Ambient Temperature Polysulfide-Based Redox Flow Batteries and Membrane Development

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DOE OE Energy Storage Peer Review
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Project Team

Core Expertise and Focus Areas

- High energy flow battery chemistries based on earth-abundant active materials
- Ion-selective polymer electrolytes with high ionic conductivity for Na-based batteries
- Advanced characterization and device integration
Acknowledgment

This work is supported by Dr. Imre Gyuk, Manager, Energy Storage Program, Office of Electricity, Department of Energy.

Thanks to Michael Starke, program manager, ORNL.
Long-duration energy storage (LDES) systems will play an integral role in achieving clean electricity from renewables to meet decarbonization goals.

**DOE Energy Earthshots 2030 Goals**
- Long duration energy storage > 10 hrs
- Reducing energy storage cost by 90%

**FY22 Technical Achievements**
- Developed liquid electrolyte to stabilize Na metal anode
- Identified novel additives to increase solubility of low-order Na polysulfides
- Fabricated mechanically robust single-ion conducting membranes for Na-Na$_2$S$_x$ RFBs

### ORNL R&D focuses on next-generation redox flow batteries (RFBs) based on earth-abundant active materials and advanced polymer electrolytes.

<table>
<thead>
<tr>
<th>Metric</th>
<th>Target Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Installed Capital Cost</td>
<td>$40/kWh (for 10 h storage)</td>
</tr>
<tr>
<td>Lifetime</td>
<td>20+ years</td>
</tr>
<tr>
<td>Storage Duration</td>
<td>10+ hours</td>
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</tbody>
</table>


Timeline of ORNL Research on Nonaqueous Redox Flow Batteries

Crosslinked PEO Membranes

In-Situ UV-Vis Crossover Setup

Glass Fiber/PEO Composites

Single-Ion Conductor Membranes

Bilayer Membrane Benchmarking

2018

Mediated Red Phosphorus Anode

Biphenyl/Na$_2$S$_x$ Cylindrical Cell

Nonaqueous Flow Cell Testbed

3 Electrode AC Impedance Method Development

2022

Reversible Na Metal Anodes

$E(i) - E_{eq} = \int_0^i Z(i')di'$

*references to these works are available upon request
Na$_2$S$_x$ is promising catholyte for nonaqueous flow batteries due to low cost and outstanding cycling stability.

**Na$_2$S$_x$ in Diglyme (2EGDME)**

- **NaS$_8$**
- **Na$_2$S$_7$**
- **Na$_2$S$_6$**
- **Na$_2$S$_5$**
- **Na$_2$S$_4$**

**Overview of Na$_2$S$_x$ Catholytes**

- Low cost, earth-abundant active material
- Outstanding reversibility and cycling stability
- Low solubility ($<0.1m$) when $x<5$
- Low sulfur utilization (125 mAh/g) when only soluble Na$_2$S$_x$ species are cycled.
- Cycling insoluble species (e.g., Na$_2$S$_4$, S) is only viable for small lab-scale prototypes.

**Soluble Species**

- S/Na$_2$S$_4$

**Precipitates**

- Na$_2$S$_4$
- NaS$_8$

*Impurities

**Electrochemical Properties**

- Specific Capacity / mAh g$_{S}$
- Cell Potential / V

**JCPDS**

- NaS$_8$: 08-2047
- Na$_2$S$_4$: 25-1112

Adding $P_2S_5$ to low-order $Na_2S_x$ yields high-capacity, highly soluble Na-P-S catholyte. FY23 will explore electrochemical properties of these new catholytes.

$$Na_{2}S_{x} + P_{2}S_{5} \rightarrow Na_{2}P_{2}S_{5+x}$$

* Assumes 2 electrons transferred per sulfur

<table>
<thead>
<tr>
<th>Composition</th>
<th>Theoretical Capacity* (mAh/g AM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Na_2P_2S_6$</td>
<td>1,070</td>
</tr>
<tr>
<td>$Na_2P_2S_7$</td>
<td>1,130</td>
</tr>
<tr>
<td>$Na_2P_2S_8$</td>
<td>1,177</td>
</tr>
<tr>
<td>$Na_2P_2S_9$</td>
<td>1,220</td>
</tr>
</tbody>
</table>

ORNL Invention Disclosure 81939560  (Submitted Sept. 13, 2022)
NaPF$_6$-based glyme electrolytes enable highly reversible Na metal anodes which opens vast opportunities for Na metal hybrid flow batteries.

**Electrolyte Formulations Investigated**

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Salts</th>
</tr>
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<tbody>
<tr>
<td>Monoglyme</td>
<td>NaOTF</td>
</tr>
<tr>
<td>Diglyme</td>
<td>NaClO$_4$</td>
</tr>
<tr>
<td>Tetruglyme</td>
<td>NaTFSI</td>
</tr>
<tr>
<td></td>
<td>NaPF$_6$</td>
</tr>
</tbody>
</table>

**Na|Na Symmetric Cell**

- **NaOtf**
- **NaClO$_4$**
- **NaTFSI**
- **NaPF$_6$**

**Na|Cu Asymmetric Cell**

- **Na Plating** (1 mAh/cm$^2$)
- **Na Stripping** (0.5V cutoff)

**Average**: 99%±1.76 CE

**Stable Na passivation and plating/stripping behavior in NaPF$_6$/2EGDME electrolyte.**

J. L. Tyler et al. 2022 (Unpublished)
Next-Generation Membranes: ORNL’s single-ion conducting polymers have outstanding properties compared to conventional polymers (e.g., PEO)

- Low cost (prepared from commercial polymer precursor)
- High Na⁺ selectivity in concentrated electrolytes
- High Na⁺ conductivity (~0.1 mS/cm at RT)
- Compatible with wide range of supporting electrolytes

Advantages of ORNL’s single-ion conducting membranes

- Ion-selective sidechain

20-30 µm

>1 GPa modulus

The performance of hybrid flow batteries containing Na metal anode and Na$_2$S$_8$ catholyte were benchmarked using commercial membranes.

**Key Findings:**
1. Hybrid Na|Nafion|Na$_2$S$_8$ hybrid flow cells exhibit high capacity and moderate cycling stability.
2. Strategies needed to stabilize Na metal anode
3. Membranes with improved selectivity (e.g., single ion conductors) needed.

J. L. Tyler et al. 2022 (Under Review)
The chemical stability and Na$_2$S$_8$ crossover rates of commercial membranes were evaluated. A bilayer membrane (Celgard|Na$^+$ Nafion) will be tested in FY23 to improve cycling stability of Na metal/Na$_2$S$_x$ hybrid flow cells.
Ongoing and Future Work

Nonaqueous Catholytes from Earth Abundant Materials
- \( \text{Na}_2\text{S}_x \) has outstanding cycling stability but limited practical capacity due to poor solubility when \( x \leq 4 \)
- New class of Na-P-S catholytes prepared by formation of solvated \( \text{Na}_2\text{S}_x-\text{P}_2\text{S}_5 \) complexes

Na Metal Hybrid Flow Batteries
- \( \text{NaPF}_6/2\text{EGDME} \) electrolyte enables outstanding reversibility of Na metal anode
- Requires membrane with excellent reductive stability and low \( \text{Na}_2\text{S}_x \) crossover

Ion selective membranes for Na-based flow batteries
- Crosslinked polymers, single ion conductors, composites
- Benchmark performance of emerging polymers from startup companies (e.g., Bettergy Corp.)
- Investigate transport using \textit{operando} FT-IR and UV-vis
- \textbf{Targets}: ASR < 50 \( \Omega \) cm\(^2\), no crossover
FY22 Manuscripts


FY22 Intellectual Property


Questions?
Backup Slides
I. High Energy, Earth Abundant Electrolytes for RFBs
- Reversible Na metal anodes
- Room temperature sulfur catholytes
- Mediated anodes/cathodes

![Na2Sx Catholyte](image)

<table>
<thead>
<tr>
<th>Catholyte</th>
<th>Discharge</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaS8</td>
<td>125 mAh/gS</td>
<td></td>
</tr>
<tr>
<td>Na2S6</td>
<td>313 mAh/gS</td>
<td></td>
</tr>
<tr>
<td>Na2S7Na2S6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na2S5Na2S6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na2S4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

II. Cost-effective Membranes for RFBs
- Crosslinked polymer composite electrolytes
- Highly selective single ion conductors
- Scalable synthesis and processing routes

III. Advanced Characterization to Optimize Device Performance
- **Spectroscopy**: Identify polymer structure/transport correlations
- **Electrochemistry**: Probe parasitic reactions, assess long-term stability
- **AC Impedance**: Quantify energy loss mechanisms
**Next-Generation Membranes**: Address major bottlenecks of existing membranes which lack the necessary conductivity, selectivity, and mechanical properties.

**Ceramic Separators** (e.g., Na⁺ β”-Al₂O₃)
- Thickness >0.5mm
- Brittle
- High manufacturing cost

**ORNL’s Next-Generation Polymer Membranes**

- **Gen I Polymer/Ceramic Filler Composites**
  - 2018
  - *ACS Energy Letters*, 3(7), pp.1640-1647

- **Gen II Crosslinked Polymers**
  - 2022

- **Gen III Polymer/Inorganic Scaffold Composites**
  - 2018
  - *Chem*, 2022, 8(6), 1-22
  - *Macromolecules*, 2022 (accepted)
  - U.S. Patent Application 63/165,865, filed March 24, 2022

- **Gen IV Single ion Conducting Polymers**
  - 2022
  - *ACS Energy Letters*, 3(7), pp.1640-1647

**ORNL Membrane Technology**
- Compatible with R2R processing (<50 µm)
- High mechanical strength (GPa)
- High Na⁺ conductivity (>0.1 mS/cm at 25°C)
Catholyte and Device Prototypes: ORNL developed custom hardware for nonaqueous biphenyl/sodium polysulfide flow batteries which operate at 25°C.

Cathode: \( \text{Na}_2\text{S}_8 + 2\text{Na}^+ + 2e^- \leftrightarrow 2\text{Na}_2\text{S}_4 \)  
\( E^0 = 2.3 \text{ V vs. Na/Na}^+ \)

Anode: \( \text{Na}^+\beta^- \leftrightarrow \beta^0 + \text{Na}^+ + e^- \)  
\( E^0 = 0.2 \text{ V vs. Na/Na}^+ \)

Full Cell: \( \text{Na}_2\text{S}_8 + 2\text{Na}^+\beta^- \leftrightarrow 2\text{Na}_2\text{S}_4 + 2\beta^0 \)  
\( E_{cell} = 2.1 \text{ V} \)

NaS₈ Na₂S₈ Na₂S₇ Na₂S₆ Na₂S₅ Na₂S₄

125 mAh/gₜₜ

313 mAh/gₜₜ

Cylindrical Cell Configuration

Flow Cell Configuration

Inner: Na₂Sₓ Catholyte
Outer: Na-Biphenyl (Na⁺β⁻) Anolyte

FY21 Recap: Biphenyl/Na$_2$S$_x$ flow cells containing ceramic exhibit outstanding cycling stability (several months continuous testing).

**Full Cell: Cycling Soluble Phases**

Na$_2$S$_5$ $\leftrightarrow$ Na$_2$S$_8$ ($Q_{theoretical} = 125$ mAh/g$_S$)

**Full Cell: Cycling Insoluble Phases**

Na$_2$S$_8$ $\leftrightarrow$ S$_8$ ($Q_{theoretical} = 209$ mAh/g$_S$)