What I learned by making the worlds worst lithium battery

JOS COOPER

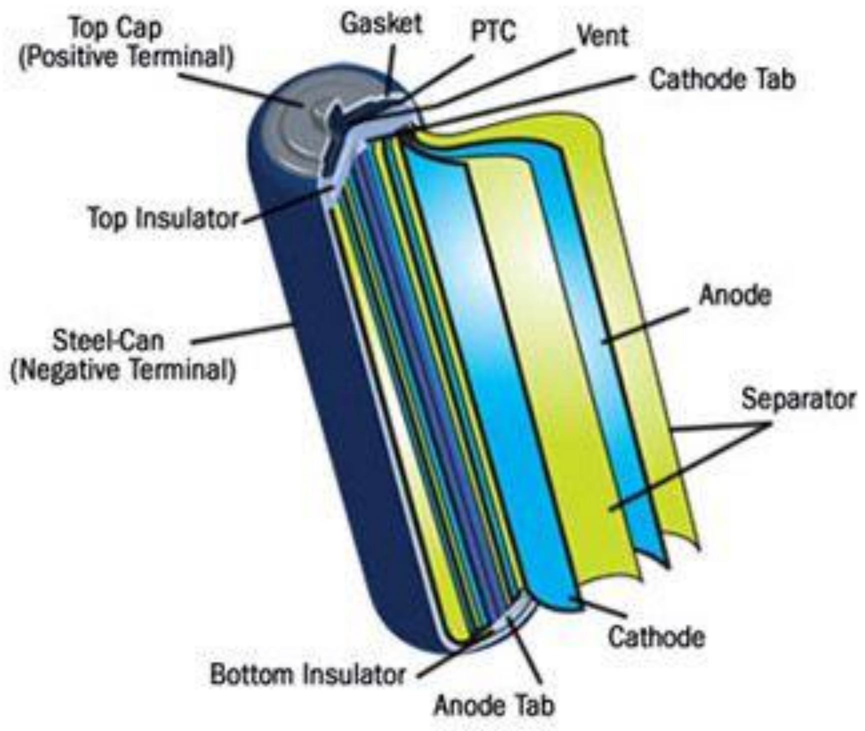
2024-10-17

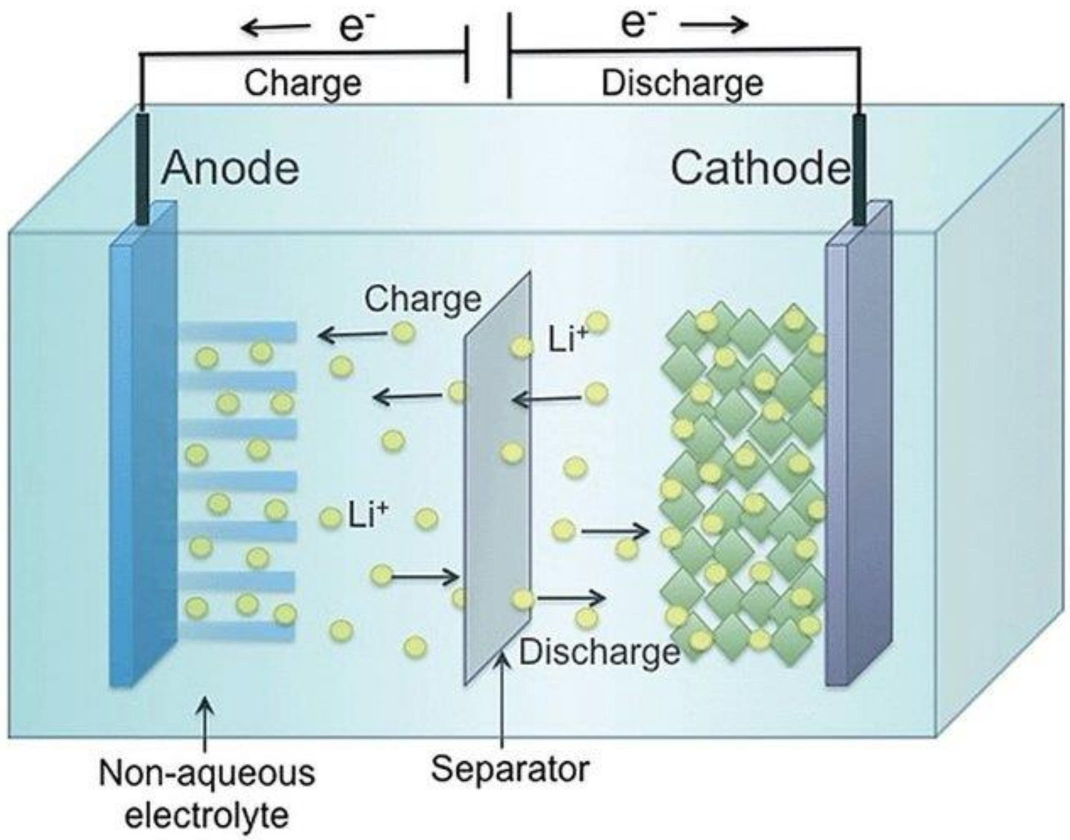
Overview

1

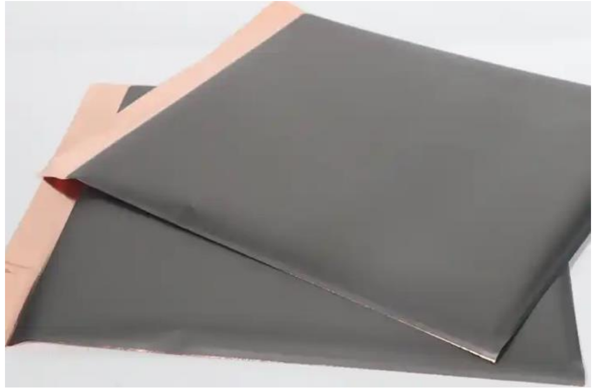
Lithium Ion Batteries

Lithium ion batteries



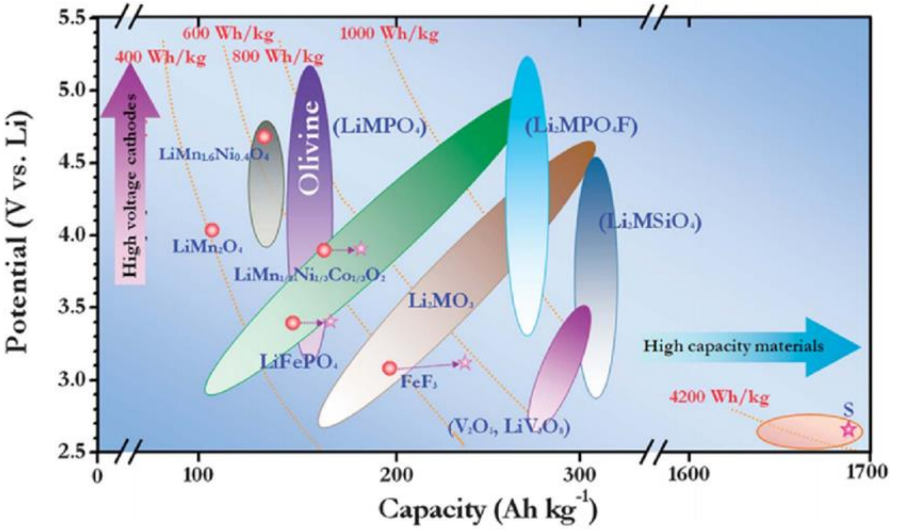


Lithium ion batteries



Anode / Cathode:

- Want the materials to be able to hold a lot of lithium
- Need them to be stable (1000's of charge cycles)
- Want them to be light (Wh/kg) and compact (Wh/cm^3)



Electrolyte:

- Stable across the voltage window
- Allow ions to flow easily

Separator:

- Allow easy ion diffusion
- Stop shorting out

also cheaper, more recyclable, faster to charge….

Lithium ion batteries

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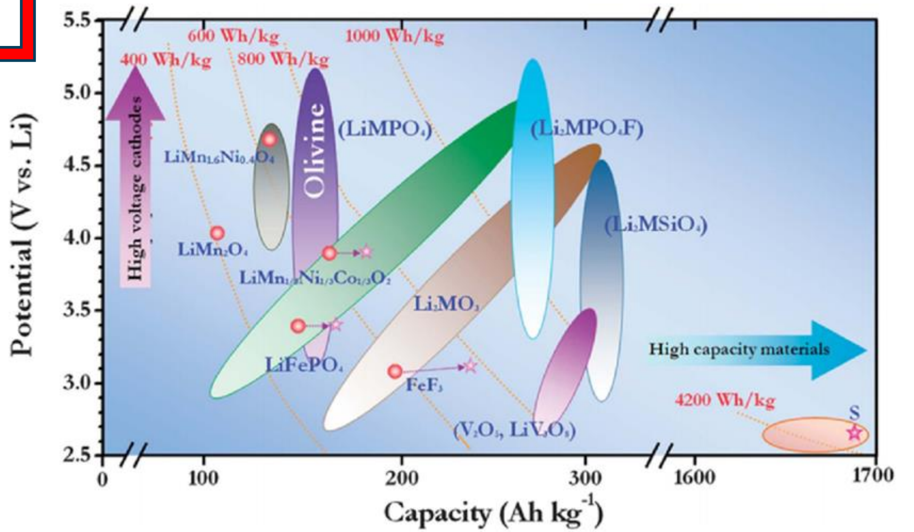

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Stability

Number of lithium batteries in the world is in billions and is growing fast

Lots of ways the batteries can fail!

- Short circuit across electrodes
  - A lot of energy stored in a battery
- Leaking electrolyte
  - Some rather unpleasant chemicals in most electrolytes

Automotive failures are highly publicised

Personal device failures are perhaps more dangerous due to proximity to body parts

https://www.mckinsey.com/industries/automotive-and-assembly/our-insights/battery-2030-resilient-sustainable-and-circular

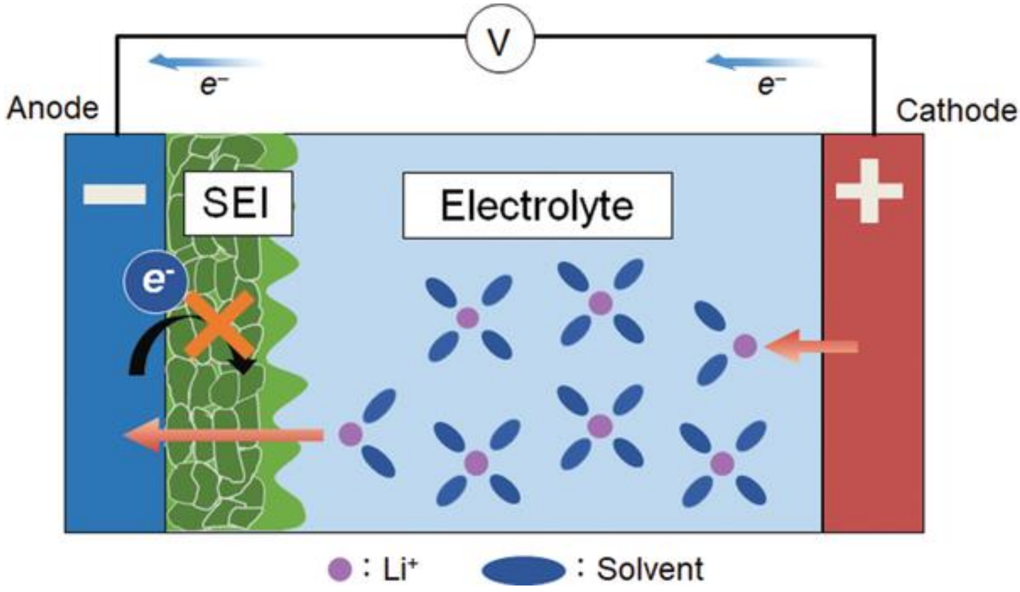
Solid electrolyte interphase

SEI

The electrolyte is actually not entirely stable across the whole voltage window, and will happily react on the anode surface when supplied below some threshold voltage

During the first charge cycle the SEI forms by breakdown of electrolyte

- Ionic conductor
- Electrical insulator
- Usually limits charge/discharge rate
- ~1-10 nm thick
- Not well understood!



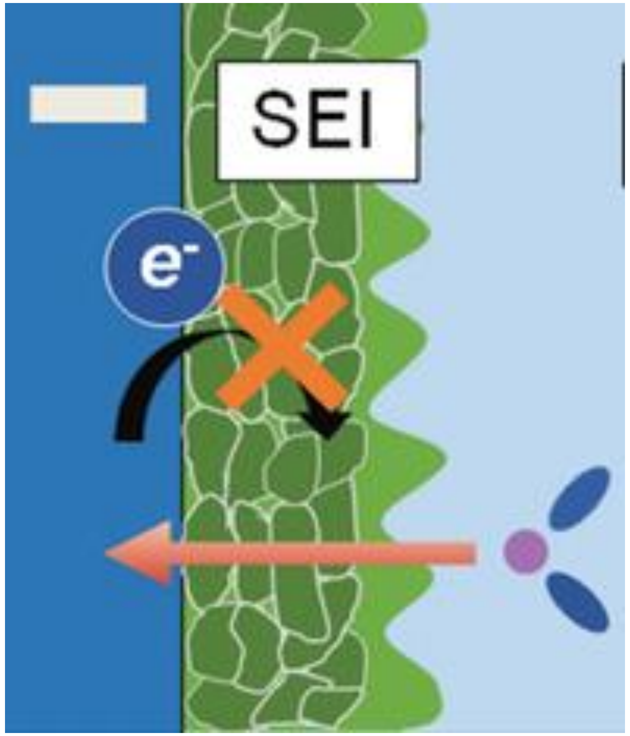
https://doi.org/10.1002/adma.202100574

Solid electrolyte interphase

SEI

Most battery companies have ”secret” first charging cycles, with different rates, voltage holds, or pauses throughout

- The key to battery longevity is a stable and well formed SEI
- Without good understanding of what it is, and why it forms, the best we have is trial and error
- Also have additives to modify the SEI
- It has to be formed by some combination of broken down electrolyte and lithium or lithium salt
- How many compounds can you really form out of:
  - C, F, Li, P, H, and O?...

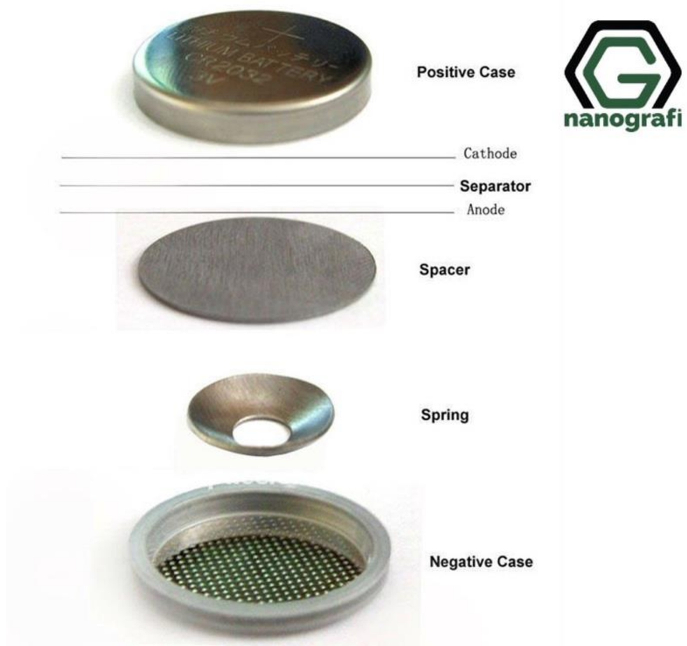


https://doi.org/10.1002/adma.202100574

Solid electrolyte interphase

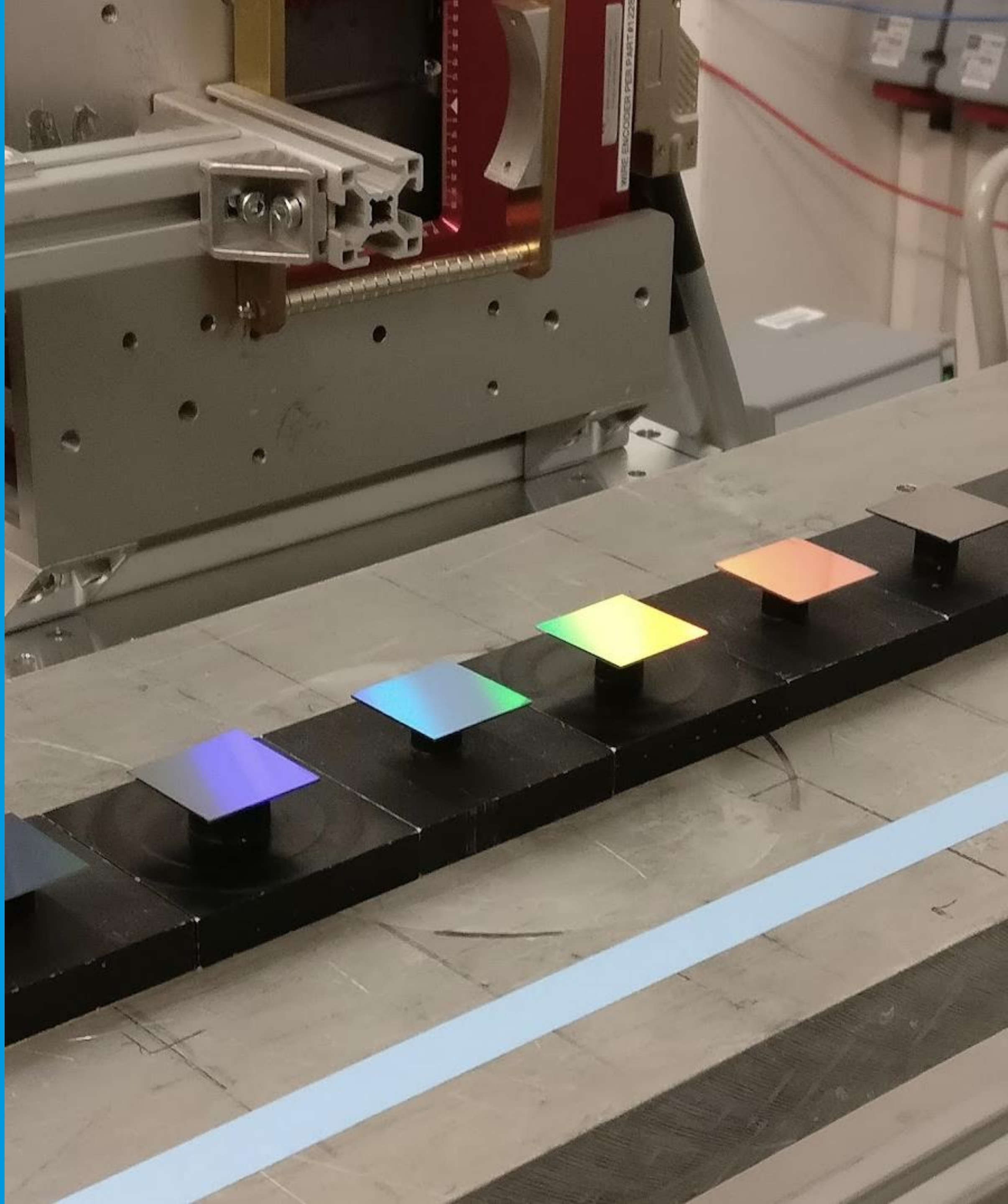
SEI

- C, F, Li, P, H, F, and O are all somewhere between “tricky” and “impossible” to probe using x-rays *in-situ*
- Opening up the cells can (probably will) change what the surface layers look like
- Cleaning off the excess electrolyte and salt from the surface could also wash off some of the SEI
- Maximum 10^{-12} g cm^{-2} of active material and ~0.1 g cm^{-2} of “background”



2

Neutron Reflectivity



Neutron reflectivity!

Sub-nanometre resolution though the film

Able to penetrate centimetres of material

Very good sensitivity to lithium!

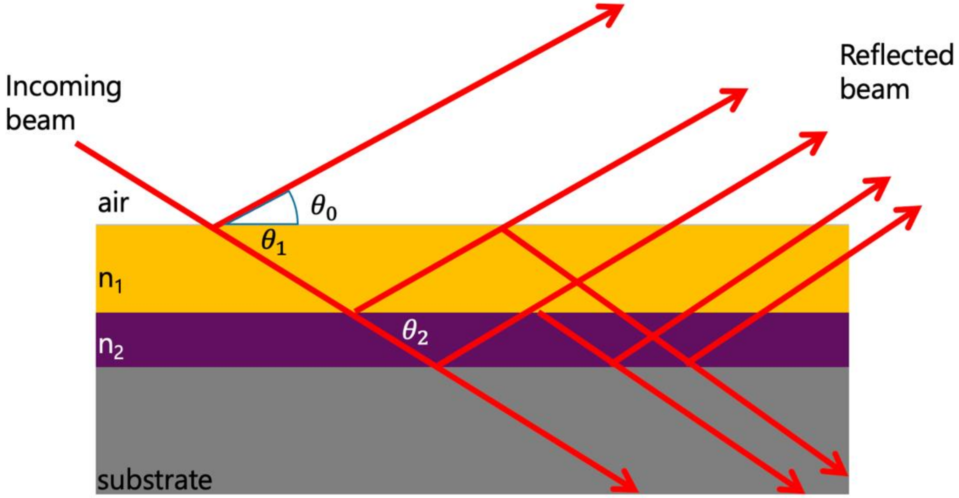
b_{Li}=-1.9

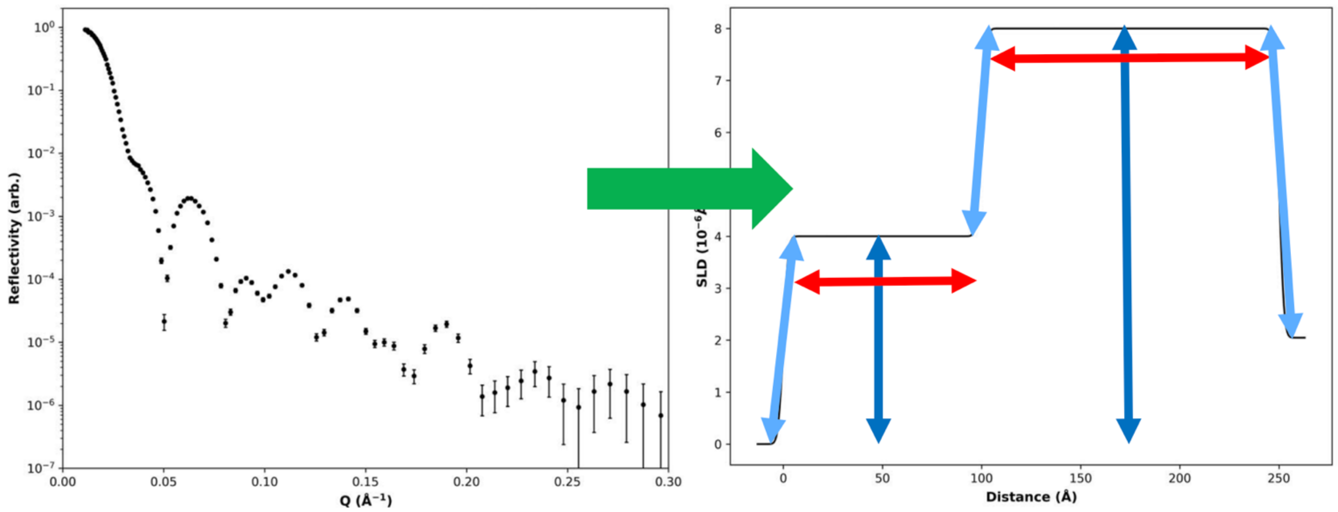
b_{C}=6.65

b_{O}=5.8

Need a large and flat electrode

Need to make a battery cell





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Worlds Worst Battery

How to make a battery?

Hard to make graphite flat and even for anode

- Don't use it!
- Just a nickel film for electrical conductivity

Too big a range of cathode materials

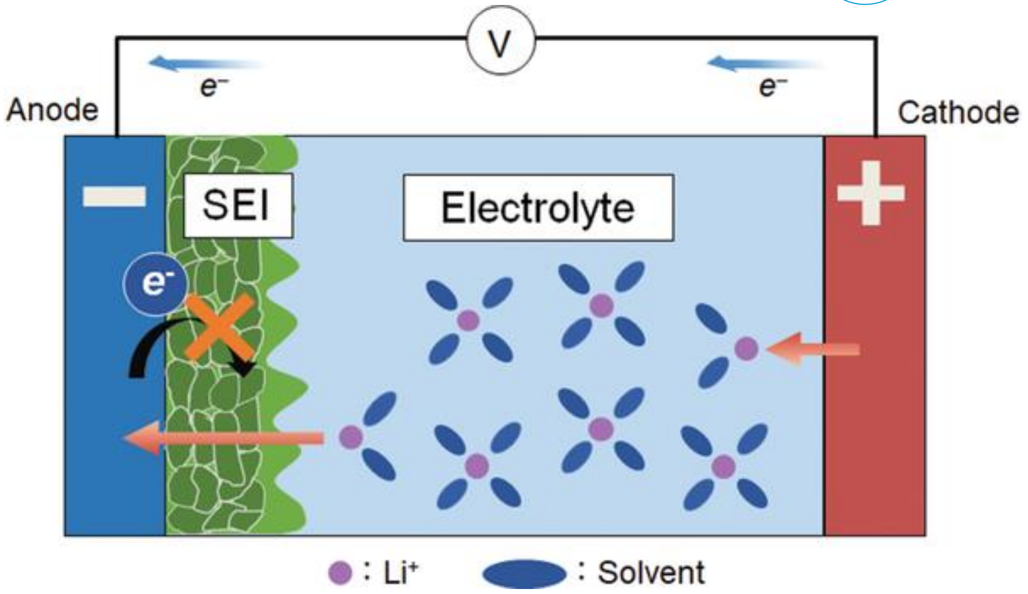
- Just use lithium

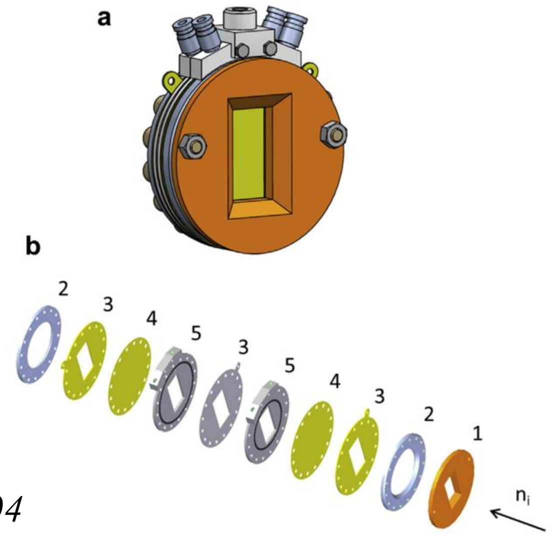
I really don't want it to explode

- Copy a design which has been shown to not explode!

EC/DMC 50/50 w. LiPF6 1M salt

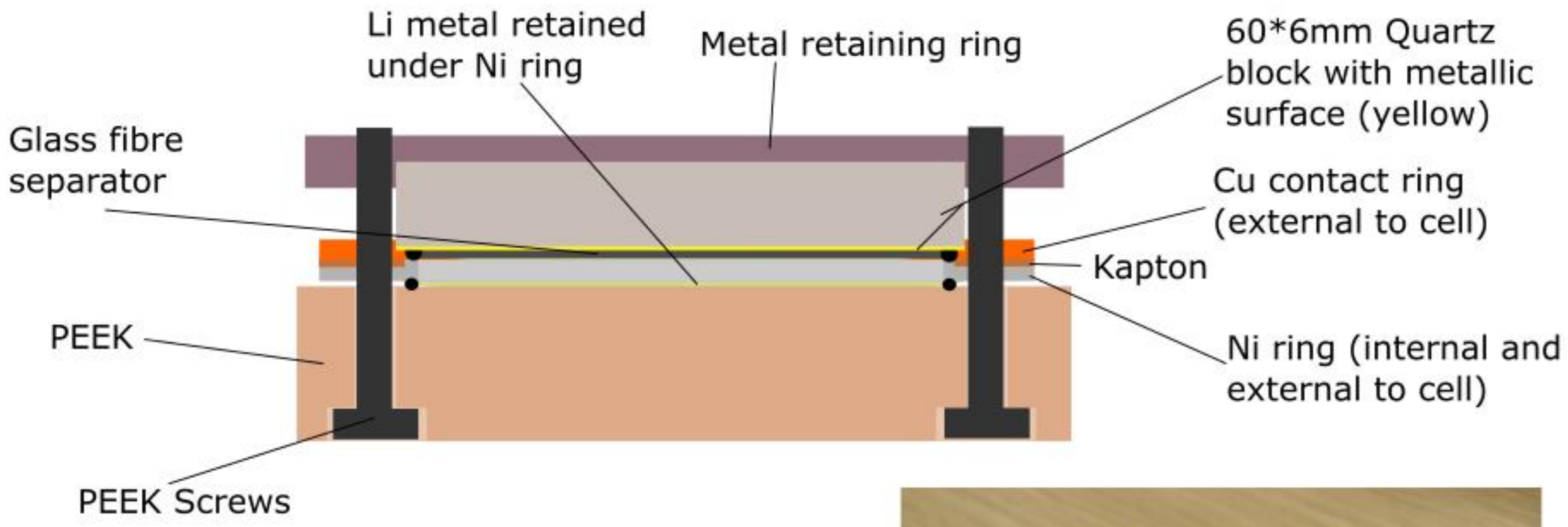
2x glass fibre separators

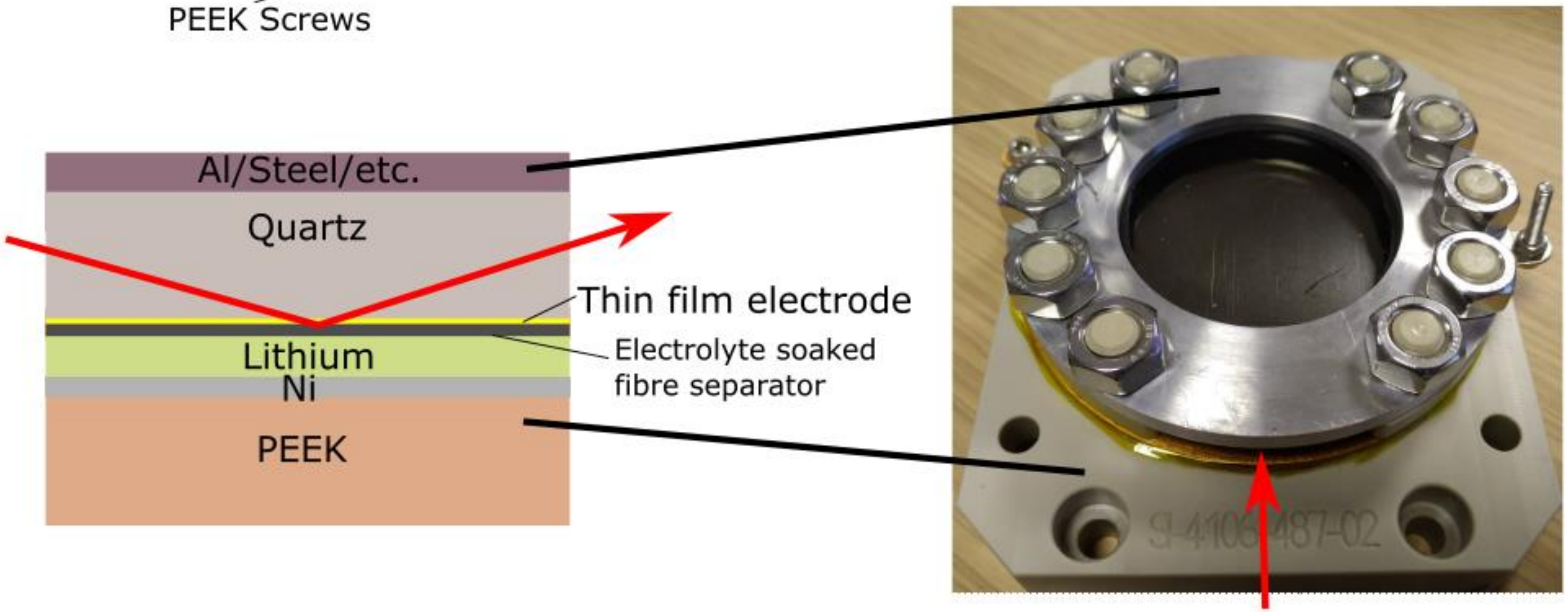




J. Pow. Source ***248*** *(2014) 900e904*

Battery cell

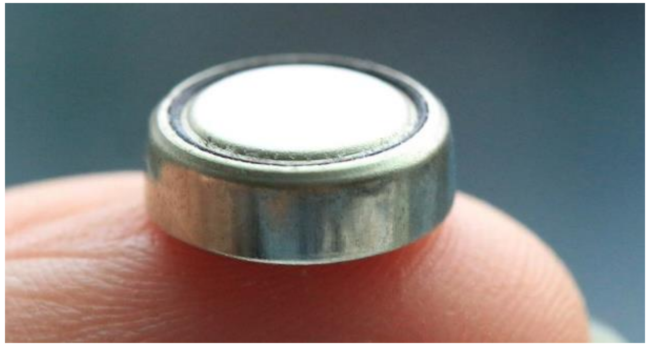




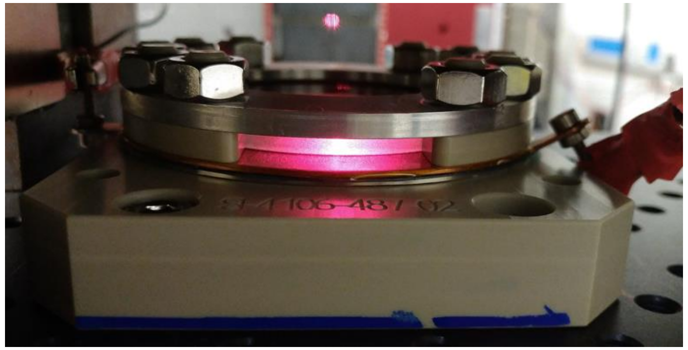
World's worst battery?

Maybe…

- High capacity anode material
- High surface area
- Minimal mass and volume of container
- Cheap



- No anode material – zero capacity!
- Flattest and smoothest possible surface
- Large PEEK plate and aluminium clamping ring with no active functions. 6mm thick quartz wafer
- Ha!



World’s worst battery?

But it **is** still a battery!

The experiment

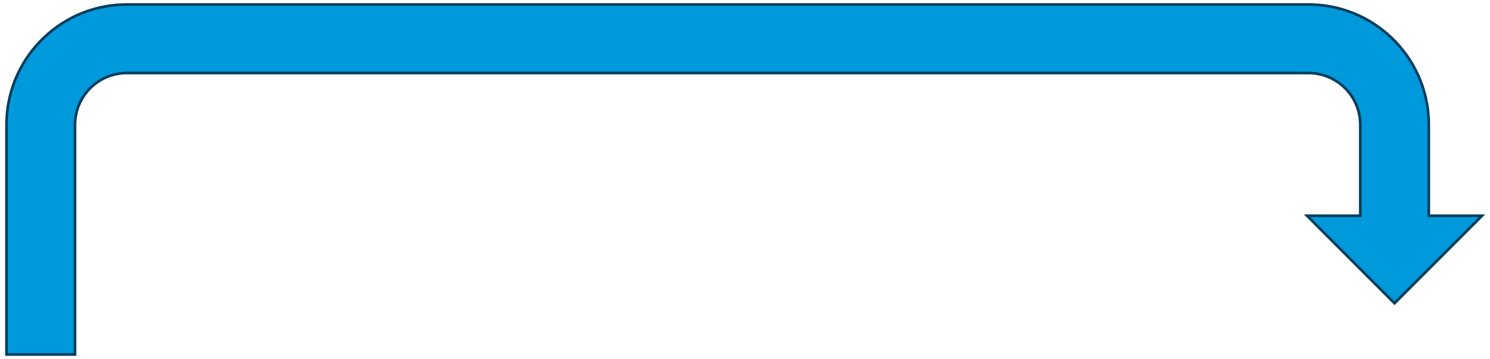
The all important first charge cycle

The experiment

The all important first charge cycle

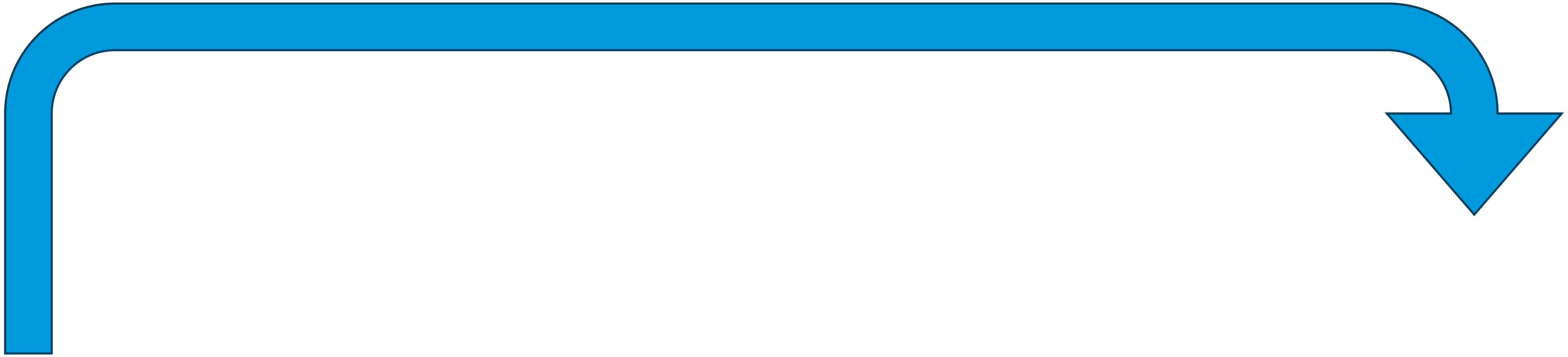
The experiment

The all important first charge cycle



The experiment

The all important first charge cycle



What is the SEI?

Element	Scattering Length (x10^{-6}Å^{-2})
C	6.64
H	-3.74
O	5.8
P	5.13
F	5.65
Li	-1.9

We can infer some chemical information

But can't pin anything down

Time for some x-rays

What is the SEI?

NEXAFS and XPS – but not *in situ*

What is the SEI?

NR + XPS for depth resolved chemistry

- We can rule out PEO's from both techniques
- No evidence for lithium oxide or hydroxide in the first layer from NR - but LiO_2 and LiOH are seen in XPS
- No pure DMC – but could be EC on the top
- Low SLD region implies a Li or H rich compound
- Can map the depth and voltage resolved chemistry
- Somewhat different to results on carbon electrodes – possible transition metal effects?
- Still open question of how opening cell affects the results

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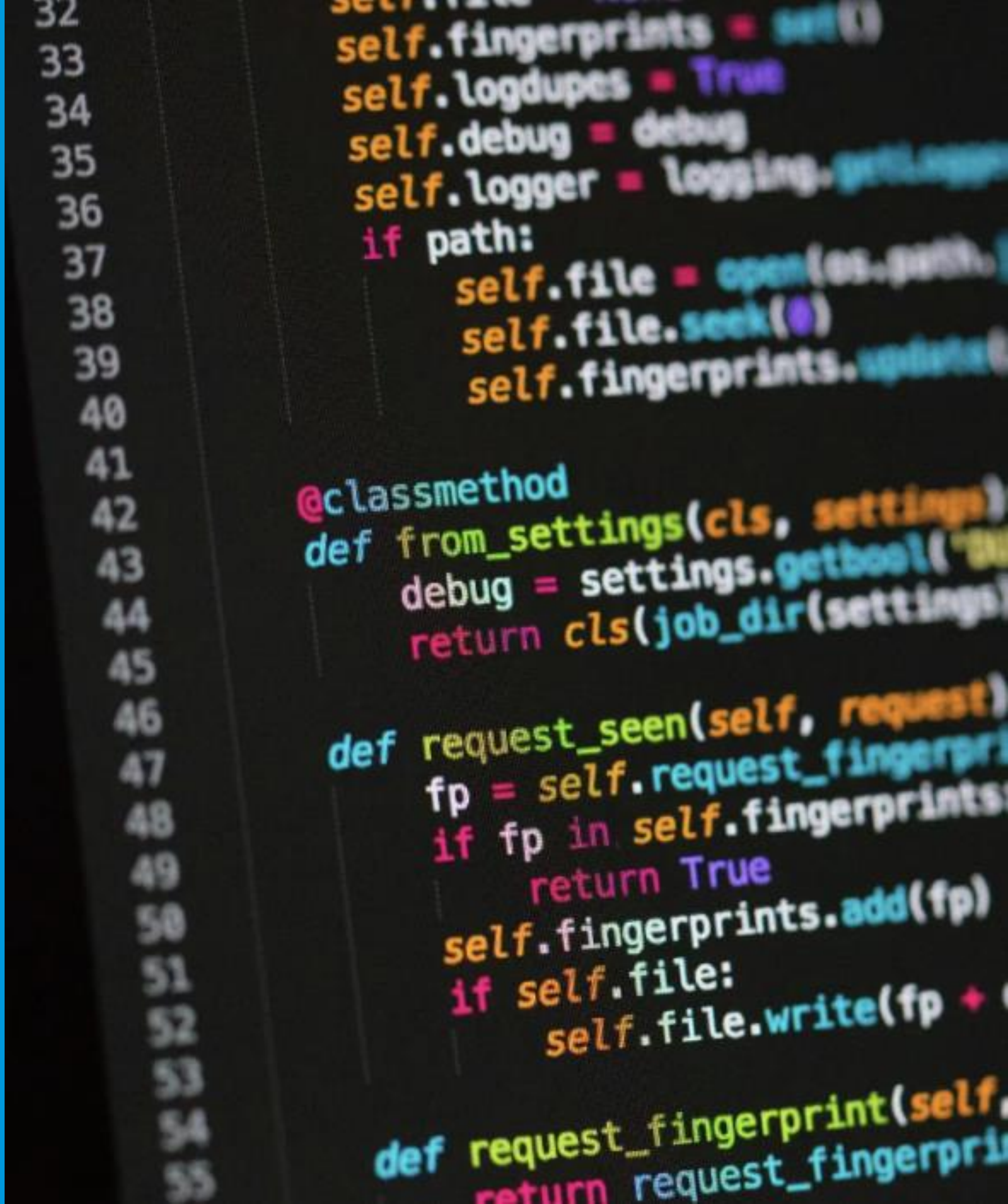
Career Change!



Instrument scientist's python code

```
os.chdir(str(folderpath))
f=FindFiles(("mccode",),(".sim",))
something=f.find_filenames(lookintosubdirs=True)
somethingalso=f.find_keyword_filenames(inputnames=something)
valuetofiledictionary={}
for filepath in somethingalso["mccode"]:
    openfile=open(filepath)
    lines=openfile.readlines()
    parameterline=lines[23] #This happend to be the line in the mccode output which gives the scanned parameter and its value. Not great that it is hard coded, but saves some reg exps...
    try:
        parameterandvalue=parameterline.split("Param:")[1].split("=") #This splits line 24 of the file twice to get the scan parameter and value, it is just for the name
        parameter=parameterandvalue[0]
        parametervalue=parameterandvalue[1].split("\n")[0] # Stupid newline character
        print("parameter="+str(parameter)+", value="+str(parametervalue))
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Research software engineering

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IOS Press

Guidelines for collaborative development of sustainable data treatment software

Joachim Wuttke [a,*], Stephen Cottrell [b], Miguel A. Gonzalez [c], Anders Kaestner [d], Anders Markvardsen [b], Thomas H. Rod [e], Piotr Rozyczko [e] and Gagik Vardanyan [c]

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[b] *ISIS Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Didcot OX11 0QX, United Kingdom*
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Abstract. Software development for data reduction and analysis at large research facilities is increasingly professionalized, and internationally coordinated. To foster software quality and sustainability, and to facilitate collaboration, representatives from software groups of European neutron and muon facilities have agreed on a set of guidelines for development practices, infrastructure, and functional and non-functional

Software developer's python code

```python
    def reflectivity(self, q: np.ndarray) -> np.ndarray:
        """Calculates the model reflectivity at given `q` points.

        Args:
            q: Q points to calculate reflectance at.

        Returns:
            numpy.ndarray: reflectivity for each Q point.

        """
        # If there are no data points, return an empty array.
        if len(q) == 0:
            return np.array([])

        return self.sample_model(q)
```

```python
def test_reflectivity(self, refnx_model):
    """
    Checks that a refnx model reflectivity generated through
    `hogben.reflectivity` is always greater than zero.
    """
    sim = SimulateReflectivity(refnx_model)
    ideal_reflectivity = sim.reflectivity(np.linspace(0.001, 0.3, 200))

    np.testing.assert_array_less(np.zeros(len(ideal_reflectivity)),
                                 ideal_reflectivity)
```

- All code comes with a test
  - Which runs automatically every time **any** code is changed
- Code is open and available for anyone to see/copy/contribute to
  - In this case `pip install hogben` to use
  - Github to view or contribute
  - Github issues to flag things which don't work or feature requests
- Clear what it does
- Clear how it does it
- Also, dark mode = pro

ISIS RSE team

Modern software development practices applied to scientific software

- Improve reproducibility in data analysis
- Reduce reliance on single author software
- Reduce wasted effort
- **Make code accessible, free and open source!**

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Optimizing experimental design in neutron reflectometry

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Using the Fisher information (FI), the design of neutron reflectometry experiments can be optimized, leading to greater confidence in parameters of interest and better use of experimental time [Durant, Wilkins, Butler & Cooper (2021). *J. Appl. Cryst.* **54**, 1100–1110]. In this work, the FI is utilized in optimizing the design of a wide range of reflectometry experiments. Two lipid bilayer systems are investigated to determine the optimal choice of measurement angles and liquid contrasts, in addition to the ratio of the total counting time that should be spent measuring each condition. The reduction in parameter uncertainties with the addition of underlayers to these systems is then quantified, using the FI, and validated through the use of experiment simulation and Bayesian sampling methods. For a `one-shot' measurement of a degrading lipid monolayer, it is shown that the common practice of measuring null-reflecting water is indeed optimal, but that the optimal measurement angle is dependent on the deuteration state of the monolayer. Finally, the framework is used to demonstrate the feasibility of measuring magnetic signals as small as 0.01 μ_B per atom in layers only 20 Å thick, given the appropriate experimental design, and that the time to reach a given level of confidence in the small magnetic moment is quantifiable.

Keywords: **neutron reflectivity**; **neutron reflectometry**; **experimental design**; **Fisher information**; **information theory**.

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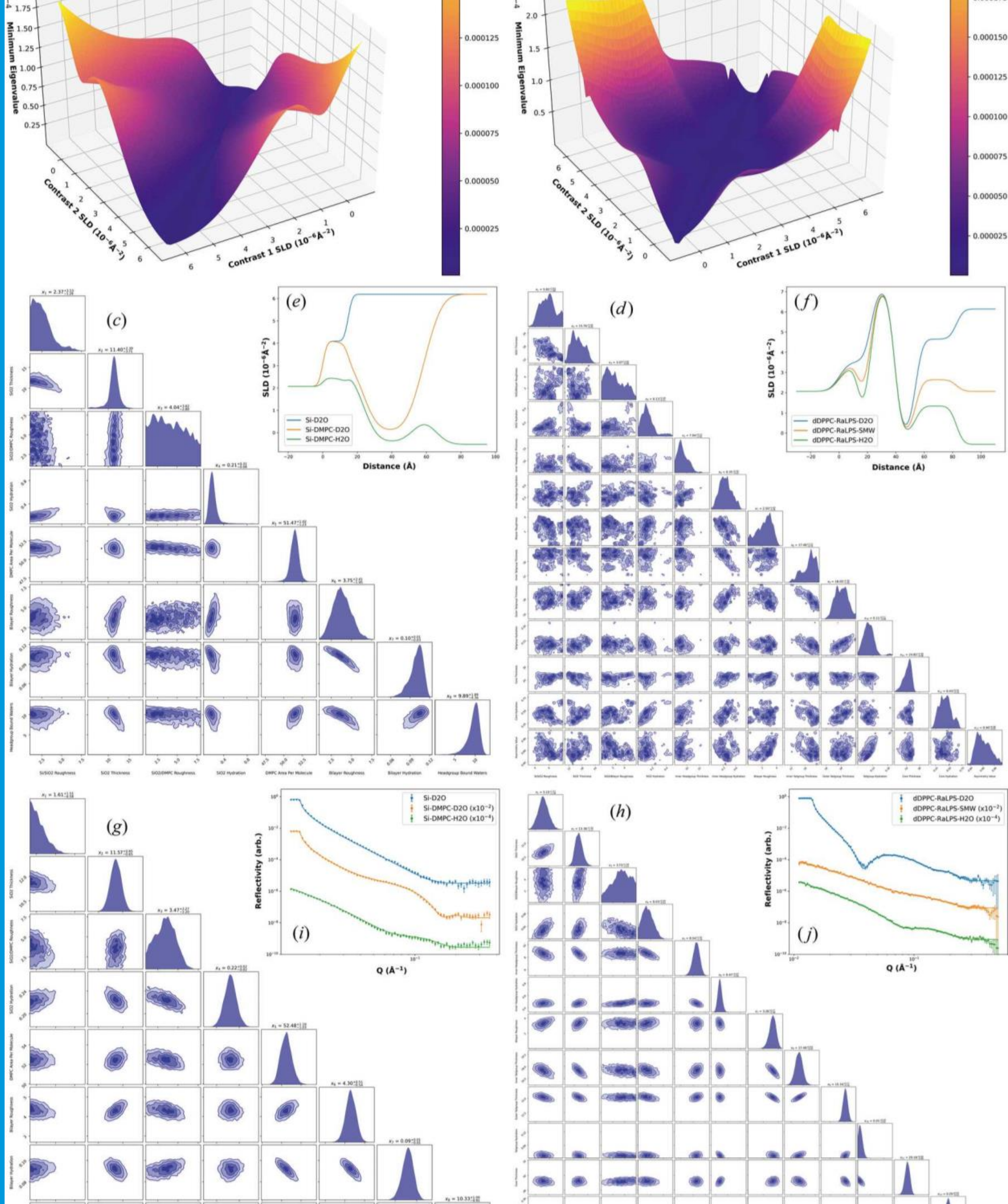
HOGBEN



Minimum Eigenvalue
Contrast 2 SLD (10⁻⁶Å⁻²)
Contrast 1 SLD (10⁻⁶Å⁻²)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
SLD (10⁻⁶Å⁻²)
Distance (Å)
Si-D2O
Si-DMPC-D2O
Si-DMPC-H2O
dDPPC-RaLPS-D2O
dDPPC-RaLPS-SMW
dDPPC-RaLPS-H2O
Si-DMPC-D2O (x10⁻²)
Si-DMPC-H2O (x10⁻⁴)
dDPPC-RaLPS-SMW (x10⁻²)
dDPPC-RaLPS-H2O (x10⁻⁴)
Reflectivity (arb.)
Q (Å⁻¹)

HOGBEN

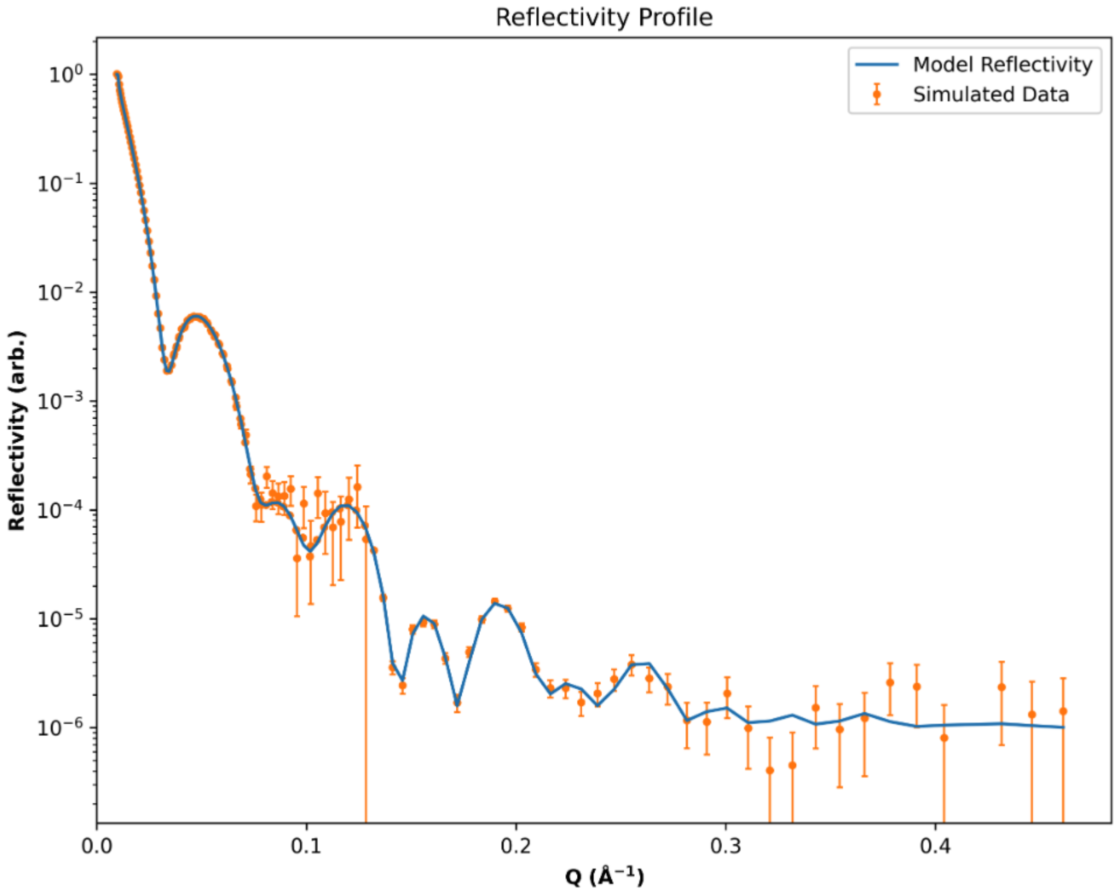
Using the Fisher information to quantify how much information a dataset contains about the model parameters of interest

- Sensitivity analysis to each parameter at each point
- Scaled by number of neutron counts
  - More counts is less uncertainty is more information

Can optimize how to run a sample on a beamline

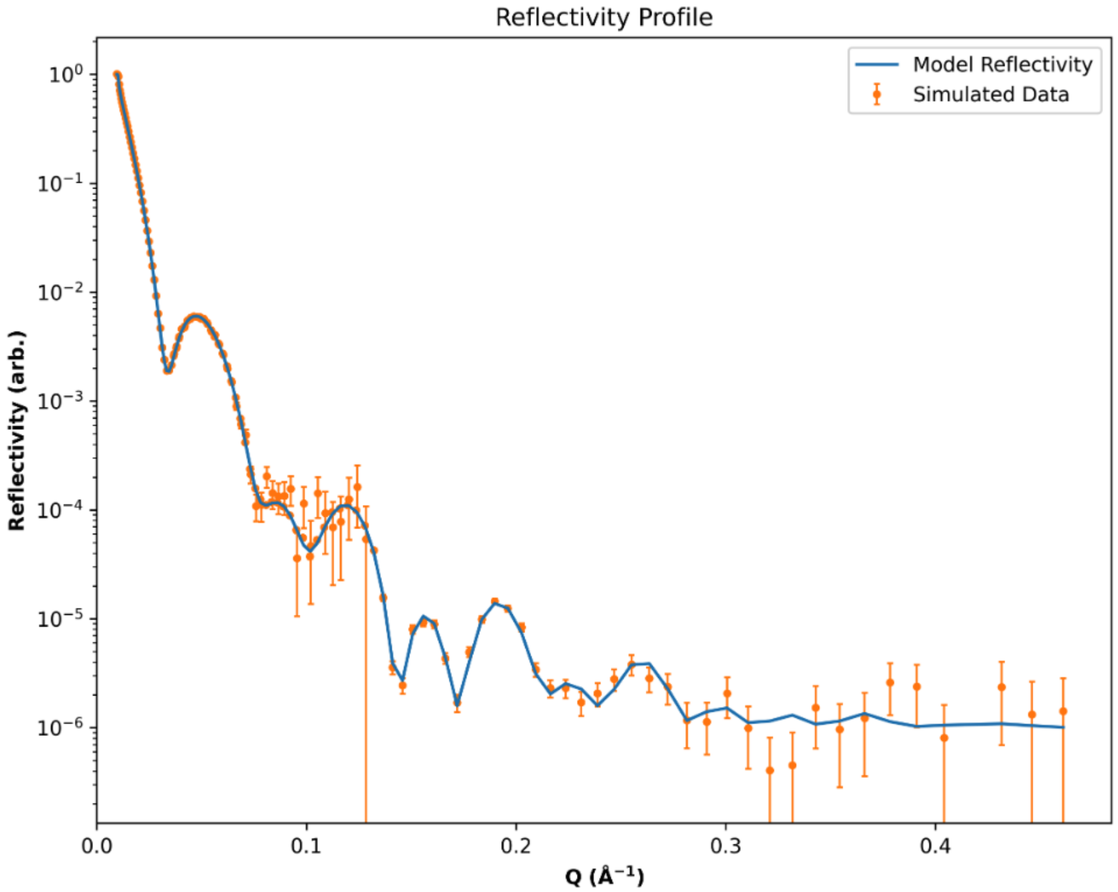
- Humans are not wired to judge sqrt(counts) error bars on a log scale transformed through an optical matrix formalism…

HOGBEN

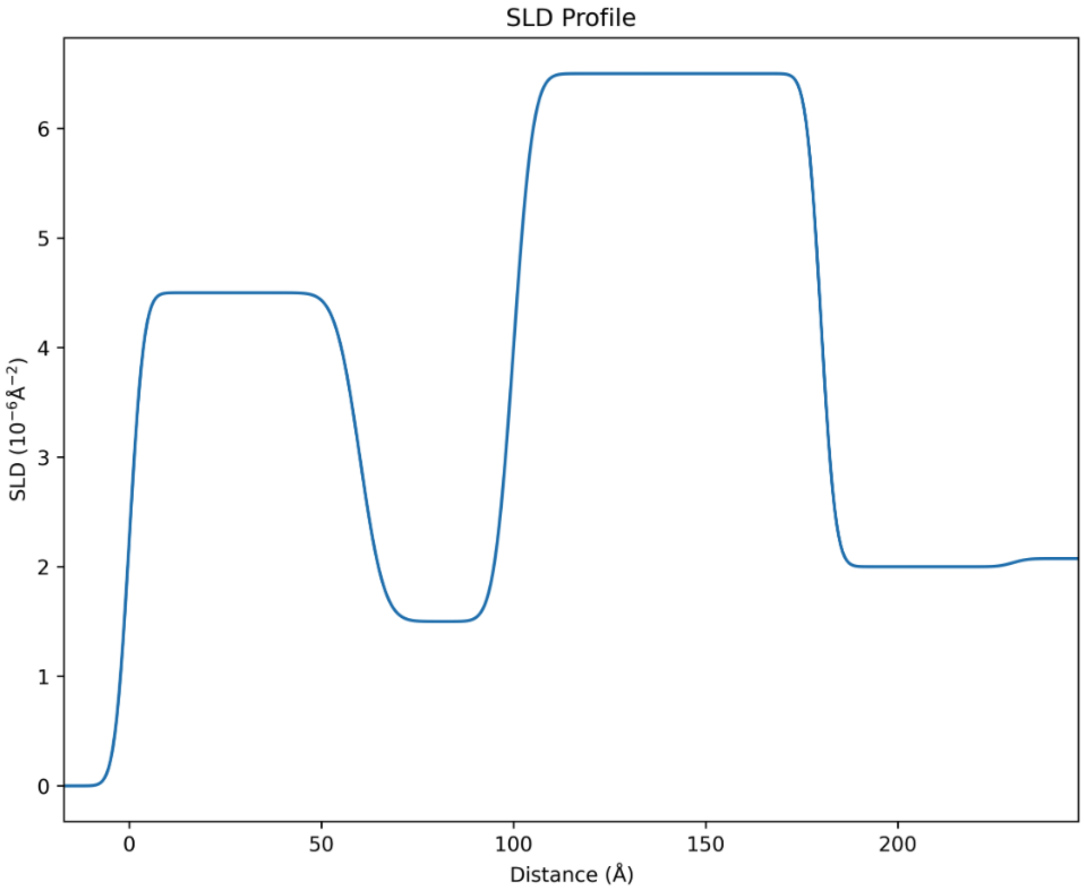


Reflectivity Profile
Model Reflectivity
Simulated Data
Reflectivity (arb.)
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
0.0
0.1
0.2
0.3
0.4
Q (Å^{-1})

HOGBEN

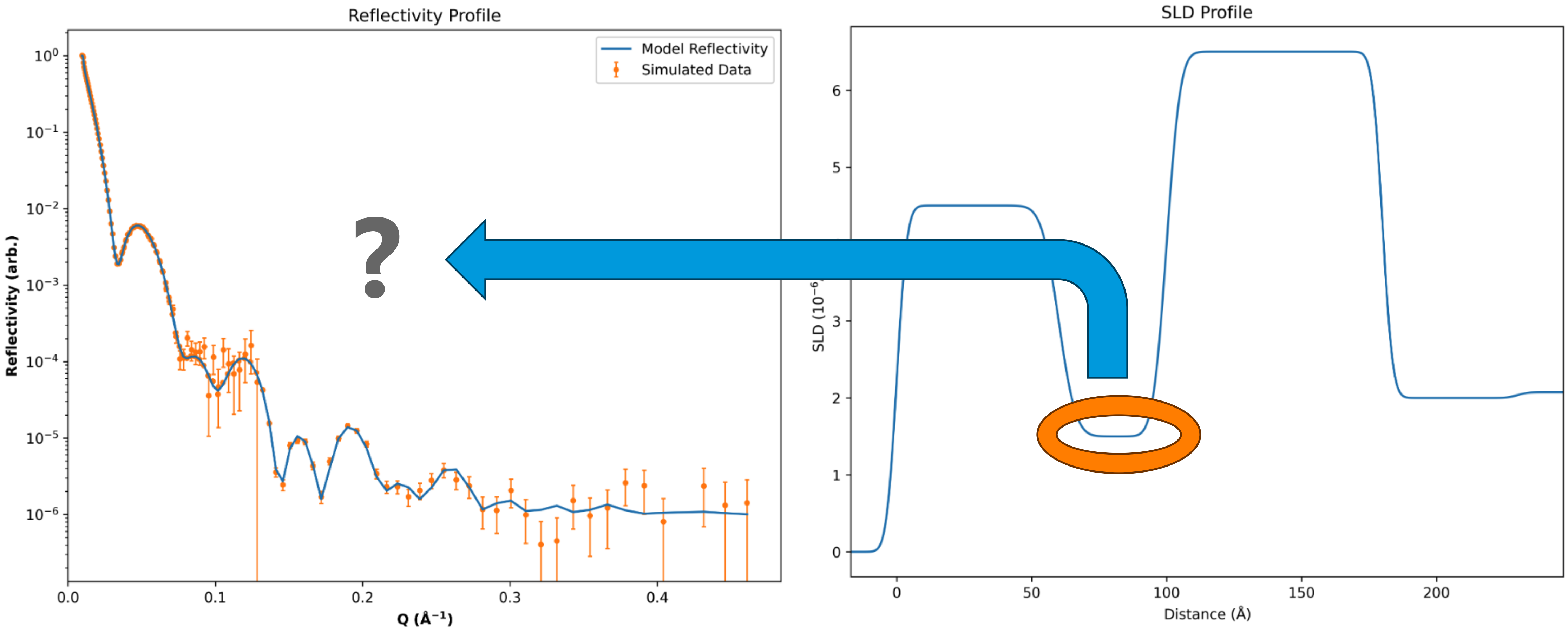


Reflectivity Profile
Model Reflectivity
Simulated Data
Reflectivity (arb.)
Q (Å⁻¹)



SLD Profile
SLD (10⁻⁶Å⁻²)
Distance (Å)

HOGBEN



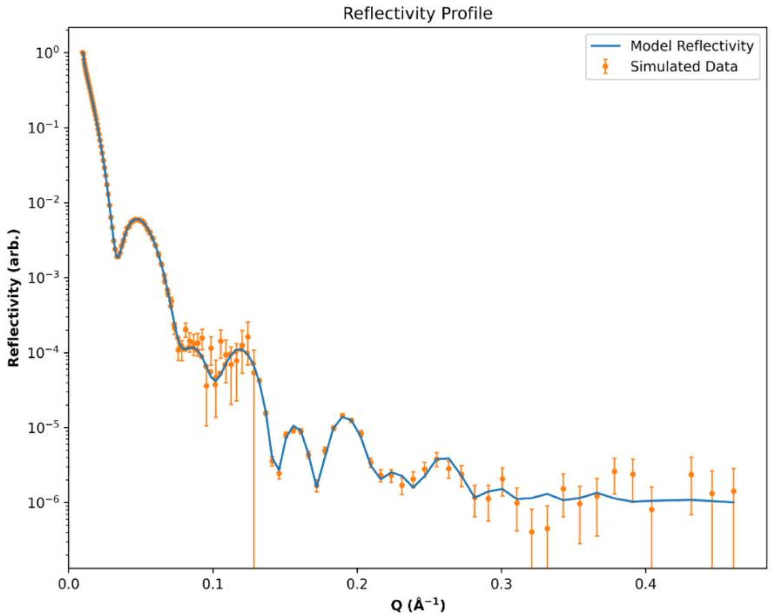
Reflectivity Profile
Model Reflectivity
Simulated Data
Reflectivity (arb.)
Q (Å⁻¹)
?
SLD Profile
SLD (10⁻⁶
Distance (Å)

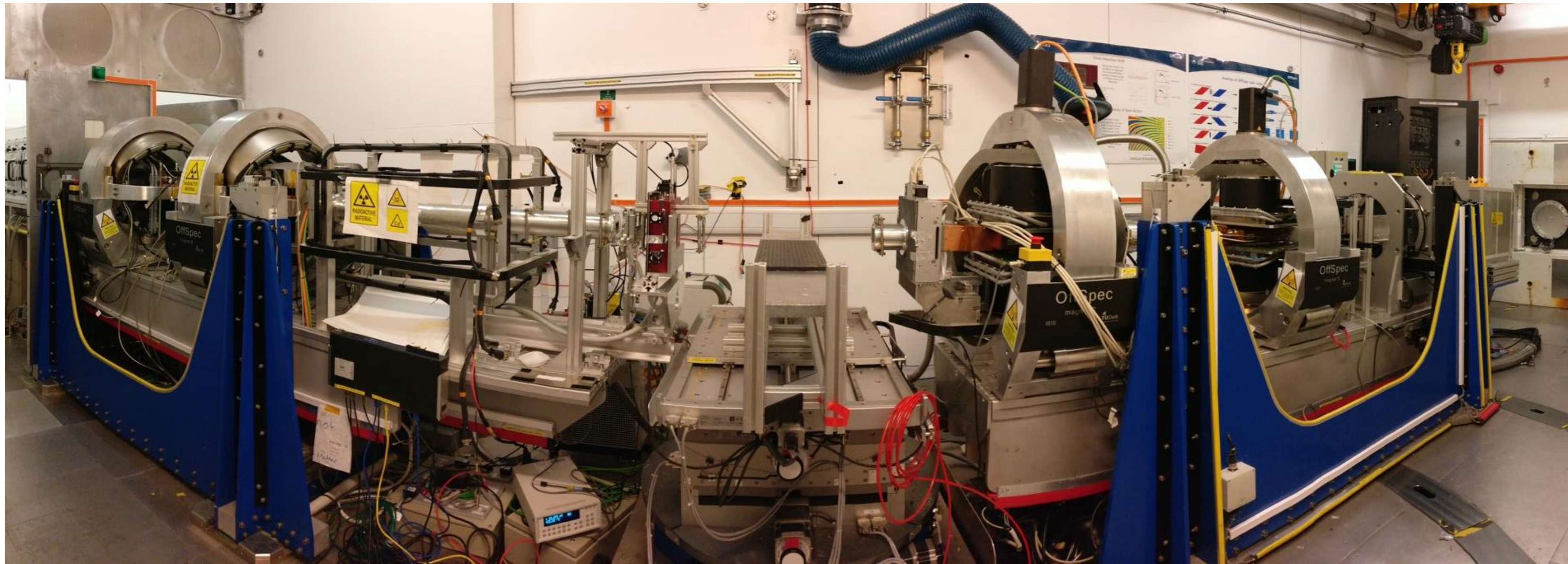
HOGBEN

"Measurements" from a dataset taken at 0.6 and 2.3 degrees for 0.5 and 1 hour respectively on OFFSPEC give an information metric* about the sample structure of **0.00307**

If we had measured instead at 0.4 and 2.3 degrees for 0.25 and 1.25 hours, then we would have **0.00488**

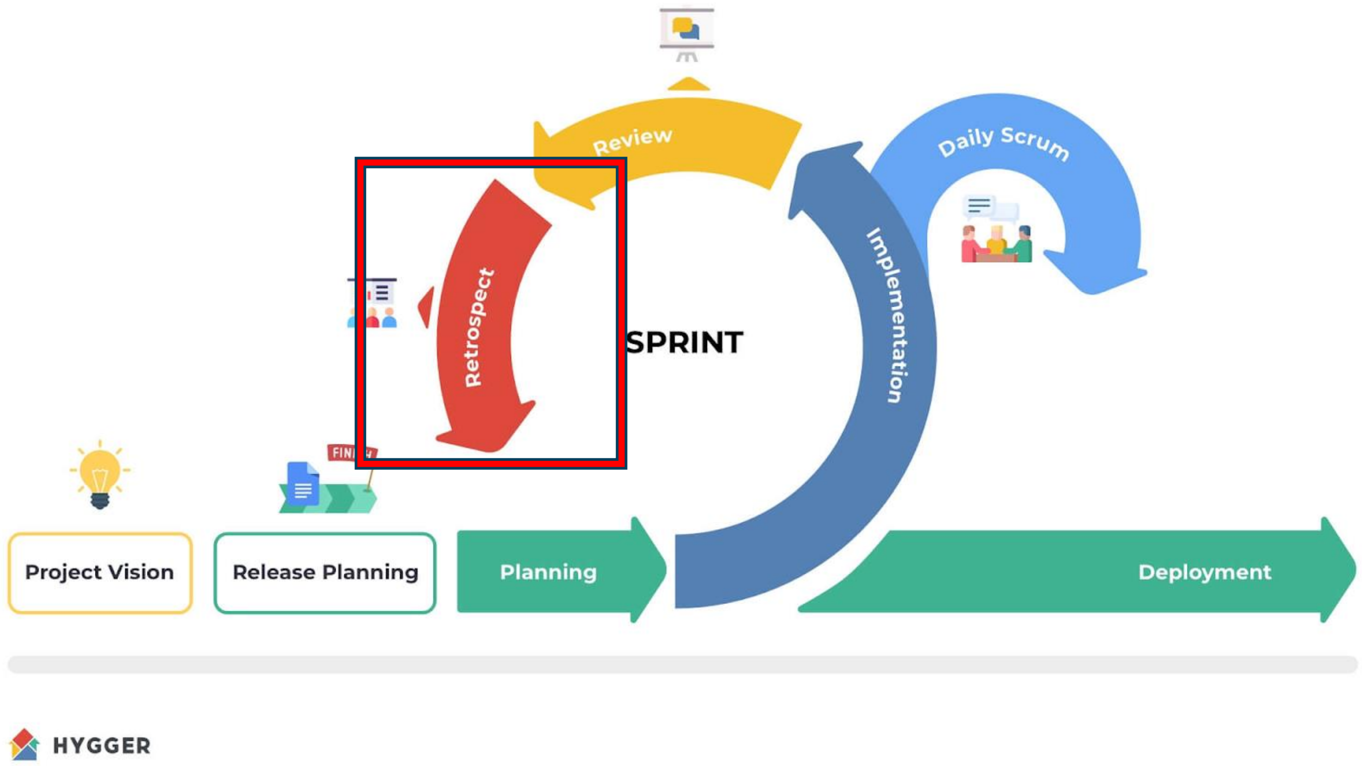
This is directly related to parameter variance ➔ 50% improvement in our (co)variances for the same time budget





Retrospectives

Retrospectives



Retrospectives

A review of things which have already been completed (both successful and unsuccessful) at the end of a work package

Actively trying to learn from previous experiences, so that next time we do them better

Often performed as a discussion amongst team members

HOGBEN for batteries

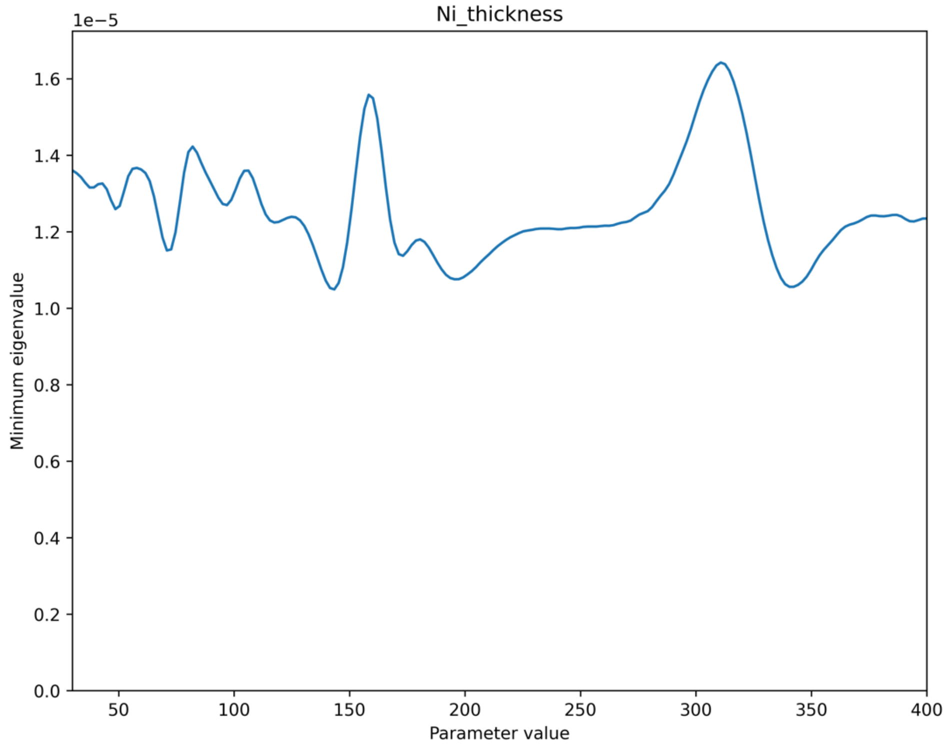
We had a Ni layer thickness of 133 Å, but there was no reason to choose this value

If we changed the layer thickness, do we get more information about the SEI layers?

YES!

Using a 311 Å thick layer gives us 40% more information

No drawbacks



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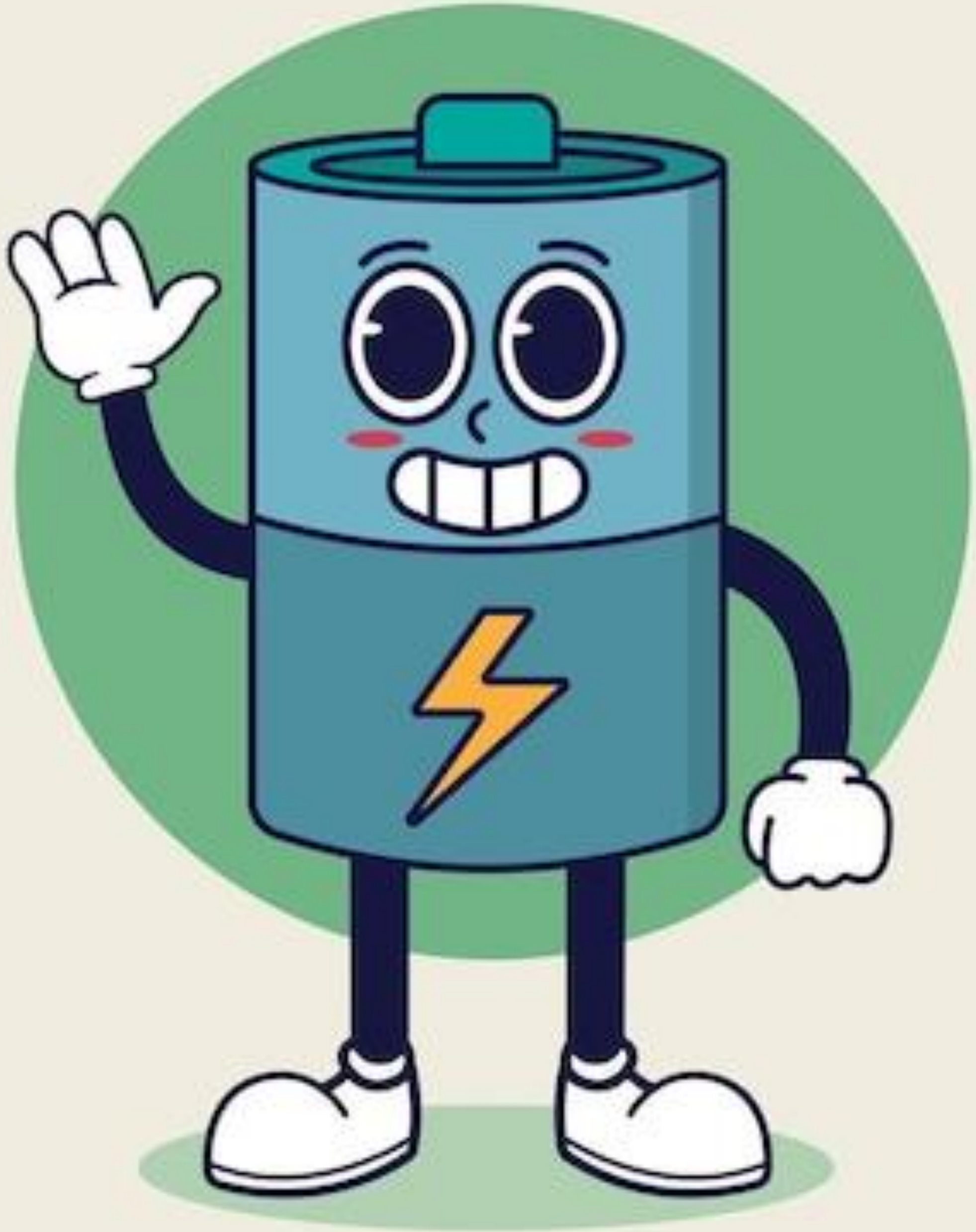
Conclusions



Conclusions

We successfully made the lowest capacity, most expensive, heaviest, and most voluminous battery ever*

We can still learn from zero capacity batteries but many open questions

- Does the anode material catalyse different electrolyte breakdown products?
- What to the additives do structurally?
- How does the SEI develop with more charge cycles?

Retrospectives are a useful tool – not just for software developers

Next time we can, and will get better data!

*maybe

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Andrew McCluskey

University of Oxford | Department of Materials

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Rob Weatherup

Sjoerd Stendahl
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