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Sandia Membrane Development for Energy Storage Devices: Industry Partnerships

Key Personnel Team Members: Tim Lambert, Leo Small, Nate Kirchhofer, Thanh Le and Cy Fujimoto

Industry Partners: BioZen Batteries (Flow battery) and Coulomb Technology (Zn battery)

Flow Batteries - #203

U.S. DEPARTMENT of ENERGY

DOE OE Energy Storage Peer Review & Annual Meeting, 2026

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U.S. DEPARTMENT of ENERGY | NNSA National Nuclear Security Administration

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Goal: Engineering membranes for flow batteries

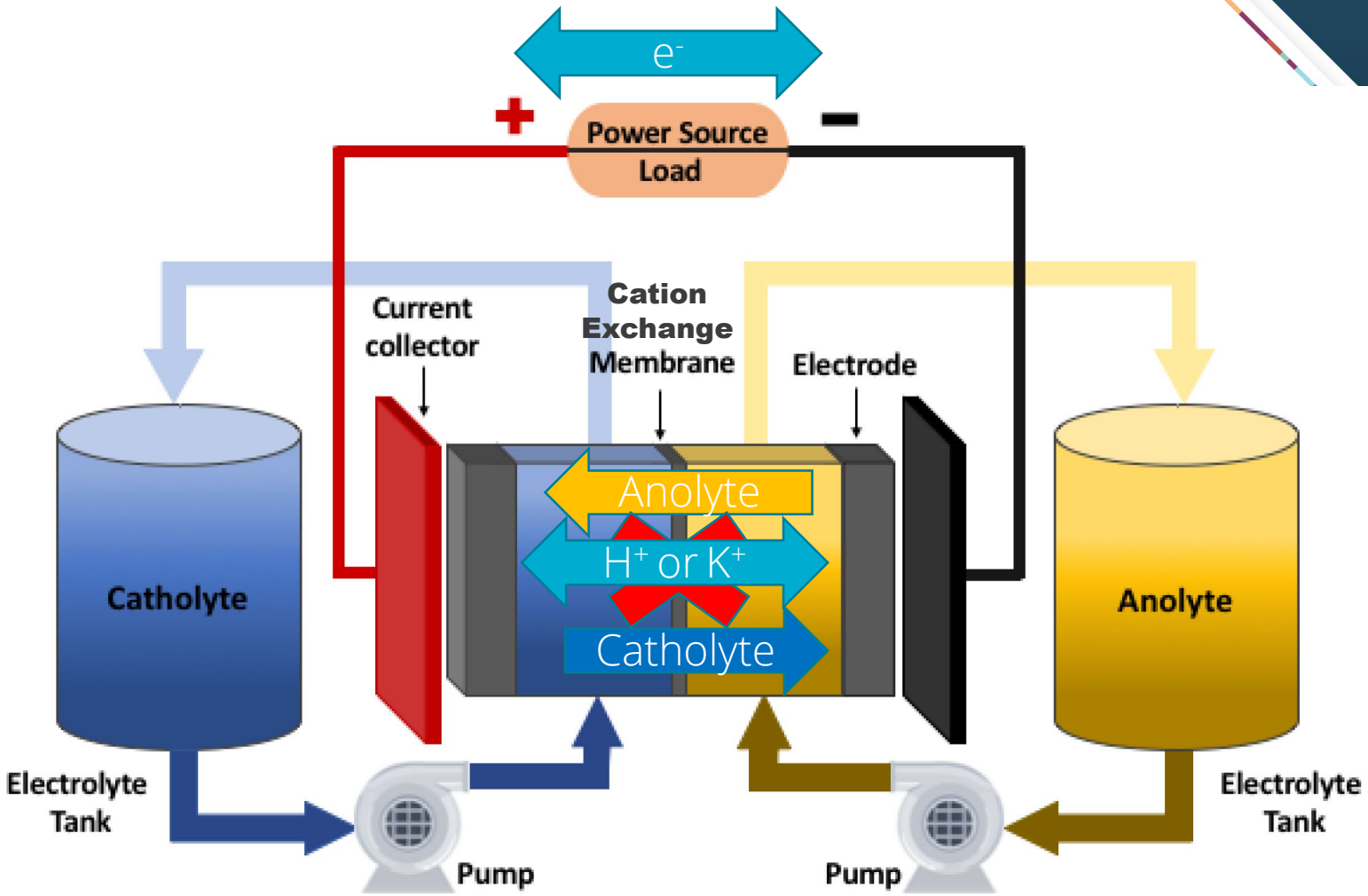
Desired Membrane Properties

1. To impede anolyte and catholyte transport. This prevents anolyte and catholyte from mixing, improves battery lifetime.

2. Allow specific ions to migrate. Faster ion mobility results in low battery resistance and higher efficiencies.

3. Low cost $\$10 m^{-2}$. Results in lowering battery capital cost.

4. Membrane required to survive highly oxidative/reductive and variety of pH environments.

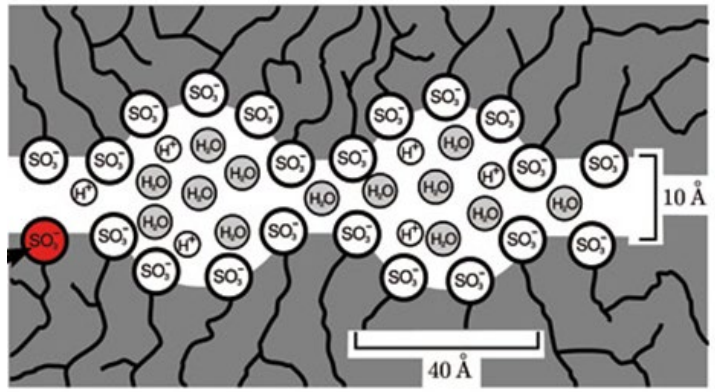


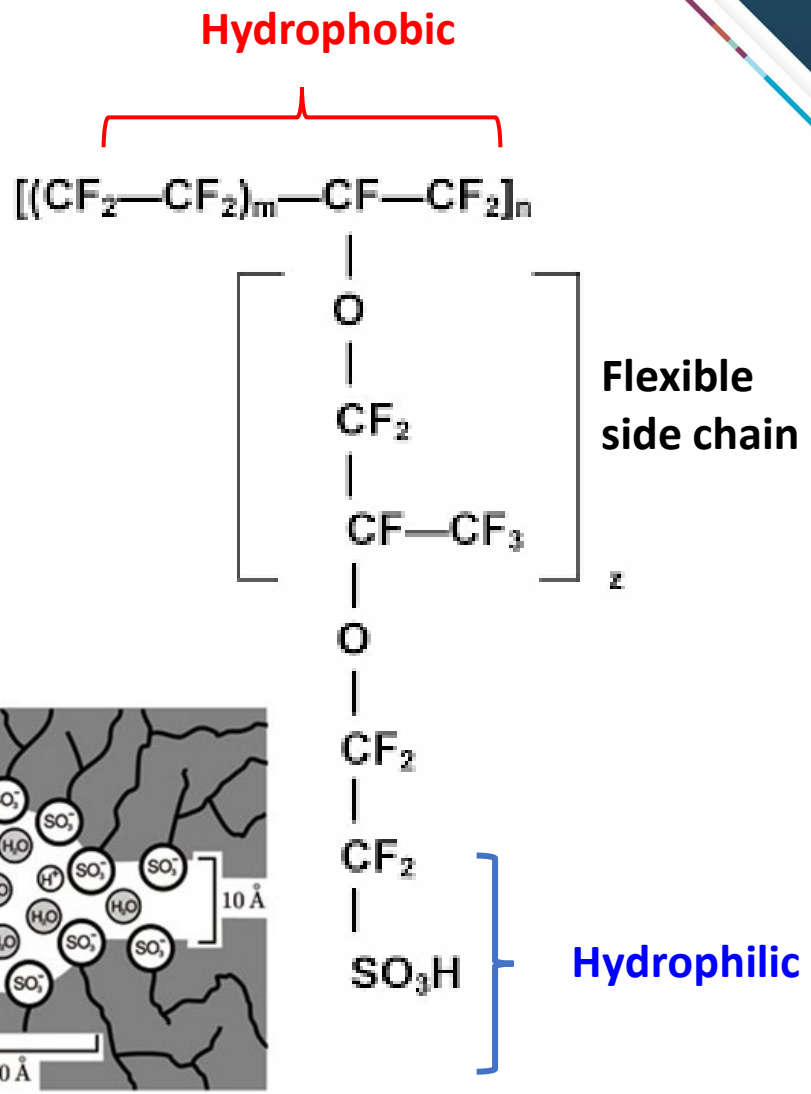
Modified from Electronics 2020, 9(10), 1567 (2020)

- **Objective: Develop ion selective, low cost, durable membrane for flow battery use.**

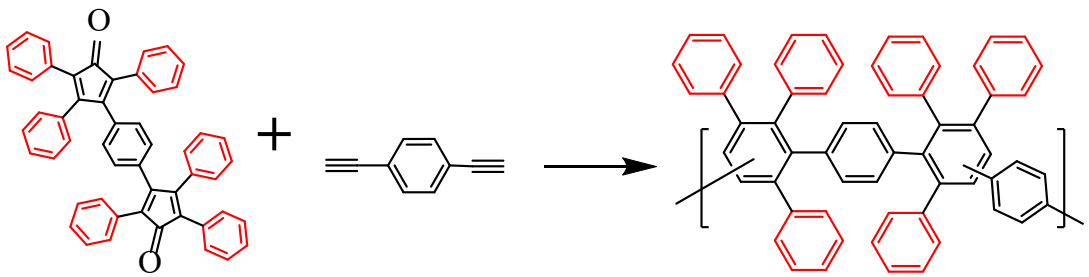
Current Practice: Perfluorinated sulfonic acid polymer (PFSA); Nafion, Aciplex, Flemion, etc.

- PFSA developed by Dupont in the late 60s. Primary market is chloro alkali industry, but is used in early market devices (PEM fuel cells, electrolysers and flow batteries).
- PFSA high ion conduction (especially for protons) and excellent chemical durability.
- High cost ($200-500 per m^2). Unable to recycle/concerns of material disposal at end use (PFAS family). There will be more regulations in the production of these chemicals and potentially bans.
- How does Nafion "work": When exposed to water hydrophobic groups aggregate and form water channels (pathways) that allow water ions to move through.
- Current market size in 2024 $0.82 billion.

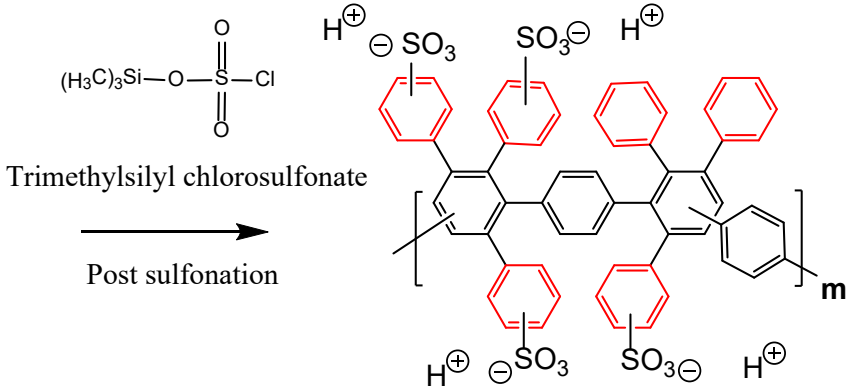




Impact: Market for non PFSA membrane technology



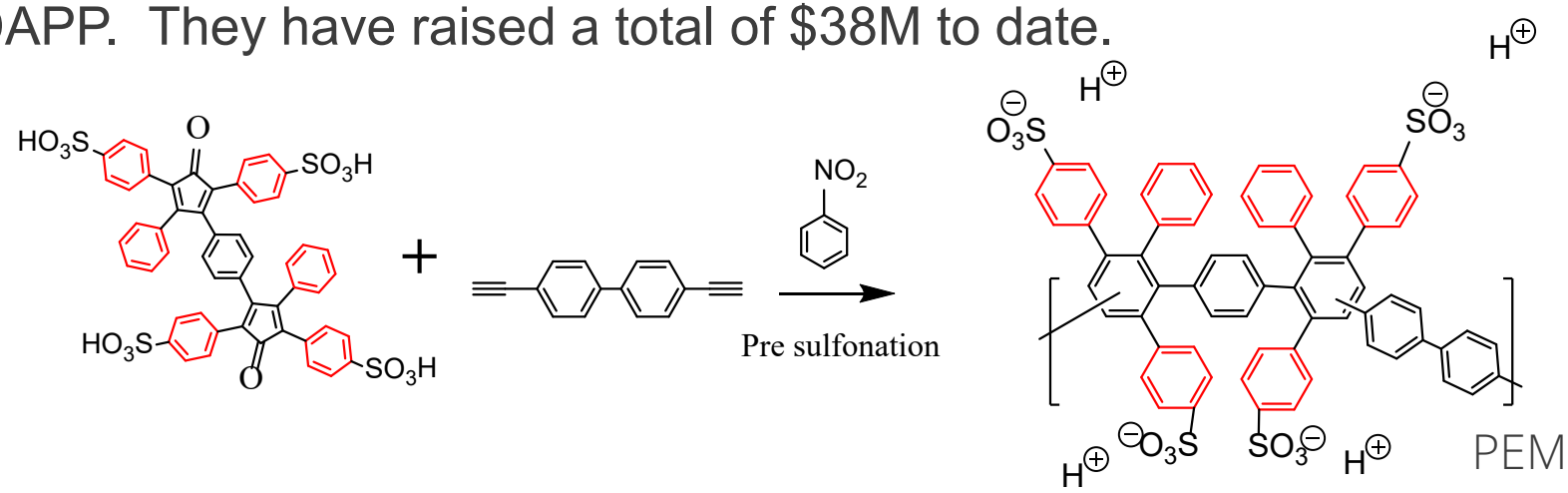
Diels Alder Poly(phenylene)



Sulfonated Diels Alder Poly(phenylene)

Sulfonated Diels Alder Poly(phenylene) SDAPP

In 2017, a Canadian membrane company called Ionomr Innovation was established using very similar structure to SDAPP. They have raised a total of $38M to date.

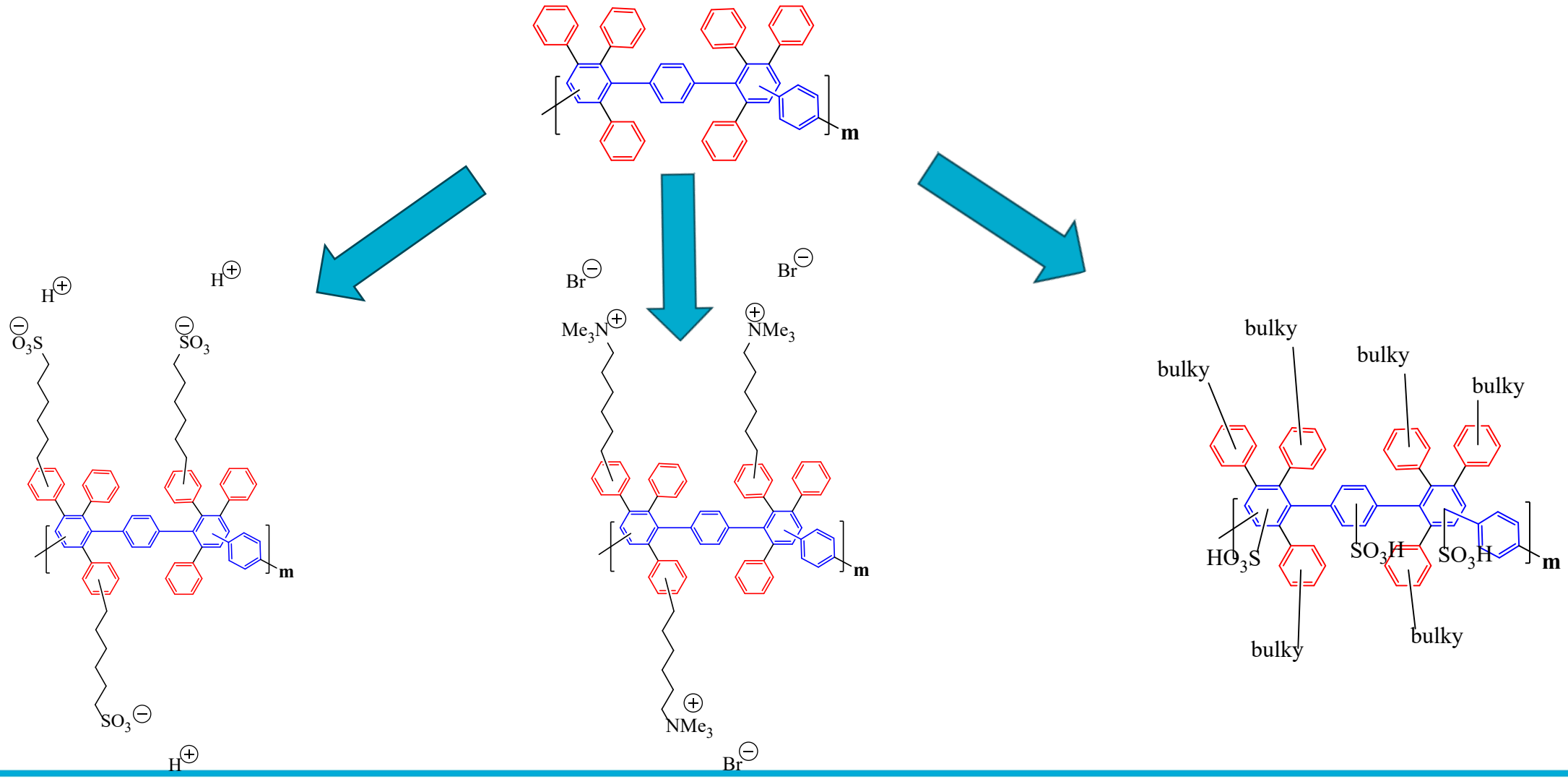


PEMION

Ionomr Innovation shows there is market demand for non PFSA materials.

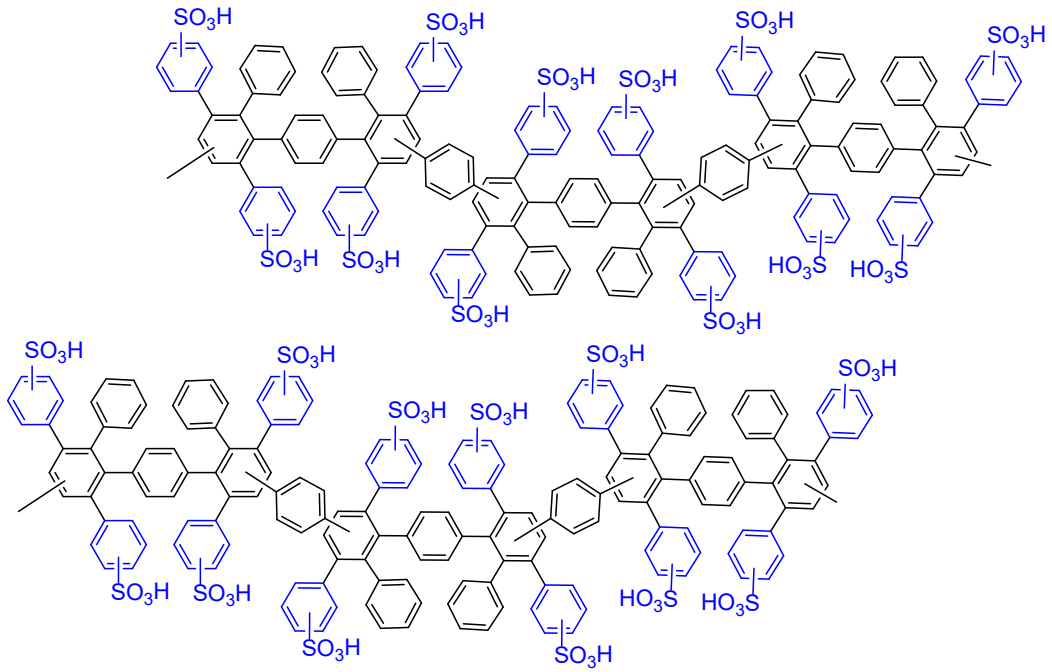
Approach: Post functionalization enables structural diversity

- Attachment is statically controlled
- Attach either positive or negative charged species (cation or anion exchange)
- Allows for pendant and backbone functionalization



Approach: Controlling ion channel by polymer structure

Pendant sulfonation

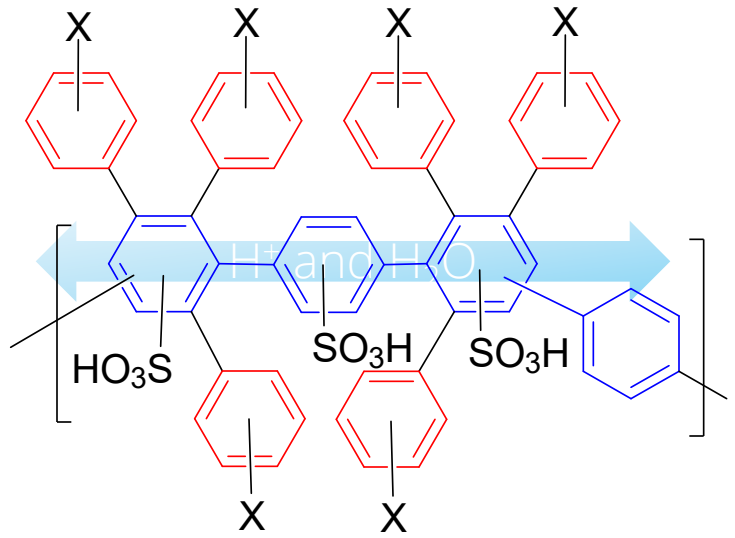


- Pendant sulfonation: external hydrophilic domains, ion channels form through neighboring sulfonic aggregation; typically large, difficult to reduce size.

Electrochemistry Communications (2012), 20, 48-51, Journal of the Electrochemical Society (2014), 161(12), A1860-A1868, 9 pp., Journal of the Electrochemical Society (2016), 163(1), A5154-A5162, Journal of the Electrochemical Society (2016), 163(1), A5229-A5235.

Backbone sulfonation

X = hydrophobic and electron withdrawing

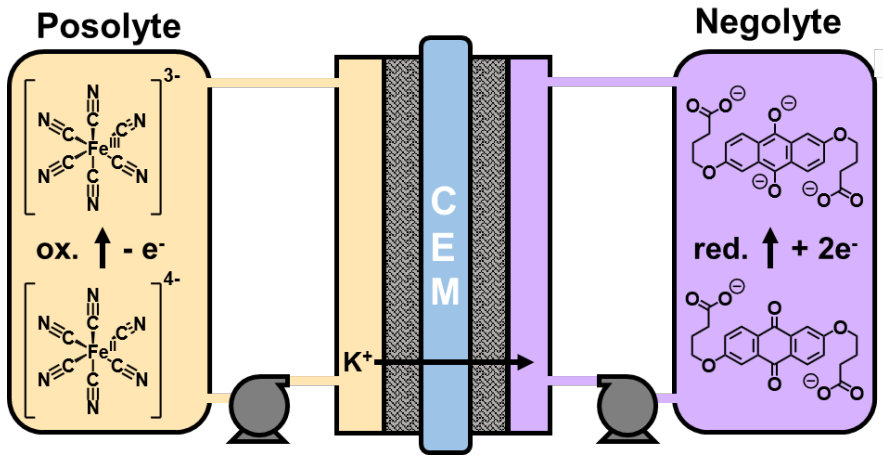


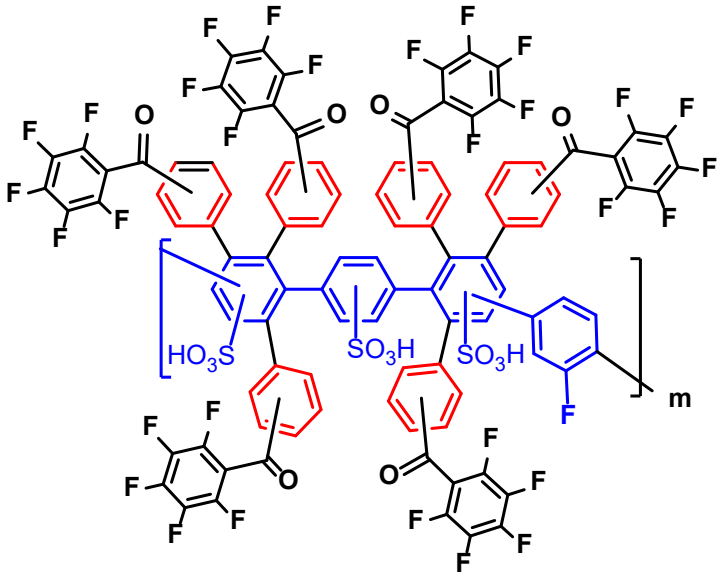
- Internal sulfonation: confined hydrophilic domain, alignment of sulfonic acid.
- Pendant substitution requires group that is electron withdrawing and hydrophobic.

Journal of Power Sources (2022), 520, 230805.
Journal of Electrochemical Society (2023), 170, 030515

High ion selectivity of Sandia membrane in alternative flow batteries

- Collaboration with Professor Michael Aziz from Harvard University (Tommy George).
- Aqueous organic electrolytes a potential low cost alternative to vanadium redox flow batteries.
- At neutral and high pH Nafion membranes are not ideal.





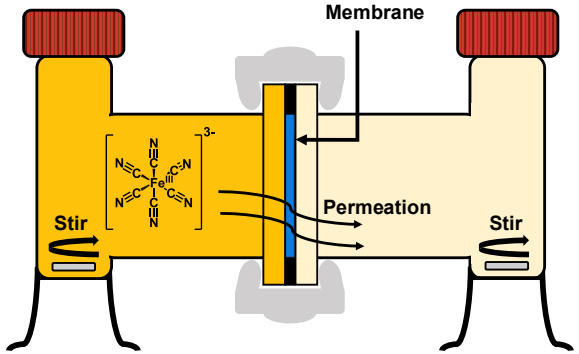
Journal of Electrochemical Society (2023), 170, 030515.

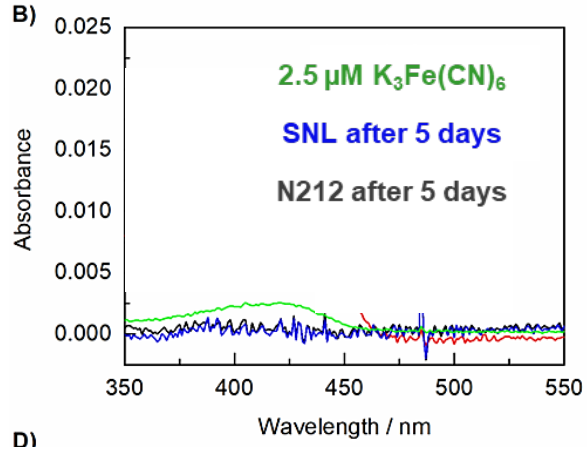
ASR in Ω cm² in 1M MCl

Membrane	H^+	Li^+	Na^+	K^+
Nafion 212	0.2	0.8	0.9	2.7
Sandia[d] 40	0.18	1.5	0.89	0.58

- **SNL membrane 4.5x less resistive to K+ than Nafion!**

Diffusion of ferricyanide



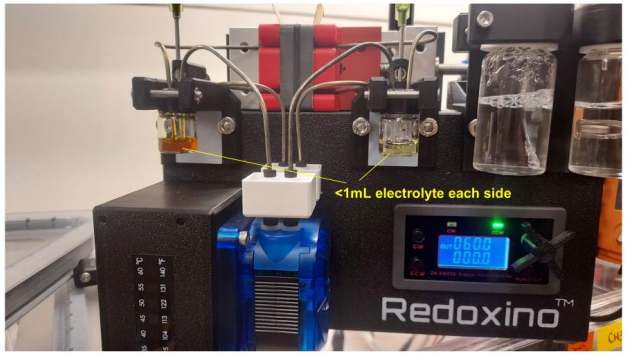


- **Nafion and SNL membrane no crossover of ferricyanide.**

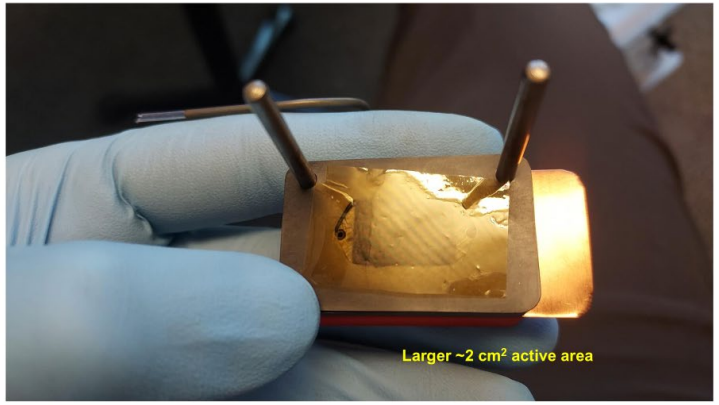
Results: Industry Testing BioZen Batteries

- Based in San Luis Obispo developing organic redox flow batteries.
- Company founded in 2019 by Nate Kirchhofer, Zachary Rengert and Eric Brigham.
- In addition to organic electroactive materials development, BioZen has developed a “mini” flow cell test system for high throughput screening of new battery materials.

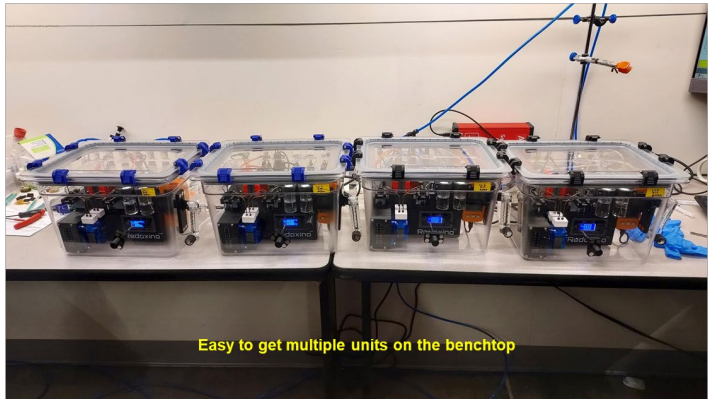
Setting up v1.1 Redoxino™ Test Systems for testing



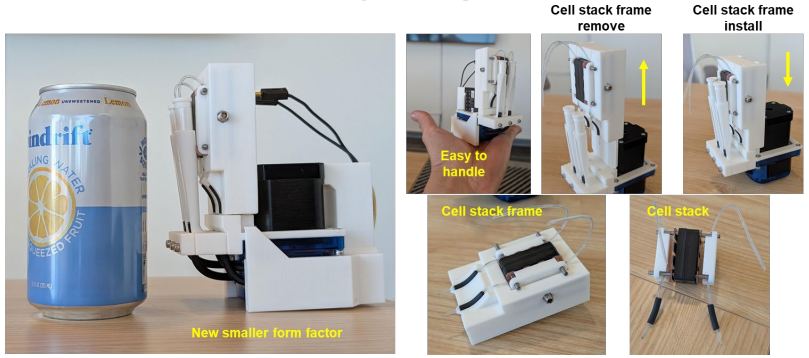
v1.1 Cell assembly with NTESS membrane



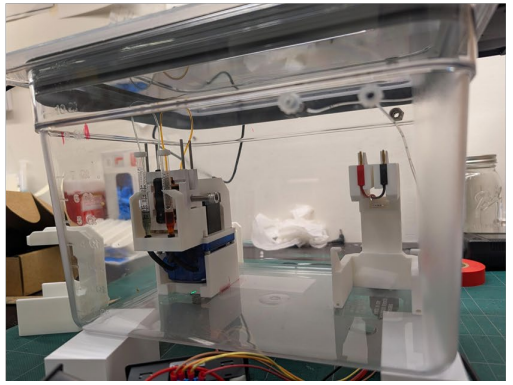
Setting up v1.1 Redoxino™ Test Systems for testing



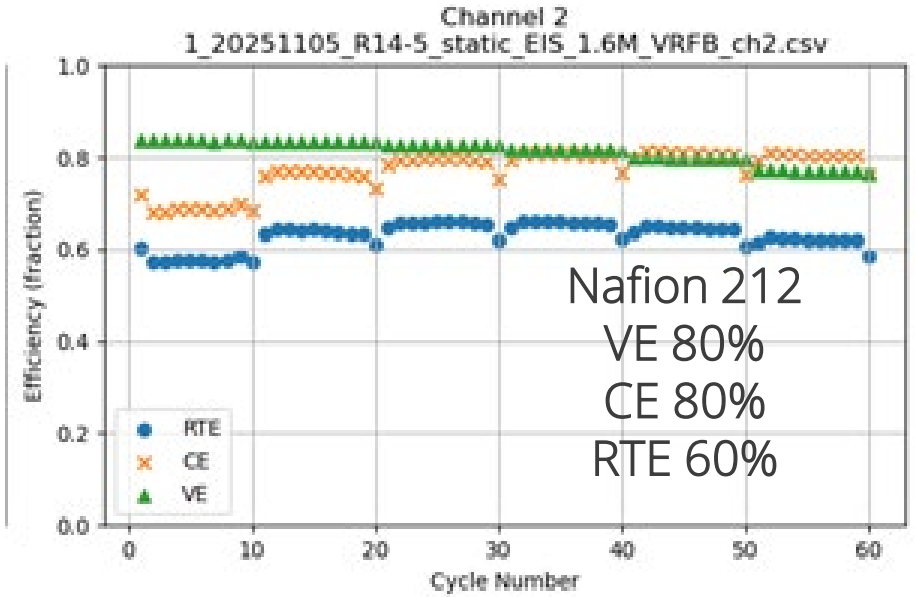
v2.0 Redoxino™ Test Systems - even smaller and easier!
Can this be a flow battery testing standard?

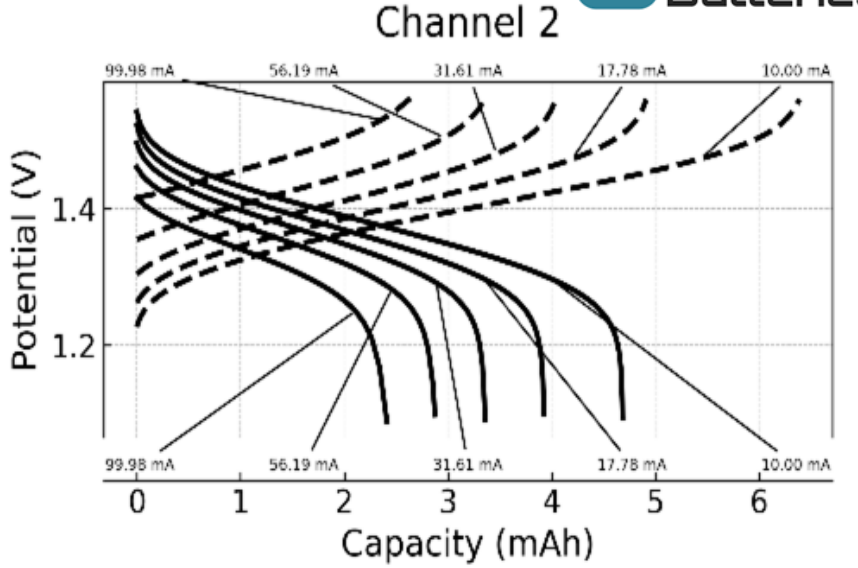


Fit ~four v2.0 Redoxino™ Test Systems in one inert box

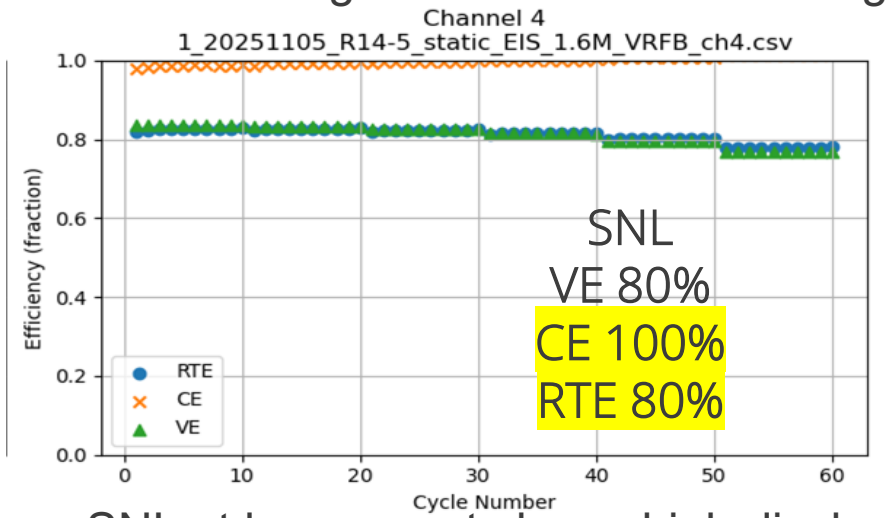


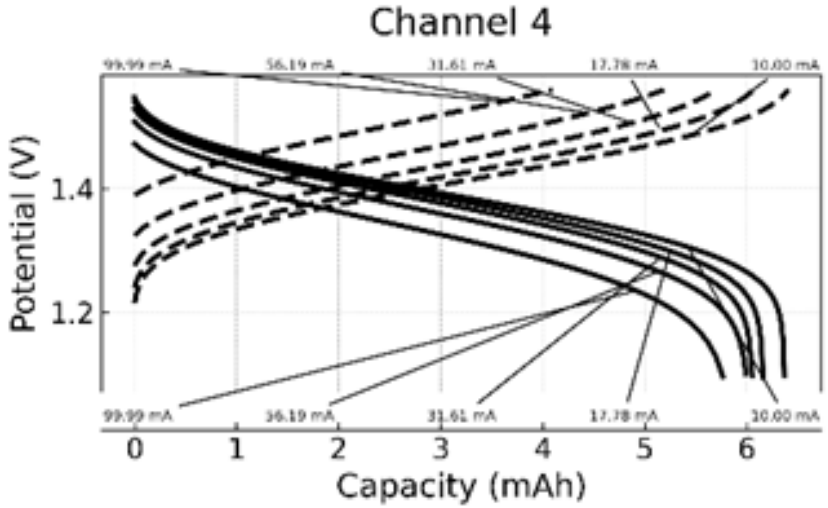
Results: Industry Testing BioZen Batteries





- Nafion at low current shows low discharge capacity due to V crossover.
- Nafion at high current show low charge capacity due to resistive losses.

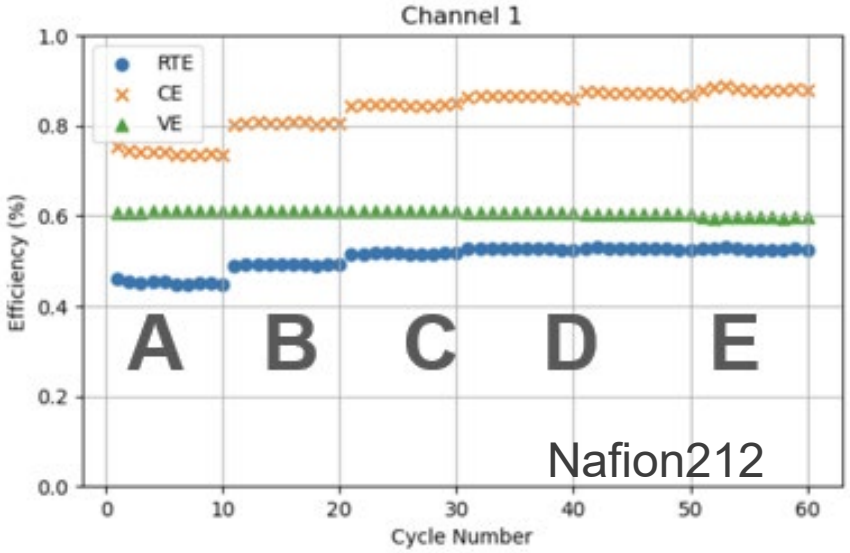


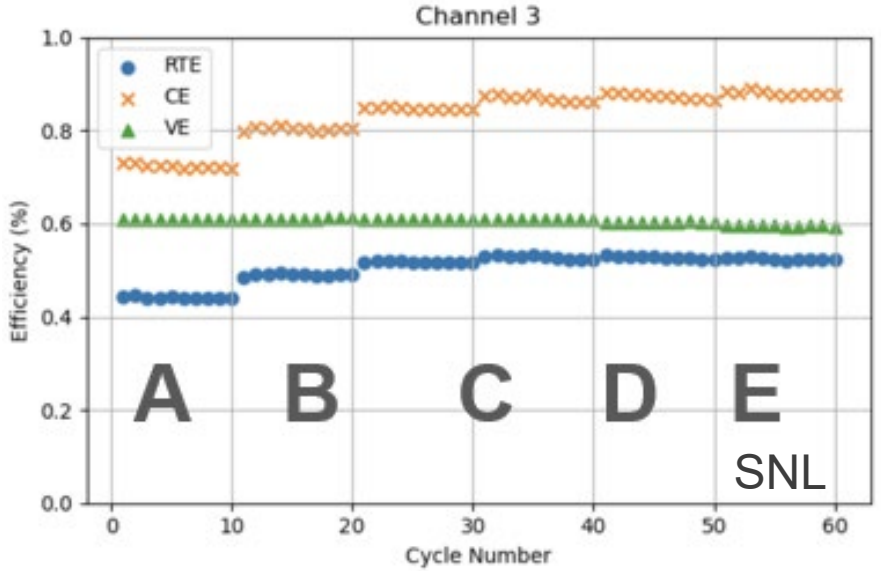


- SNL at low current shows high discharge capacity due low V crossover.
- SNL at high current show good charge capacity due to low resistive losses.

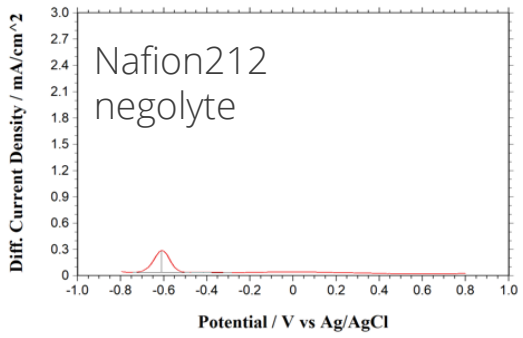
Results: Industry Testing BioZen Batteries

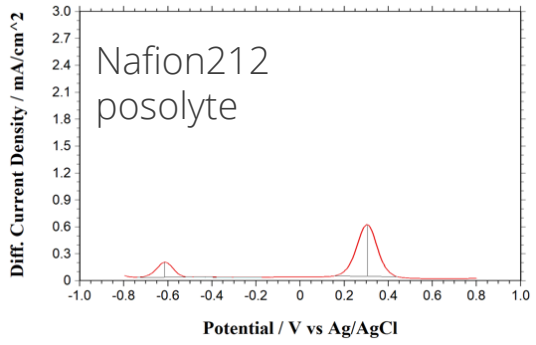
BioZen anolyte/catholyte with Nafion212 (channel 1) and Sandia polymer (channel 3).
Results membranes nearly identical; CE 80%, VE 60% and RTE 50%.

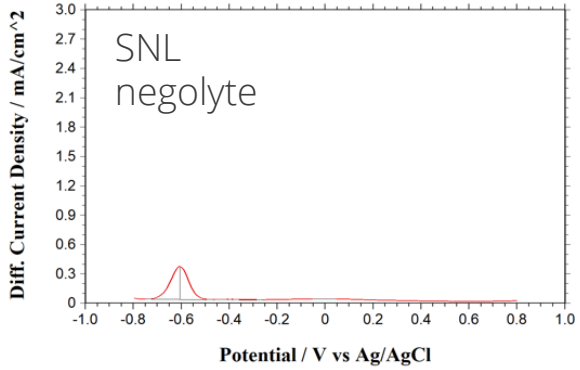


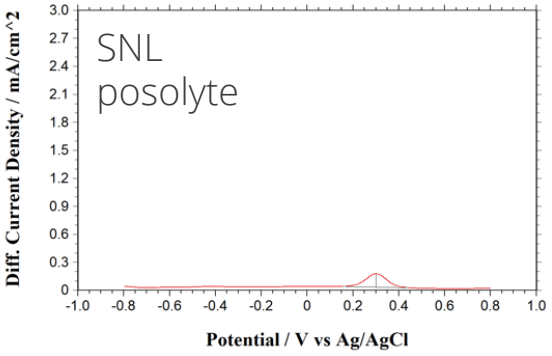


After testing complete negolyte and catholyte compartments were analyzed to measure crossover.







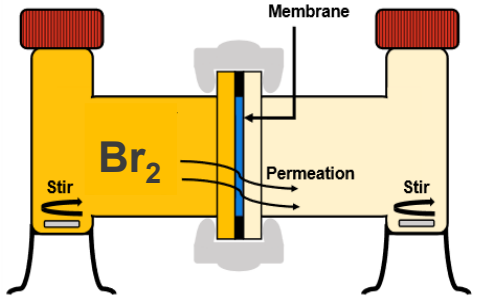


Crossover degradation in Nafion due to negolyte passing membrane into posolyte.
No crossover degradation in SNL, negolyte only contains negolyte, vice versa.

Results: Industry Testing Coulomb Technology

- Project funded by DOE Office of Technology Commercialization FY23-25.
- Initially partnered with Redflow. Australian Zn/Br_2 battery manufacturer.
- Redflow interested in membrane that would prevent Br_2 crossover, while still allowing high conductivity of charge balancing ion.
- Before building battery Redflow requested evidence of selectivity [prevent Br_2 allow H^+].

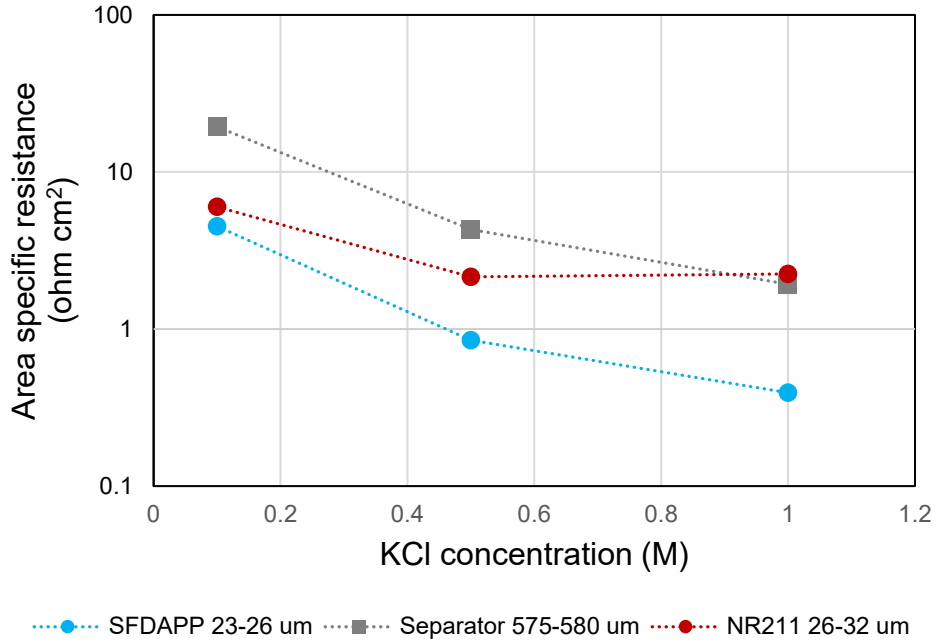
Br_2 Diffusion



Membrane	Diffusion coefficient of Br_2
Daramic	$1.23*10^{-6}cm^2/s$
Sandia	$1.5*10^{-10}cm^2/s$

- SNL four orders magnitude lower Br_2 compared to Daramic

H^+ area specific resistance



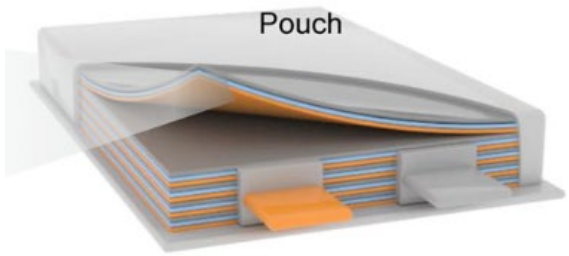
- SNL membrane 5x lower ASR compared to Daramic

Performed by Tommy George of Professor Aziz's Group

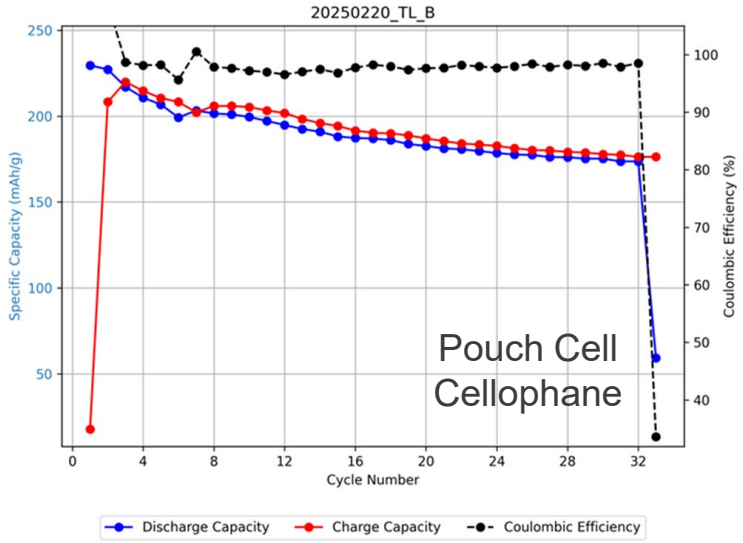
Industry Testing Coulomb Technology

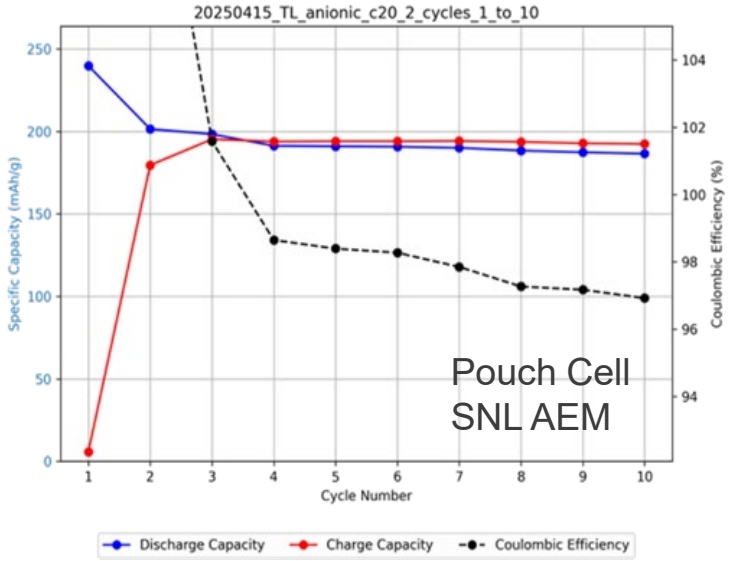
- Coulomb Technology is a battery developer based in Knoxville, Tennessee.
- In addition to Na ion batteries, Coulomb is also investigating Zinc based systems.
- Cellophane is used as state of the art. Will ion exchange membranes perform better?

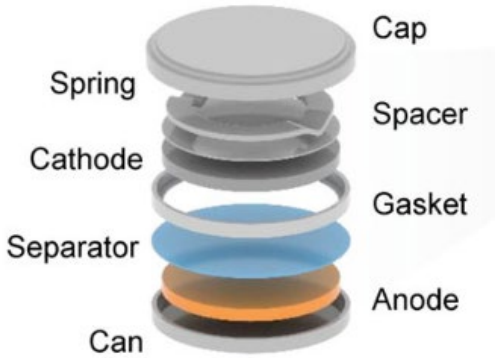
By Thanh Le



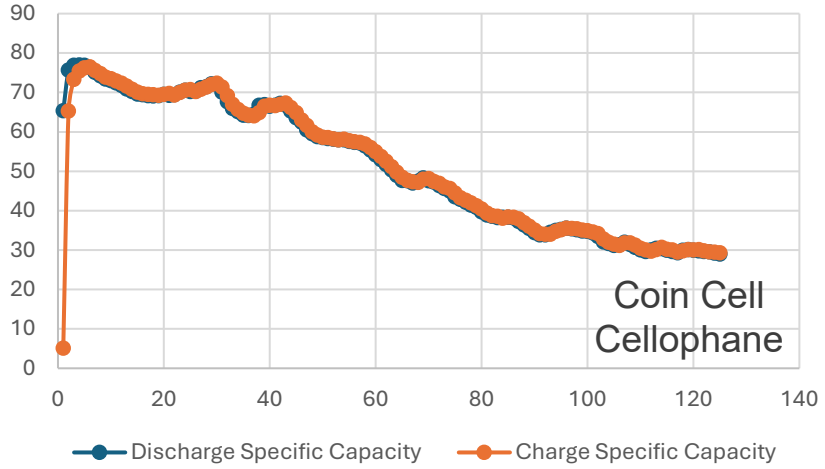
Pouch-type cell

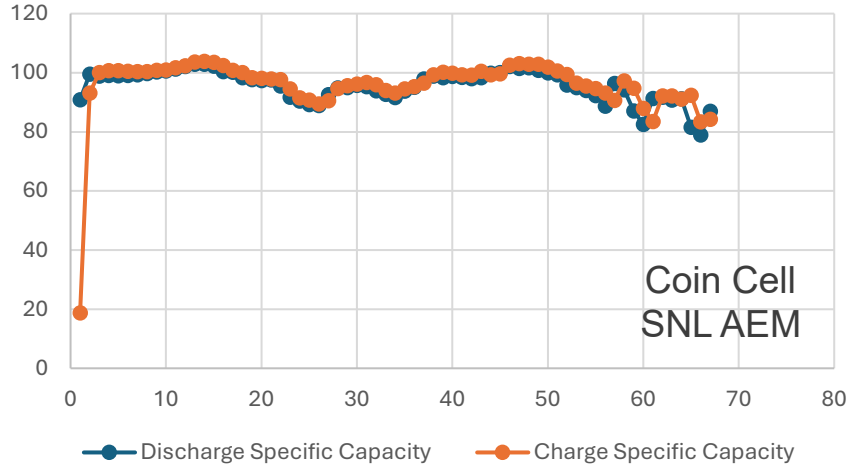






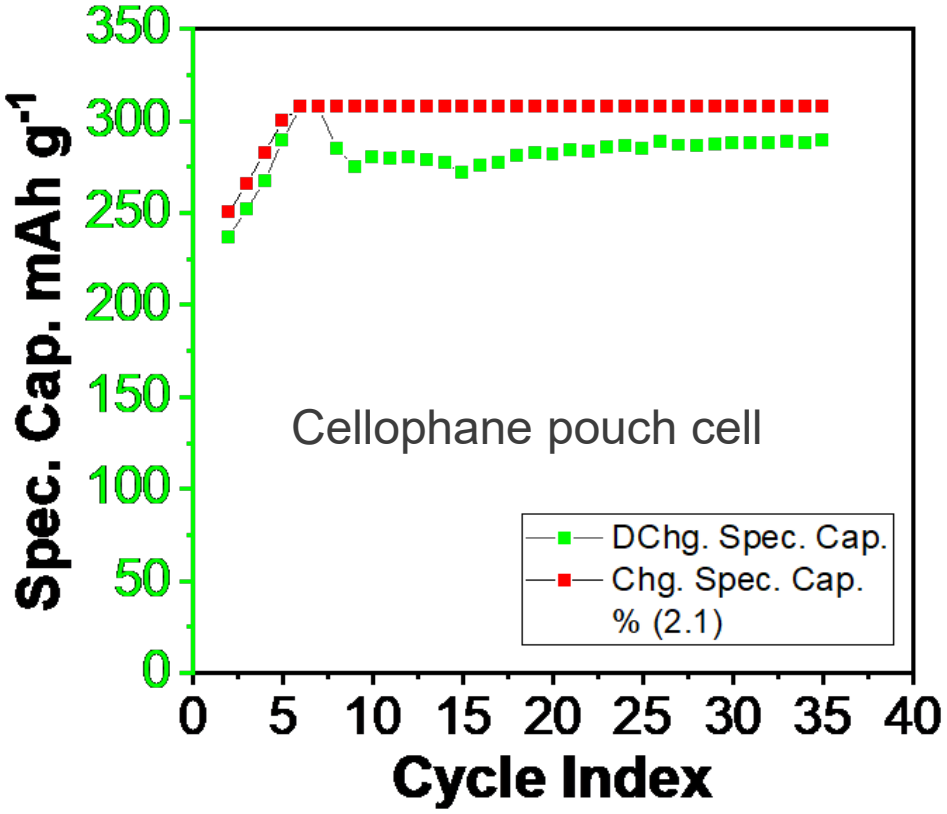
Coin-type cell

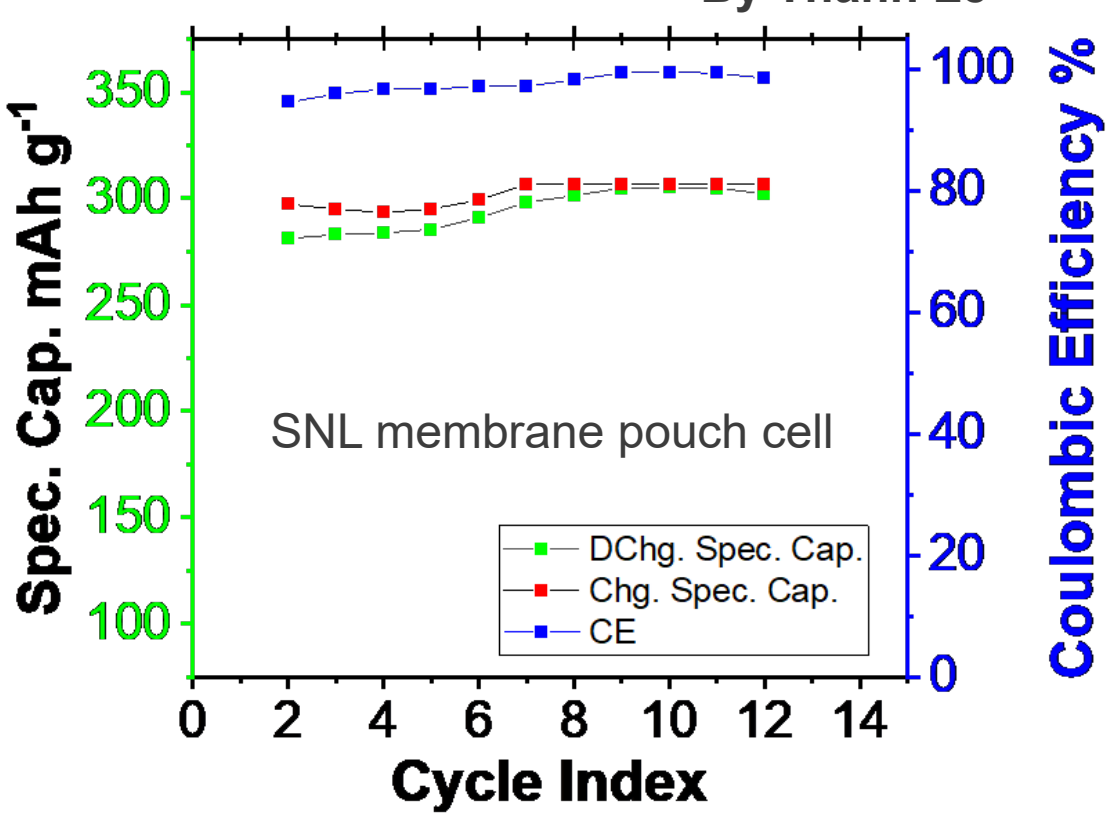




Industry Testing Coulomb Technology

By Thanh Le





- Ladder-like activation cycling with an initial discharge capacity dip before reaching a stable plateau.
- Lower discharge capacity compared to charge capacity.

- No activation as seen in cellophane cell.
- High coulombic efficiency 99.5%.
- Consistent charging voltage curves indicate good interfacial contact and active material utilization.

Conclusions

- Developing membrane material that can be readily modified for multitude of applications.
- Testing by industrial collaborators show promising performance in various battery types/configurations.

Impact

- Four patents developed under OE funds are currently being commercially licensed.
- Materials have shown good properties as battery makers can handle/process films by techniques utilized with state of the art materials.

Future Directions

- Looking to replace fluorinated aryl rings with non fluorinated substances.

ACKNOWLEDGEMENTS

- *This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division.*

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