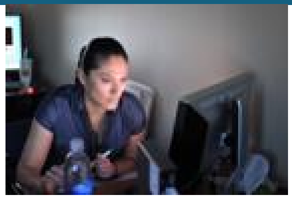
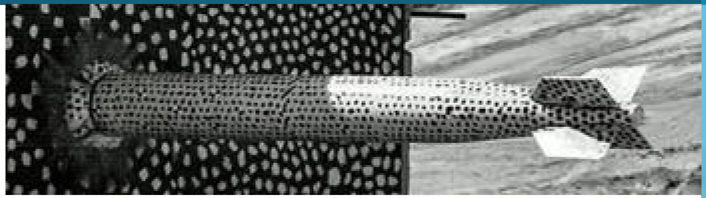
SAND2022-6370C

Sandia National Laboratories

Low-Temperature Molten Sodium Batteries for Large-Scale Storage: Fundamental Studies of Metal Halide Catholyte and Cathode Materials

241st ECS Meeting – Vancouver, BC

June 2, 2022

PRESENTED BY

Adam Maraschky

Rose Lee, Melissa Meyerson, Martha Gross, Stephen Percival, Amanda Peretti, Erik Spoerke, Leo Small

OFFICE OF ELECTRICITY
ENERGY STORAGE PROGRAM

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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This work was funded by the DOE Office of Electricity, managed by Dr. Imre Gyuk.

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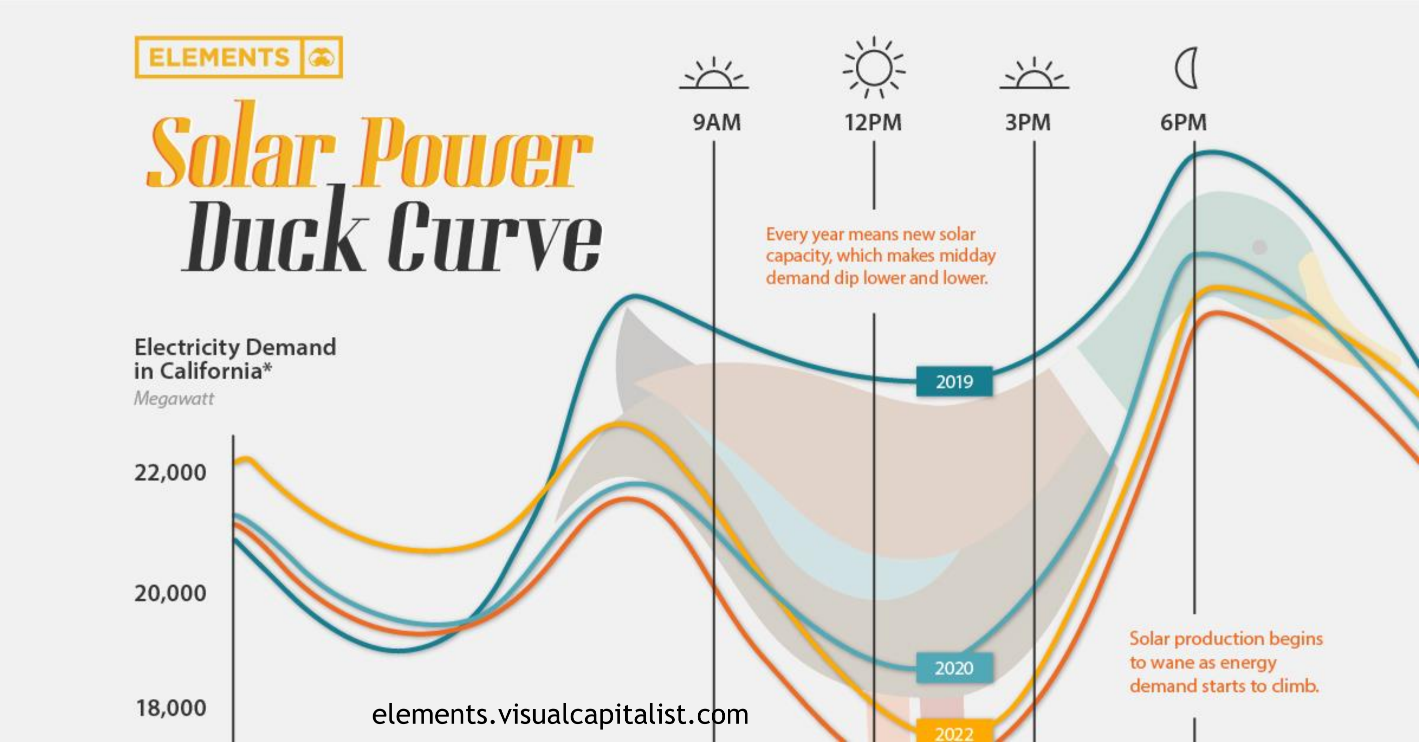
Safe, Low-Cost Energy Storage is Critically Needed

- Decarbonization of industry requires a reliable grid powered by renewables
- Without storage, wind and solar capacity requirements are much greater!
- Energy demands do not always align with supply (*i.e.*, duck curve)
- Seasonal changes also drive a need for long-duration storage
- **Batteries must be affordable and safe to be used on a large scale**

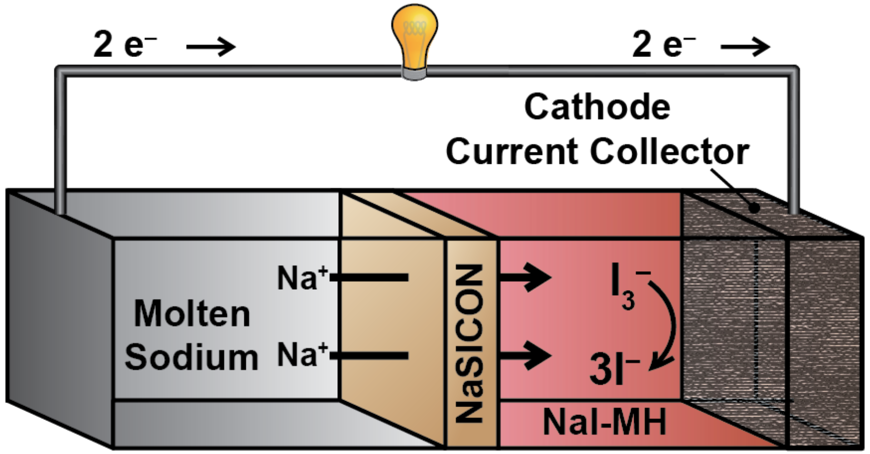


Our Approach

Develop enabling technologies for safe, low-cost, ***molten sodium batteries***

Attractive for resilient and reliable grid-scale energy storage:

- Employ earth-abundant, energy-dense materials (Na, Al, Si)
- Minimize dendrites with ***molten*** sodium
- Prevent crossover/shorting with NaSICON ceramic separator
- Leverage inorganics to limit reactivity upon mechanical failure
- Enable applications for long-duration energy storage



Anode

$Na \rightarrow Na^+ + e^-$

Cathode

$I_3^- + 2e^- \rightarrow 3I^-$

$$2Na + I_3^- \rightarrow 2Na^+ + 3I^- \qquad E^0_{cell} = 3.24\ V$$

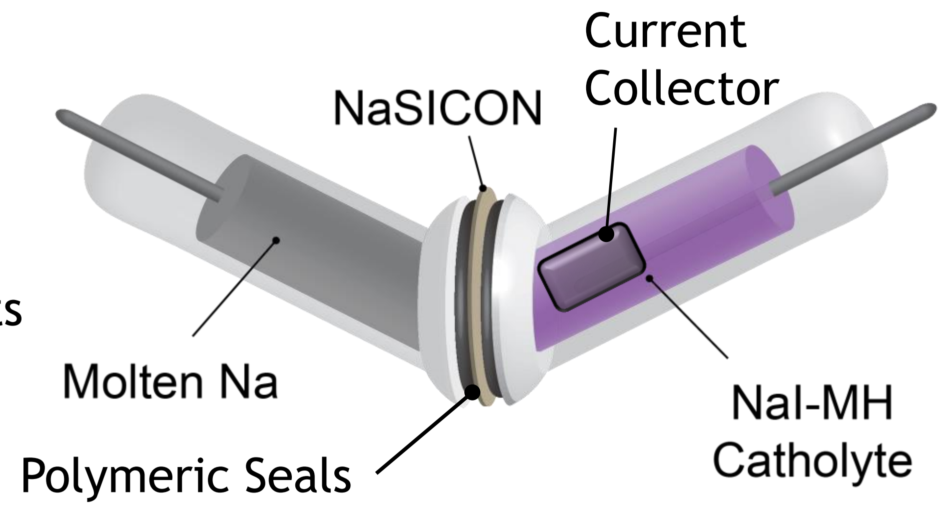
L. J. Small, A. Eccleston, J. Lamb, A. C. Read, M. Robins, T. Meaders, et al. *J. Power Sources,* **360**, 569 (2017).

Why Low Temperature?

Commercial molten sodium batteries operate near 300 °C (Na-S) or 270 °C (ZEBRA).

We are driving down battery operating temperature to near sodium's melting point (98 °C)

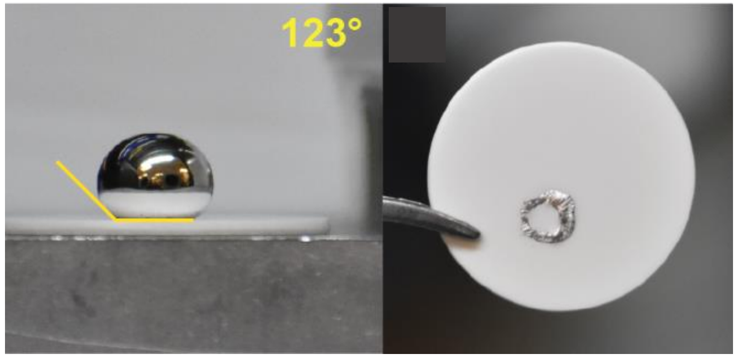
- Lower Cost
  - Less expensive materials (*e.g.*, wiring)
  - Insulation
- Reliability
  - Lower temperatures → slower aging on all system components
  - System level heat management not as extensive
  - Fewer side reactions
- Lower Start-up Energy

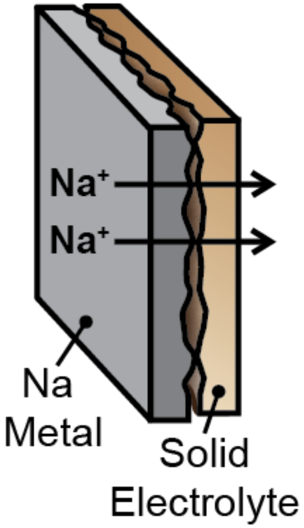


While lower temperatures can improve cost and reliability, materials challenges arise.

Tin Coating Improves Molten Sodium Anode

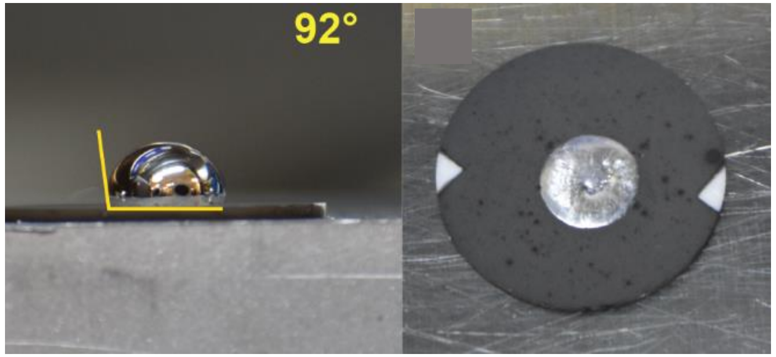
Bare NaSICON

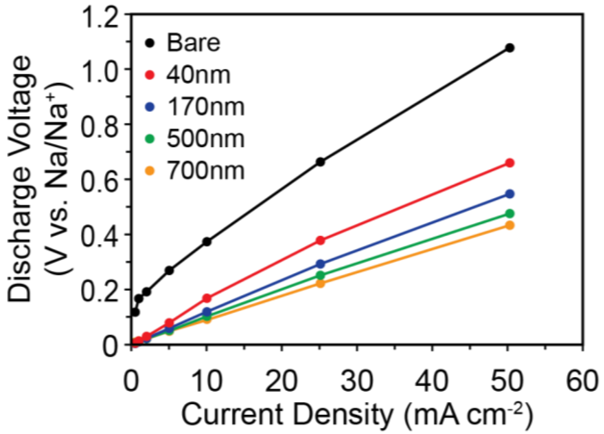




High interfacial resistance between molten Na and solid electrolytes typically prevents low-temperature operation

Sn Coating on NaSICON





Sn coating on NaSICON decreases resistance at the sodium-separator interface.

M. M. Gross, L. J. Small, A. S. Peretti, S. J. Percival, M. A. Rodriguez and E. D. Spoerke. *J. Mat. Chem. A*, **8**, 17012 (2020).

M. M. Gross, S. J. Percival, L. J. Small, J. Lamb, A. S. Peretti and E. D. Spoerke. *App. Energy Mat.*, **3**, 11456 (2020).

Molten Salt Catholyte

- Composed almost entirely of ions → high ionic conductivity
- NaI-based molten salt is redox-active
- I^- behaves as a Lewis-base with metal halide MX_3 as the acid to form a Lewis adduct
- Phase behavior, speciation, and Lewis acidity depend on composition of NaI/MH mixture
- Composition changes with state of charge (SOC)

MX_3 where M = Al or Ga and X = Cl or Br

$NaI/GaCl_3$ Phase Diagram

Temperature (°C)	0	10	20	25	30	35	40	50
130	L	L	L	L	L	L+S	L+S	S
120	L	L	L	L	L	L+S	L+S	S
110	L	L	L	L	L	L+S	S	S
100	L	L	L	L	L+S	L+S	S	S
90	L	L	L	L	L+S	S+L	S	S
80	L	L	L	L	L+S	S+L	S	S
70	S	S+L	L	L+S	L+S	S+L	S	S
60	S	S+L	L	L+S	S+L	S+L	S	S
50	S	S+L	L	S+L	S+L	S+L	S	S
40	S	S	S+L	S	S	S	S	S
30	S	S	S	S	S	S	S	S

mol % of NaI in $GaCl_3$

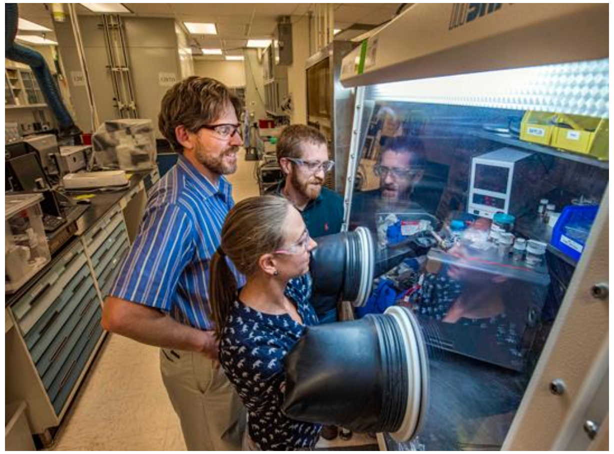
S.J. Percival, L.J. Small, and E.D. Spoerke. J. Electrochem. Soc., **165**, A3531 (2018).

S. J. Percival, R.Y. Lee, M.M. Gross, A.S. Peretti, L. J. Small, and E. D. Spoerke. J. Electrochem. Soc., **168**, 036510 (2021).

R.Y. Lee, S.J. Percival, and L.J. Small. *J. Electrochem. Soc.*, **168** 126511 (2021).

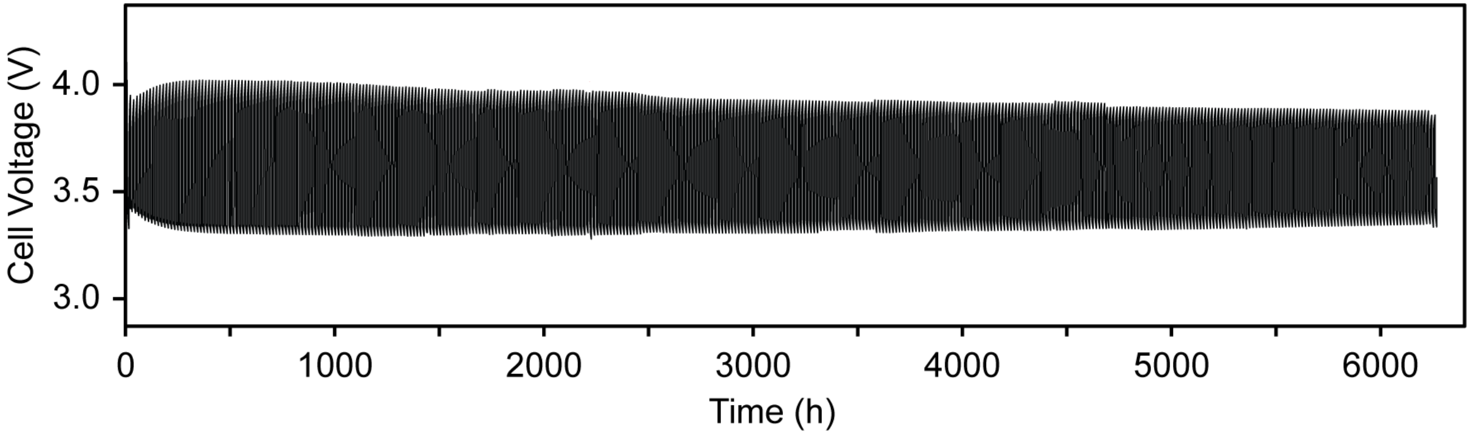
M.M. Gross, S.J. Percival, R.Y. Lee, A.S. Peretti, E.D. Spoerke, and L.J. Small. *Cell Reports Physical Science* **2,** 100489 (2021).

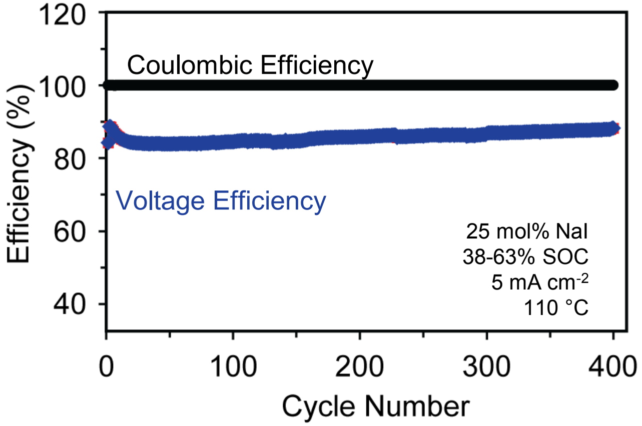
High-Performance, Low-Temperature $GaCl_3$-Based Battery



Implemented high-voltage NaI-$GaCl_3$ catholyte in molten sodium batteries at 110 °C

- Ran >400 cycles (>8 months) at 5 mA cm^{-2} (25% DoD) with 85.3% energy efficiency
- Nominal voltage of 3.62 V is 40% higher than standard ZEBRA chemistry



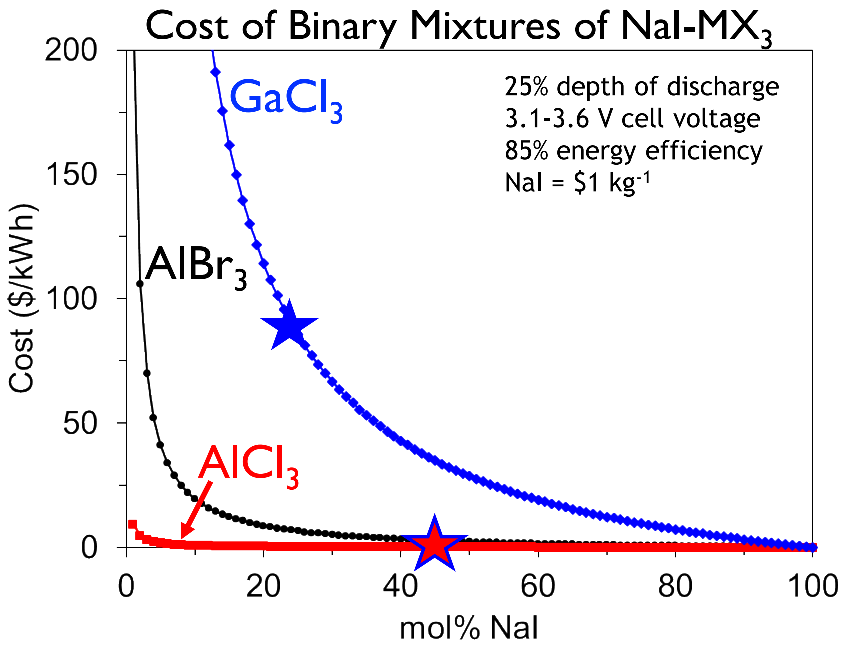


Cycled molten sodium battery with NaI-GaCl3 catholyte for >8 months with >85% energy efficiency at 40% increase in cell voltage vs. ZEBRA at < half the temperature.

M.M. Gross, S.J. Percival, R.Y. Lee, A.S. Peretti, E.D. Spoerke, and L.J. Small. *Cell Reports Physical Science* **2** (2021) 100489.

Catholyte Materials Control Costs

- NaI-$GaCl_3$ catholyte showed great performance…
- But ***$GaCl_3$ is relatively expensive (>$100 kg^{-1})***
- After evaluating costs across many NaI-MX_3 combinations, we decided to reinvestigate NaI-$AlCl_3$
- Previously investigated at higher temperature



Despite its great performance, NaI-$GaCl_3$ is too expensive!
Reinvestigate NaI-$AlCl_3$, with materials cost <$1 kWh^{-1}.

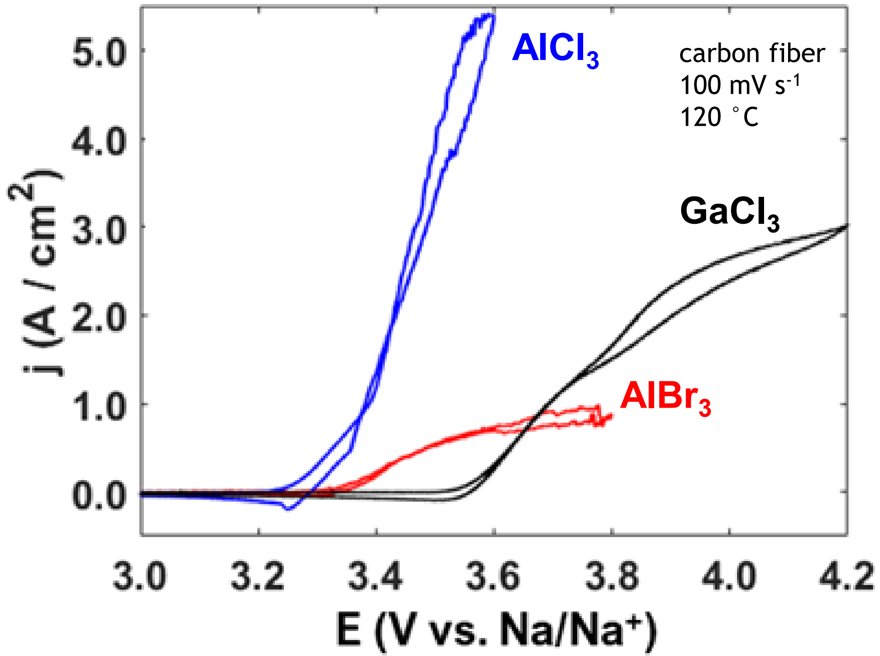
L. J. Small, A. Eccleston, J. Lamb, A. C. Read, M. Robins, T. Meaders, et al. *J. Power Sources,* **360**, 569 (2017).

Modeling NaI-MX_3 Speciation Reveals Kinetic Limitations

We coupled microelectrode studies with electrochemical simulations to understand the differences between NaI-$AlCl_3$, NaI-$AlBr_3$, and NaI-$GaCl_3$

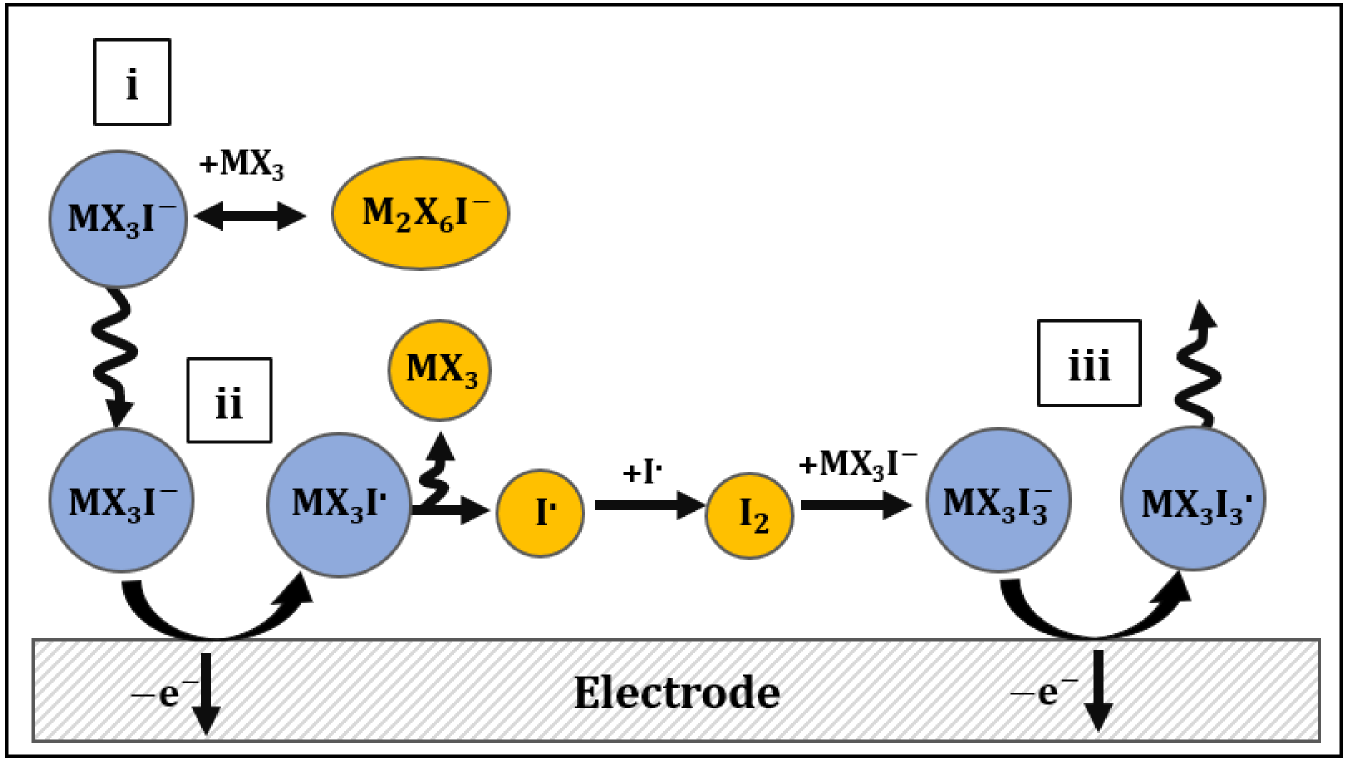
- Fit model to data to determine chemical equilibrium and electrochemical kinetics parameters
- NaI-$AlCl_3$ had slowest electron transfer rates, highest currents

What explains the observed differences in kinetics?



R.Y. Lee, S.J. Percival, L.J. Small, *J. Electrochem. Soc.*, **168** 126511 (2021).

Iodide Oxidation Reaction Scheme



R.Y. Lee, S.J. Percival, L.J. Small, *J. Electrochem. Soc.*, **168** 126511 (2021).

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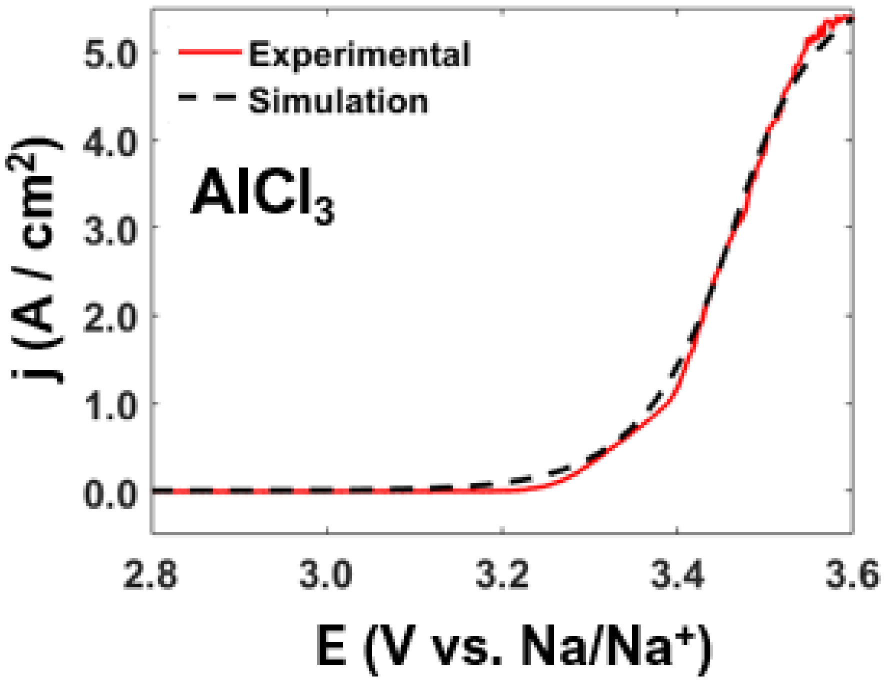
- Fit model to data to determine chemical and electrochemical parameters
- NaI-$AlCl_3$ had slowest electron transfer rates, highest currents
- Multiple species exist in the molten salt – Al_2Cl_6, $Al_2Cl_6I^-$, $AlCl_3I^-$, etc.
- Some species "lock up" reactant, making it unavailable for redox

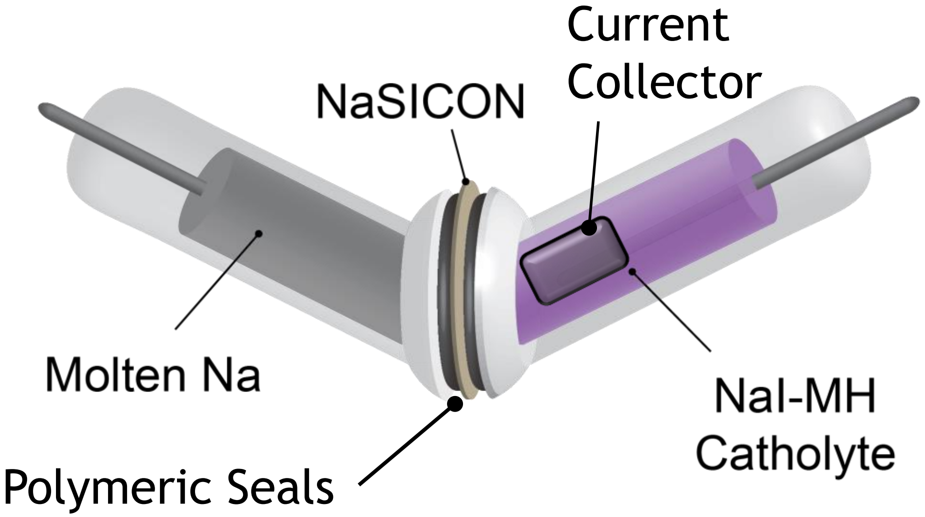


Iodide oxidation kinetics depend on the availability of reactive species, as determined by chemical equilibria. This can be used to understand electrochemical performance and screen catholytes.

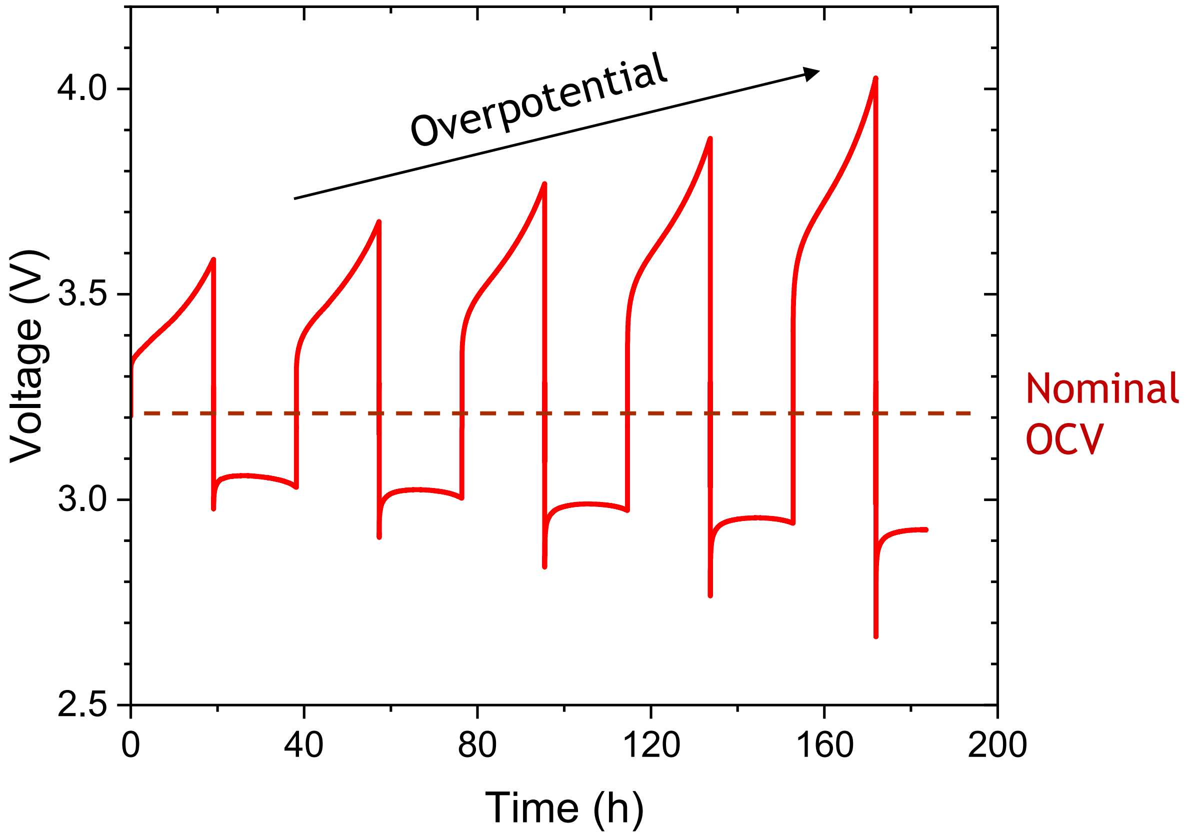
R.Y. Lee, S.J. Percival, L.J. Small, *J. Electrochem. Soc.*, **168** 126511 (2021).

Battery Symptoms

110 °C Operation
45% NaI
55% $AlCl_3$
7.5% SOC build (add I_2)



Typical cell cycled 30% DOD at 2.5 mA cm^{-2}

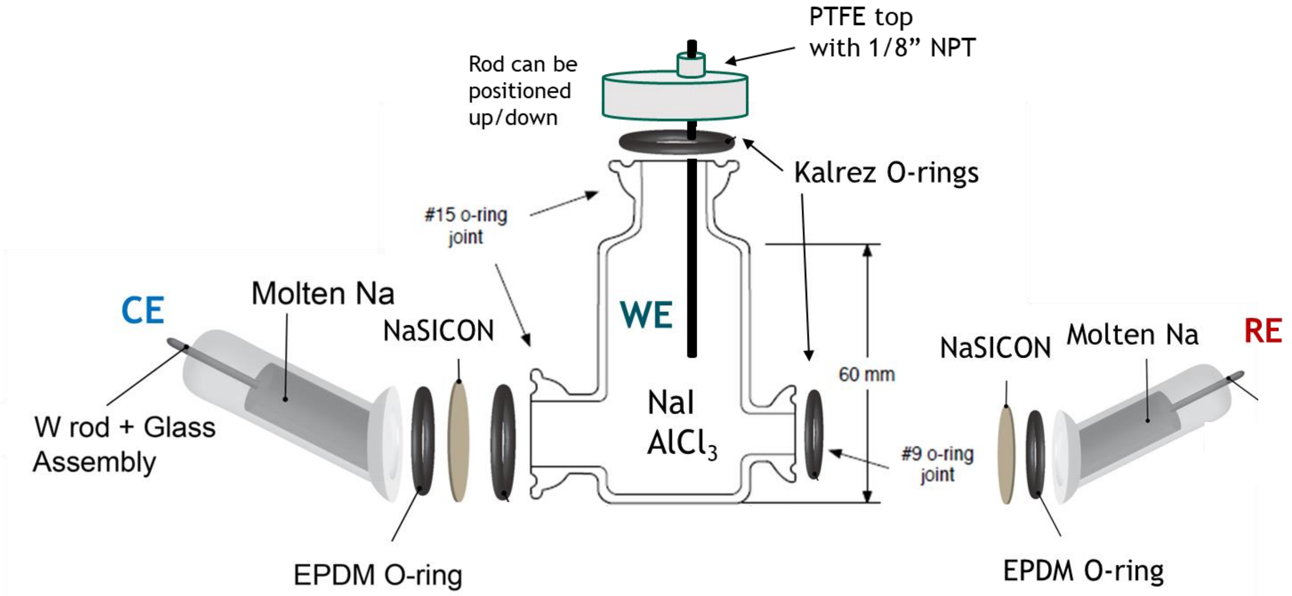


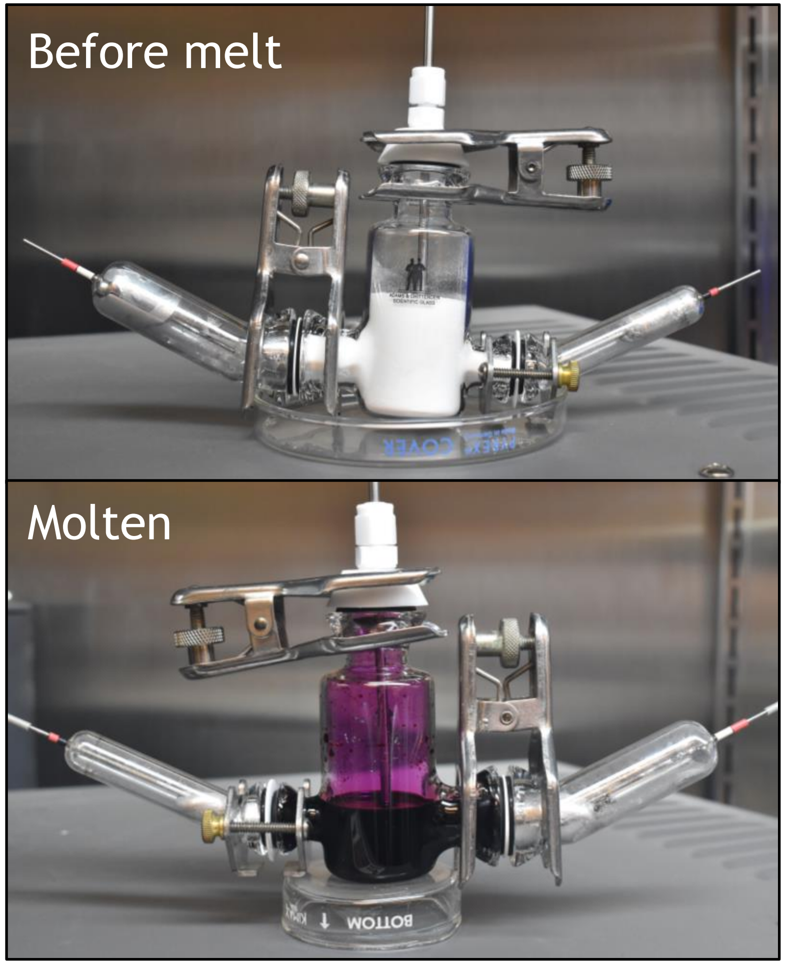
Cycling profile shows steady overpotential increase, loss of efficiency.
Something in the cell is degrading!

Optimizing the Current Collector

3-Electrode Cell Design

- In a battery, hard to tell what process/component contributes most to overpotential
- Another approach: use 3-electrode cell to isolate electrode of interest
- De-couple current and voltage using a reference electrode (RE)





Benefits:

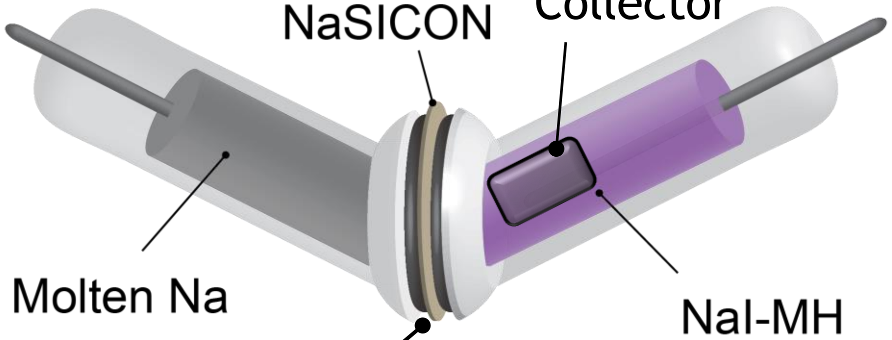
- Interchangeable WE, control area & material
- Isolate WE potential from separator, CE
- Hermetically sealed against I_2 escape
- Stable composition (excess salt volume, capacity)
- Same catholyte composition and CE as full cells!

Current Collector Optimization

Task: redesign current collector for cathode

1. What material?
   - Molybdenum (Mo)
   - Tungsten (W)
   - Tantalum (Ta)
   - Glassy Carbon (GC)

More catalytic?



2. What high-surface area configuration? (microstructure, size)
   - Foam
   - Mesh
   - Felt

Maximize surface area

$$i = \frac{I}{A}$$

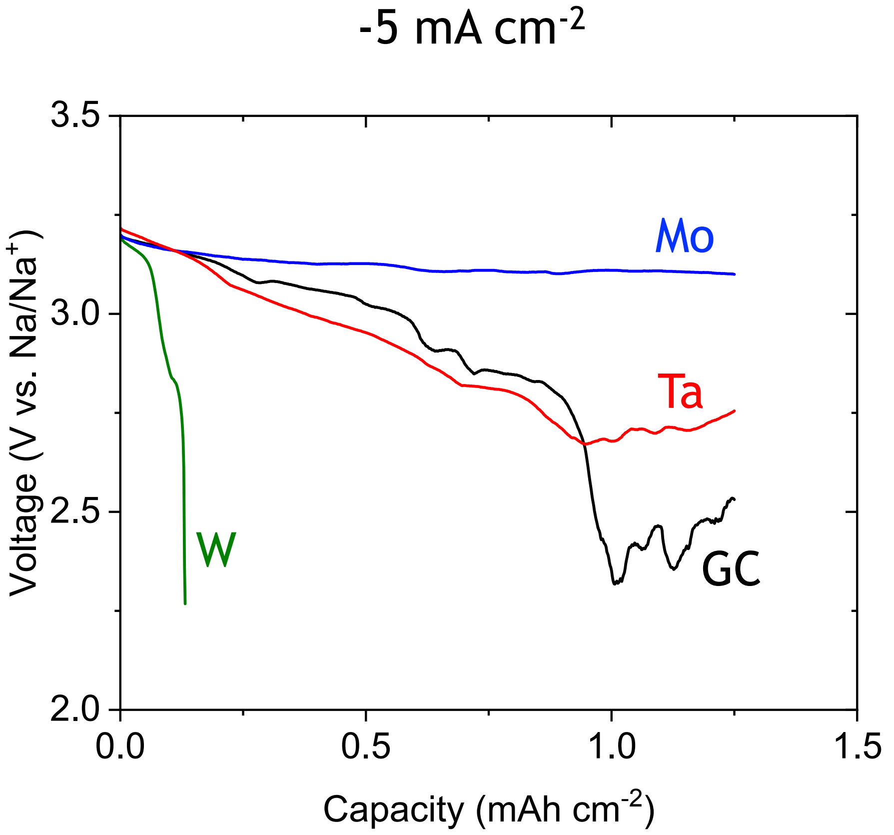
$$V_{app} = E_0 + iR_\Omega + \frac{RTi}{nFi_0} + \frac{RT}{nF}\left(1 - \frac{|i|}{i_L}\right)$$

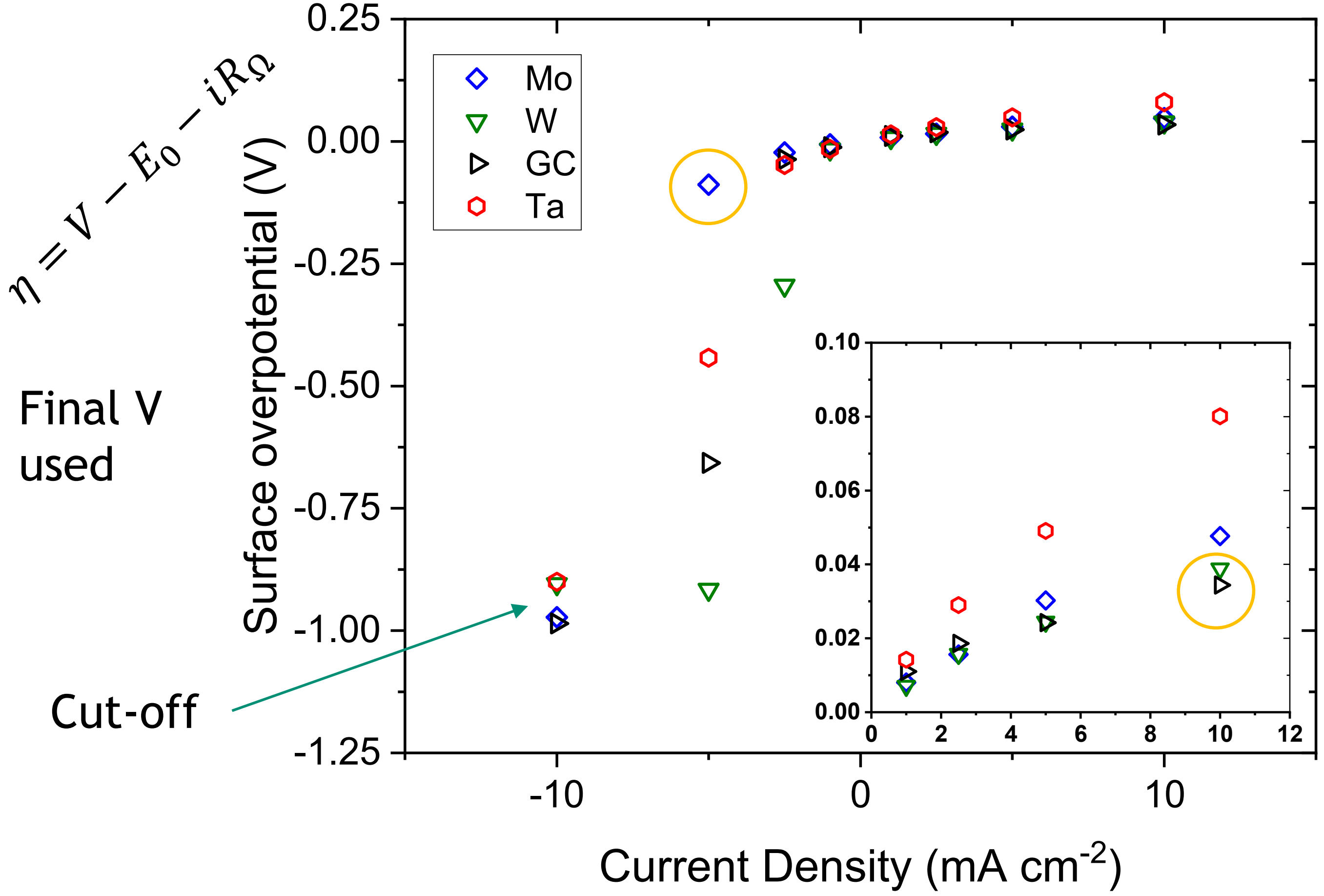
Overpotentials

Electrochemically active surface area controls overpotential (voltage inefficiency) for given current.

Galvanostatic Experiments on Disk Electrodes

Experiment conditions: +/- 1.0 , 2.5, 5.0, 10 mA cm^{-2} for 900 s each (charge then discharge)

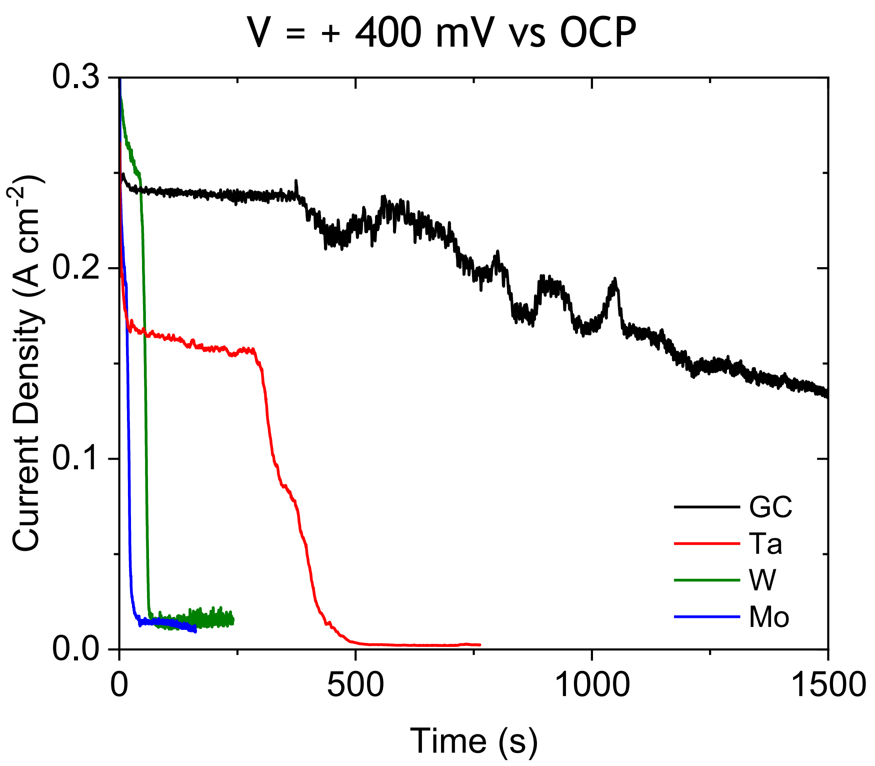


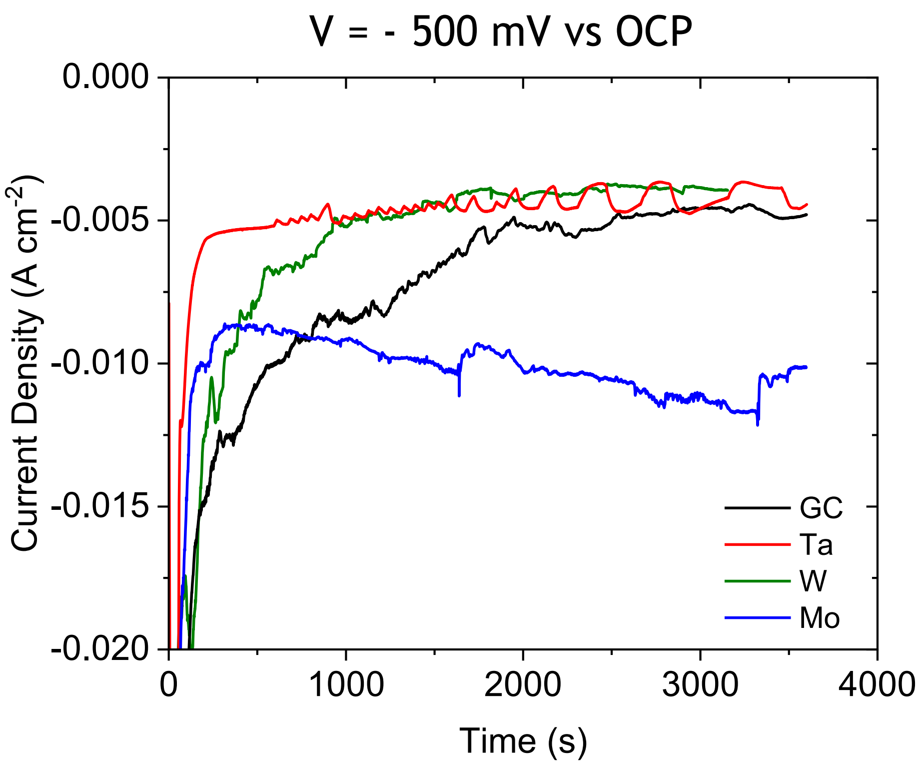


Glassy carbon showed lowest overpotential on charge, while Mo had lowest overpotential on discharge.

110 °C, 45% NaI/55% $AlCl_3$, 7.5% SOC build

Potentiostatic Experiments on Disk Electrodes





Glassy carbon showed very stable charge (+) current, while Mo had greatest (-) current on discharge.
May be due to differences in iodine/triiodide adsorption.

110 °C, 45% NaI/55% $AlCl_3$, 7.5% SOC build

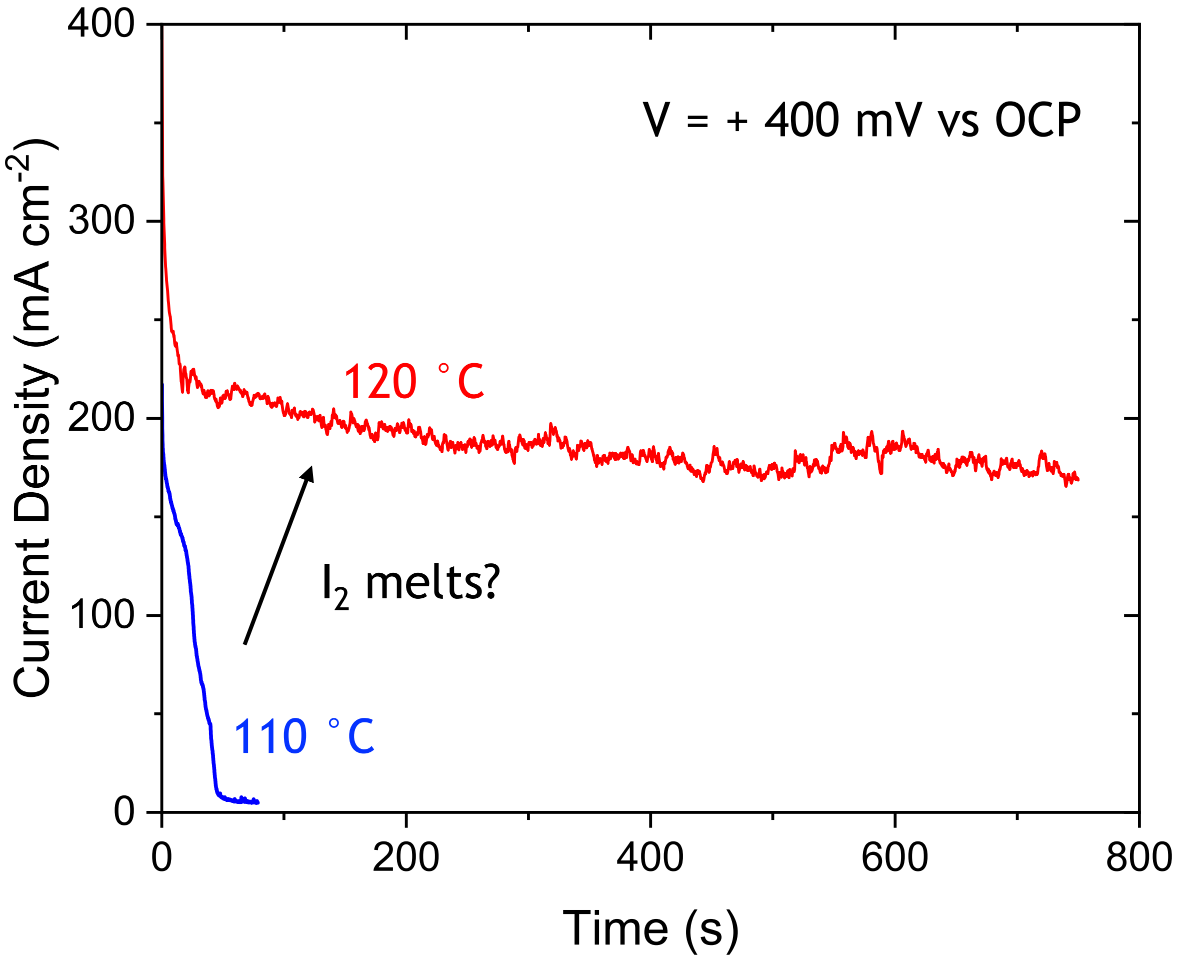
Effect of Temperature on Mo's Charging Stability

Electrochemical rxn:

$$2I^- \rightarrow I_2 + 2e^-$$

Chemical rxn:

$$I^- + I_2 \leftrightarrow I_3^- \text{ (high K)}$$



Hypothesis: below I_2 melt point (114 °C), Mo surface readily saturates; oxidation shuts off. Above that temperature, charge reaction proceeds unhindered for > 700 s.

110 °C, 45% NaI/55% $AlCl_3$, 7.5% SOC build

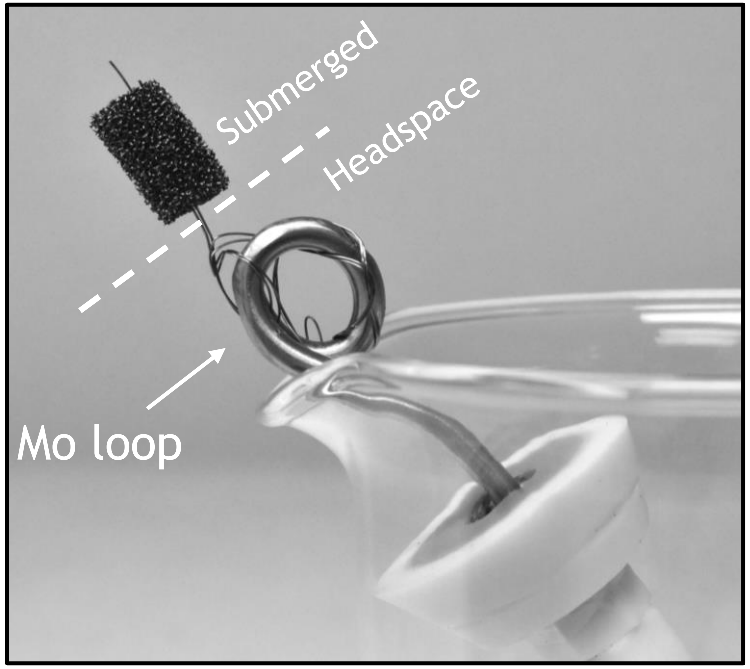
Materials Selection Summary

Material	electrical resistivity at 25 °C (W cm)	cost for solid rod ($/cm^3)	overpotential at +5 mA/cm^2 (V)	overpotential at -5 mA/cm^2 (V)	steady current density at +400 mV (mA/cm^2)	Stable performance? (Y/N)
GC	5.00E-03	85	0.024	-0.657	150-250	Y most stable charge
Mo	5.34E-06	15	0.030	-0.088	10	Y less on charge
Ta	1.31E-05	84	0.049	-0.442	2	N oxide
W	5.60E-06	24	0.024	-0.906	16	Y less on charge

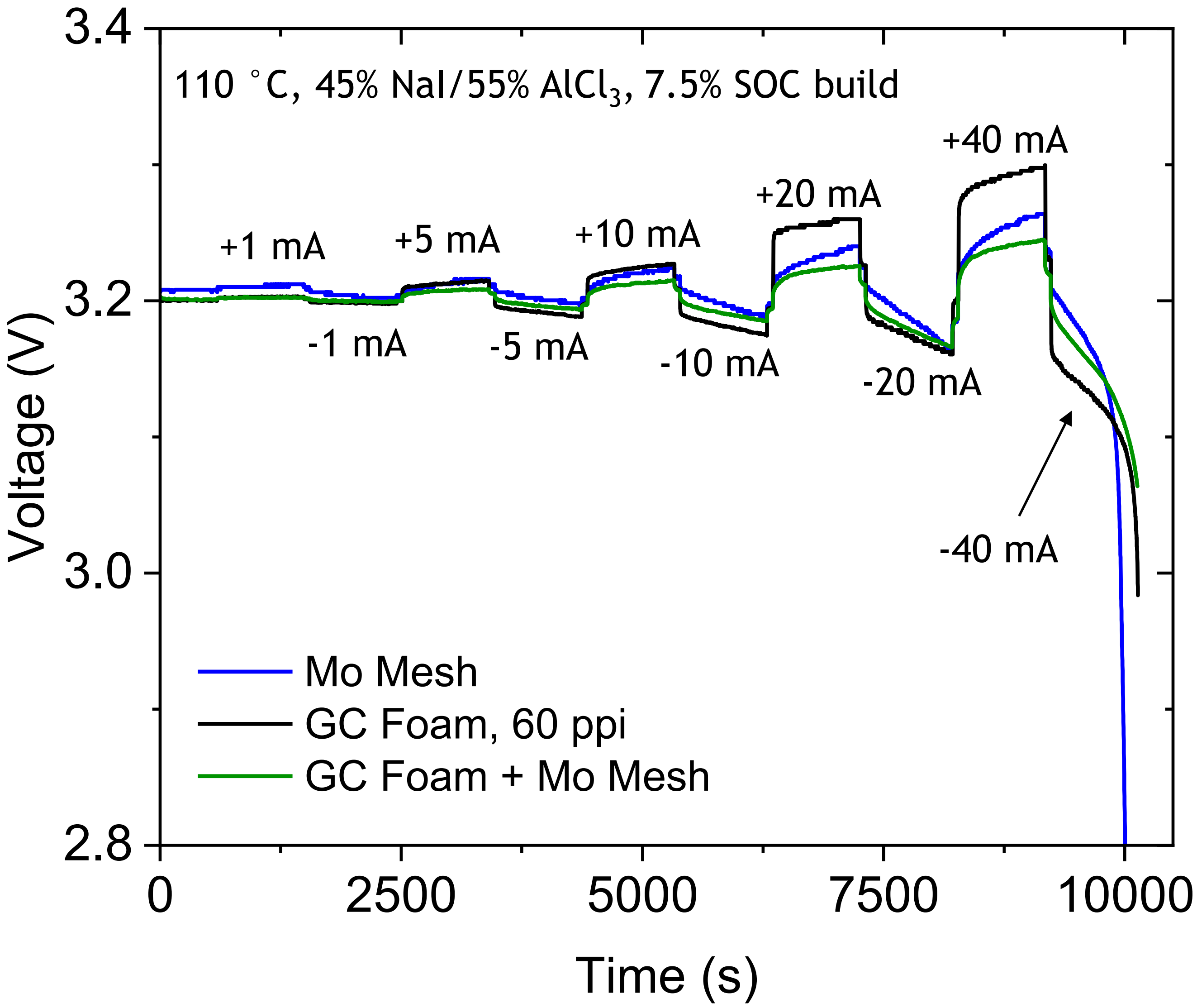
Pursue **Mo** and **GC** for high surface area electrode materials.

Evaluation of High Surface Area Materials

GC Foam



Mo Mesh

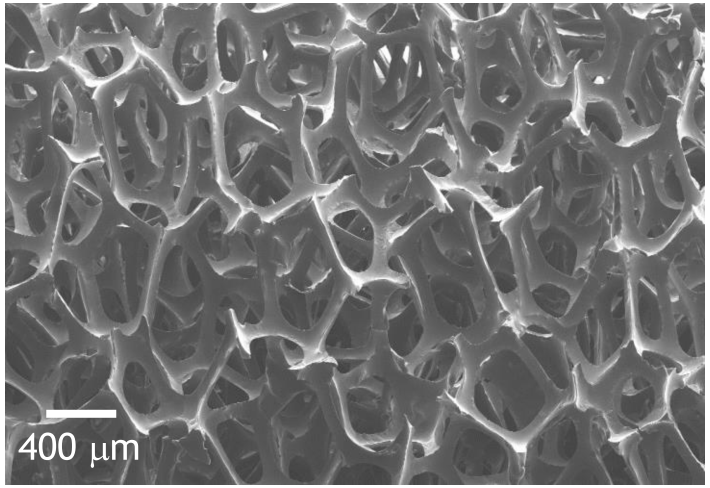


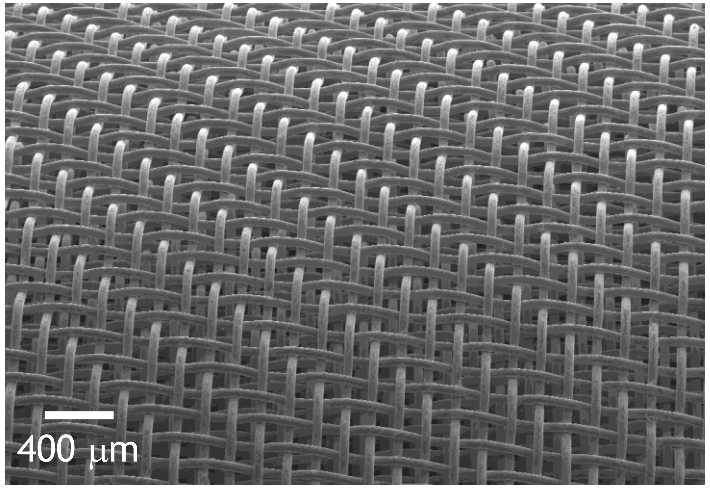
Combining GC Foam with Mo Mesh lowers charge overpotential!

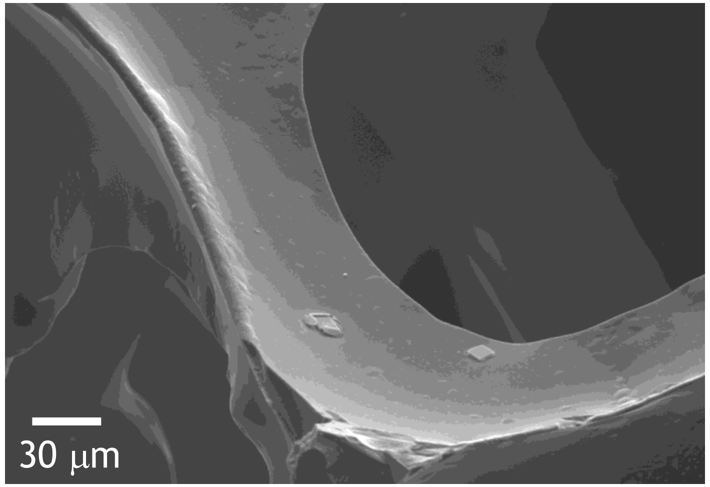
SEM Confirms Material Stability

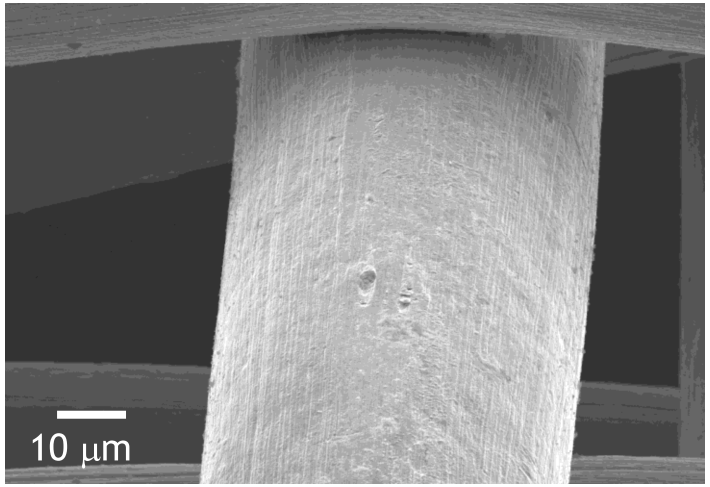
GC Foam

Mo Mesh





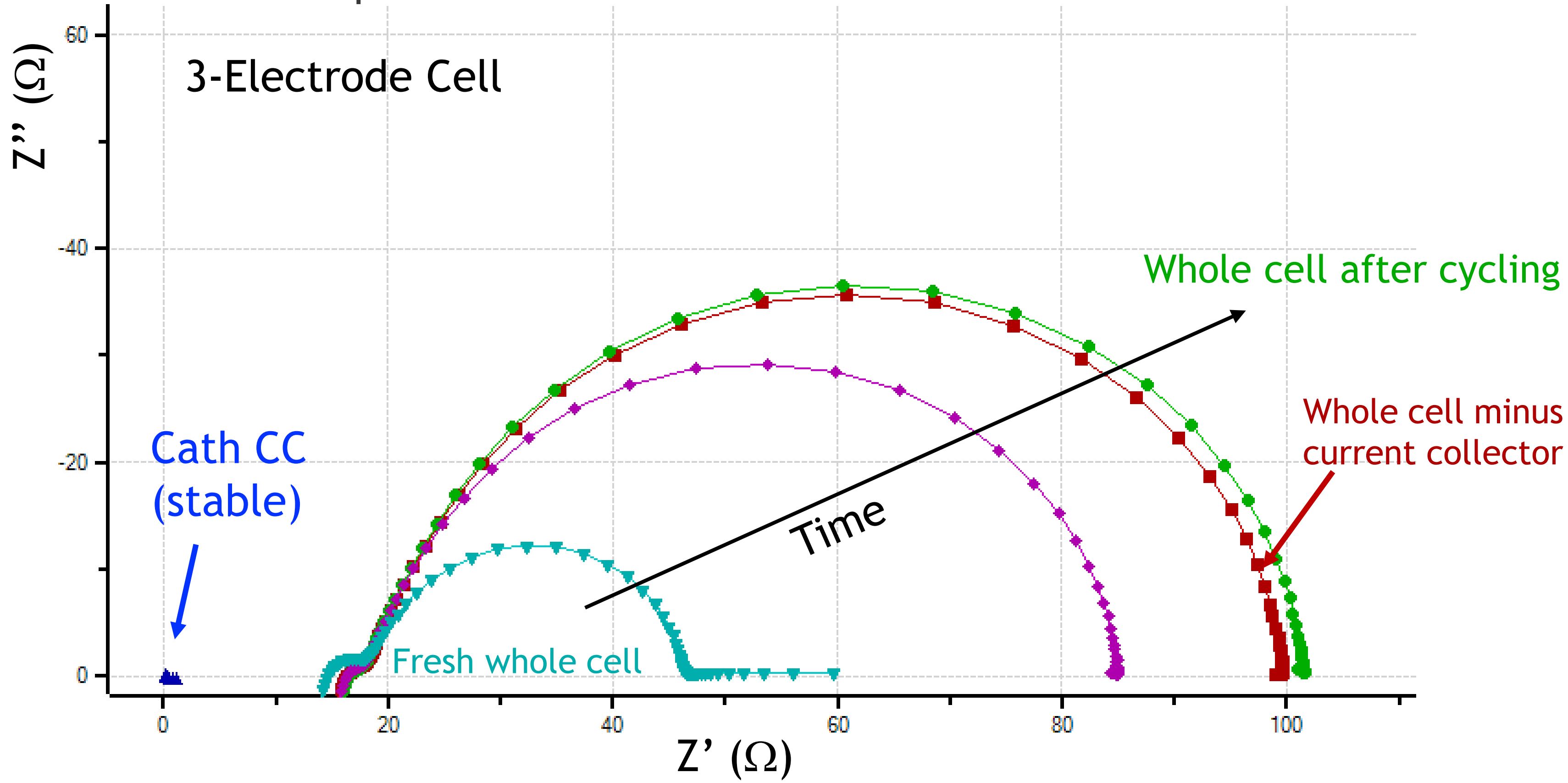




After cycling and cleaning, no evidence of microstructural changes.

A Surprising Discovery

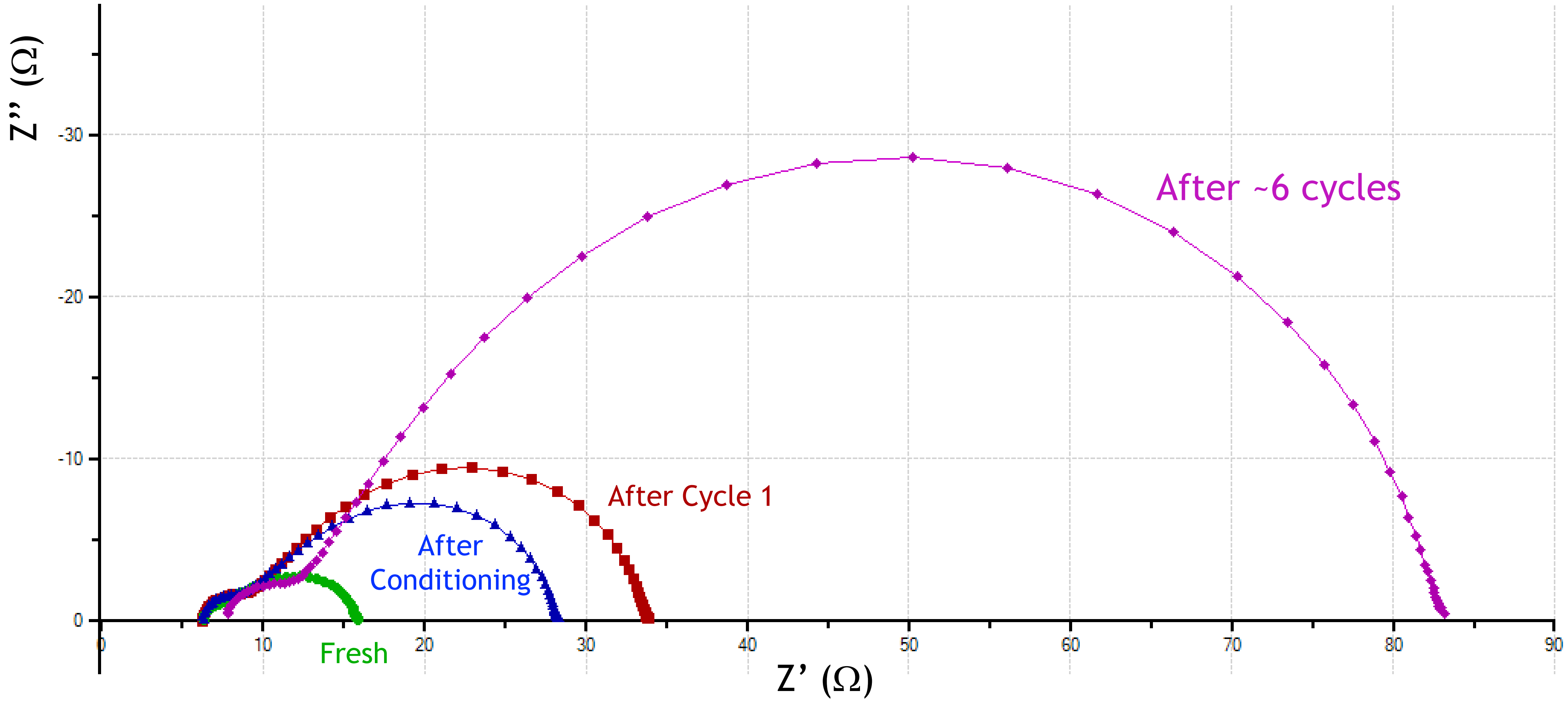
- We noticed that 3-electrode cells saw similar total impedance increase as full batteries
- Impedance on catholyte current collector remained small and stable
- Total cell increase was independent of WE



Analysis reveals that this impedance increase is on the CE/NaSICON interface!

110 °C, 3.0 Ah, 45% NaI/55% $AlCl_3$, 7.5% SOC build, GFD WE

Full Battery Impedance

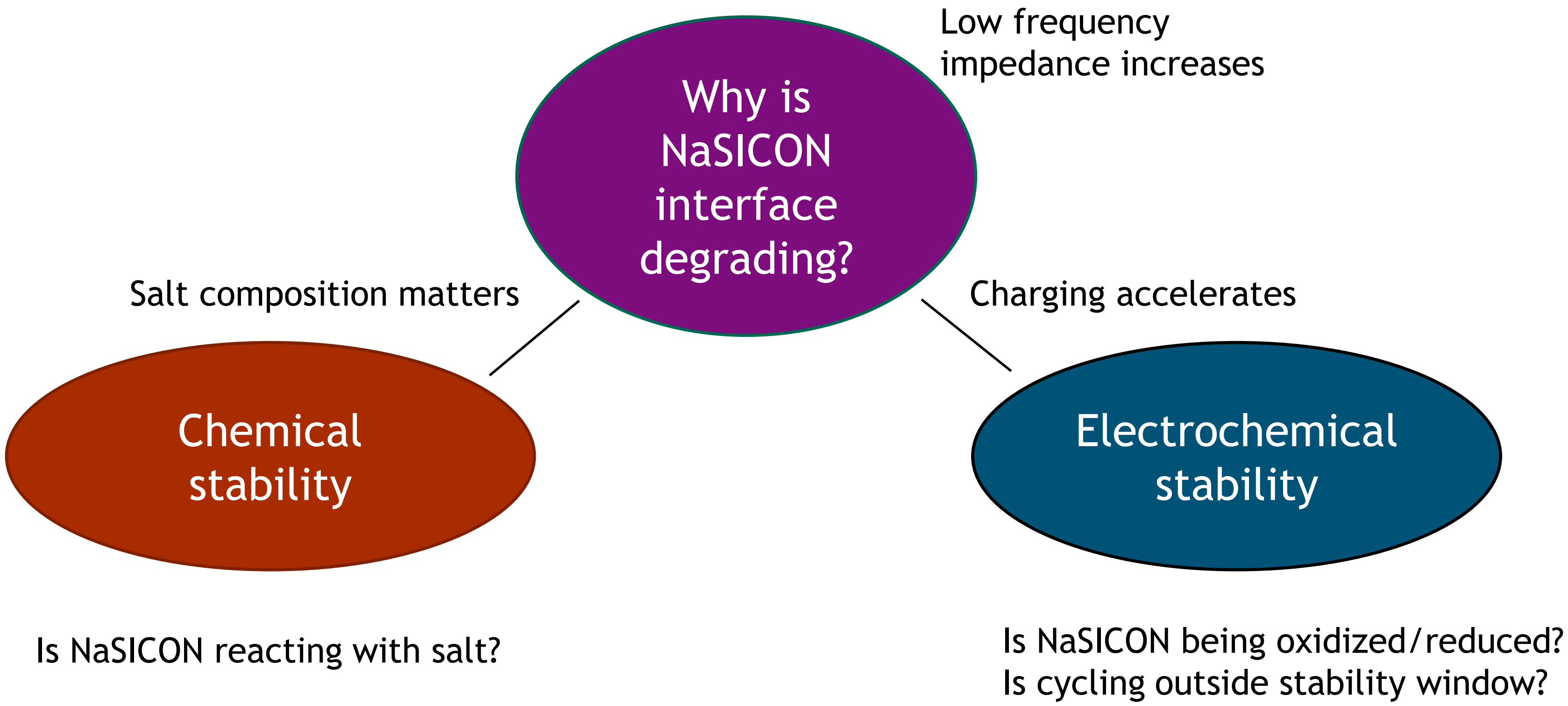


Batteries see same degradation as 3-electrode cell! Not current collector, but NaSICON/salt interface.

110 °C, 0.18 Ah, 45% NaI/55% $AlCl_3$, 7.5% SOC build, GFD WE

NaSICON Stability

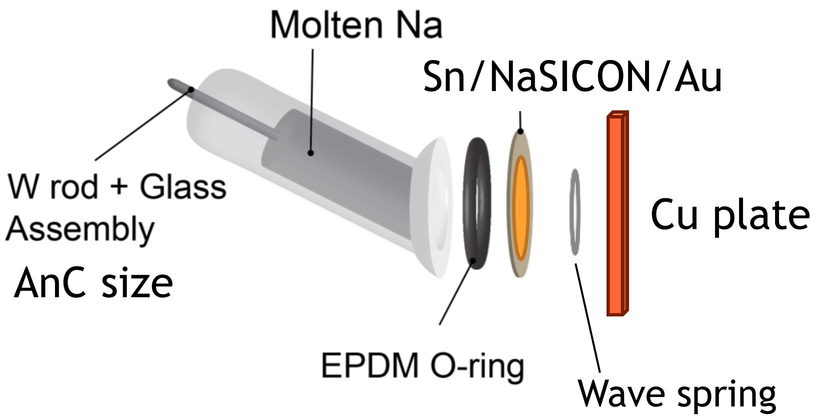
In Progress: NaSICON Degradation Analysis

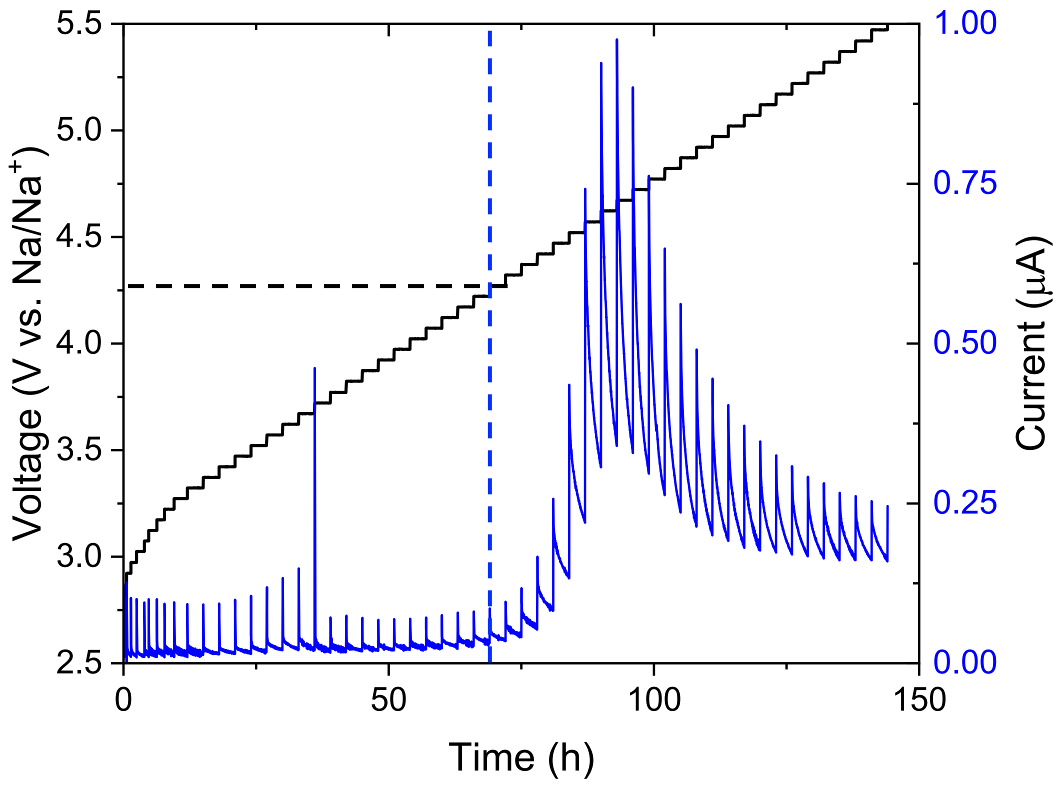


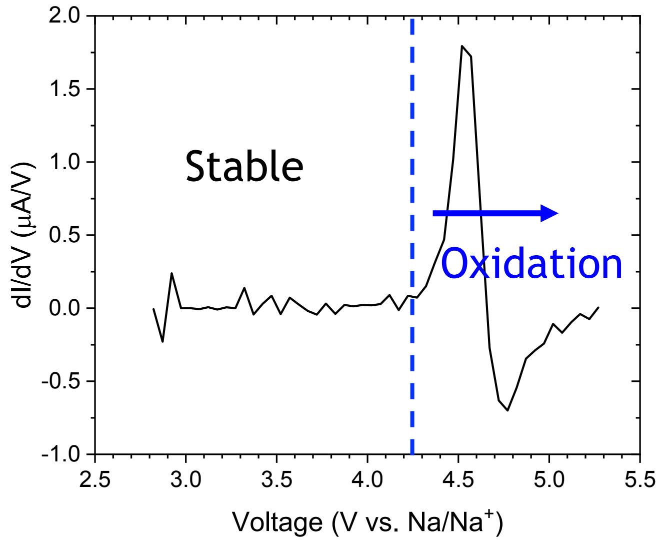
NaSICON Oxidative Stability

Potentiostatic Intermittent Titration Technique (PITT) to assess at what potential NaSICON begins to oxidize

Blocking Electrode







NaSICON begins to oxidize at ~ 4.25 V – above our V cutoff limit. Cycling outside Electrochem. Stability Window is not the issue.

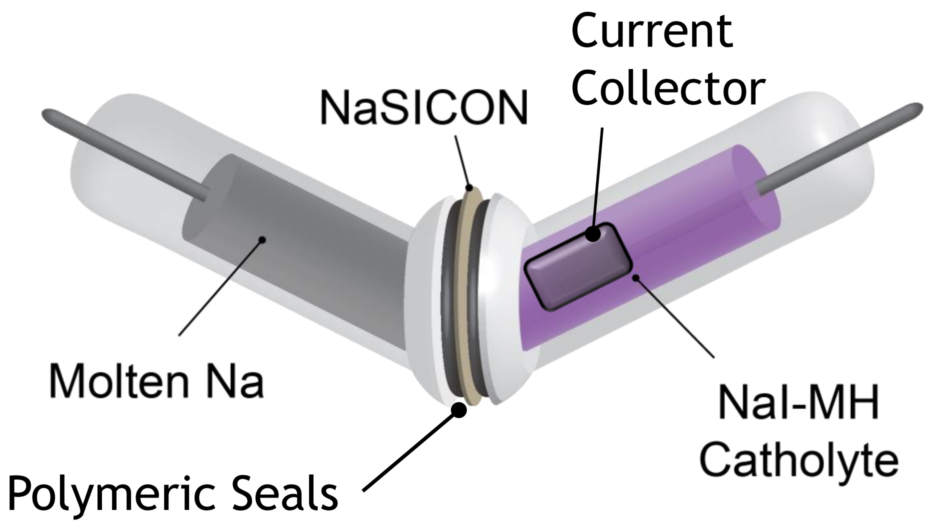
A.M. Maraschky, M.M. Meyerson, S.J. Percival, A.S. Peretti, E.D. Spoerke, and L.J. Small. *In Preparation.*

Chemical Stability Concerns

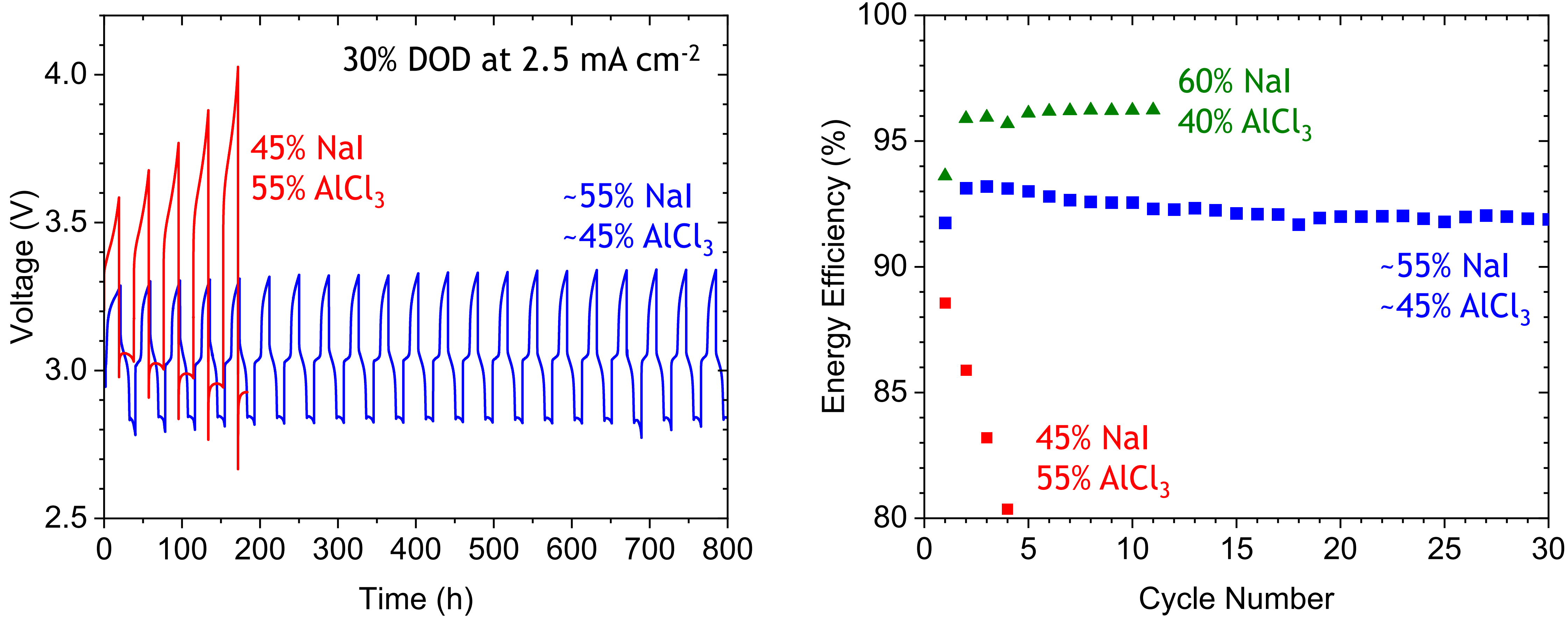
Remember, NaI-MX_3 forms a Lewis adduct

$GaCl_3$ is softer acid (more tightly associated with soft iodide base)

$AlCl_3$ as a harder acid could be attacking materials at the interface



Keep It Basic: Cycling Improves with More NaI in Catholyte



Initial results suggest cycling is more stable when NaI is used at >50 mol%.
Hypothesis: catholyte is less acidic, and therefore less aggressive to materials.

110 °C, 7.5% SOC build, GFD current collector

Summary and Next Steps

- Low-temperature molten sodium batteries are viable for low-cost, large-scale energy storage
- Glassy carbon: best material tested for charge (I^- oxidation): most stable, high current
- Molybdenum: best material tested for discharge (I_3^- reduction): lowest overpotential
- Concept: combine the two materials to take advantage of different catalytic properties or I_2/I_3^- adsorption constants
- High surface area current collectors showed no degradation via SEM
- Cell performance loss observed in cells with acidic $AlCl_3$ melts (<50% NaI); not outside ESW – further characterization in progress
- Next: rate test full batteries with HSA current collectors, aiming for high current densities

Acknowledgements

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Questions?

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