Time-resolved neutron reflectometry study of lithium-mediated nitrogen reduction

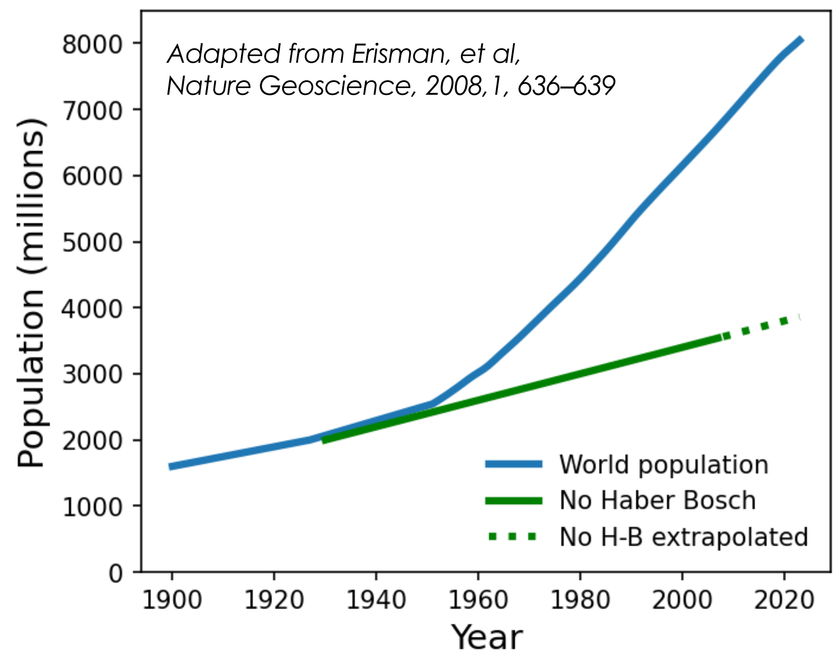
Studying transient phenomena with NR

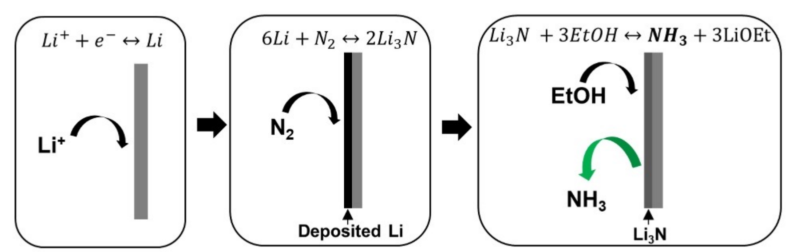
Mathieu Doucet

Oak Ridge National Laboratory

Green ammonia production

- The Haber-Bosch production process requires high temperatures (~400° C) and high pressure (>200 bar), and is responsible for >2% of global CO_2 emissions.
- ~185 Mton/year of ammonia produced in recent years.
- Electrochemical nitrogen reduction reaction (NRR) would allow a more environmentally friendly production of ammonia, including the possibility of point-of-use production.
- The complex mechanism at the electrode-electrolyte interface remains to be fully understood.



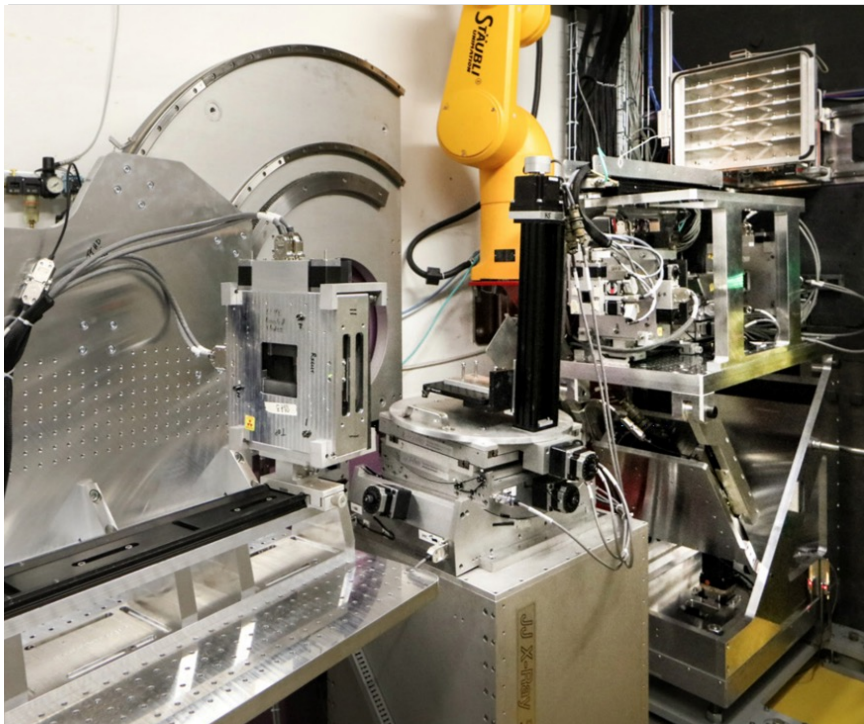


Blair et al, ACS Energy Lett., 2022, 7, 6, 1939–1946

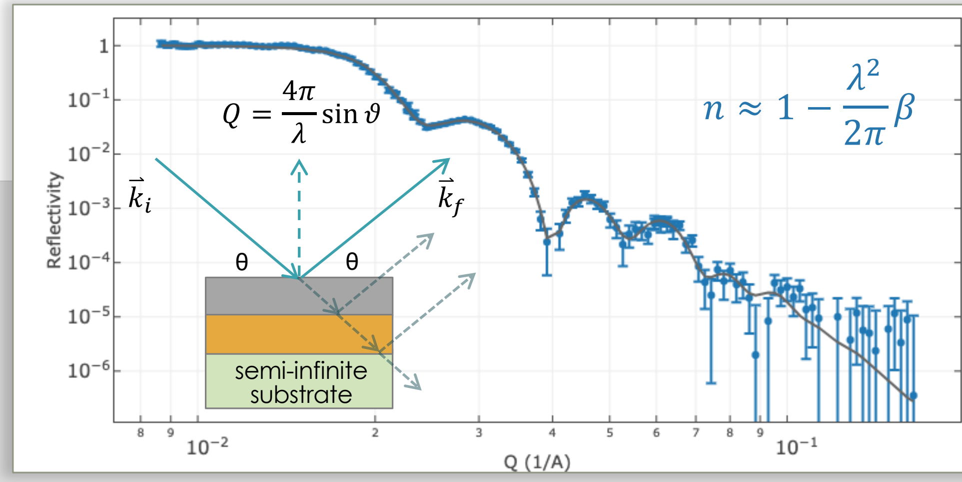
OAK RIDGE National Laboratory

Oak Ridge National Laboratory

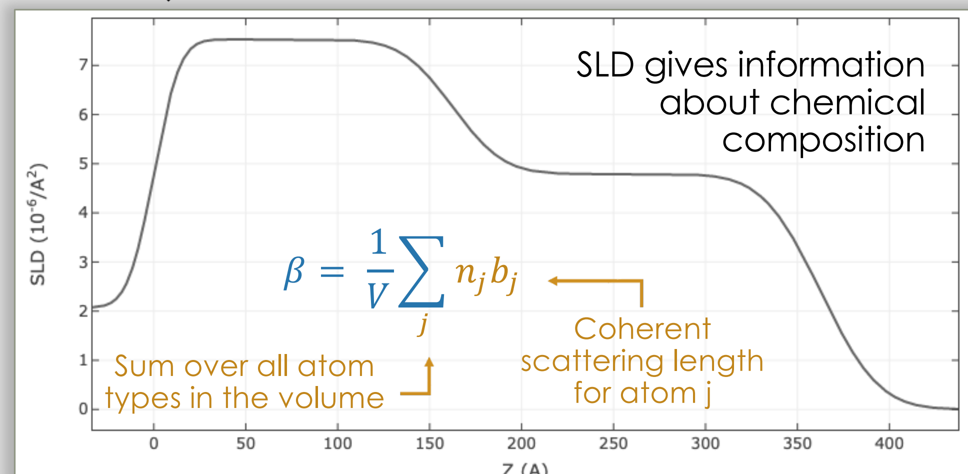
Liquids Reflectometer at SNS



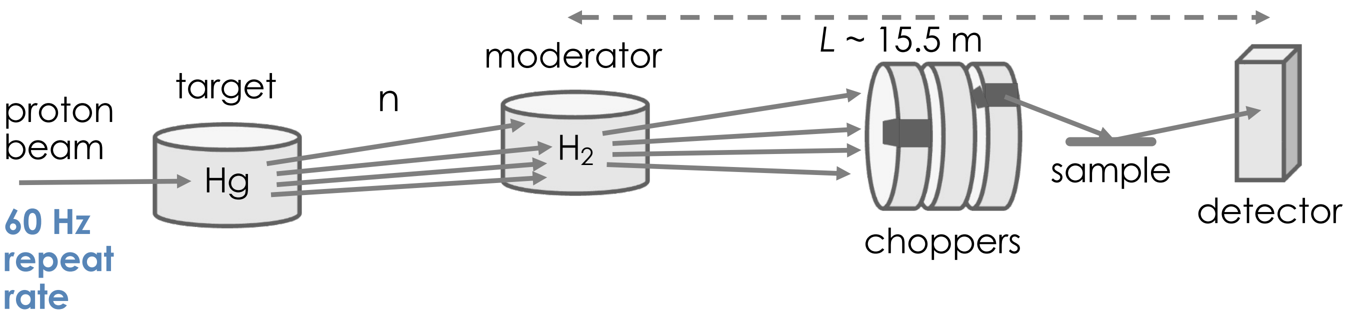
Measuring the probability of a neutron beam to reflect off a thin-film surface allows us to determine the structure of the film on nm scale

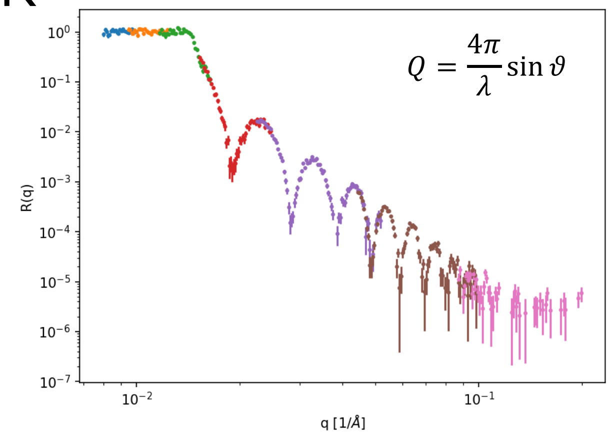


$$R(Q) = rr^* \approx \frac{16\pi^2}{Q^4} \left| \int_{-\infty}^{\infty} \frac{d\beta}{dz} e^{-izQ}\, dz \right|^2$$

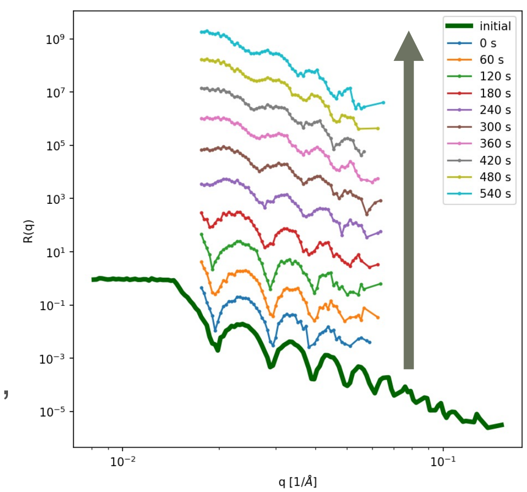


From steady-state NR to time-resolved NR





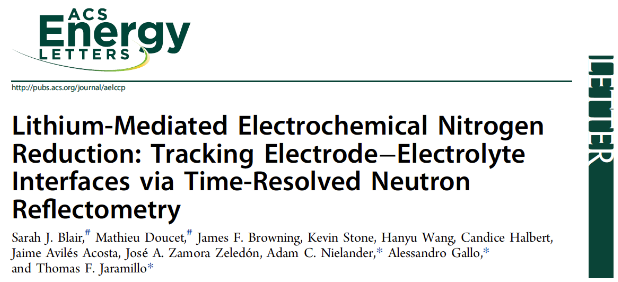
- LR is a TOF reflectometer with a neutron wavelength band ~ 3.5 Å.
- A measurement in the range of 0.008 < Q < 0.2 1/Å is typically made in 7 measurements over 45 minutes.
- For time-resolved measurements, we select the appropriate scattering angle and wavelength band center for our system and measure each neutron event while the system is in transition.
- Events are then binned in time intervals during post-processing to optimize the measurement.
- A wider Q range can be achieved by skipping every second pulse, effectively operating at 30 Hz, producing a 7 Å band. In the present case, we obtain a Q range of (0.017 < Q < 0.05 1/Å).



Time-resolved reflectometry at the Liquids Reflectometer

This study follows the initial formation of a lithium-rich layer at the surface of a Mo electrode in contact with a N_2 saturated $THF/LiClO_4$ + EtOH electrolyte under constant current at -0.1 mA/cm^2.

THF-based solvent is used because aqueous solutions have lower faradaic efficiency due to competition with hydrogen evolution reaction.

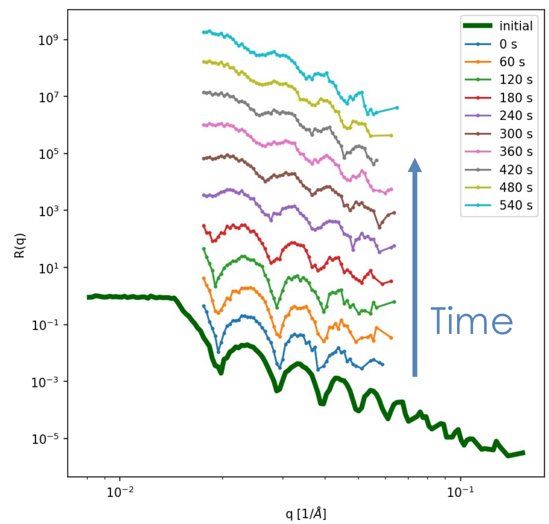

ACS Energy LETTERS

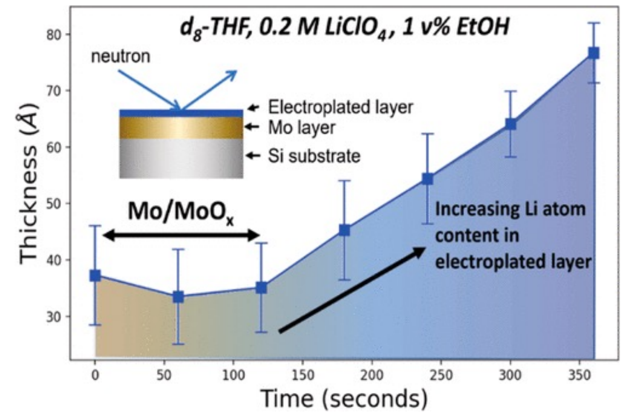
http://pubs.acs.org/journal/aelccp

Lithium-Mediated Electrochemical Nitrogen Reduction: Tracking Electrode–Electrolyte Interfaces via Time-Resolved Neutron Reflectometry

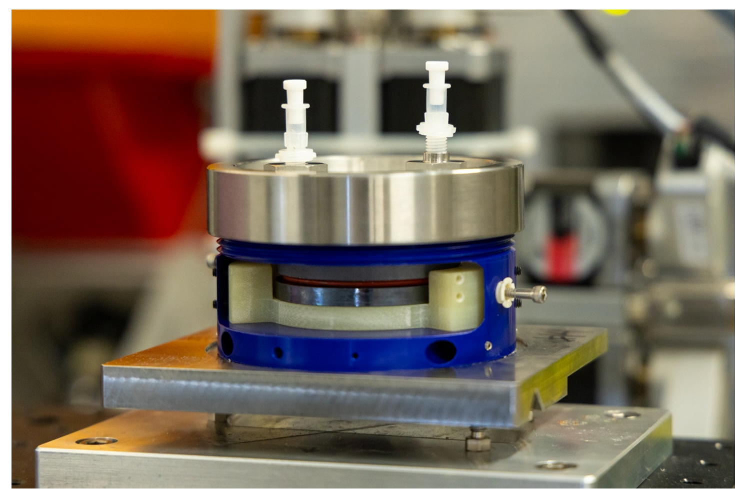
Sarah J. Blair,[#] Mathieu Doucet,[#] James F. Browning, Kevin Stone, Hanyu Wang, Candice Halbert, Jaime Avilés Acosta, José A. Zamora Zeledón, Adam C. Nielander,* Alessandro Gallo,* and Thomas F. Jaramillo*

LETTER



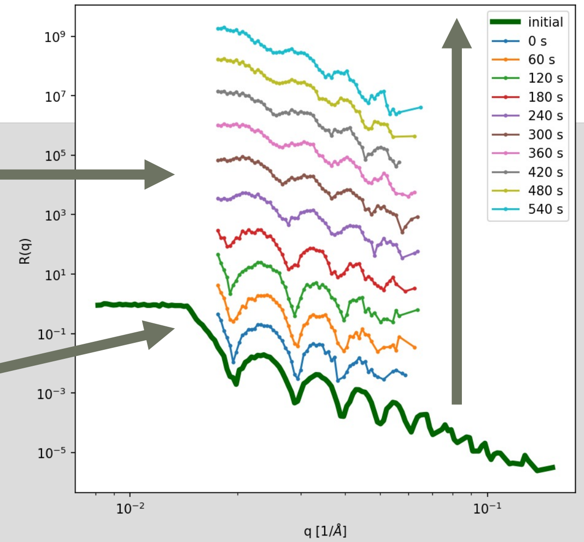


Blair et al, ACS Energy Lett., 2022, 7, 6, 1939–1946



OAK RIDGE National Laboratory

t-NR for nitrogen reduction



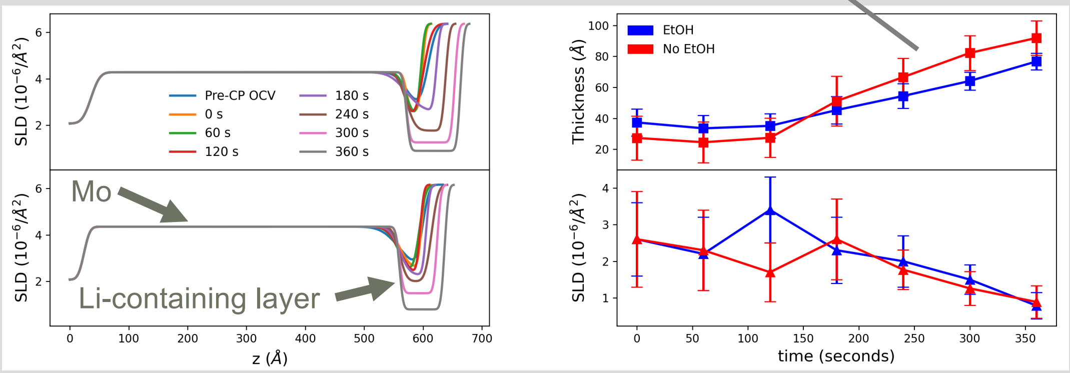
Each curve corresponds to 60 seconds.

In this case, we only analyzed the first few minutes and modeled the data curves individually.

The initial (steady) state is measured carefully to give us a good starting point for analysis.

The plated layer is thicker without EtOH since it's not being used.

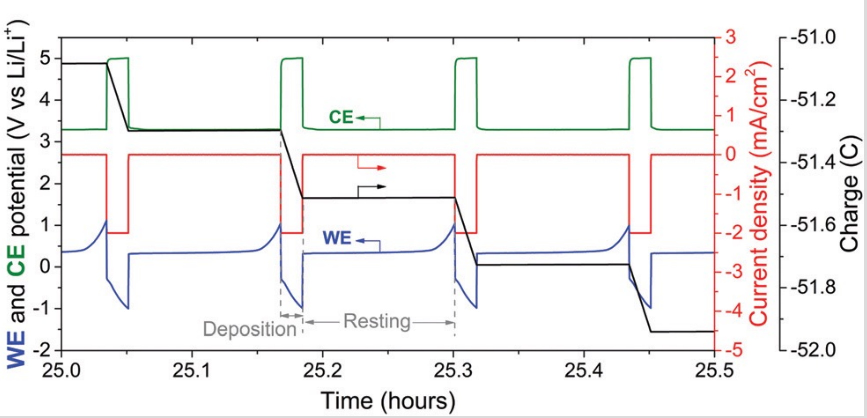
- We observed the formation of a Li-containing layer, supporting the model of an initial plated layer with no thick SEI.
- This supports the proposed approach of short cycles during real-world applications to help limit SEI formation.



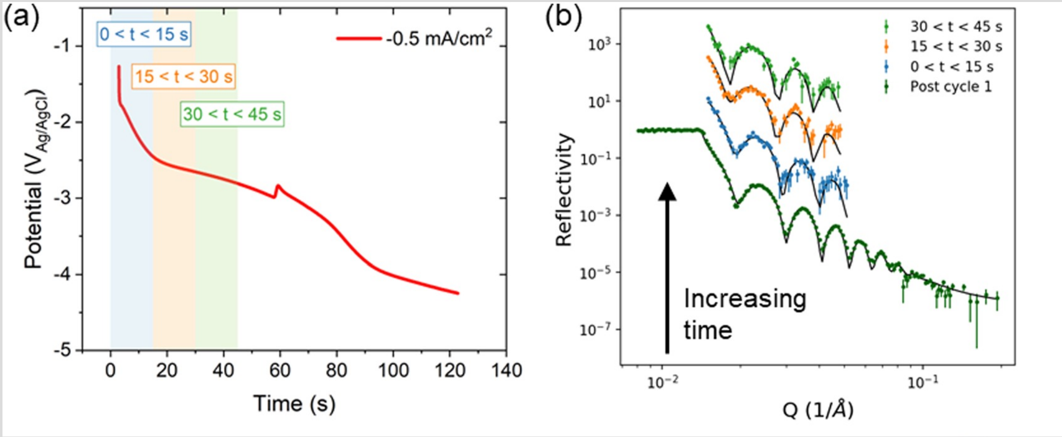
Short cycles to limit SEI growth

- Short cycles of 1 min at constant current of -2 mA/cm^2 following by 3-8 min at open circuit has been shown to increase faradaic efficiency.

- In our case, we have to limit the current to ensure the film still stays smooth at the nm level, so we use -0.5 mA/cm^2.

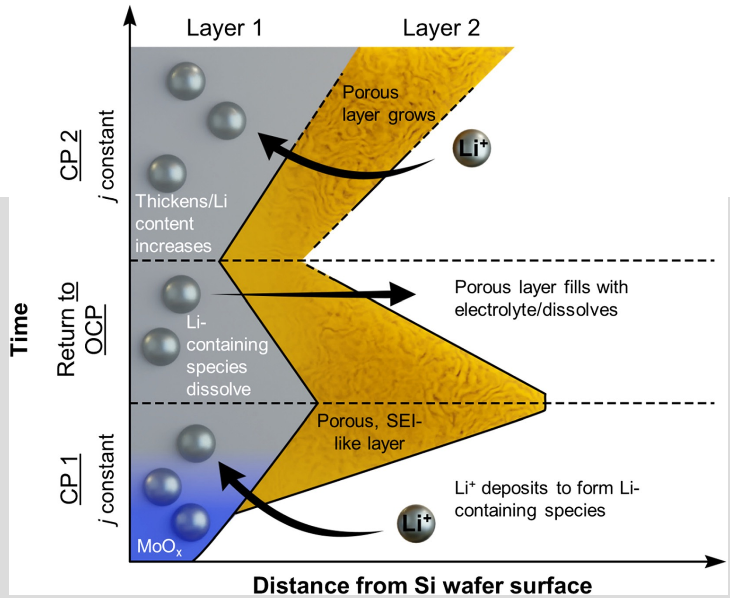


Anderson et al, Energy Environ. Sci., 2020, 13, 4291



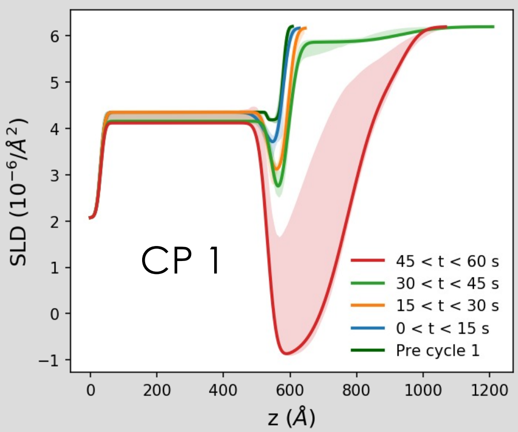
Blair et al, Energy Environ. Sci., 2023, 16, 3391–3406

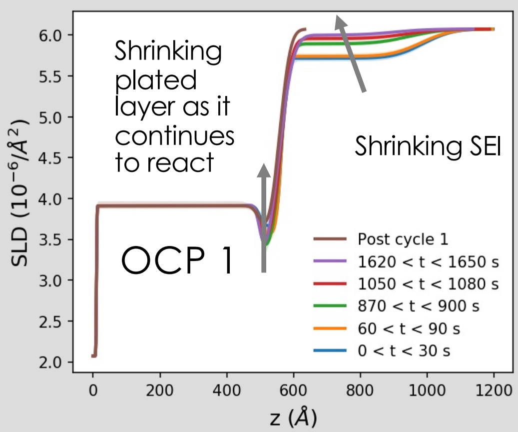
Looking at SEI formation with short cycles

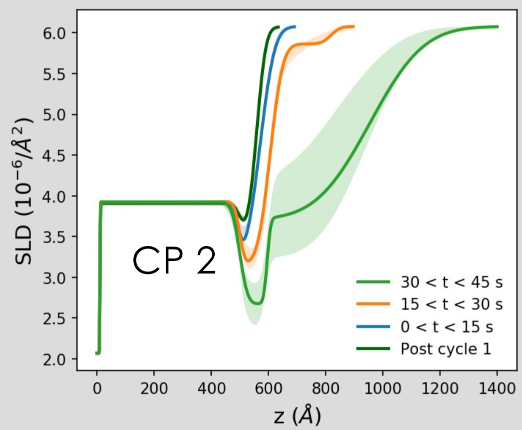


- In a follow-up experiment, we followed the electrode surface for 2-minute cycles of applied current.
- We could see the behavior of the SEI with plating and as it relaxes at open-circuit.
- Our time resolution was 15 seconds.
- The data was still (mostly) modeled individually.

Blair et al, Energy Environ. Sci., 2023, 16, 3391–3406





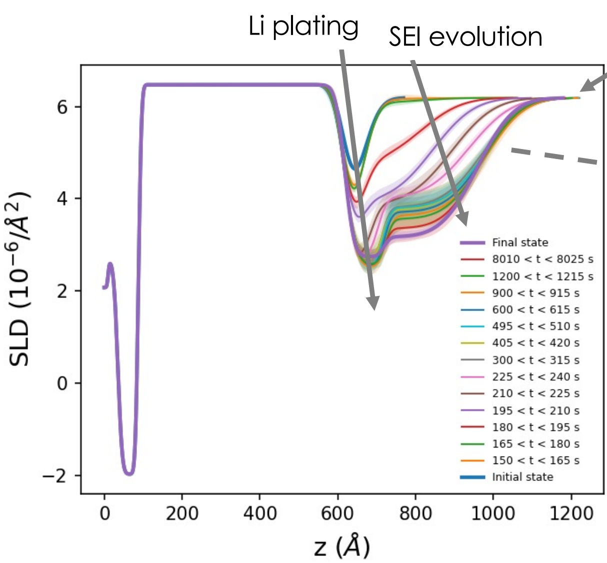


Seeing the evolution of complex systems

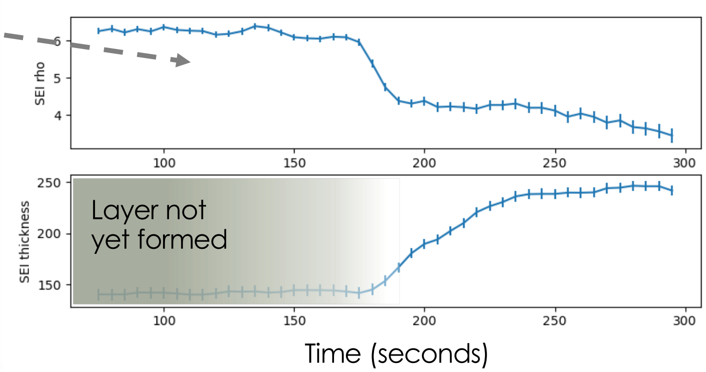
- The measurements shown here were done on a similar system, replacing Mo with Cu and using $LiBF_4$.
- An automated Bayesian approach can be used to fit the data.

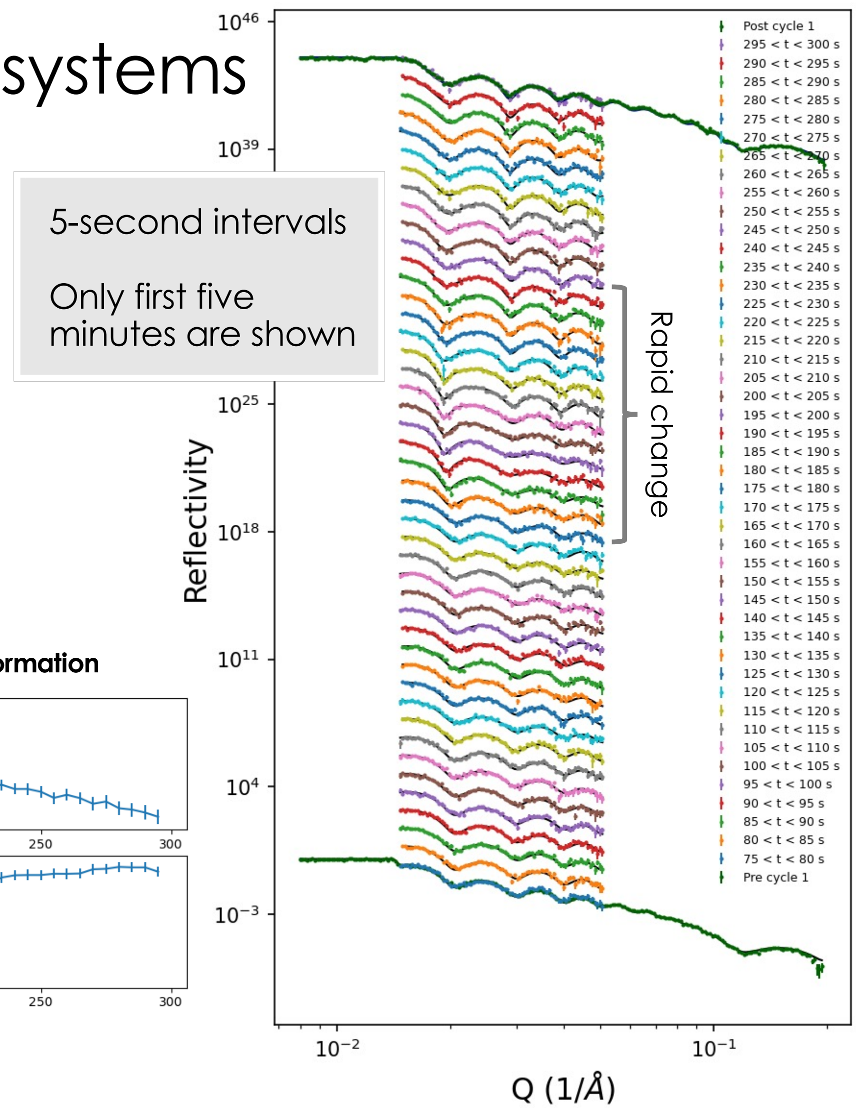
$$\text{cost} = \chi_t^2 + \alpha \sum_k^M \left(\frac{p_{k,t} - a_{k,t-1}}{\epsilon_{k,t-1}} \right)^2$$

- The result of each fit becomes the prior for the subsequent one.



Following the dynamics of the SEI formation

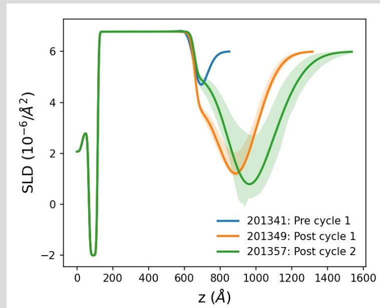




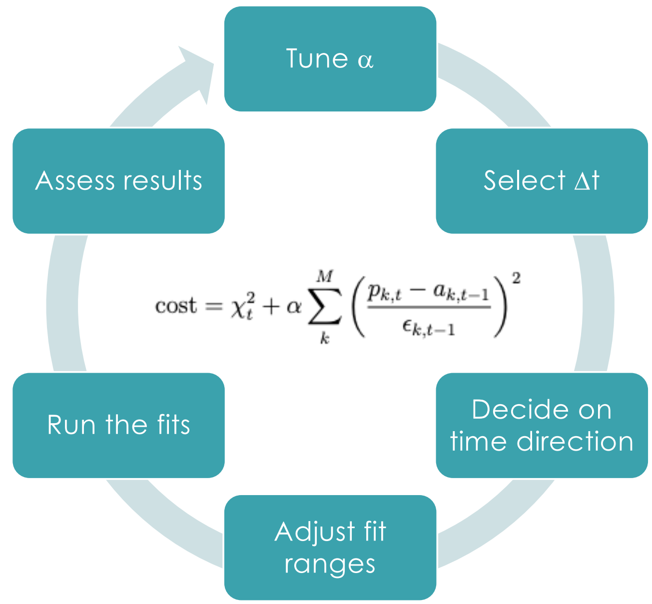
Oak Ridge National Laboratory

Challenges of a simple Bayesian approach

- What if the initial/final states are not well known? The prior becomes less useful regardless of how well the uncertainties are estimated.



- The sampling rate R_S must match the rate of change R_C.
  - ➢ When $R_S >> R_C$, numerous incremental shifts wash out the prior.
  - ➢ When $R_S << R_C$, the prior penalizes the needed large changes.
- There's a balancing act in how you slice the data, and how you use prior information.
- The main issue is that we are only considering the previous time slice when fitting a particular one.



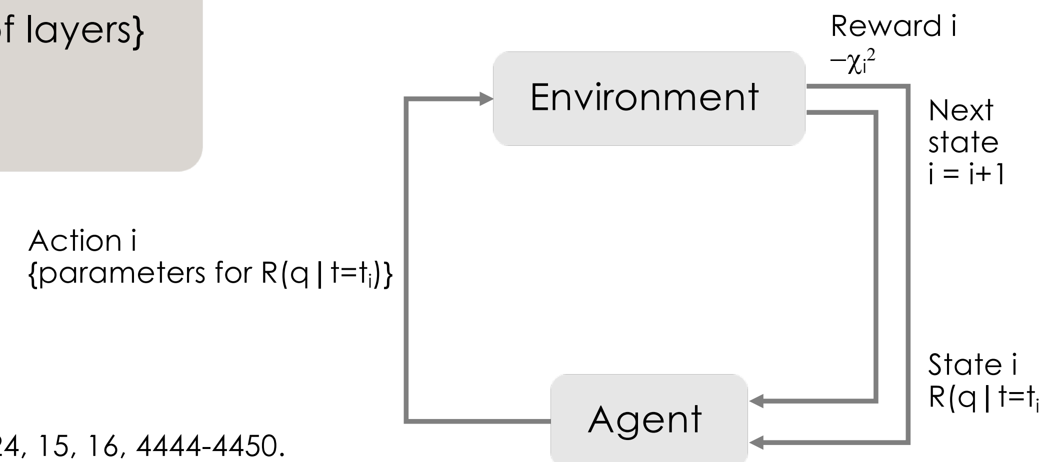
Can we use other algorithms inspired from ML?

Reinforcement Learning for t-NR

- Reinforcement learning tries to optimize **action** given a **state,** within an **environment**, following a trajectory (timeline of actions).
- Each action get a **reward**. The optimization process determines the **action**, given a **state**, that will lead to the overall best reward (summed over the whole trajectory).
- In our case:
  - State = R(q, t)
  - Action = {thickness, SLD, roughness of layers}
  - Reward = - χ^2

Time series of states is predetermined…
We are trying to solve the best sequence of “actions” for this particular trajectory.

Generated with Adobe Firefly

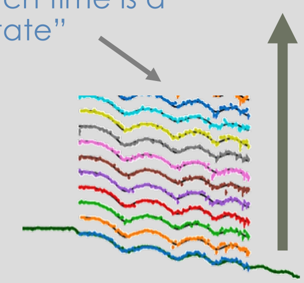


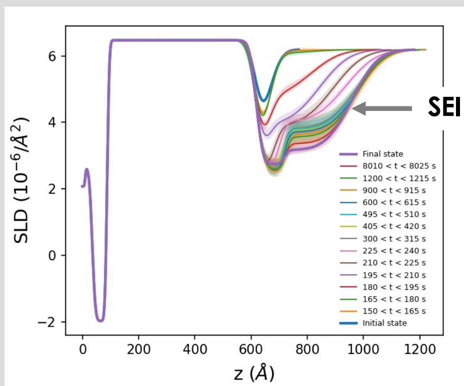
Doucet et al, *J. Phys. Chem. Lett*. 2024, 15, 16, 4444-4450.

Reinforcement Learning for to time-series fitting

- Instead of fitting one curve at a time iteratively, we **consider the whole timeline**?

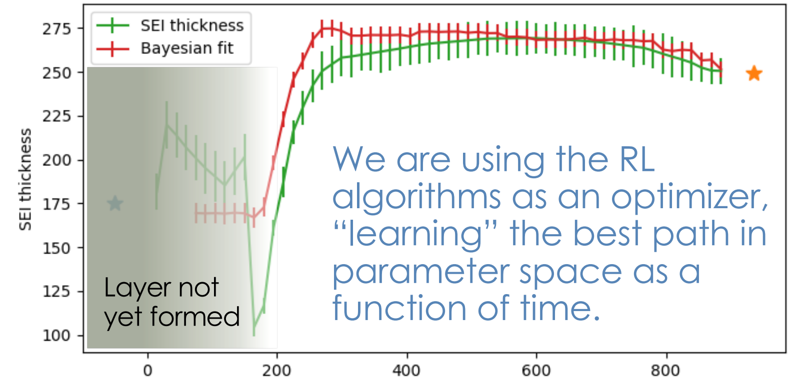
Each time is a "state"

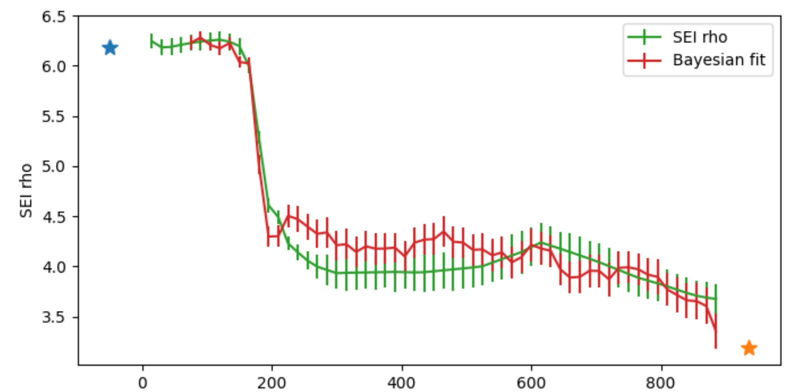




SEI evolution

Delay because of Bayesian prior.





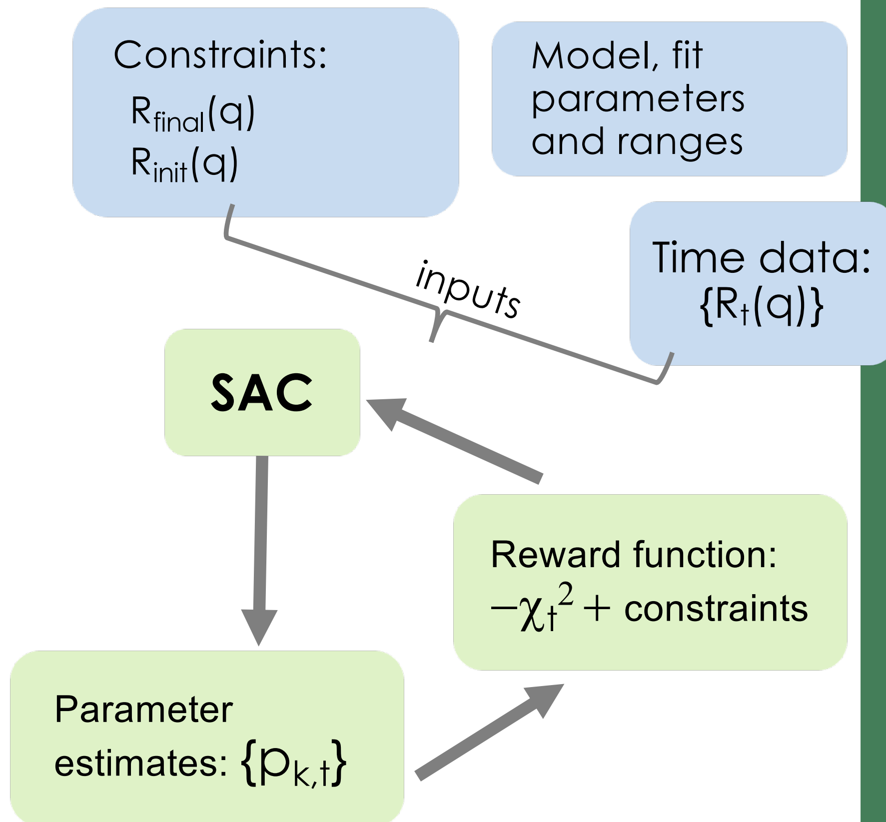
- Fitting takes minutes instead of hours.

* Here we used a Soft Actor Critic (SAC) policy

OAK RIDGE National Laboratory

Why does it work?

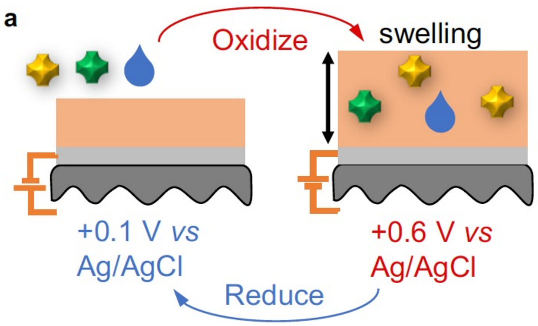
- The Soft-Actor Critic maximizes both the reward and “entropy”.
- Promotes wider exploration of parameter space, while keeping this exploration in check with the usual reward term.
- The SAC algorithm is stochastic and allows us to assess the probability distribution of the predicted parameters.
- **User inputs**:
  - Reward function may be tuned according to the problem (superposition of states, initial and final states, etc…)
  - Fit parameter ranges need to be set, just like for any other fitter.



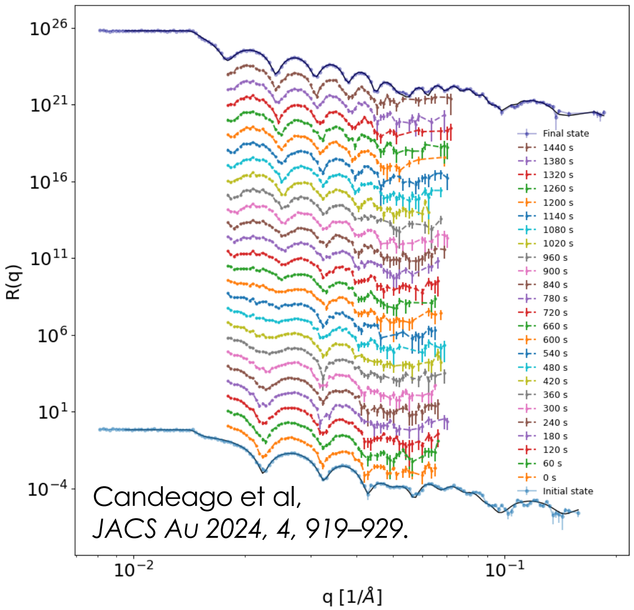
”[…] in problem settings where multiple actions seem equally attractive, the policy will commit equal probability mass to those actions.”

Haarnoja et al, 2018

Redox active polymers for ion separation



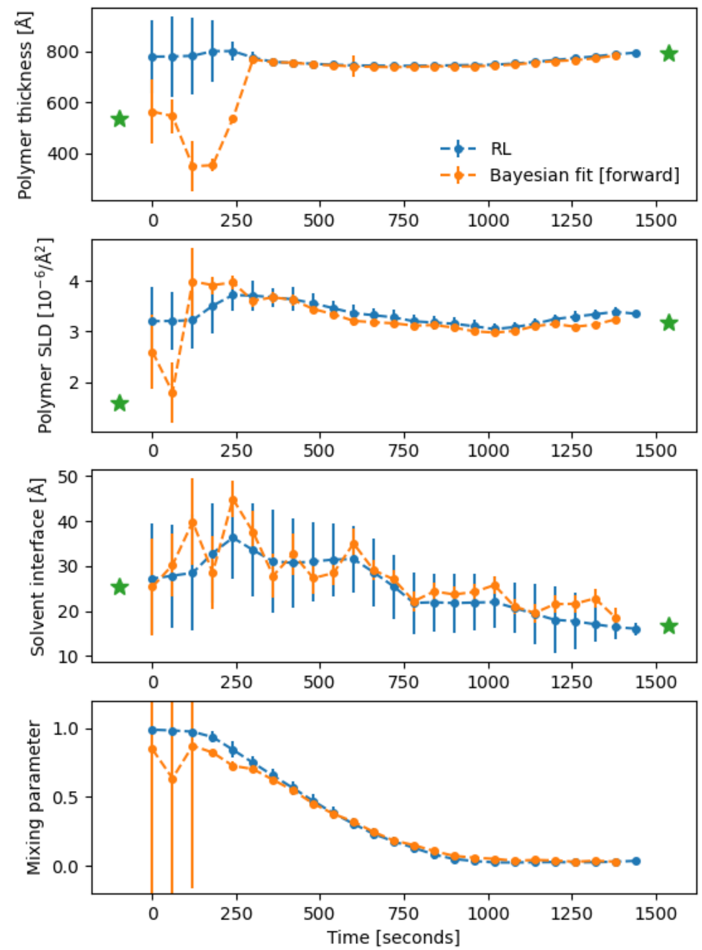
PFPMAm uptake of ReO_4-



Candeago et al, *JACS Au 2024, 4, 919–929.*

Mixed model with a fraction of the film kept in its initial state and the rest evolving into another phase.

RL approach agrees with the Bayesian approach but is much faster.



Doucet et al, *J. Phys. Chem. Lett*. 2024, 15, 16, 4444-4450.

Thanks to all our colleagues: it takes a village…

OAK RIDGE National Laboratory | 80

- Chen Zhang
- Hanyu Wang
- Jeehye Kim
- Qiu Zhang
- Tyler Boullie
- Andrew Payzant
- Ray Unocic
- Jim Browning
- Candice Halbert
- Rhonda Moody
- Instrument Hall Coordinators
- Mechanical Engineers
- Radiological Control Technicians

SUNCAT
CENTER FOR INTERFACE SCIENCE AND CATALYSIS

- Thomas Jaramillo
- Valerie Niemann
- Adam Nielander
- William Tarpeh
- Peter Benedek
- Sang-Won Lee
- Wrayzene Willowghby
- Isa Rios Amador

Past collaborators:
- Sarah Blair (now NREL)
- Alessandro Gallo (now Sila)

Acknowledgments: A portion of this research used resources at the SNS, a Department of Energy (DOE) Office of Science User Facility operated by ORNL.