Characterization and Modeling of an All-Aqueous Thermally Regenerative Redox Flow Battery

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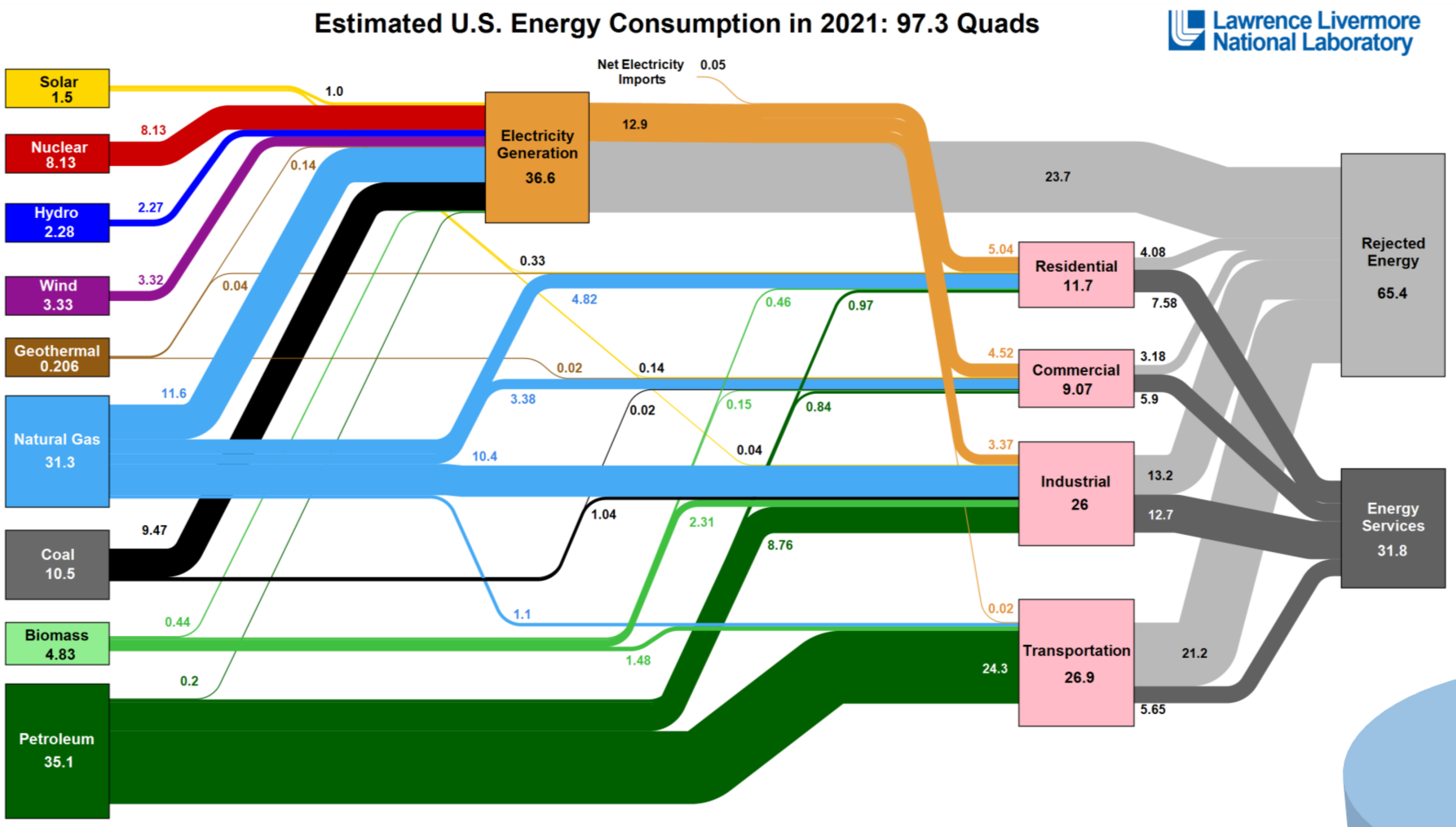
Project Title: Development of an All-Aqueous Thermally Regenerative Redox Flow Battery to Support Fossil Fuel Assets

PennState College of Engineering

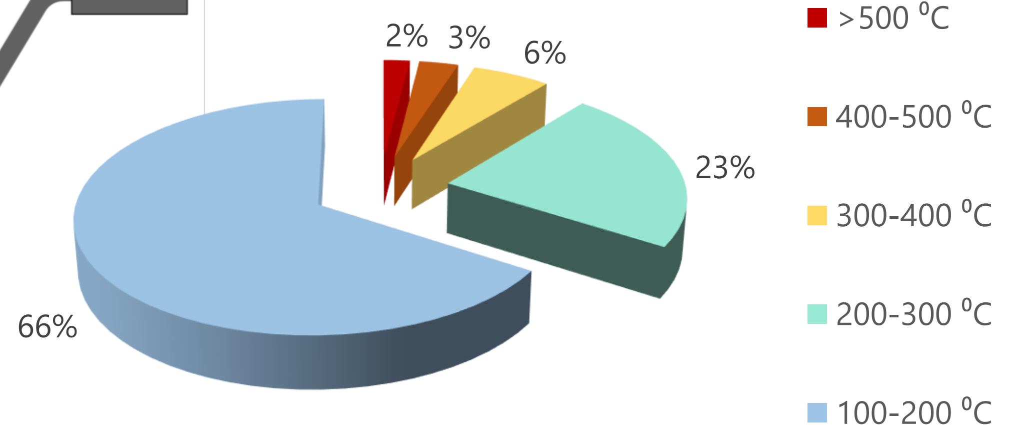
U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

Award Number: FE0032030-FOA 2332

“Low-grade” heat is abundant

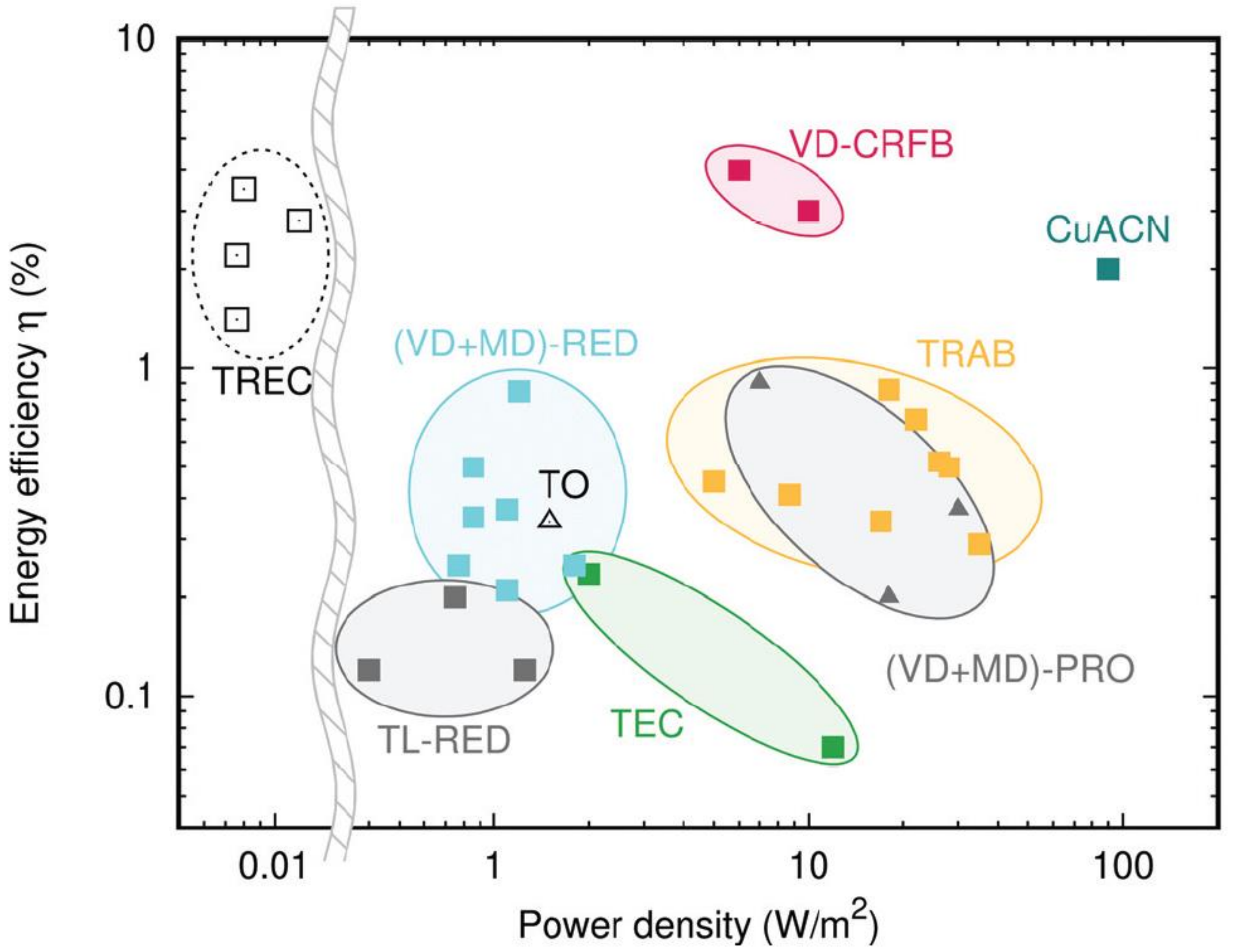


Temperature of waste heat



https://flowcharts.llnl.gov/sites/flowcharts/files/2022-04/Energy_2021_United-States_0.png
Adapted from “Some efficient solutions to recover low and medium waste heat: competitiveness of the thermoacoustic technology”, Haddad et al., 2014

Many technologies can take advantage of low-grade heat



TREC – Thermally Regenerative Electrochemical Cycle
VD – Vacuum Distillation
MD – Membrane Distillation
RED – Reverse ElectroDialysis
TEC – ThermoElectrochemical Cell
PRO – Pressure Retarded Osmosis
CRFB – Concentrated Redox Flow Battery
CuACN – Copper Acetonitrile battery
TRAB – Thermally Regenerative Ammonia Battery

“Innovative technologies for energy production from low temperature heat sources: critical literature review and thermodynamic analysis”, Brogioli and La Mantia, 2021

Flow battery + distillation column = Thermally regenerative battery

Flow battery

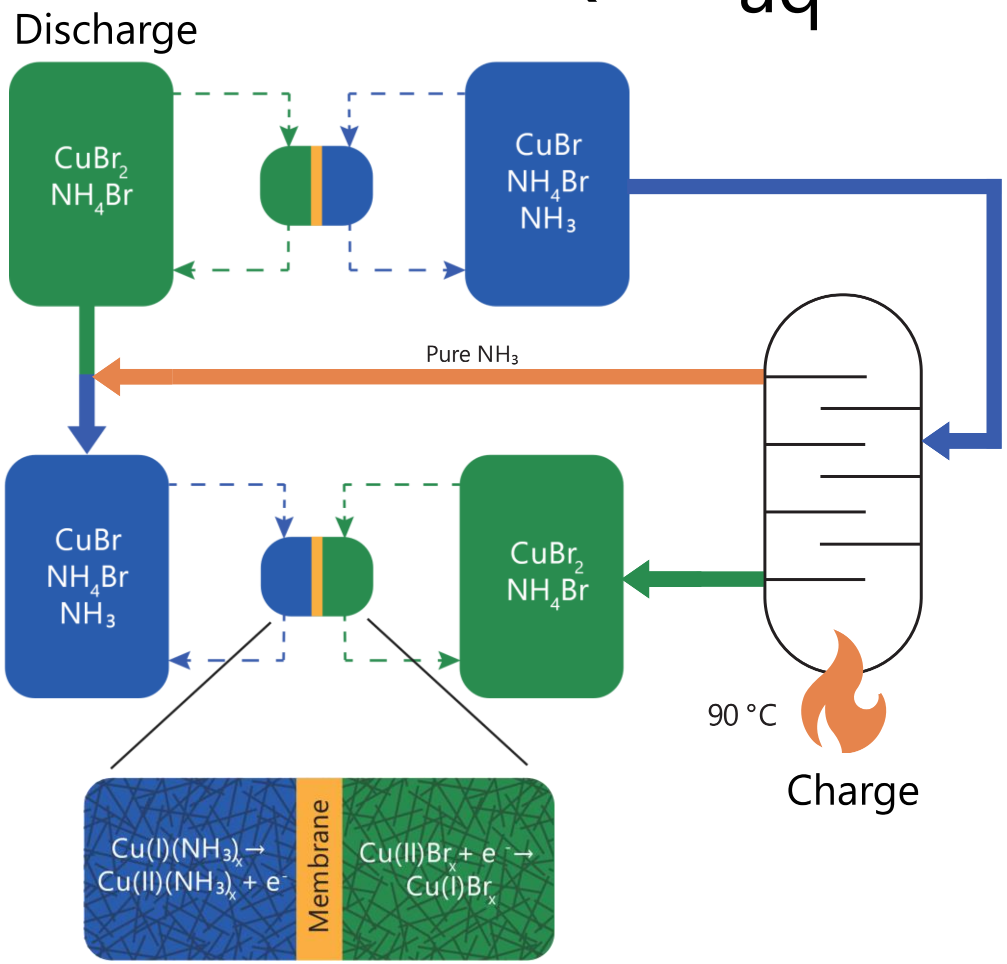
Large scale batteries

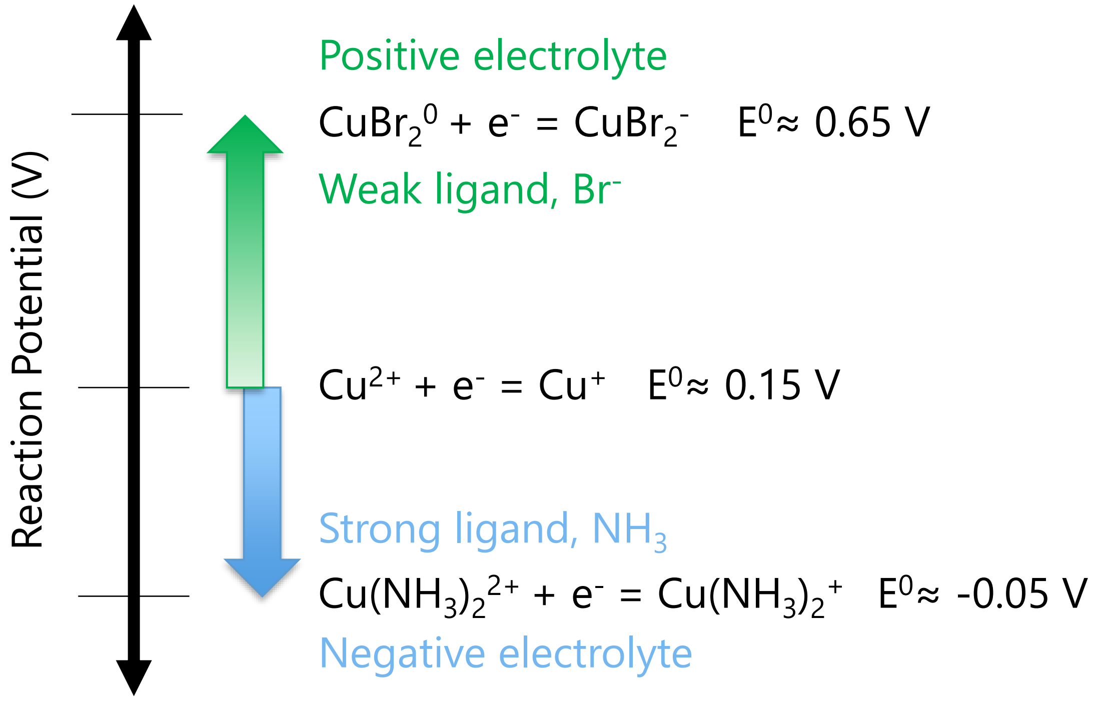
Distillation column

Large scale thermal separations

https://organics.co.uk/en/products/20/ammonia-stripping-systems
https://www.cellcube.com/casestudy/gw-microgrid-campus/

How the All-Aqueous Cu-TRAB (Cu_{aq}-TRAB) works

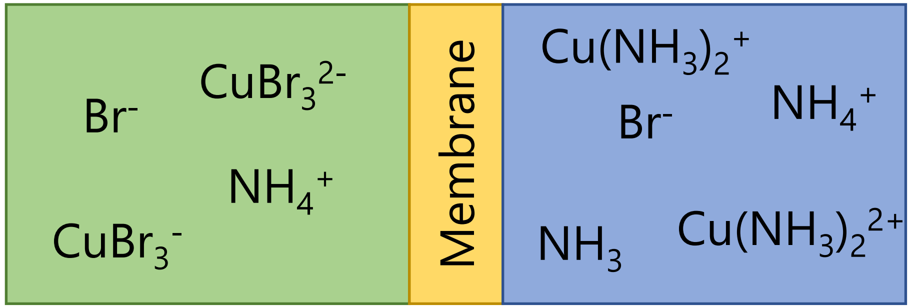




"Power and energy capacity tradeoffs in an all-aqueous copper thermally regenerative ammonia battery", Cross, et al., 2022

Milestone 3: Identify performance characteristics of suitable membrane types

The best membrane for the Cu_{aq}-TRAB is not obvious



Cation Exchange Membrane

vs.

Anion Exchange Membrane

vs.

Uncharged Membrane

Power

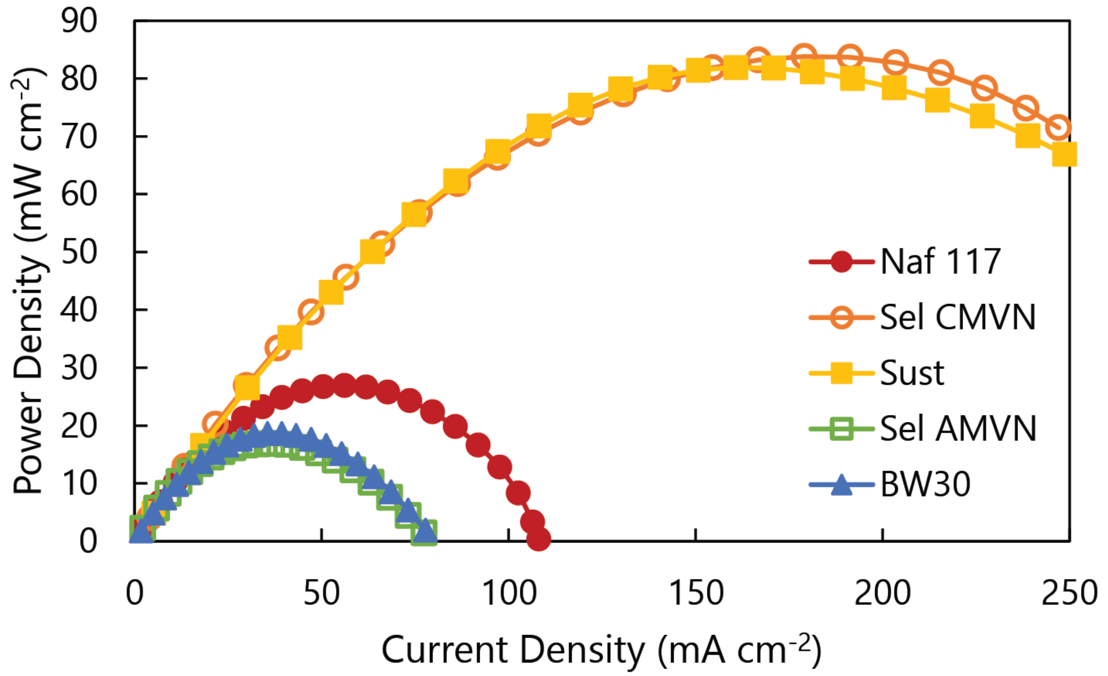
Energy

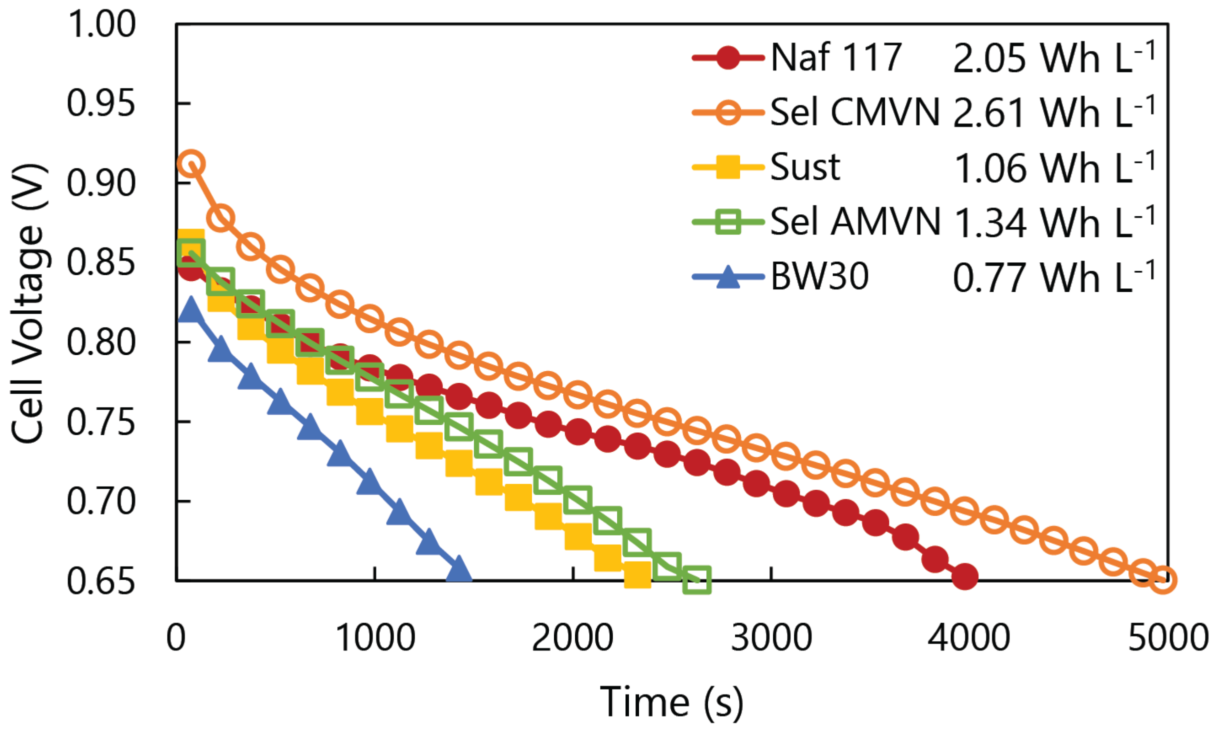
CEMs:
Nafion 117
Selemion CMVN

AEMs:
Sustainion E30-50
Selemion AMVN

Uncharged:
FilmTec BW30

Selemion CMVN showed the highest peak power and energy density



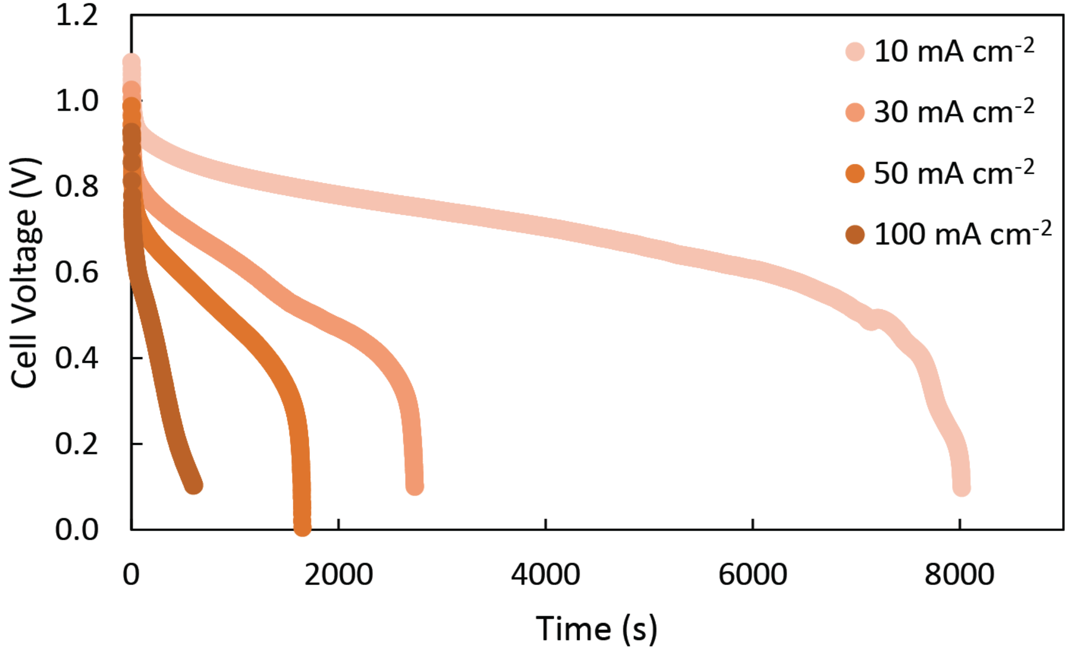


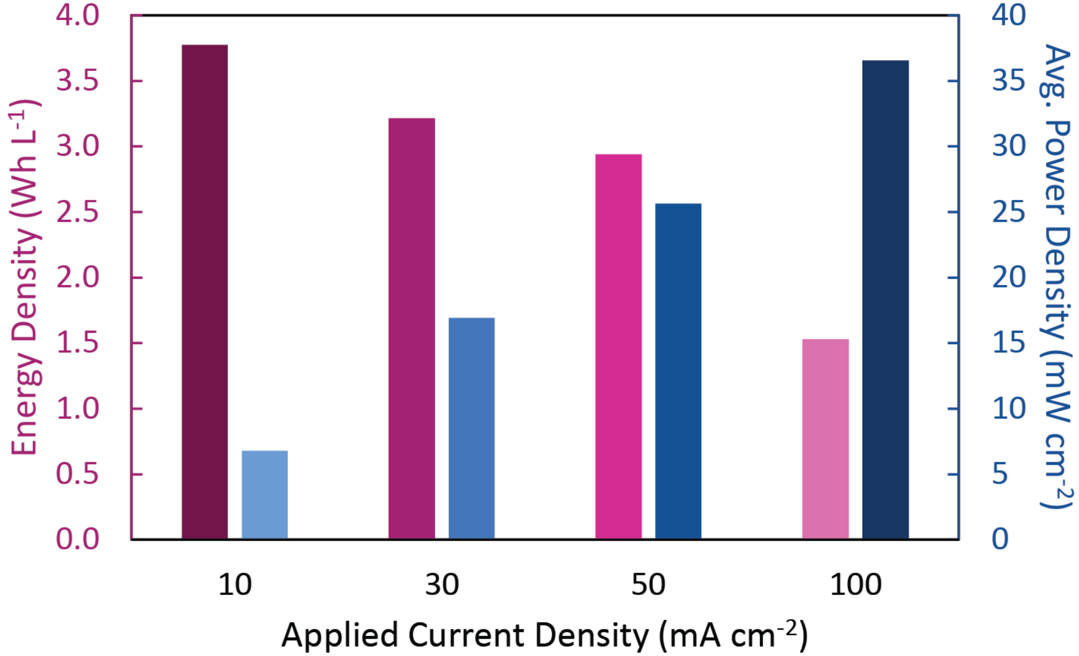
10 mA cm^{-2}, 50 ml reservoir
0.65 V cutoff

0.5 M $CuBr_2$, 5 M NH_4Br
0.5 M CuBr, 5 M NH_4Br, 4 M NH_3
50 ml min^{-1}, 25 cm^2
AvCarb G300A Felts 400 °C for 5 hours

"Alternative membranes cost-effectively…", Cross, et al., *Energy and Environmental Science*, *Submitted*

Higher applied currents resulted in higher power, lower energy



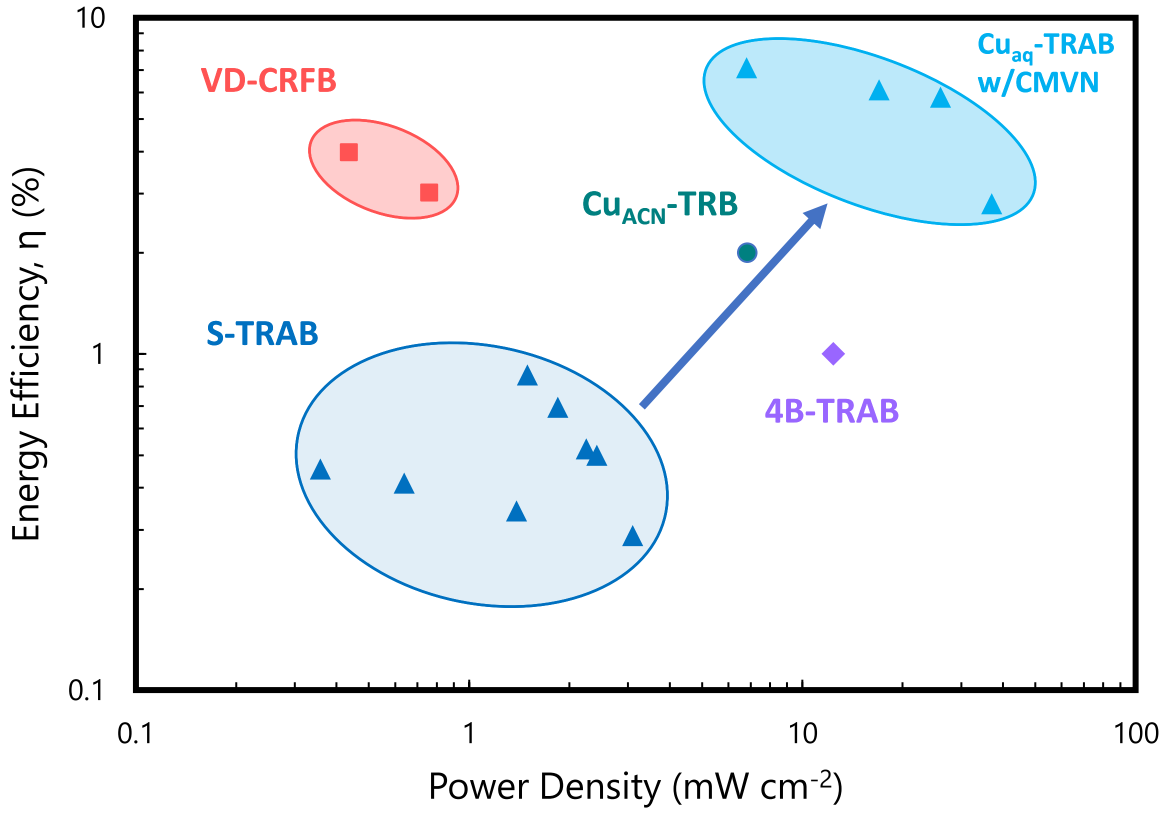


- Average power increased linearly with applied current density
- Energy density fell sharply after 50 mA cm^{-2}
- 50 mA cm^{-2} showed good balance of high power and energy densities

Selemion CMVN
50 ml reservoir
0.1 V cutoff

“Alternative membranes cost-effectively…”, Cross, et al., *Energy and Environmental Science*, *Submitted*

Where are we in comparison?

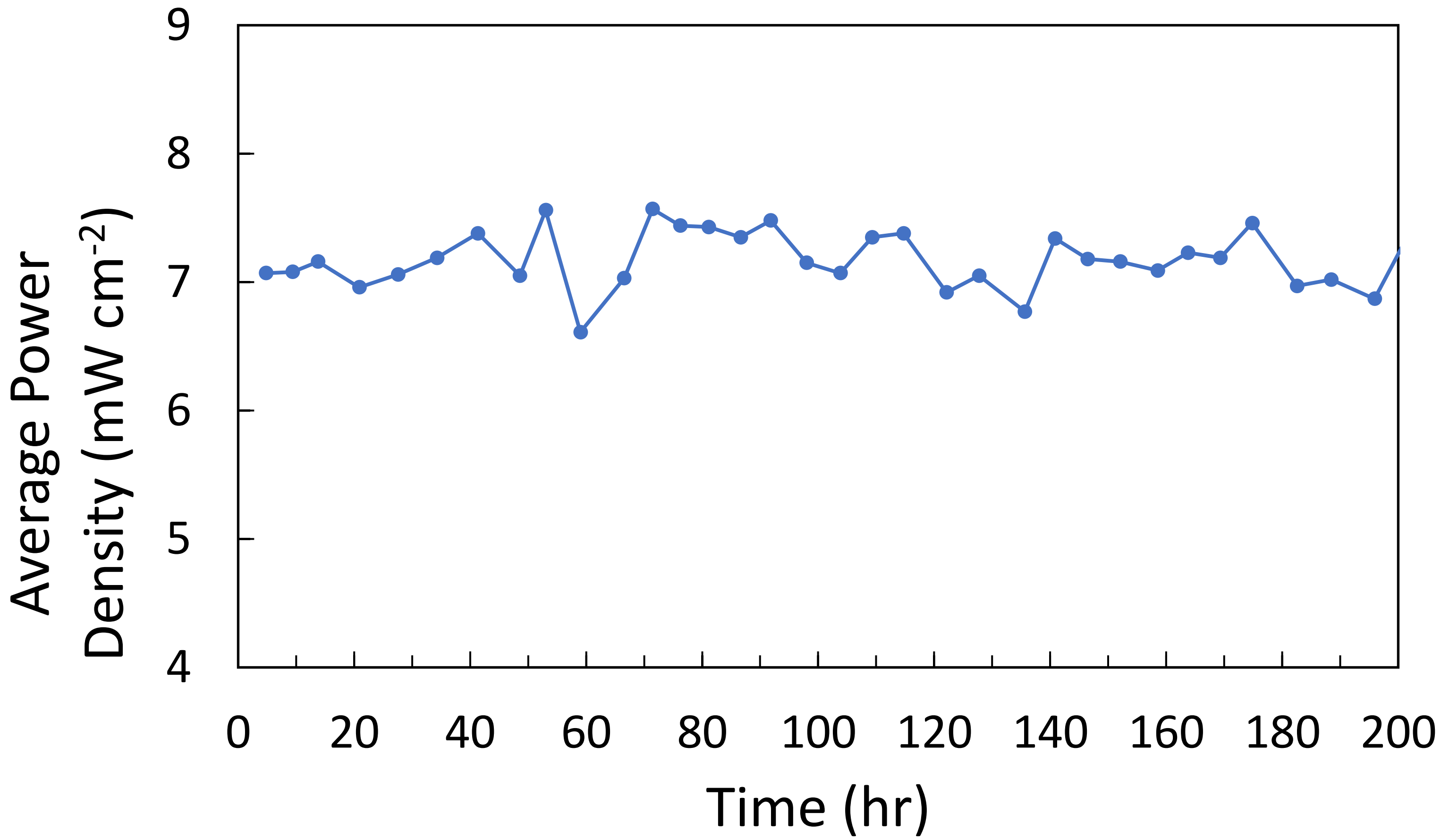


Milestone 3: Identify performance characteristics of suitable membrane types

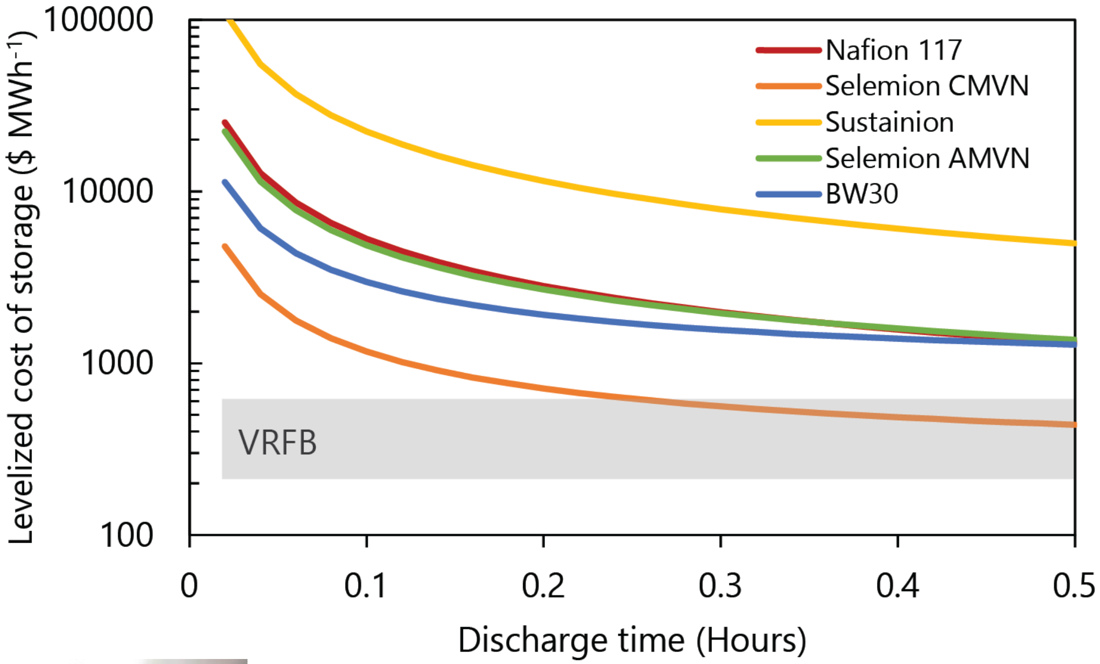
Power density remained constant over 200 hours

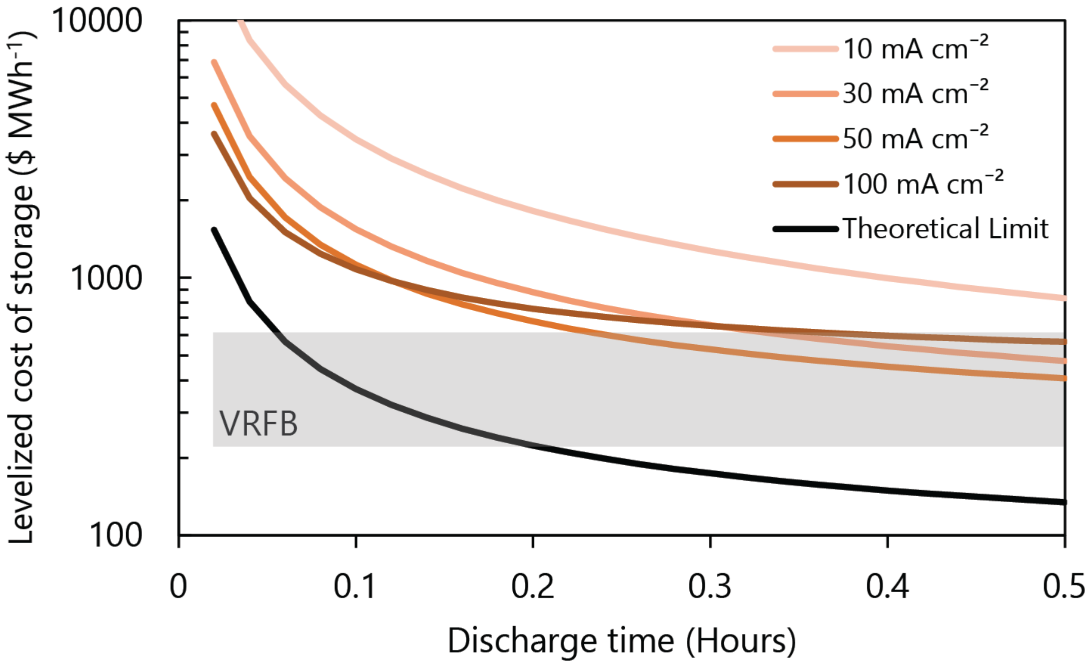
- Numerous cycling for 200 hours of continuous discharge

- Power density was unchanged during cycling



Selemion CMVN is cost-competitive with commercial flow batteries



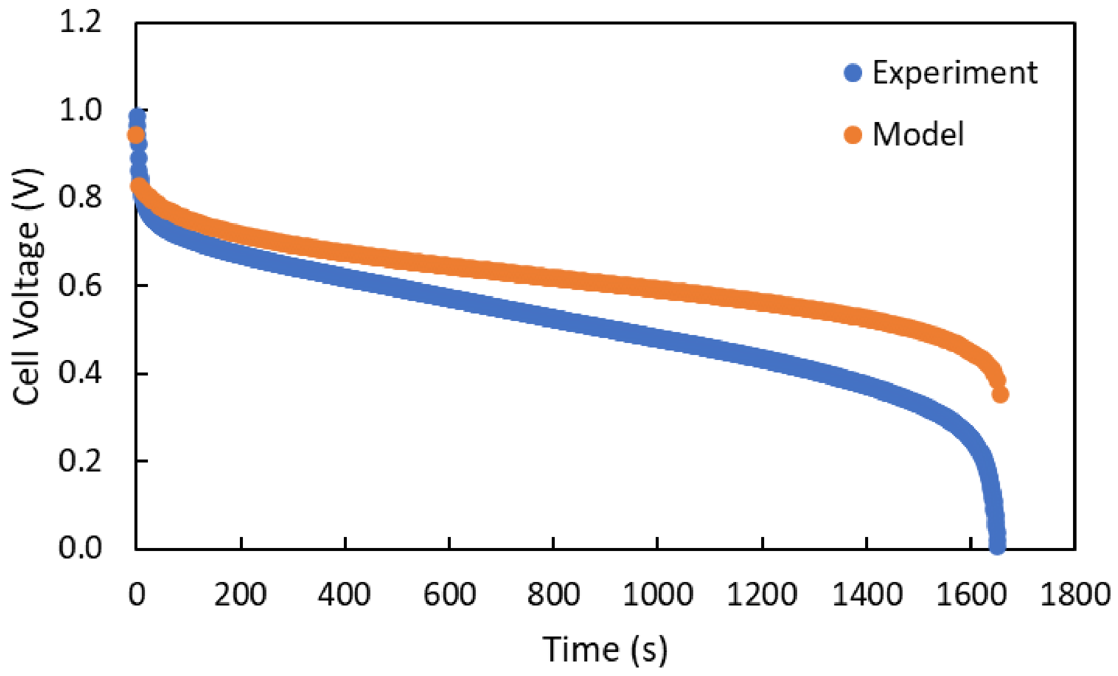


- CMVN was the lowest cost of storage due to being an inexpensive material
- Applied current of 50 mA cm^{-2} for CMVN was lowest cost of storage
- Theoretical limit of the battery approaches $150 per MWh

"Alternative membranes cost-effectively…", Cross, et al., *Energy and Environmental Science*, *Submitted*

Milestone 4: Verify basic COMSOL model with experimental data obtained from lab-scale RFB test system

The COMSOL model with no ammonia crossover did not match experimental discharge curves

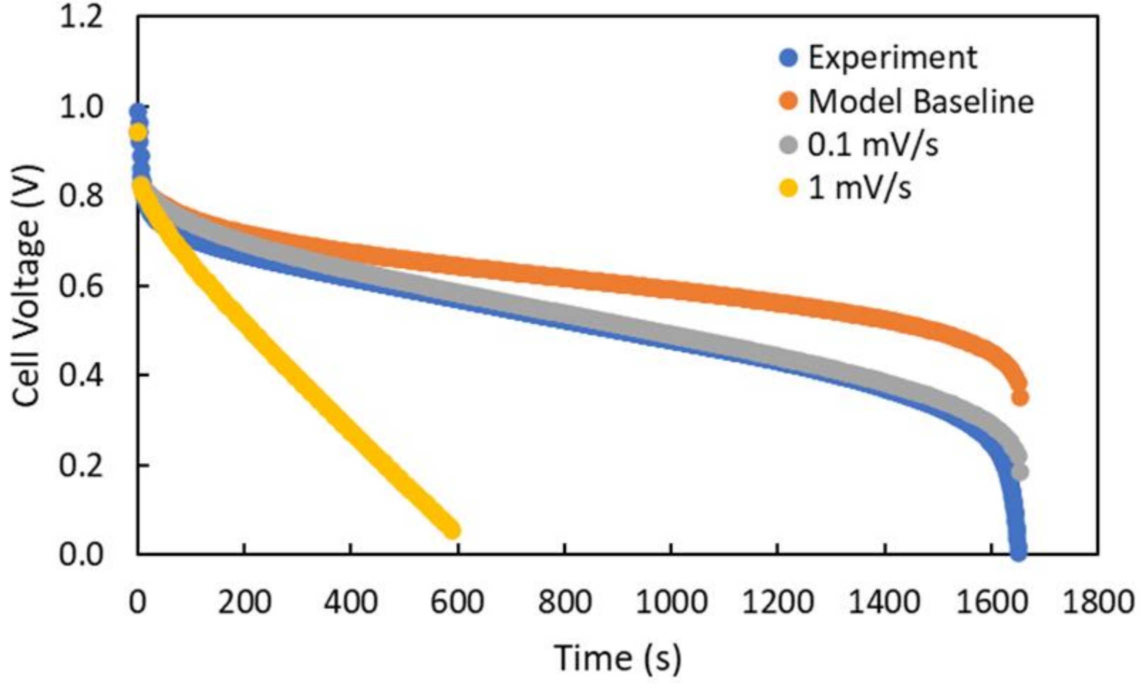


	Energy Density ($Wh\ L^{-1}$)	Avg. Power Density ($mW\ cm^{-2}$)
Experiment	2.94	25.7
Model	3.54	30.7

Difference of ~20%!

Selemion CMVN at 50 mA cm^{-2}

Model-experiment agreement was achieved through a positive electrode potential "decay" caused by crossover



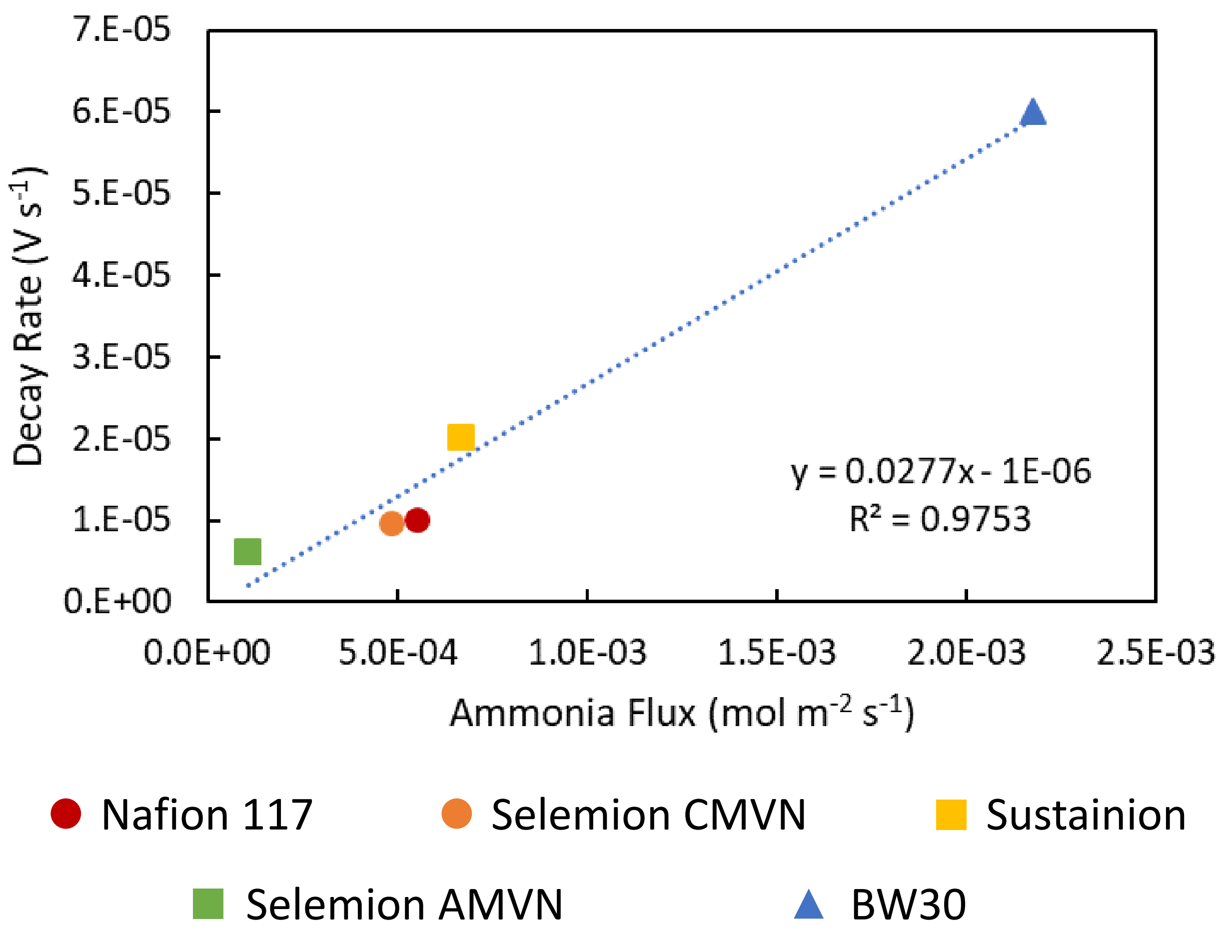
$$E_{eq,pos} = \left(E^0_{pos} - E^0_{pos,decay} * t\right) - \frac{RT}{nF}\ln(Q)$$

Where $E^0_{pos,decay}$ is the decay rate and t is time

$E^0_{pos} = 0.73$ V
$E^0_{neg} = -0.01$ V

Selemion CMVN
50 mA cm^{-2}, 50 mL reservoir, 0.5 M $CuBr_2$

Trends in fitted decay rates correlated well with ammonia flux

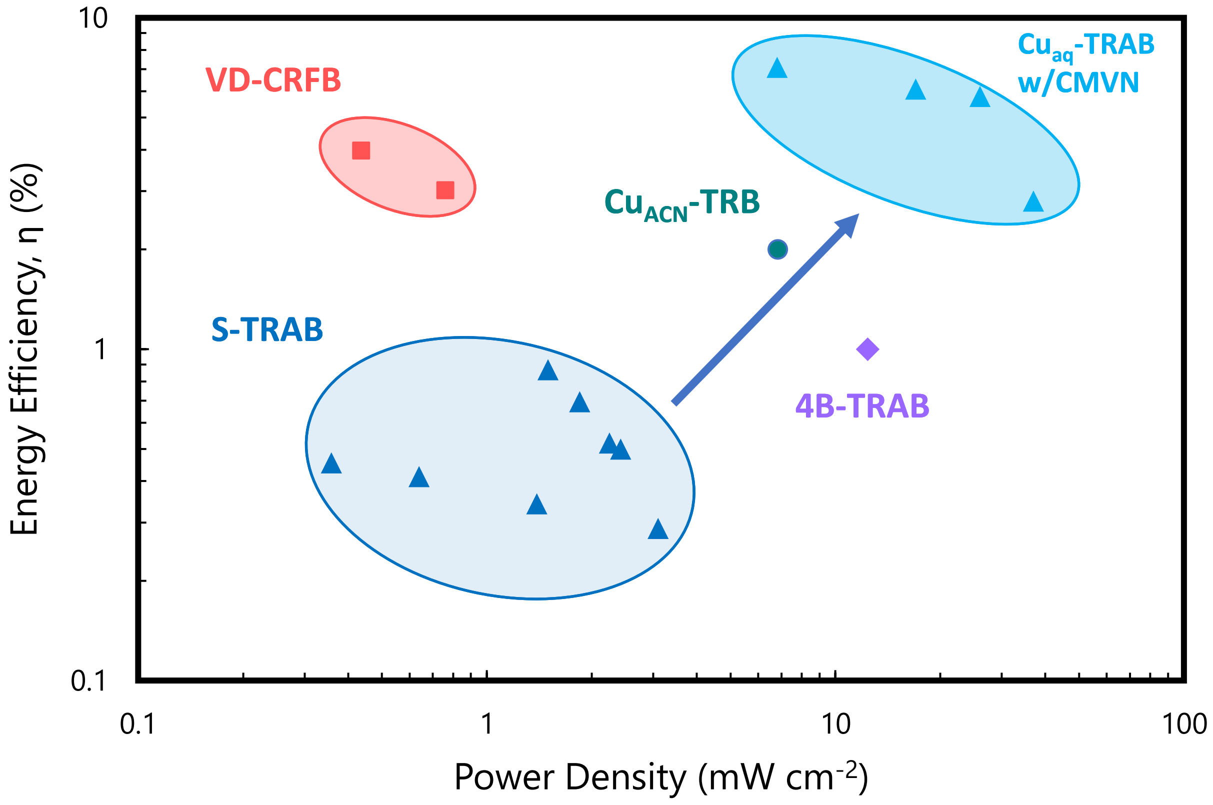


- Ammonia flux previously measured in diffusion experiments

- Consistent with what would be expected at low applied current density

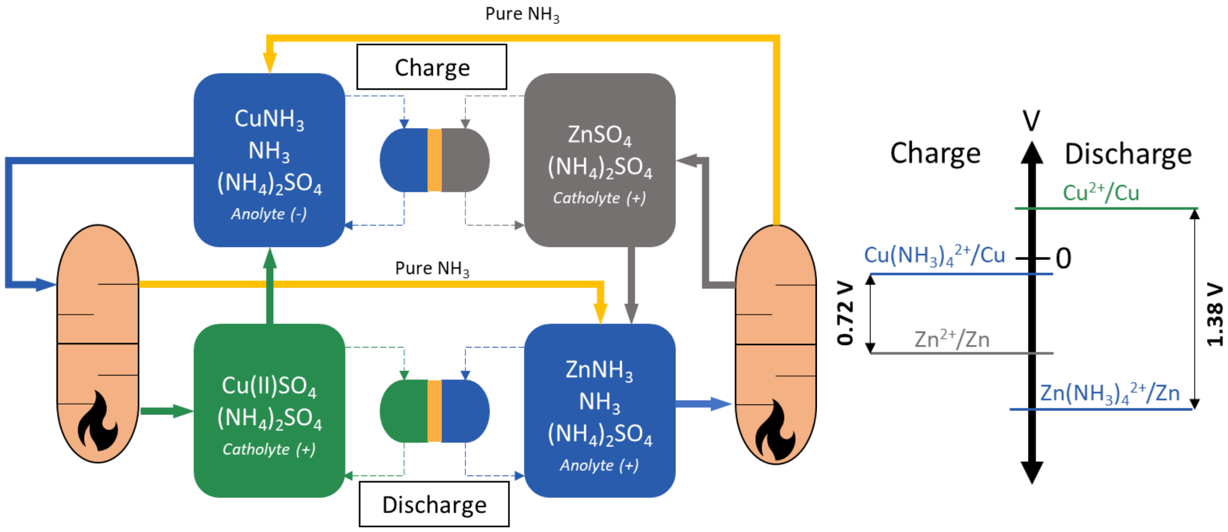
Milestone 4: Verify basic COMSOL model with experimental data obtained from lab-scale RFB test system ✓

Bimetallic Thermally Regenerative Ammonia Battery (B-TRAB)



Development of a new B-TRAB

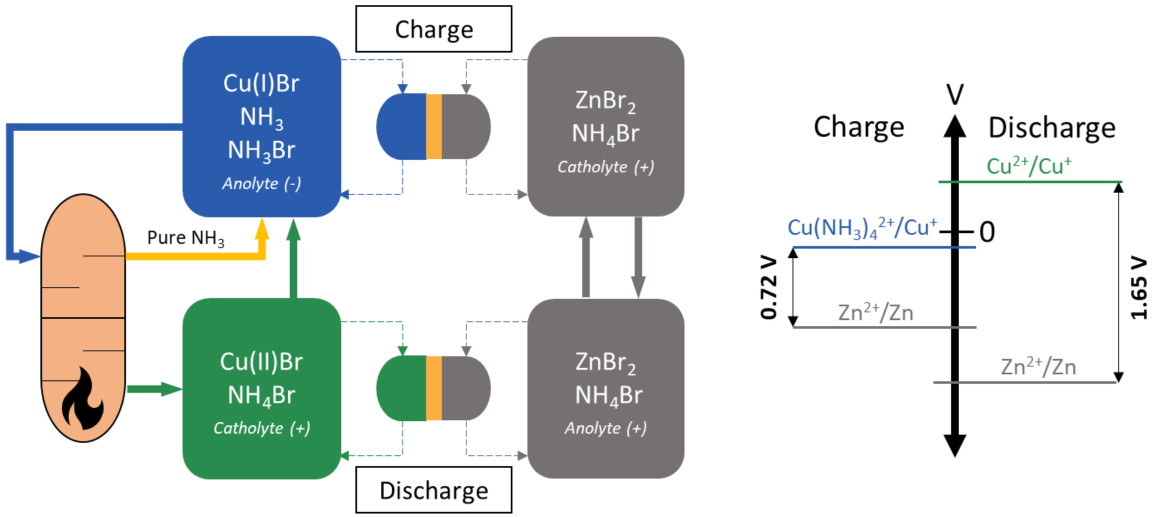
Current 4-Step (4B-TRAB)



Step 1 Electrical Charge → **Step 2** Distillation of NH_3 → **Step 3** Electrical Discharge → **Step 4** Distillation of NH_3

- Two dissimilar metals Cu/Zn for higher potential
- Cu and Zn are deposited/dissolved

Our 3-Step (3B-TRAB)



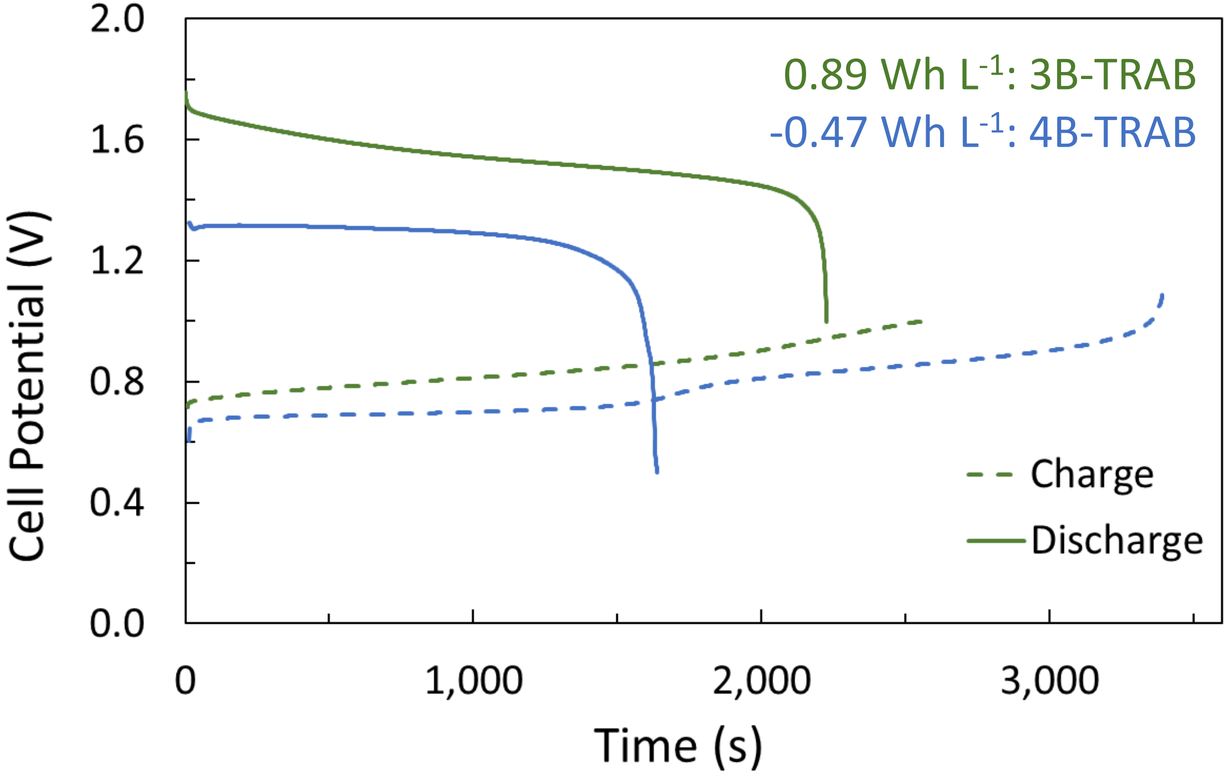
Step 1 Electrical Charge → **Step 2** Distillation of NH_3 → **Step 3** Electrical Discharge

Modifications:

- Eliminating the ammonia addition step in the negative solution (3-step)
- Keeping Cu in solution with Br^- ligand

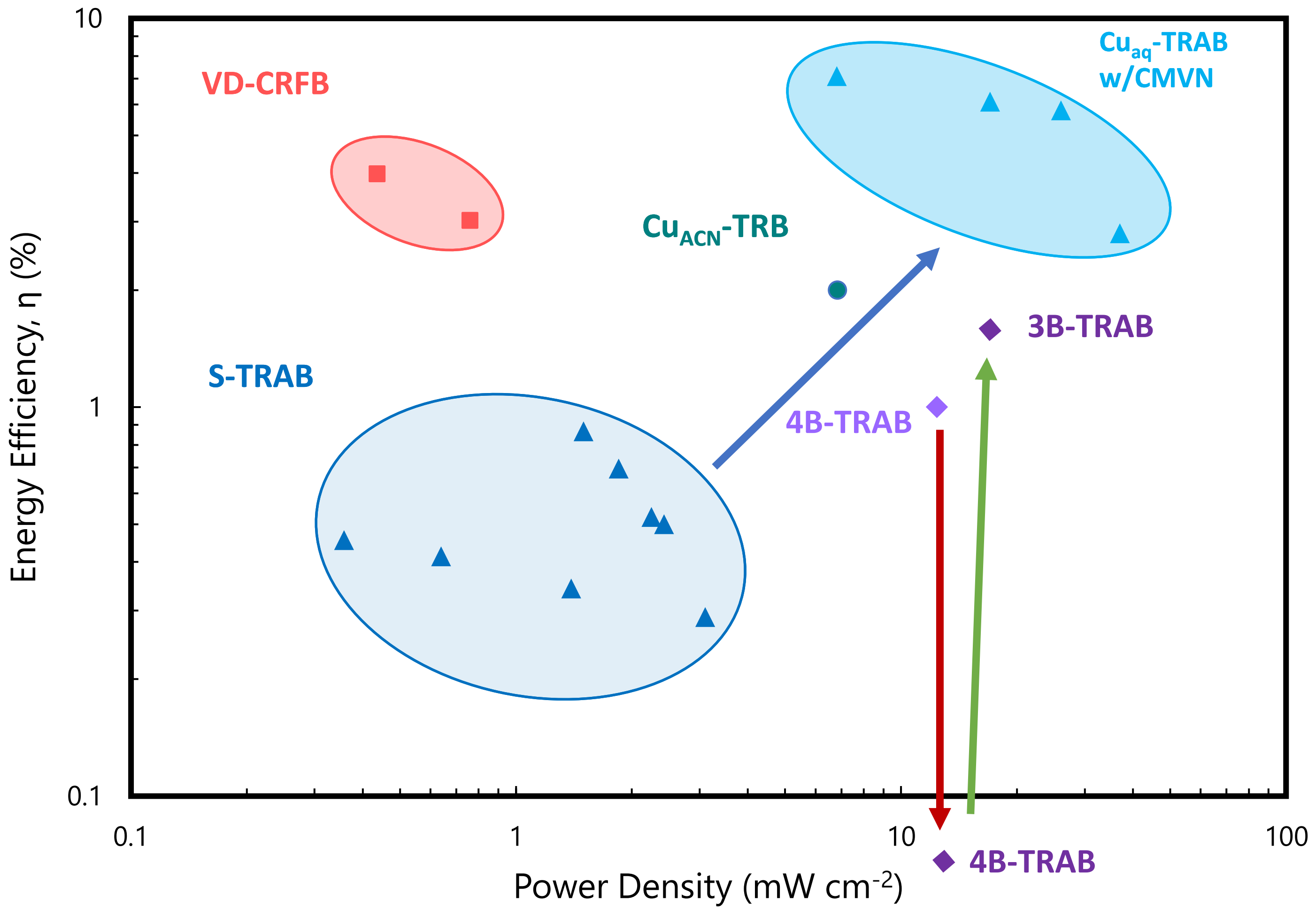
Our new 3-step B-TRAB outperforms the current 4-step B-TRAB

Performance Parameters	3B-TRAB	4B-TRAB
Net Energy Density (Wh L^{-1})	0.89 ± 2%	-0.47 ± 30%
Coulombic Efficiency (%)	85 ± 2%	48 ± 8%
Electrical Energy Efficiency (%)	160± 2%	75 ± 9%
Average Discharge Power Density (mW cm^{-2})	16 ± 1%	12 ± 2%



10 mA cm^{-2}, 50 mL reservoir
50 ml min^{-1}, 25 cm^2
Char: 0.1 M $ZnBr_2$, 5 M NH_4Br | 0.2 M Cu(I)Br, 5 M NH_4Br, 4 M NH_3
Dis: 5 M NH_4Br | 0.2 M Cu(II)Br, 5 M NH_4Br
Char: 0.1M $ZnSO_4$, 1M $(NH_4)_2SO_4$ | 4M NH_3, 1 M $(NH_4)_2SO_4$
Dis: 4M NH_3, 1M $(NH_4)_2SO4_4$| 0.1M $CuSO_4$, 1 M $(NH_4)_2SO_4$

Aqueous copper improves single and bimetallic TRAB systems



Project extension:

- Cell architecture
- Battery materials
- Operating conditions

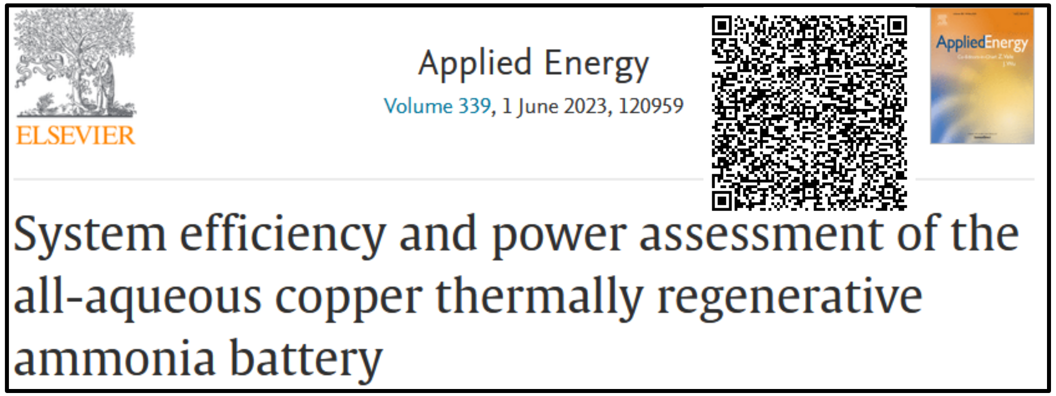
Summary of communications

Publications:

- Springer et al., “An All-Aqueous Thermally Regenerative Ammonia Battery Chemistry Using Cu(I, II) Redox Reactions” (***2021, J. Electrochem. Soc.***)
- Cross et al., “Power and Energy Capacity Tradeoffs in an All-Aqueous Copper Thermally Regenerative Ammonia Battery” ***(2022, Journal of Power Sources***)
- Cross et al., “System Efficiency and Power Assessment of the All-Aqueous Copper Thermally Regenerative Ammonia Battery” (***2023, Applied Energy***)

Presentations:

- “Membrane Transport and Performance in the All-Aqueous Copper Thermally Regenerative Battery” (**242nd ECS Meeting**)
- “Improving the Performance of Bimetallic Thermally Regenerative Ammonia Batteries” (**242nd ECS Meeting**)
- “A 3-Step Bimetallic Thermally Regenerative Ammonia Battery” (**Upcoming @ 243rd ECS Meeting**)
- “Recent Advances in Thermally Regenerative Batteries: A New Approach for Generating Electrical Power from Low-Grade Heat” (**Upcoming @ 243rd ECS Meeting**)



Thank you and please contact us if you have any questions!

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