005)

Strmcnik et al., Nat. Catal. 1, 255 (2018)

Sonoki et al., JES 166 A3593 (2019)



Method of choice to probe interfacial electrochemistry

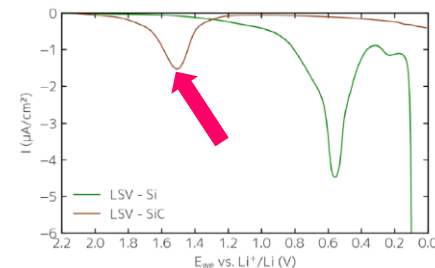
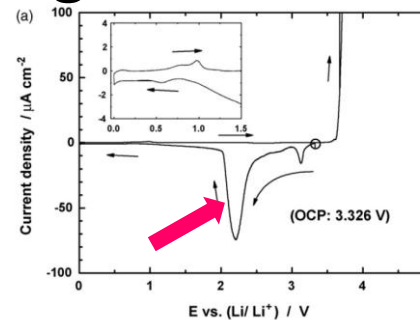
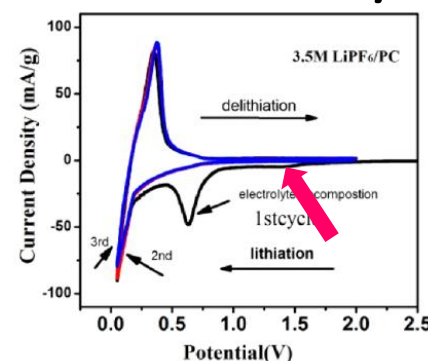
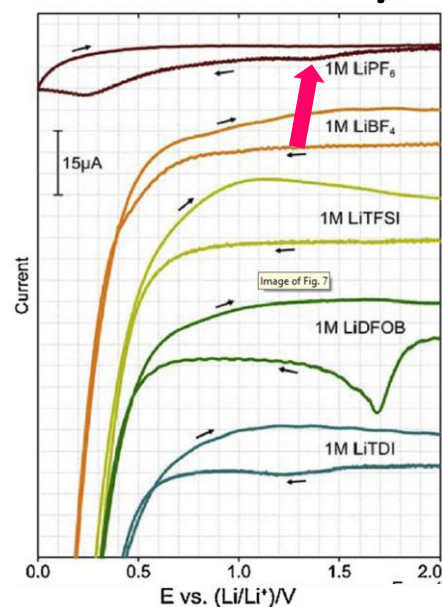
Cyclic voltammetry using model electrodes

Delp et al., Electrochim. Acta 209, 48 (2016)

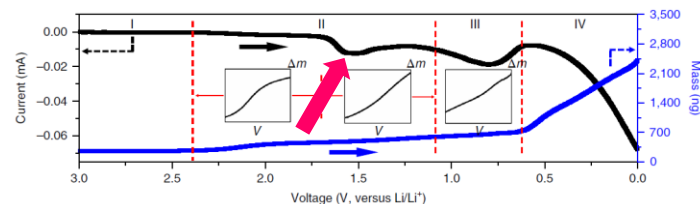
Wang et al., JPCB 115, 5381 (2013)

Muller et al., Electrochim. Acta 55, 488 (2009)

Gao et al., Joule 3, 762 (2019)



Liu et al., Nat. Nanotechnol 14, 50 (2019)

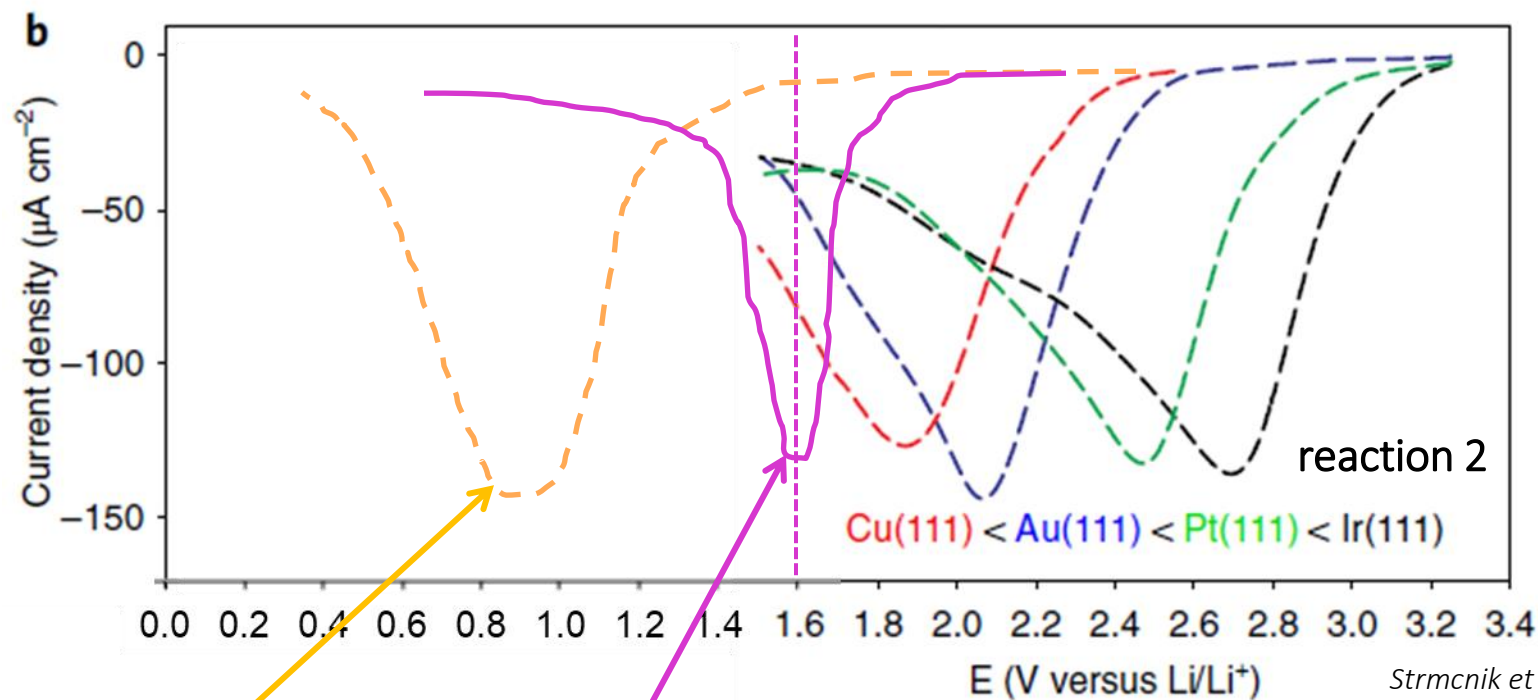
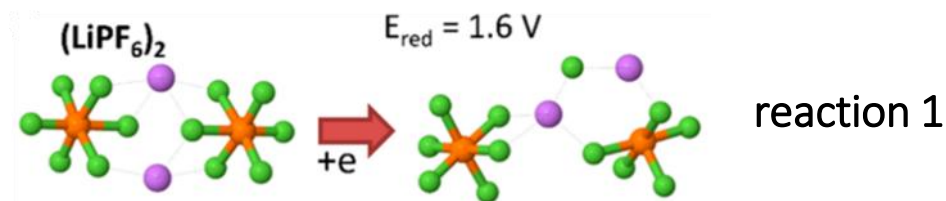


Can we design an unambiguous CV experiment
to distinguish **reaction 1** and **reaction 2**?

Can we observe **reaction 1**?

How can we observe reaction 1 ?

reaction 1: direct PF_6^- red
reaction 2: HF splitting

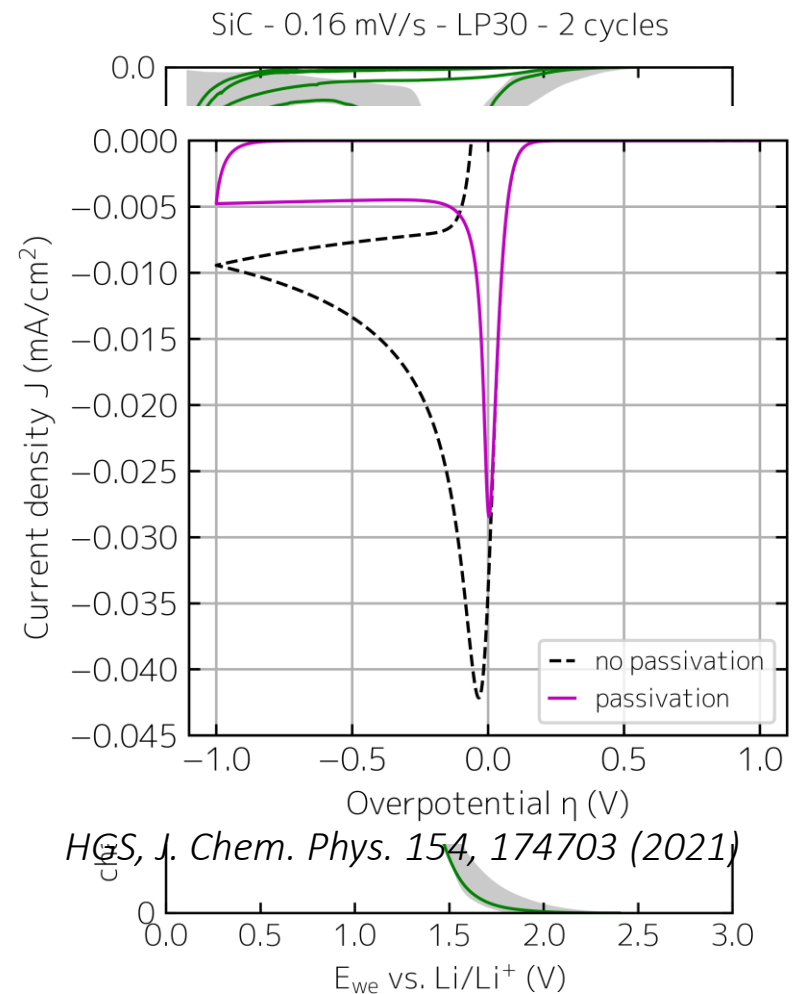
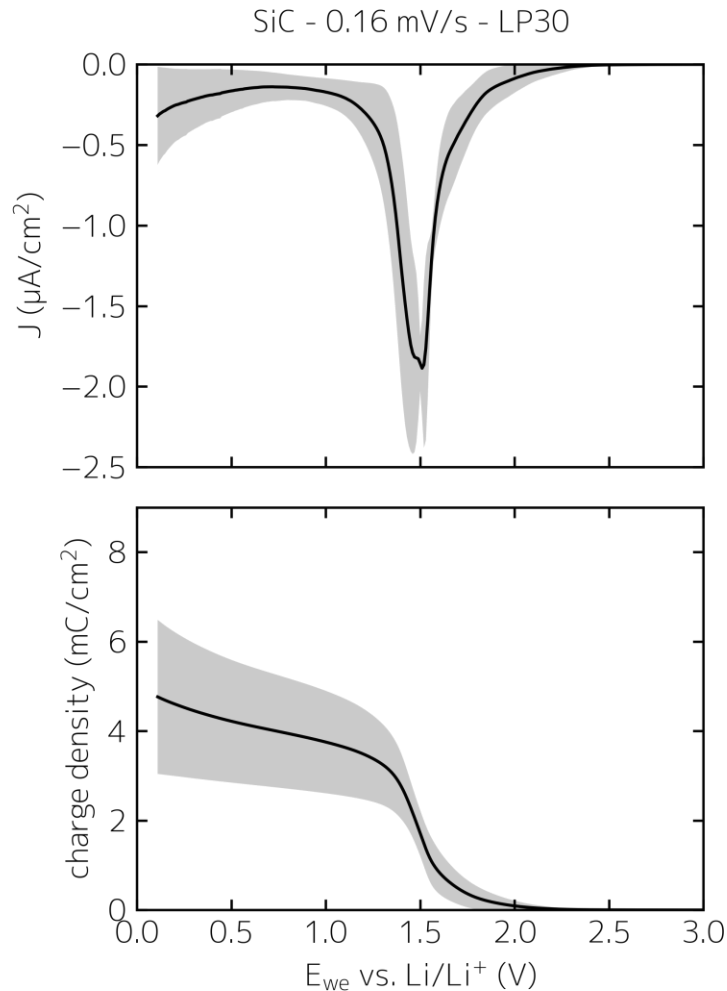


Strmcnik et al.,
Nat. Catal. 1, 255 (2018)

Nitrogen-doped silicon carbide (N-SiC)

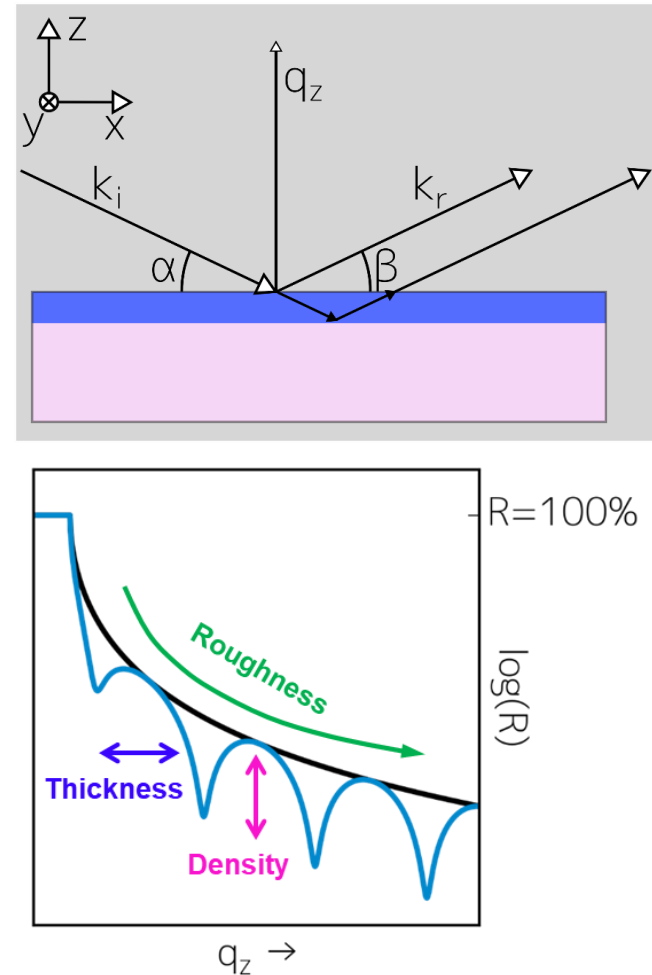
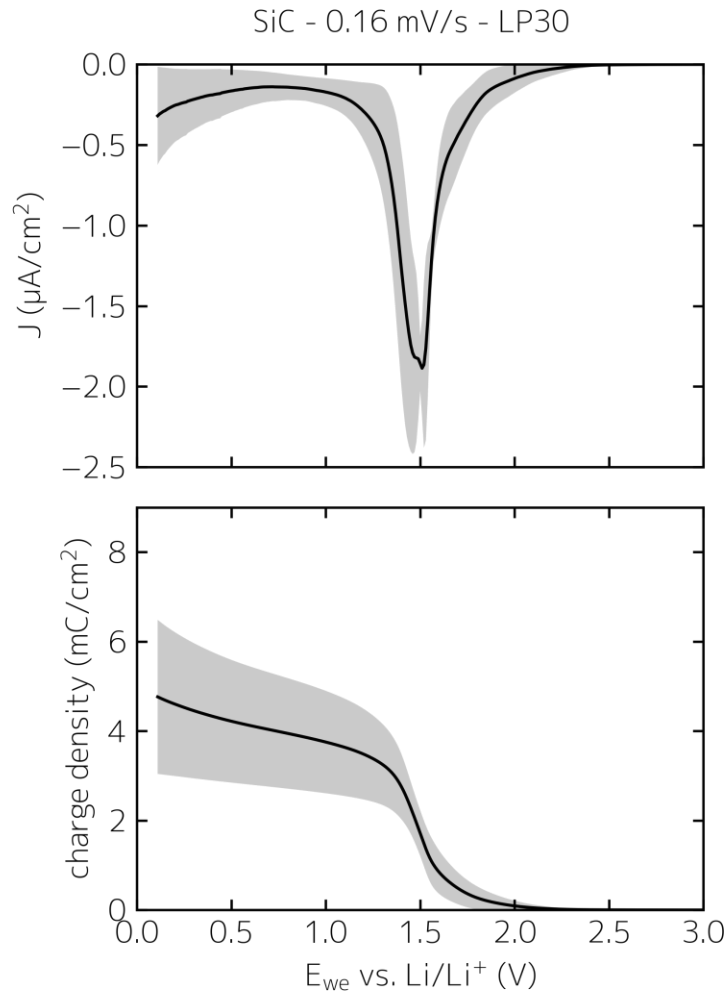
Estimated voltage for reaction 2: 1.4 V

Baseline Data: Voltammetry in 1 M LiPF₆ in EC:DMC



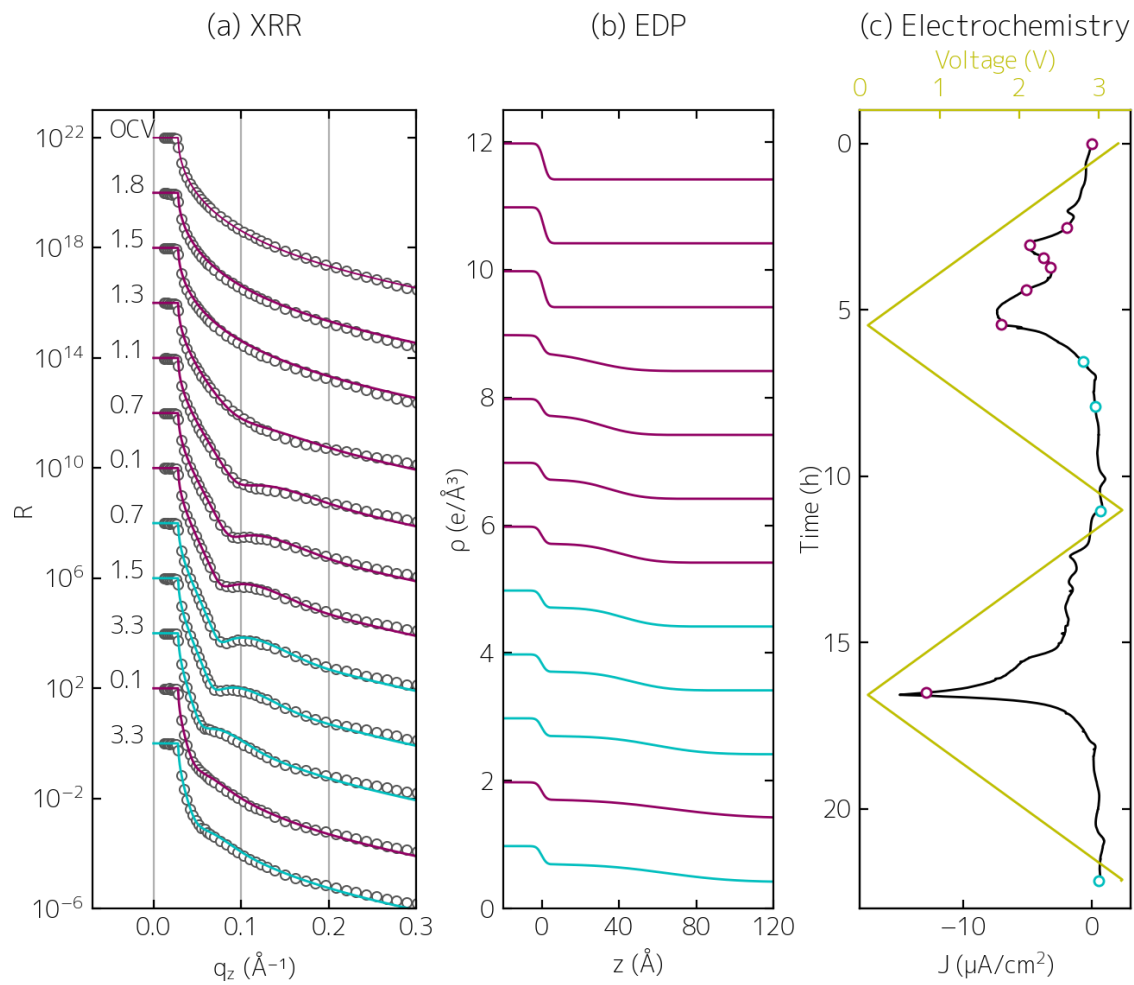
- Single feature at 1.5 V – “very” sharp peak (compared to metals)
- Surface becomes passivated by corresponding charge density → SEI layer

Baseline Data: Voltammetry in 1 M LiPF₆ in EC:DMC



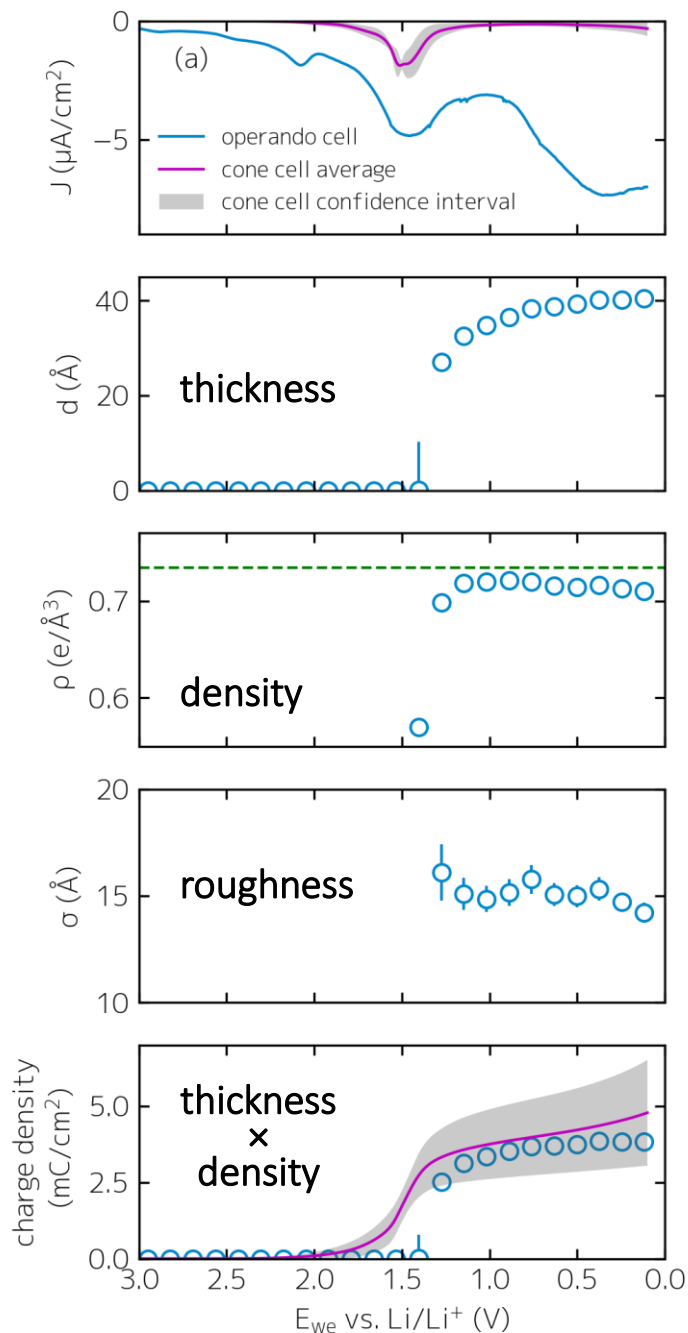
- Single feature at 1.5 V – “very” sharp peak (compared to metals)
- Surface becomes passivated by corresponding charge density $\rightarrow$ SEI layer

Operando X-ray Reflectivity



Operando XRR

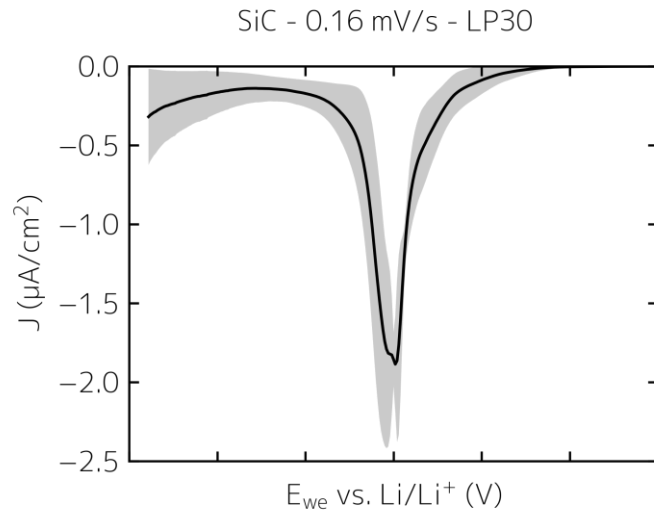
IS QUANTITATIVE: $\rho_{\text{charge}} = d \frac{zF \rho_{\text{mass}}}{m_{\text{molar}}}$



- Onset of growth at ≈ 1.5 V $\rightarrow$ matches CV
- Formation of a single layer
- SEI passivation thickness: ≈ 40 $\text{\AA}$
- SEI passivation electron density: ≈ 0.71 $\text{e}/\text{\AA}^3$
 $\rightarrow$ Matches LiF
- SEI passivation roughness: ≈ 15 $\text{\AA}$
 $\rightarrow$ Rough "gravel-on-flat-road" type film
- Electrochemical SEI charge density matches XRR SEI charge density throughout growth
 $\rightarrow$ LiF is majority component and effectively passivates the surface

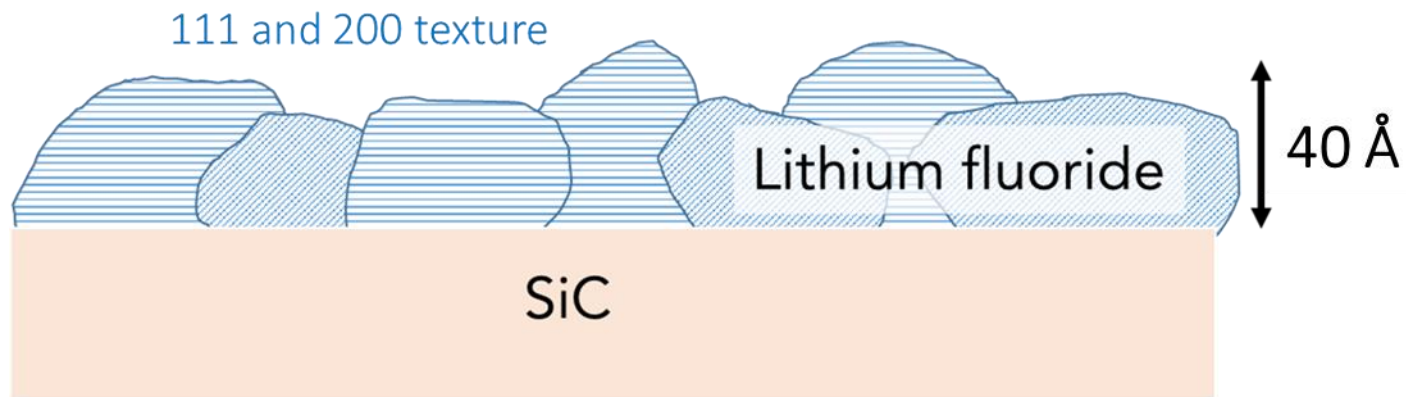
Chemistry and Structure

Results from XPS and *operando* X-ray reflectivity and (GI)WAXS



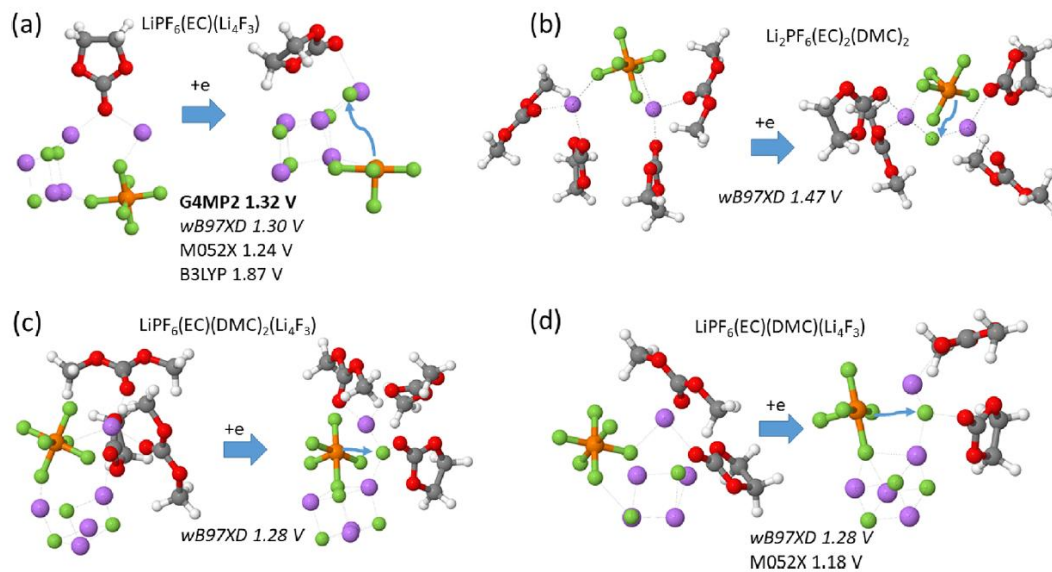
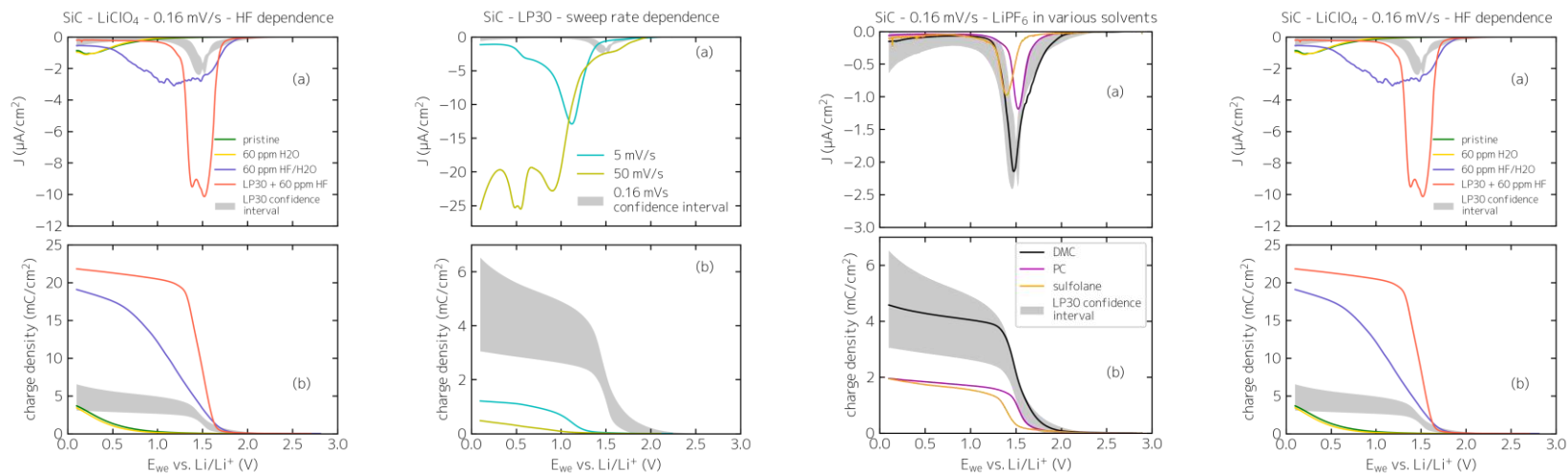
Slow cathodic scan of N-SiC in LP30:

- 40 Å SEI film
- Passivating
- Solely consists of LiF
- No organic SEI components
- Textured

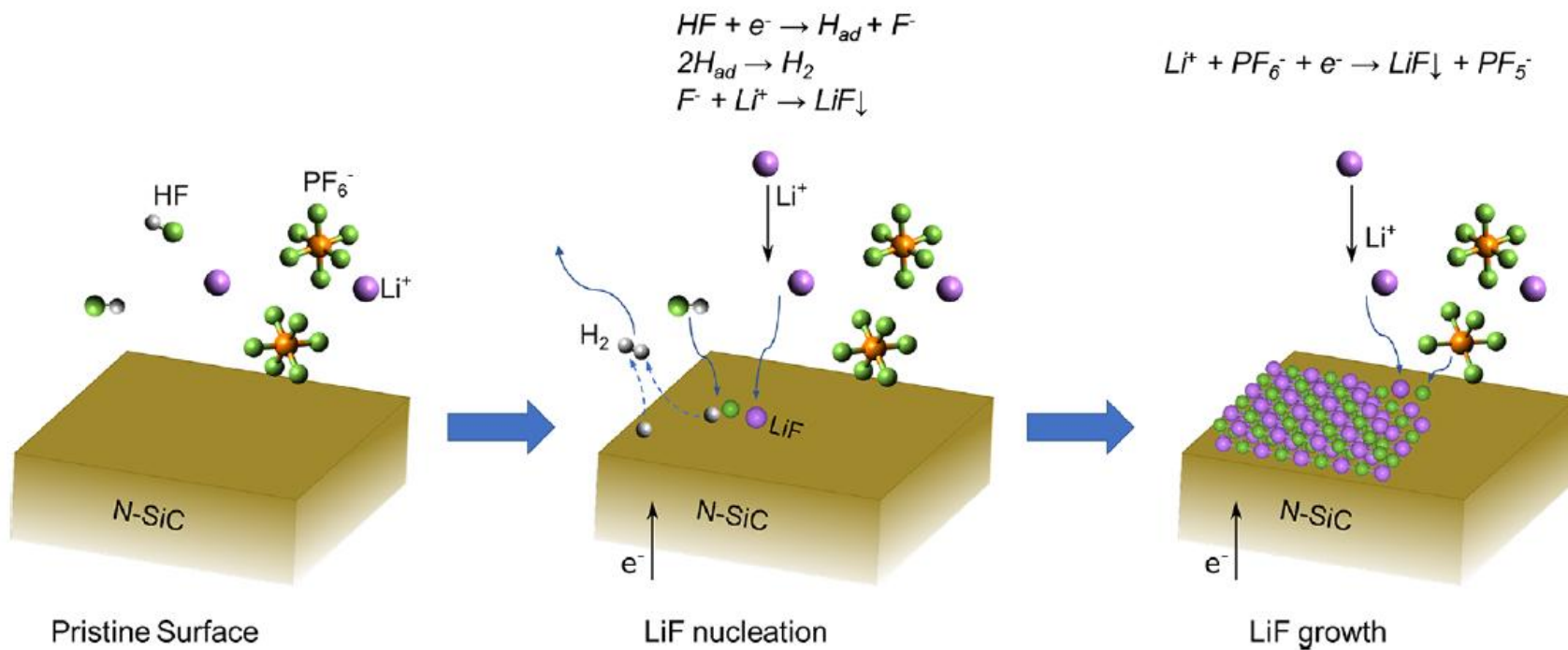


No insight into origin of LiF yet

Cyclic Voltammetry and Quantum Chemical Calculations

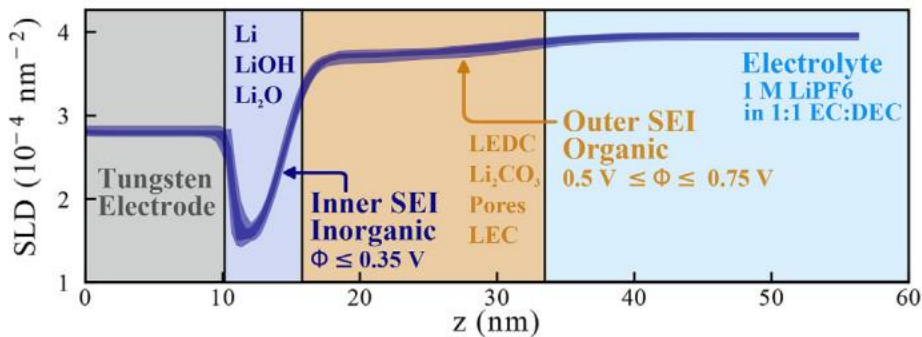
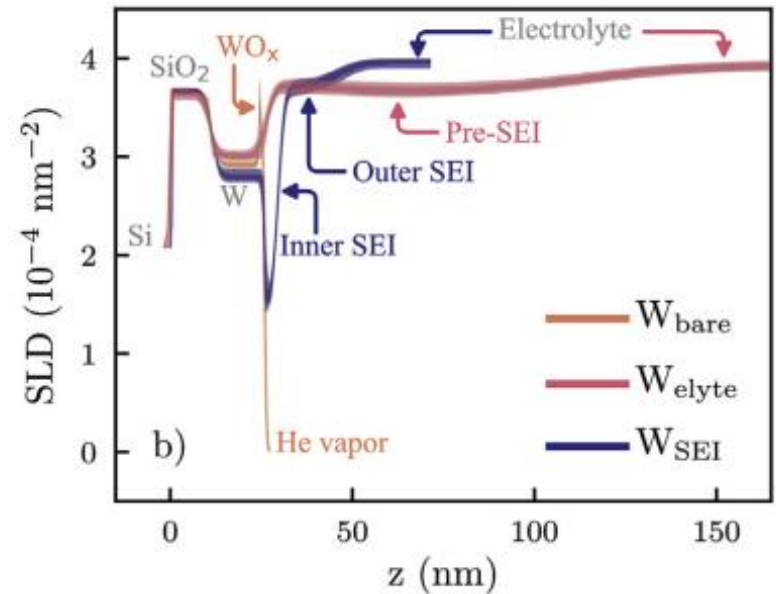
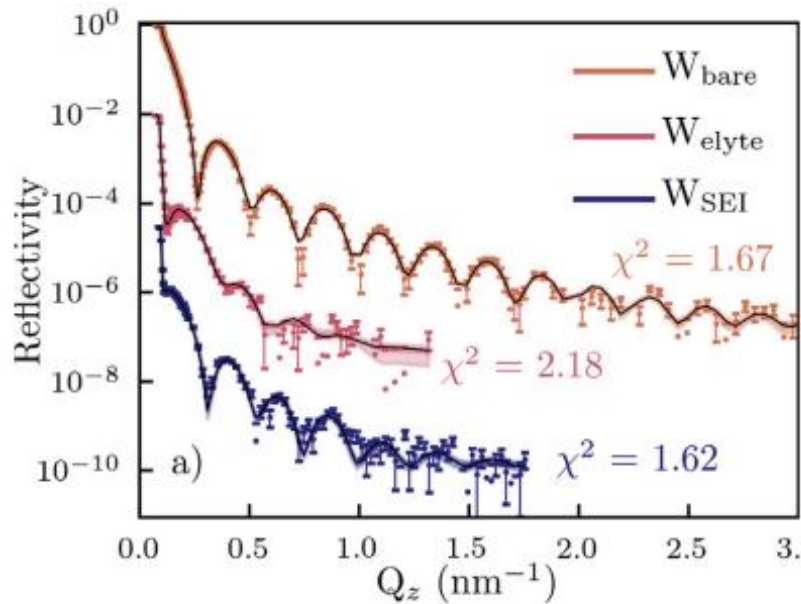


Reaction mechanisms



- LiF nucleates on the initially pristine electrode surface via **electrocatalytic HF reduction**
- Subsequently, **direct PF_6^- anion reduction** becomes significant

Neutron reflectometry



- Identification of SEI chemical composition
- Primarily inorganic, dense inner layer
- Primarily organic, porous outer layer
- Confirming proposed structures

X-ray Coulomb counting

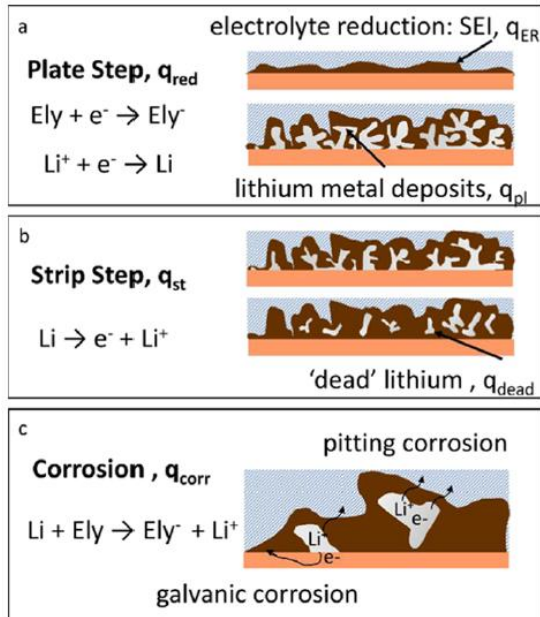
Li metal plating

Li metal batteries

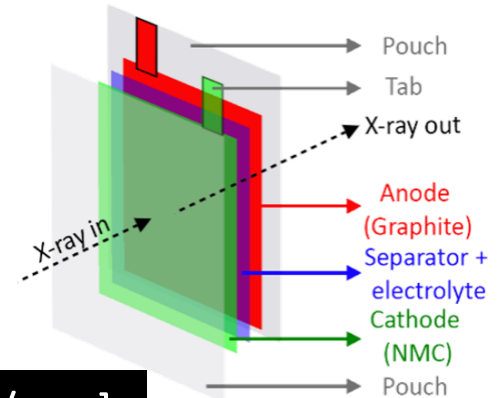
Quant. loss mechanism (GI-XRD)

Extreme fast charging

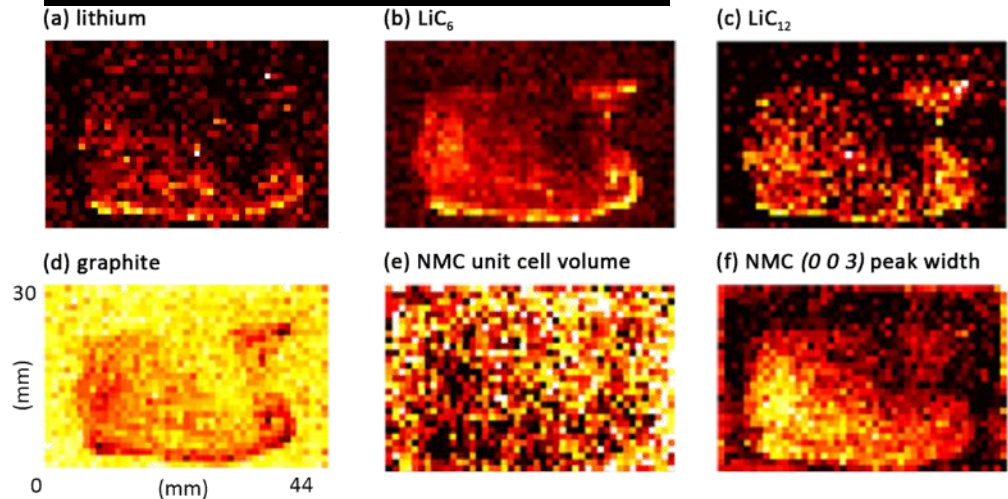
Quantifying degradation mode (HE-XRD)



Relate to growth mechanism

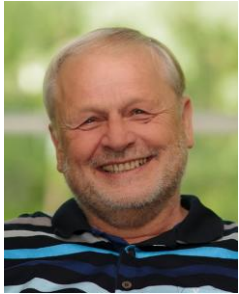


Maps in [mol/area] $\triangleq$ [C/area]



McShane et al., *J. Mater. Chem. A* 10, 23927 (2022); Paul et al., *ACS Appl. Energy Mater.* 4, 11590 (2021); *Energy Environ. Sci.* 14, 4979 (2021); *Adv. Energy Mater.* 11, 2100372 (2021); Geise et al., *Chem. Mater.* 33, 7537 (2021); Kasse et al., *J. Mater. Chem. A* 8, 16960 (2020); Tanim et al., *Cell Rep. Phys. Sci.* 1, 100114 (2020).

Acknowledgement



Andreas Magerl
FAU



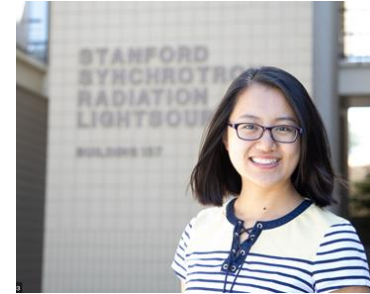
Ben Ocko
BNL



Moshe Deutsch
Bar-Ilan University



Chuntian Cao
CU Boulder



Chuntian Cao
BNL

- All group members and collaborators
- Beamline and accelerator staff

Thank you for your attention!

Q&A

Coherent X-ray scattering

Surface-sensitive X-ray scattering

X-ray Coulomb counting

