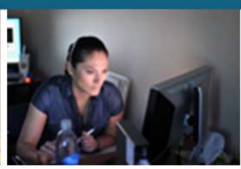
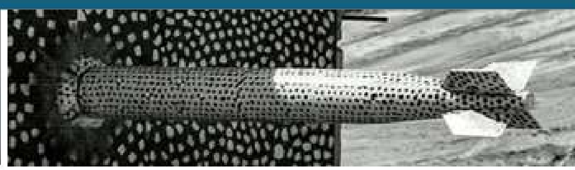
SAND2022-13827C

Sandia National Laboratories

Optimizing the Current Collector for Sodium Iodide-Metal Halide Catholytes in Low-Temperature Molten Sodium Batteries

242nd Electrochemical Society Meeting, L02-2135

October 13, 2022

PRESENTED BY

Adam Maraschky

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

OFFICE OF ELECTRICITY
ENERGY STORAGE PROGRAM

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

SAND2022-XXXX PE

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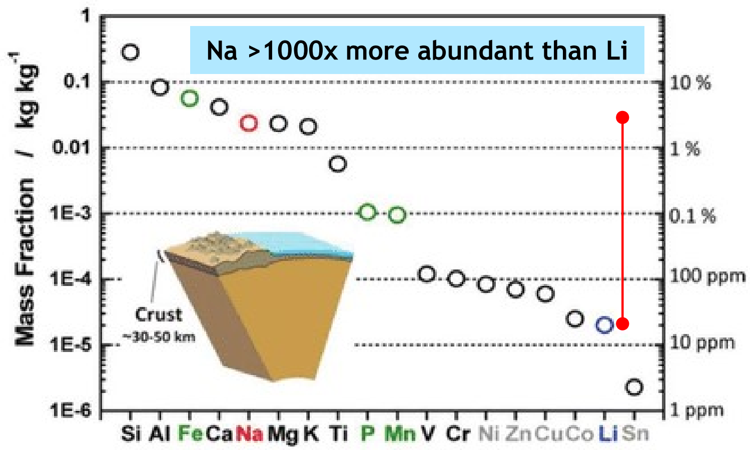
New Energy Storage Technologies are Critically Needed

- Energy storage will play an increasingly important role!
- Materials should be cost-effective, secure, and sustainable
- **Large scale batteries must be affordable and safe**

designnews.com



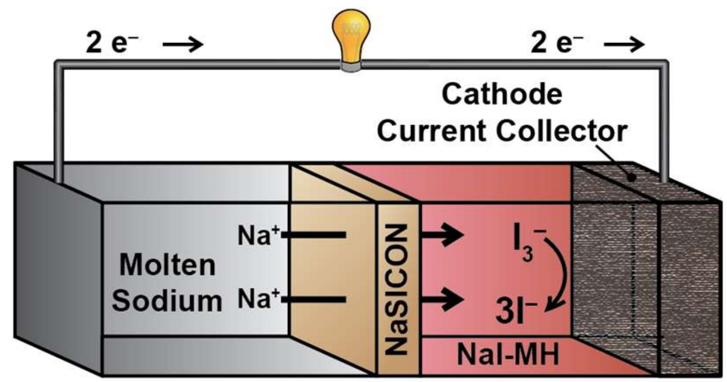
Y.E. Durmus et al. Adv. Energy Mater. 2000089 (2020).

Our Approach

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

Attractive for resilient and reliable grid-scale energy storage:

- Employ earth-abundant materials (Na, Al, Cl, I)
- Molten Na: no dendrites up to 100 mA cm^{-2}
- NaSICON separator, Na^+ conductor



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

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

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

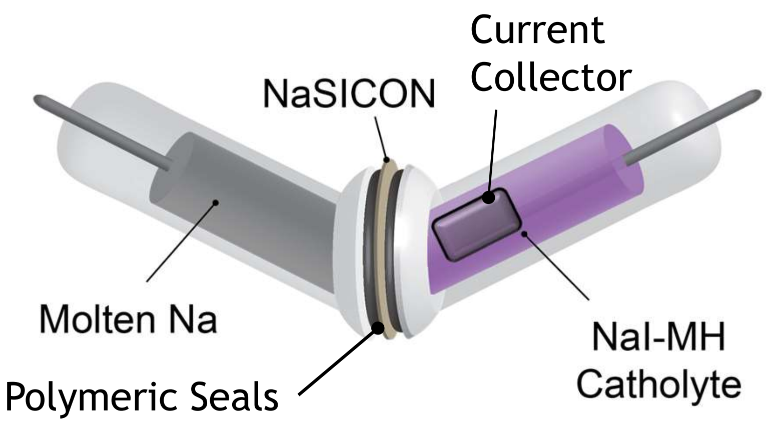
L. J. Small, A. Eccleston, J. Lamb, A. C. Read, M. Robins, T. Meaders, et al. *J. Power Sources,* **360**, 569 (2017).

Why 'Low Temperature'?

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

This newer chemistry operates near sodium's melting point (98 °C), providing:

- Lower Cost
- Greater reliability
- Lower Start-up Energy



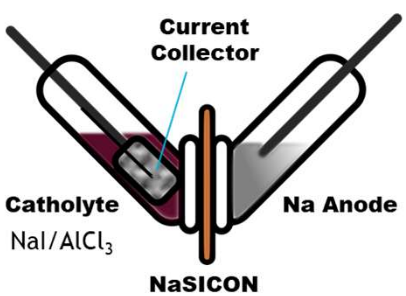
While lower temperatures can improve cost and reliability, new materials challenges arise. Here, we focus on the catholyte current collector.

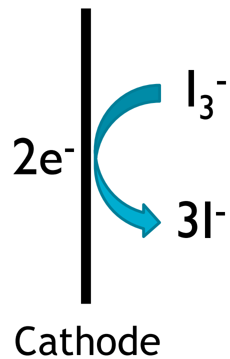
M. M. Gross, L. J. Small, A. S. Peretti, S. J. Percival, M. A. Rodriguez and E. D. Spoerke. *J. Mat. Chem. A*, **8**, 17012 (2020).

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

- Phase behavior, speciation, and Lewis acidity depend on composition of $NaI/AlCl_3$ mixture
- Composition changes with state of charge (SoC)





$NaI/AlCl_3$ Phase Diagram

Temperature (°C)						
120	S+L	L	L	L	L + S	L + S
110	S+L	L	L	L + S	L + S	L + S
100	?	S + L	L	L + S	S + L	S + L
90	?	S + L	S + L	S + L	S + L	S + L
	25	35	40	45	50	55

Composition (% NaI)

Legend

Mostly Solid | Mostly Liquid | Liquid

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).

Current Collector Optimization

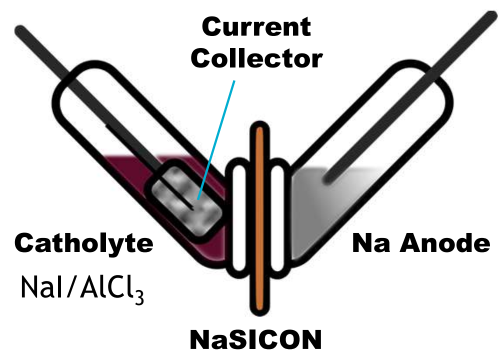
In order to increase cycling rates, redesign current collector for cathode

What material?

Desired: inert in molten salt and cost-effective:

- Molybdenum (Mo)
- Tungsten (W)
- Tantalum (Ta)
- Glassy Carbon (GC)

More catalytic?
Or…
More stable?



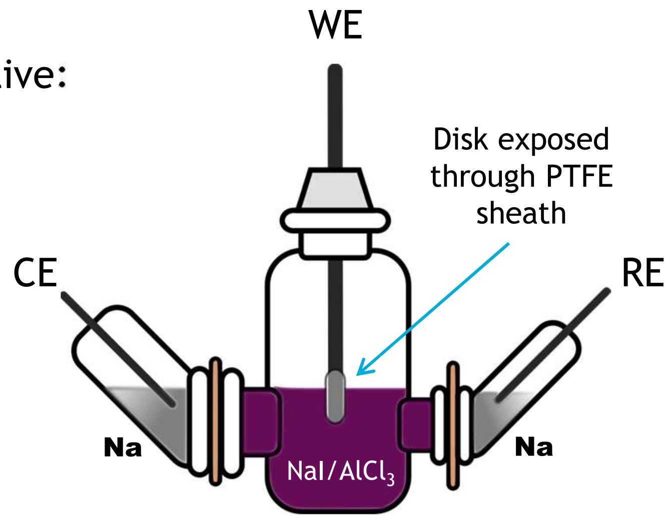
Will show:

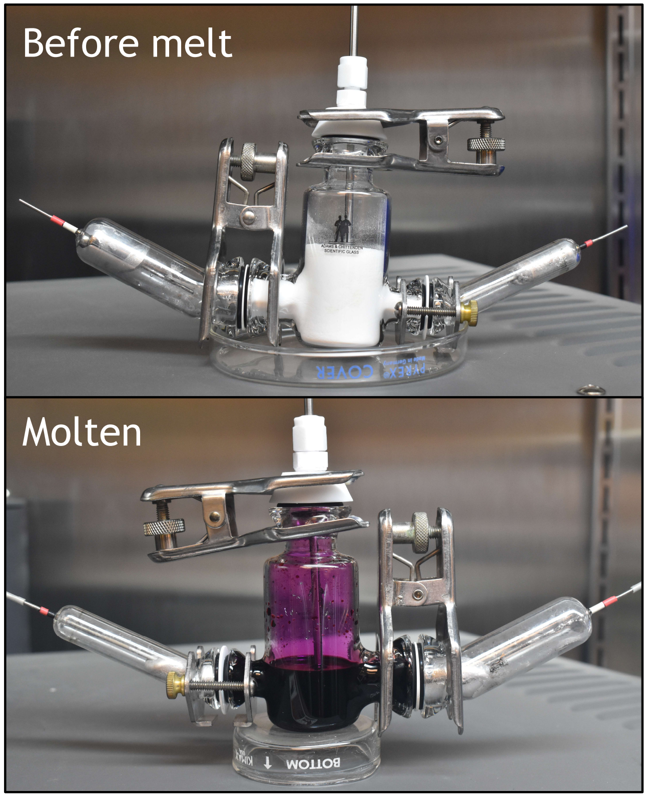
Differences in charge transfer kinetics are minor compared to surface stability.

3-Electrode Cell Design

In a battery: difficult to tell what component contributes most to overpotential.

Alternative:

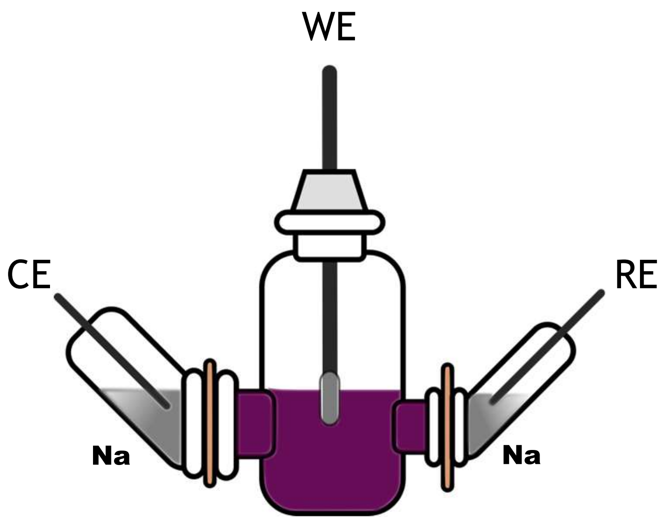




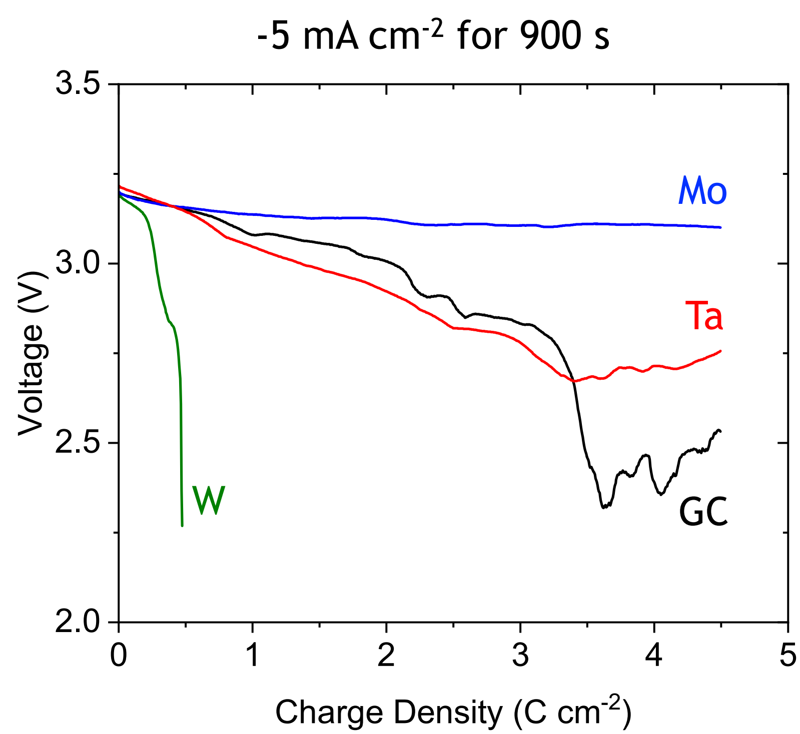
Benefits:

- Interchangeable electrodes; control area & material
- Probe specific interfaces
- Stable composition (excess salt volume, capacity)

Materials Selection: Discharge on Disk Electrodes



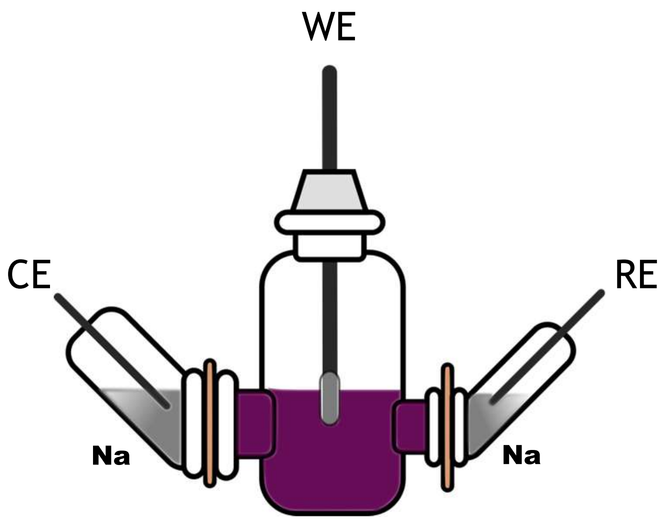
110 °C, 45% NaI/55% $AlCl_3$, 7.5% SOC build



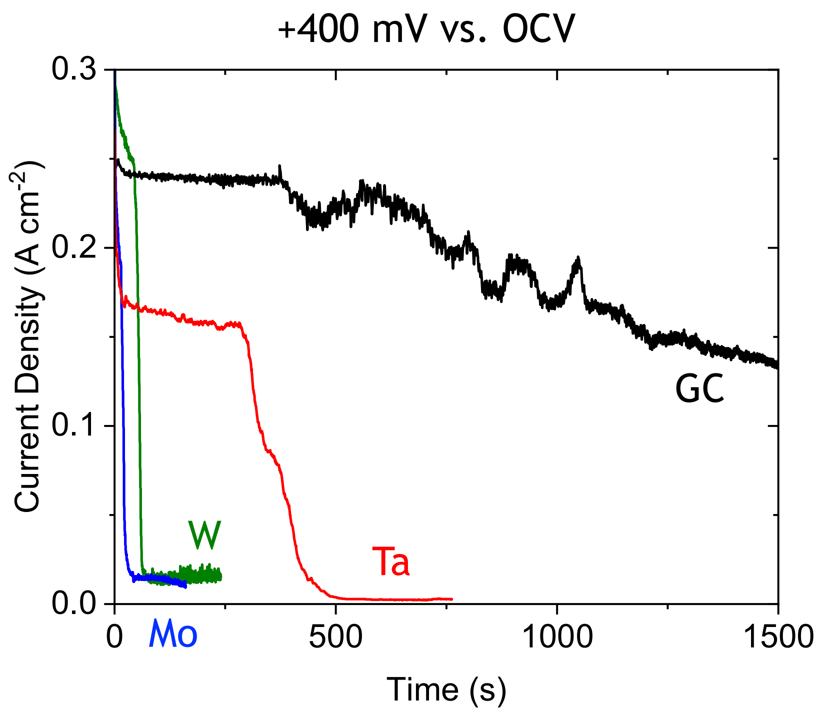
In acidic catholyte, Mo had the most stable voltage on discharge.

A.M. Maraschky et al. Tailoring Electrode Materials for Iodide/Triiodide Redox in Low-Temperature Molten Sodium Batteries. (2022) *In Preparation*.

Materials Selection: Charge on Disk Electrodes



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

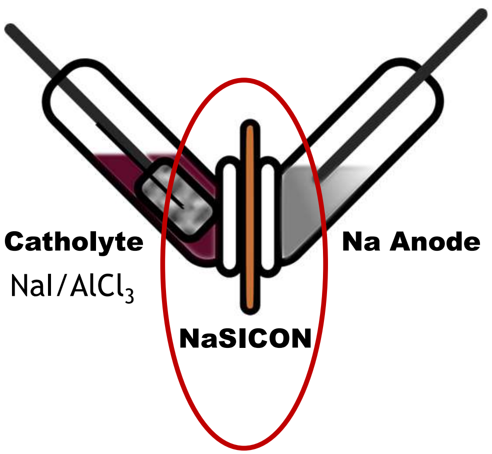


In acidic catholyte, GC had the highest, most stable current at positive potential.

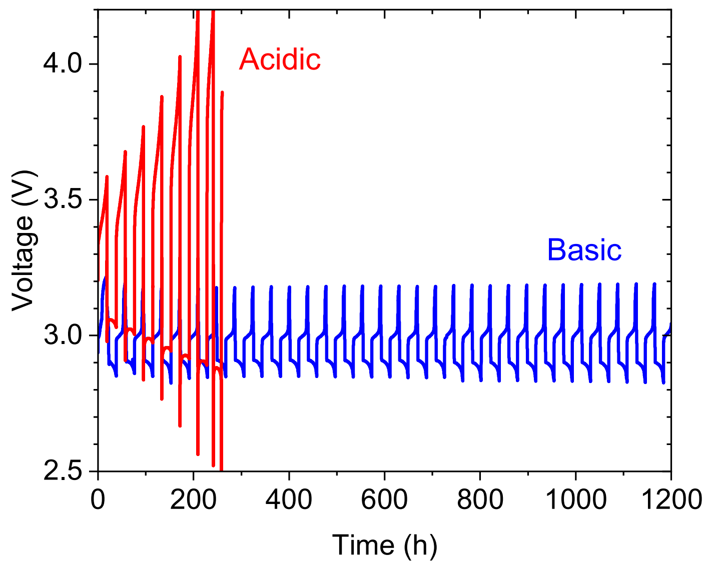
A.M. Maraschky et al. Tailoring Electrode Materials for Iodide/Triiodide Redox in Low-Temperature Molten Sodium Batteries. (2022) *In Preparation*.

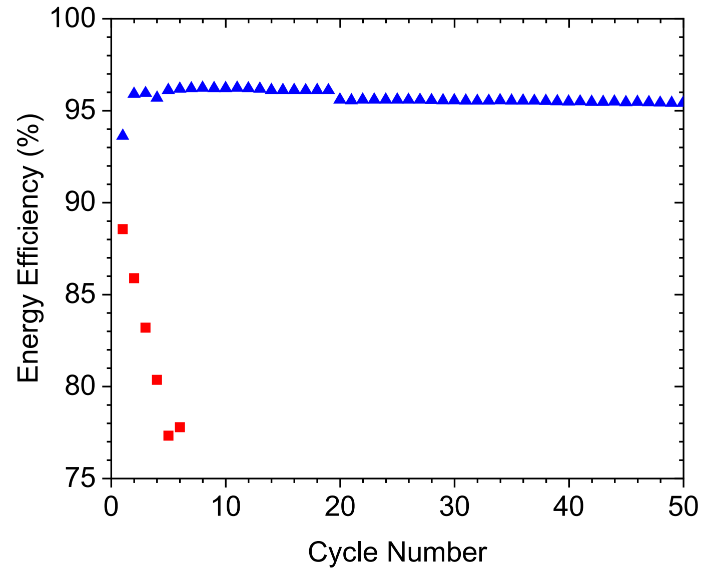
Basic Catholyte: Better for NaSICON Separator

For batteries, salt composition had a big impact on performance



Acidic: >50 mol% $AlCl_3$
Basic: <50 mol% $AlCl_3$



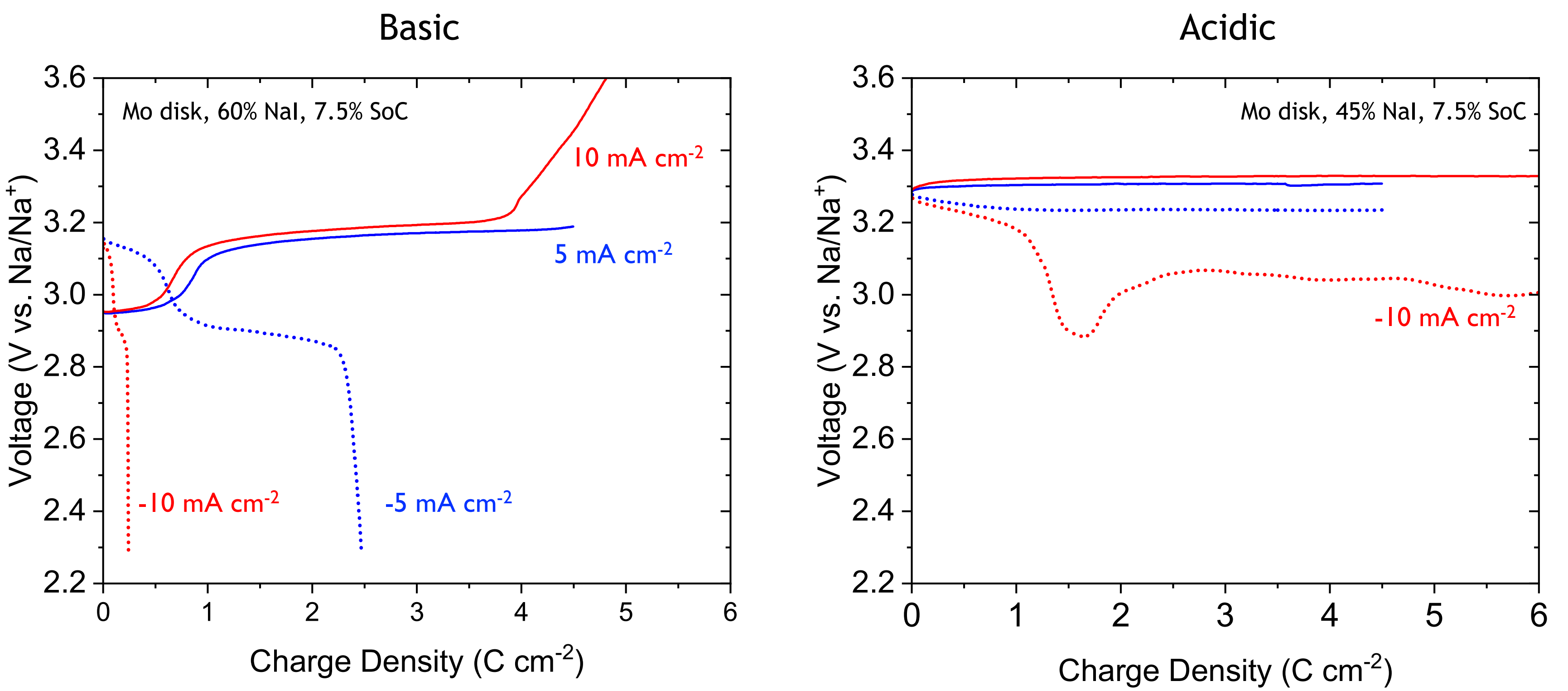


110 °C, 2.5 mA cm^{-2}, 7.5% SOC build, GFD current collector

Cycling life is longer when catholyte is Lewis Basic.
Basic catholyte is less aggressive to NaSICON.

A.M. Maraschky et al. Impact of Catholyte Lewis Acidity at the Molten Salt-NaSICON Interface in Low-Temperature Molten Sodium Batteries. *J. Phys. Chem. C.* (2022) *In Revision*.

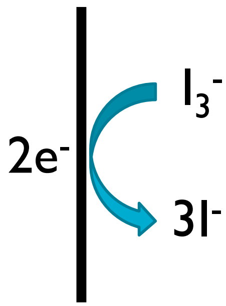
But… Greater Electrode Instability in Basic Molten Salt



In basic catholyte, electrode instability on charge and discharge is much more severe.

A.M. Maraschky et al. Tailoring Electrode Materials for Iodide/Triiodide Redox in Low-Temperature Molten Sodium Batteries. (2022) *In Preparation*.

What prevents stable discharge? Especially in basic catholyte



Possible reasons:

1. Mass transport limitations (low I_2/I_3^- concentration)

2. Electrode surface change, such as precipitation, adsorption, or passivation

$NaI/AlCl_3$
Phase Diagram

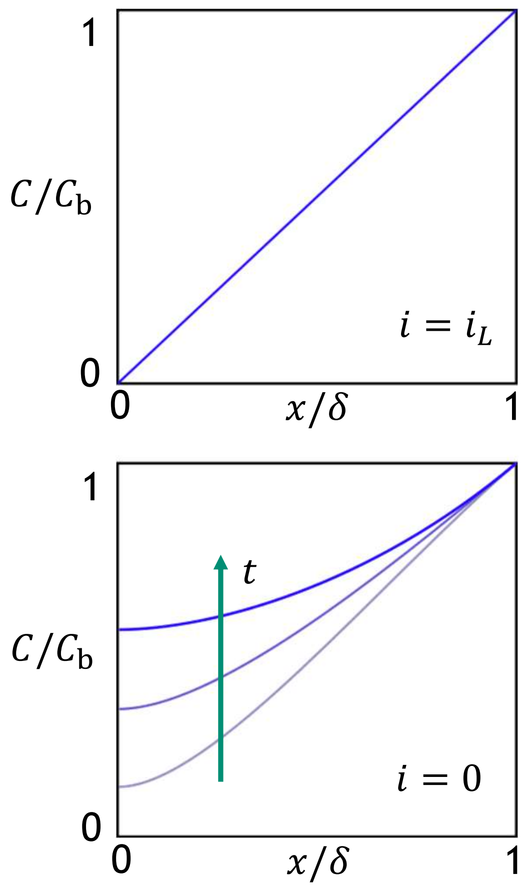
Temperature (°C)						
120	S+L	L	L	L	L + S	L + S
110	S+L	L	L	L + S	L + S	L + S
100	?	S + L	L	L + S	S + L	S + L
90	?	S + L	S + L	S + L	S + L	S + L
	25	35	40	45	50	55

Composition (% NaI)

Legend

Mostly Solid (green) · Mostly Liquid (yellow) · Liquid (red)

Mass Transport Limit? Check Concentration Relaxation



If reaction is at mass transport limit…

$$\tau = \frac{\delta^2}{\mathcal{D}} \sim 10\ s$$

Transient effects should 'reset'
With concentration relaxation

$\delta \sim 0.01\ \mathrm{cm}$
$\mathcal{D} \sim 10^{-5}\ \mathrm{cm^2\ s^{-1}}$

Can diffusion refresh the electrode? Current interrupt

Discharge

-5 mA cm^{-2}
up to V_{cutoff}

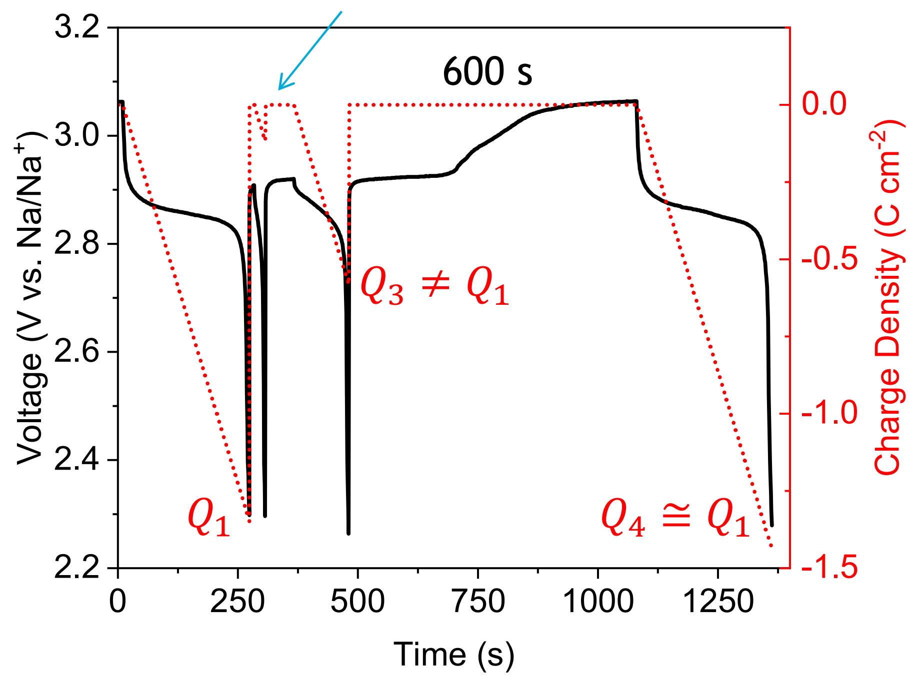
Relax Concentration Gradient

$$\tau = \frac{\delta^2}{\mathcal{D}} \sim 10\ s$$

Discharge

$$Q_n = Q_1?$$

Increasing 'relaxation' time beyond τ



Relaxation time suggests a species is slowly removed from the electrode surface.

A.M. Maraschky et al. Tailoring Electrode Materials for Iodide/Triiodide Redox in Low-Temperature Molten Sodium Batteries. (2022) *In Preparation*.

Mo disk, 60% NaI, 50% SoC

What prevents stable discharge? Especially in basic catholyte

Cathode

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

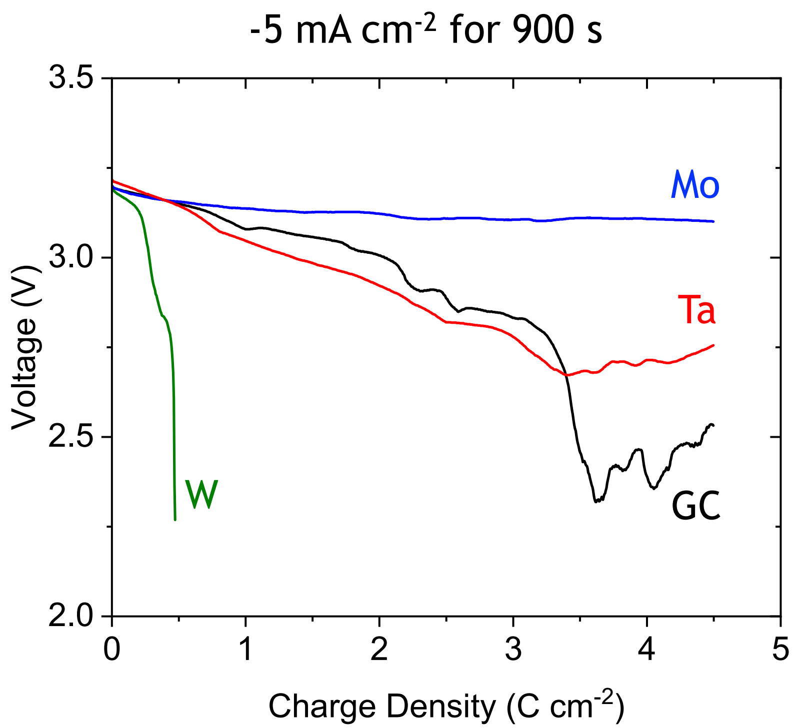
Possible reasons:

1. ~~Mass transport limitations (low I_2/I_3^- concentration)~~

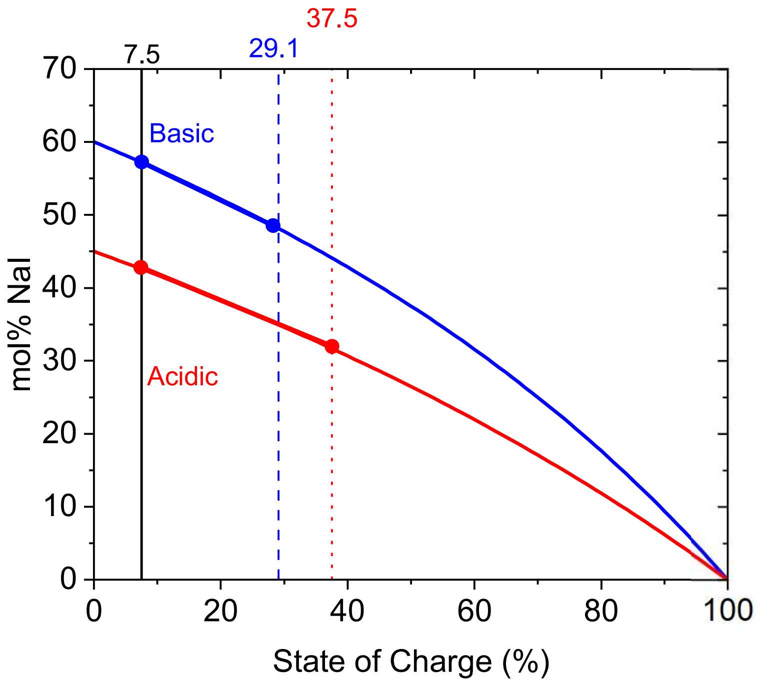
   - Relaxation: ~600 s
   - Stability depends on electrode material

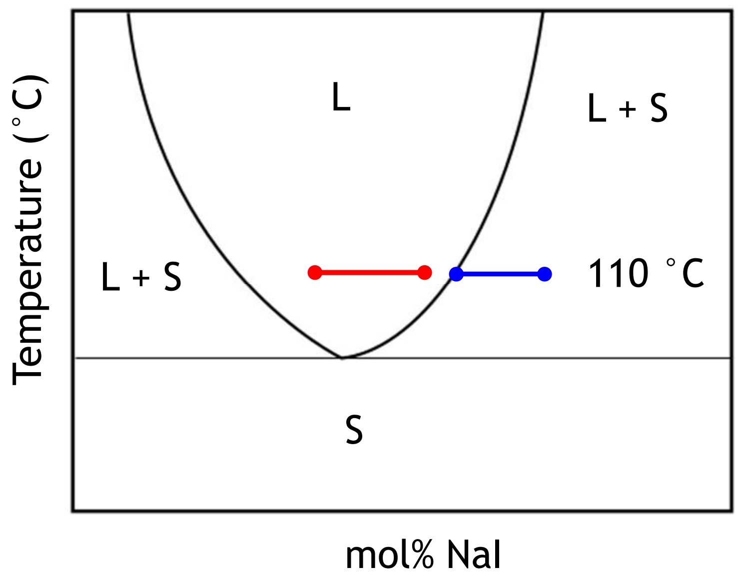
2. Adsorption or local phase instability on electrode surface
   - NaI film covers surface?
   - ~~Another species adsorbs?~~

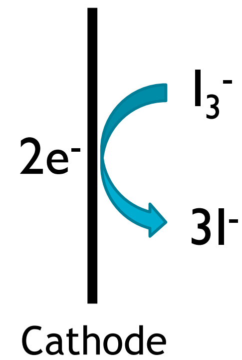
   Too thick (>>100s of $\mu C/cm^2$)



Phase Stability Depends on Composition



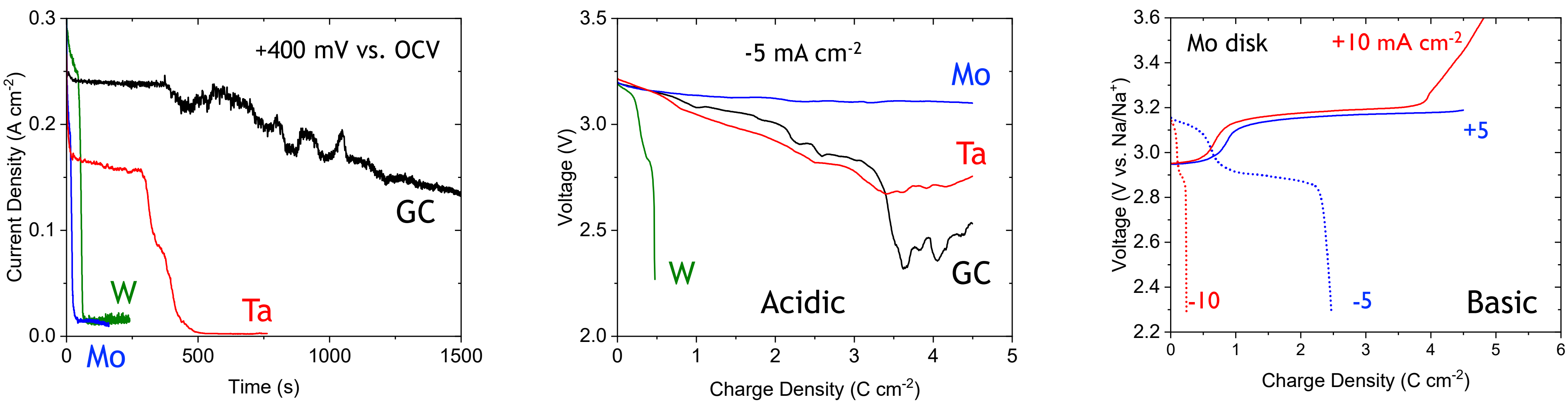




Discharge may precipitate locally high iodide concentrations on electrode.
Basic catholyte cycles in phase diagram where NaI solids are stable.

Conclusions

- Phase stabilities limit the current and charge that an electrode can sustain in $NaI/AlCl_3$
- Different materials show large differences in phase stability on electrode surfaces
- Basic catholyte shows greater local phase-instability, possibly precipitating NaI on the electrode surface during discharge



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Acknowledgements

We thank the DOE Office of Electricity, Energy Storage Program managed by Dr. Imre Gyuk for funding this work!

OFFICE OF ELECTRICITY
ENERGY STORAGE PROGRAM

Questions?

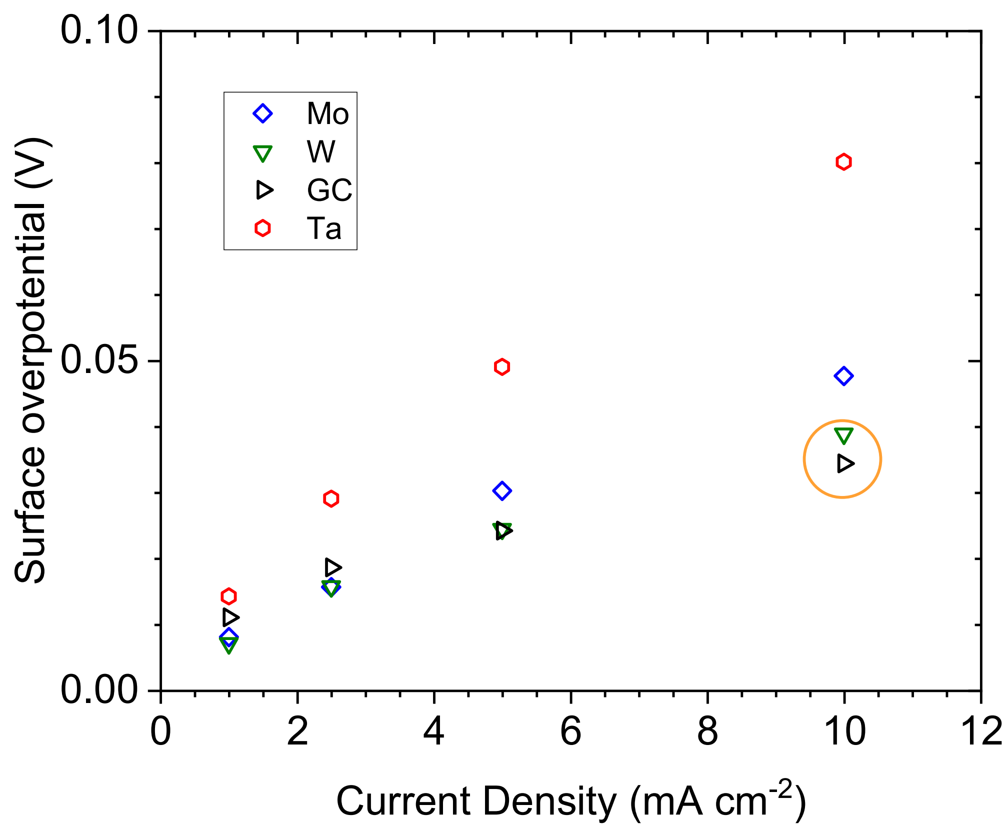
Adam Maraschky
ammaras@sandia.gov

Backup Slides

Electrode Polarization on Charge

$$\eta_s = V - E_0 - iR_\Omega$$

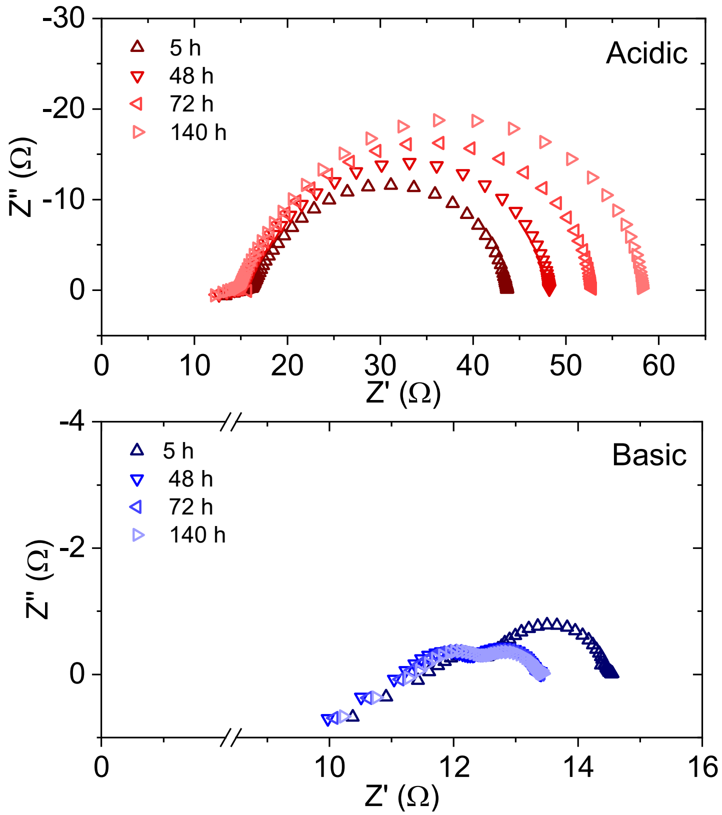
Final V used:
After 900 s

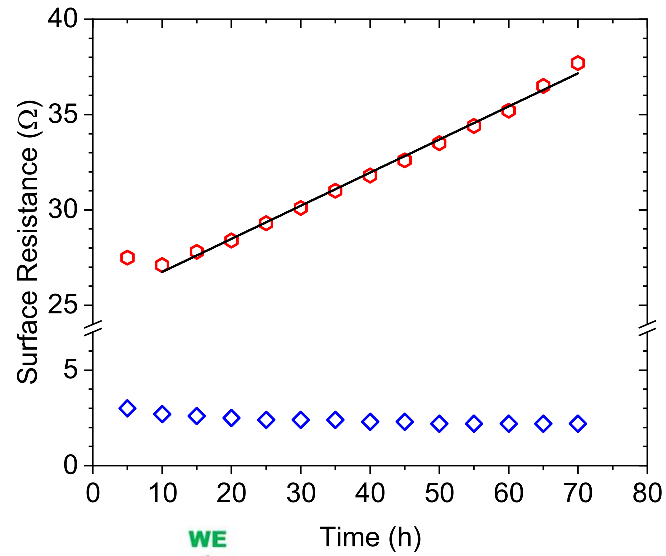


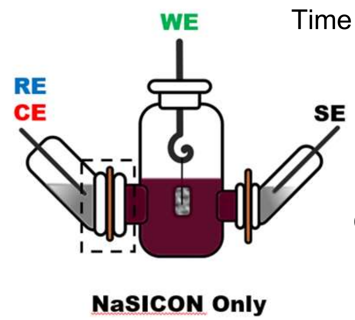
GC had the lowest overpotential on charge at +10 mA cm^{-2}.

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

NaSICON Stability Probed with EIS in 3-Electrode Cell







Electrode configuration

Surface resistance on NaSICON interface increased only in acidic catholyte.

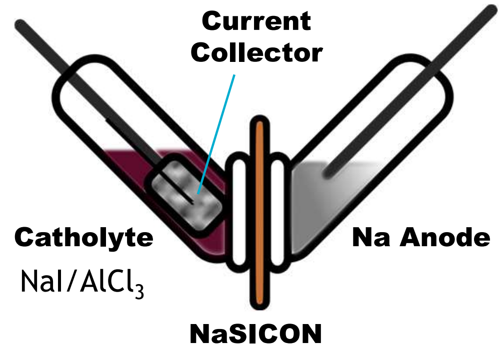
A.M. Maraschky et al. Impact of Catholyte Lewis Acidity at the Molten Salt-NaSICON Interface in Low-Temperature Molten Sodium Batteries. *J. Phys. Chem. C.* (2022) *In Revision*.

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

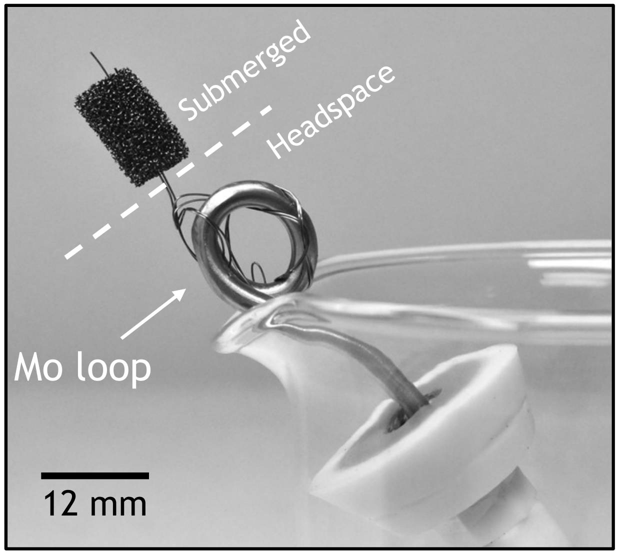
$$i = \frac{I}{A}$$

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

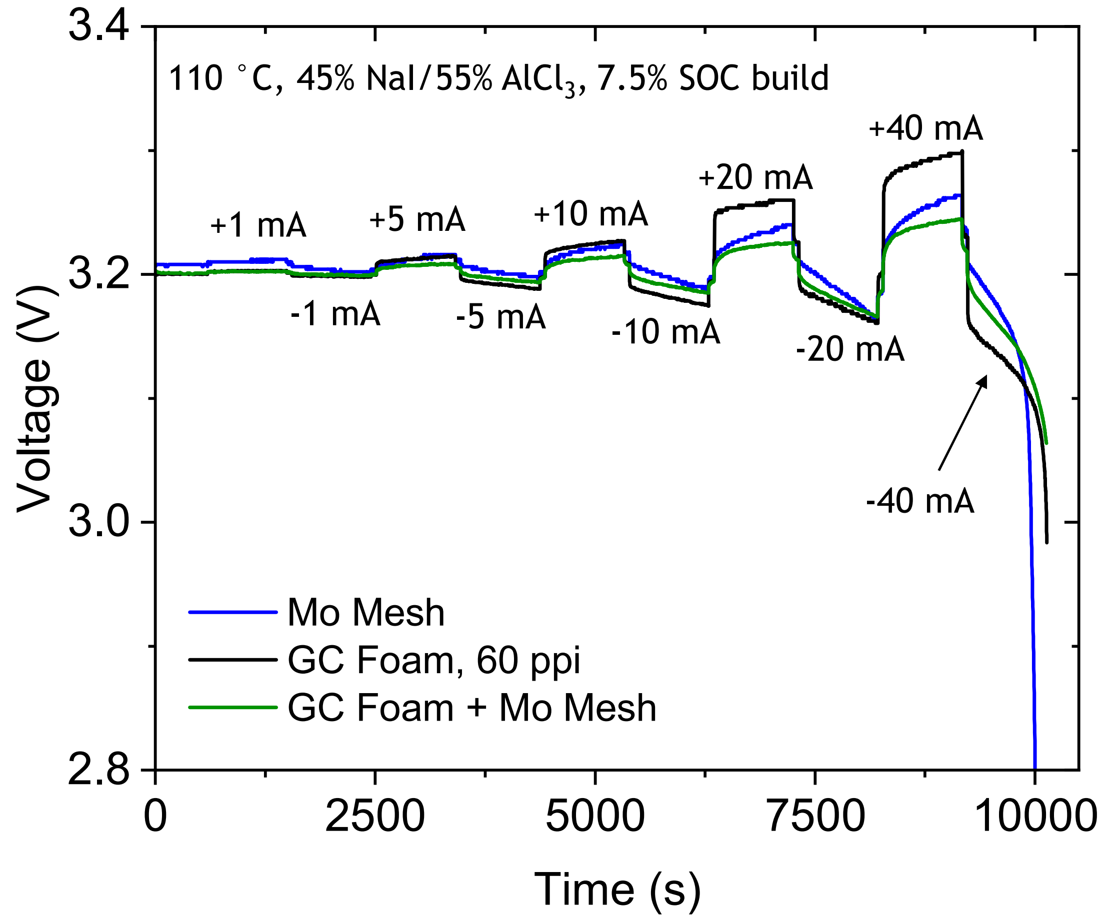
Electrochemically active surface area modulates overpotential (voltage inefficiency) for given current.

Evaluation of High Surface Area Materials

GC Foam



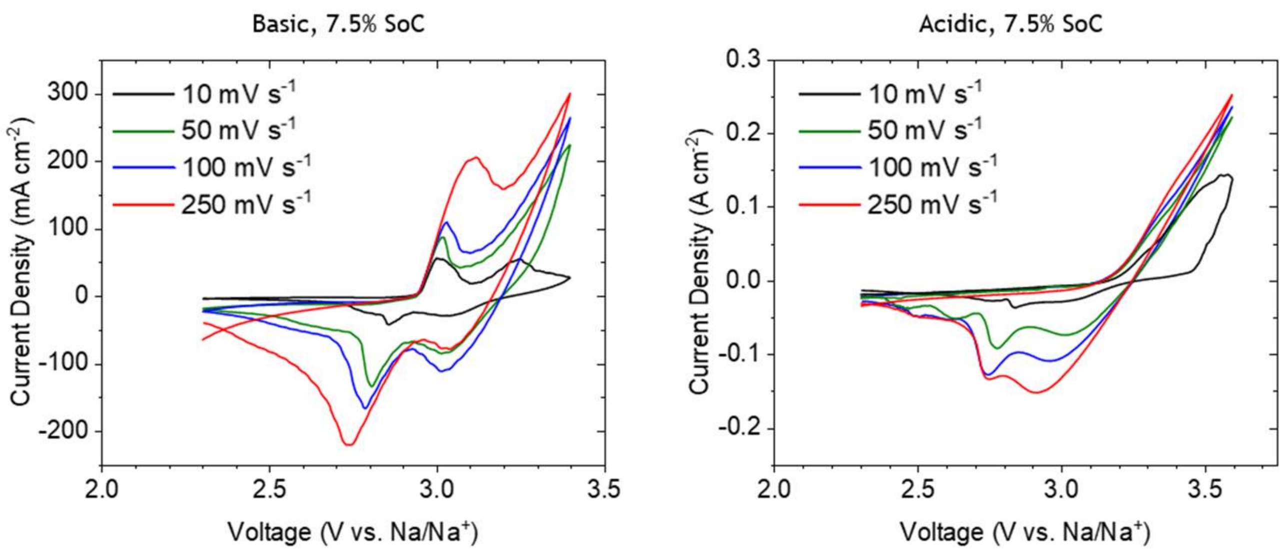
Mo Mesh



Combining GC Foam with Mo Mesh lowers charge overpotential!

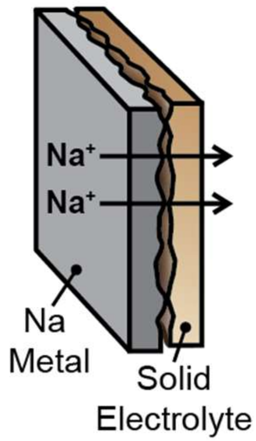
A.M. Maraschky et al. Tailoring Electrode Materials for Iodide/Triiodide Redox in Low-Temperature Molten Sodium Batteries. (2022) *In Preparation*.

Cyclic Voltammetry Reveals a New Peak



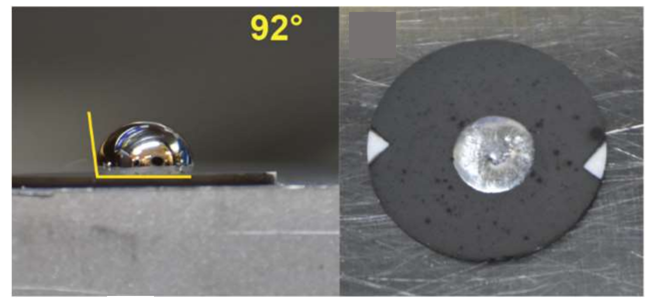
Tin Coating Improves Molten Sodium Anode

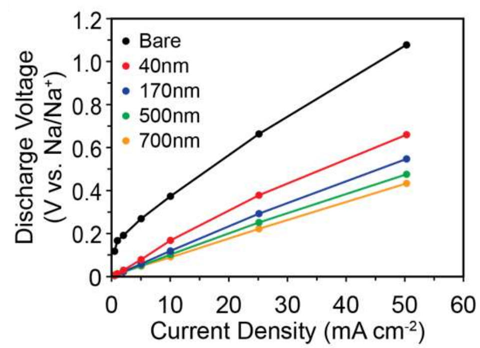
Bare NaSICON



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

Sn Coating on NaSICON



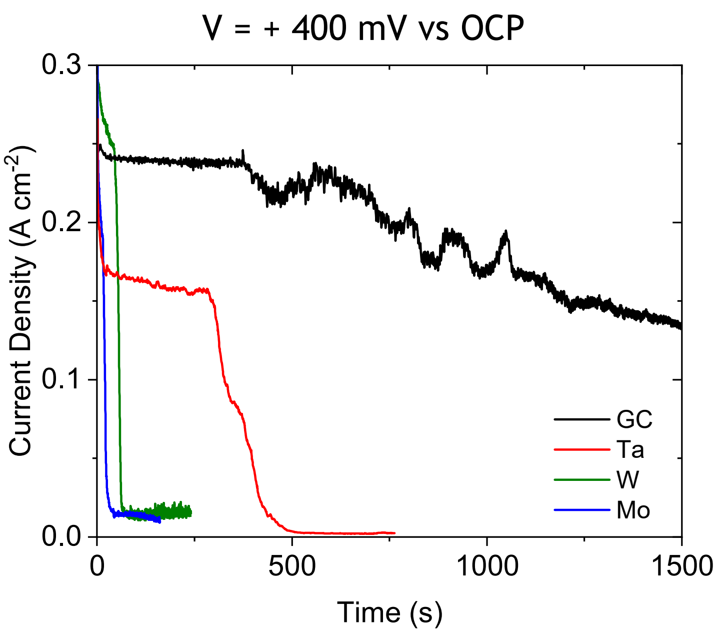


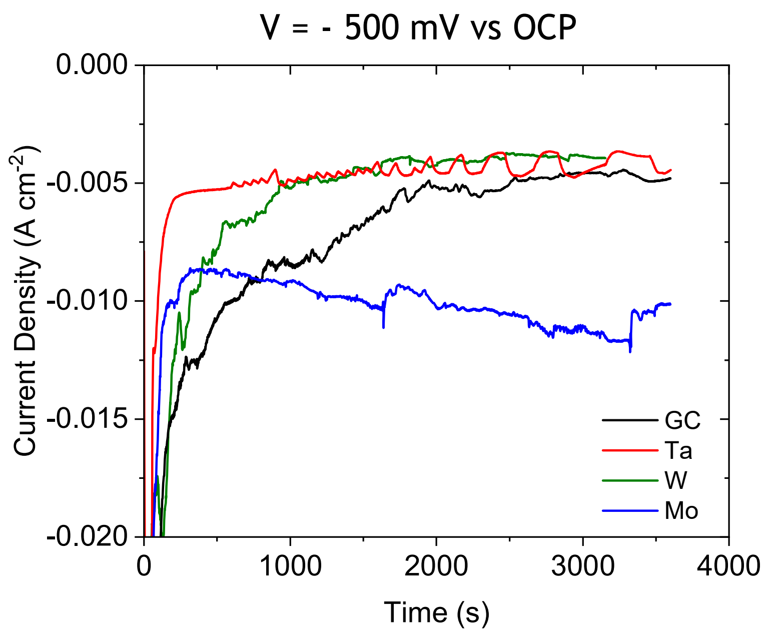
Sn coating on NaSICON decreases resistance at the sodium-separator interface.

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).

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.

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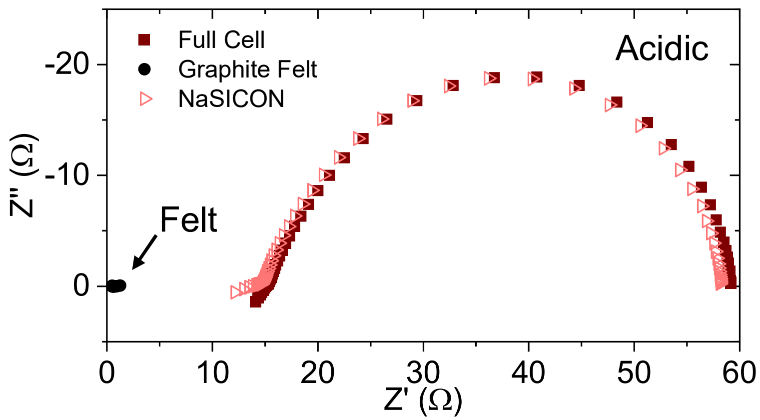
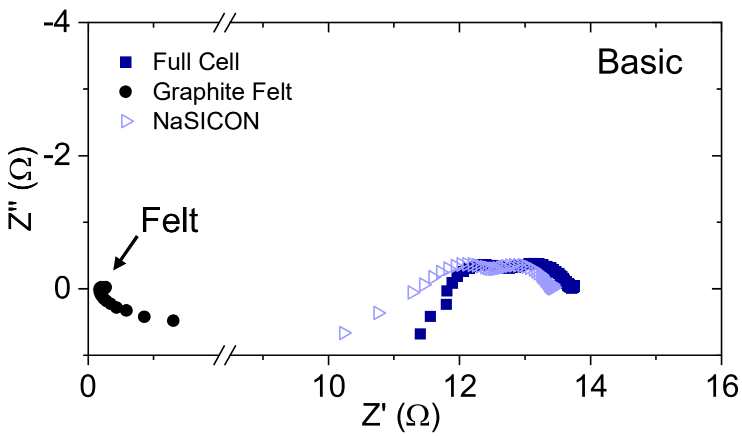
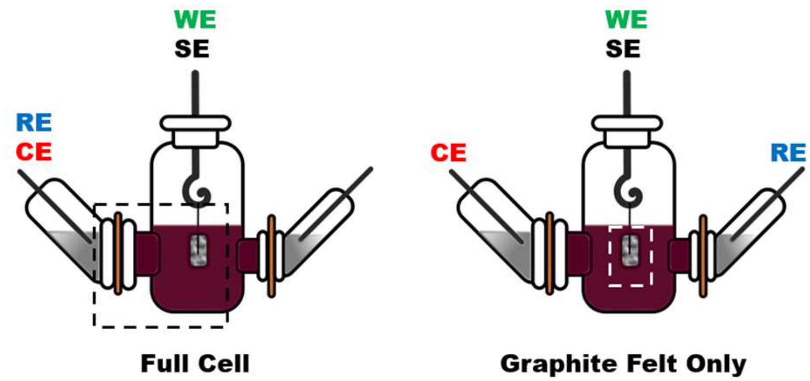
110 °C, 45% NaI/55% $AlCl_3$, 7.5% SOC build

Probing Different Interfaces after Salt Exposure





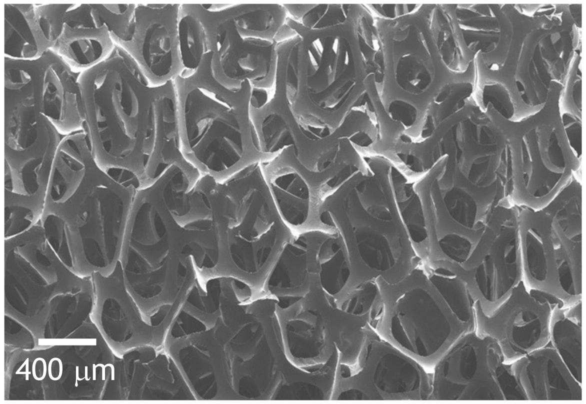


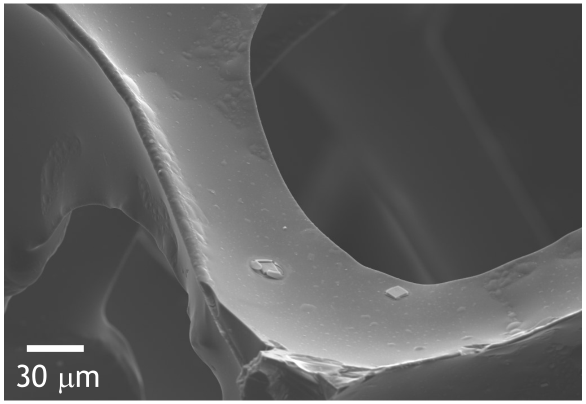
NaSICON interface is the site of the impedance increase in acidic catholyte

140 h exposure

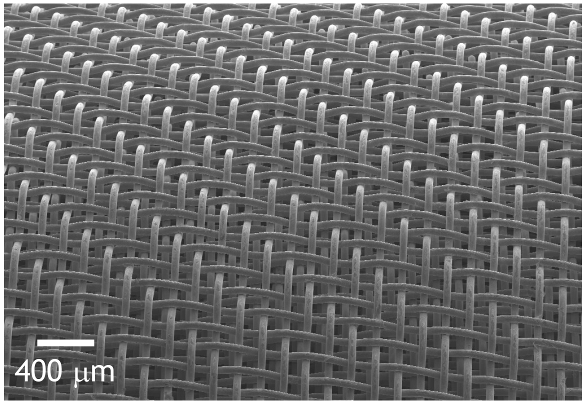
SEM Confirms Material Stability

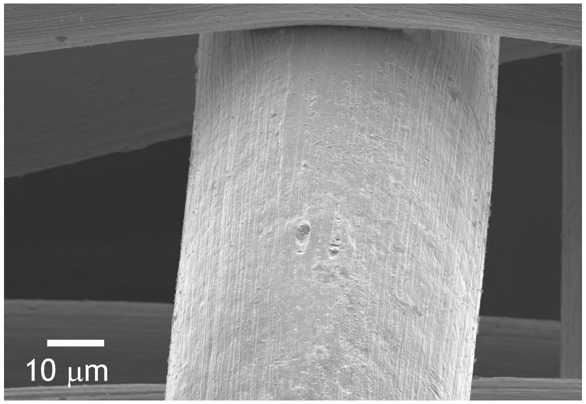
GC Foam





Mo Mesh





After cycling and cleaning, no evidence of microstructural changes.

A.M. Maraschky et al. Tailoring Electrode Materials for Iodide/Triiodide Redox in Low-Temperature Molten Sodium Batteries. (2022) *In Preparation*.