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

Nicholas Cross, Renaldo Springer, Christopher Gorski, Serguei Lvov, Matthew Rau, Derek Hall

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

Award Number: FE0032030-FOA 2332
“Low-grade” heat is abundant

Estimated U.S. Energy Consumption in 2021: 97.3 Quads

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

“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\textsubscript{aq}-TRAB) works

Positive electrolyte
CuBr\textsubscript{2}^0 + e\textsuperscript{-} = CuBr\textsubscript{2}^−

Weak ligand, Br\textsuperscript{-}

Strong ligand, NH\textsubscript{3}
Cu(NH\textsubscript{3})\textsubscript{2}^{2+} + e\textsuperscript{-} = Cu(NH\textsubscript{3})\textsubscript{2}^{+}

Negative electrolyte

"Power and energy capacity tradeoffs in an all-aqueous copper thermally regenerative ammonia battery", Cross, et al., 2022
Milestone 1: Quantify thermodynamic energy storage density

Milestone 2: Preliminary power density assessment using a COMSOL model
Solubility limits and equilibrium potentials were measured at varying ligand concentrations

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Concentration (mol kg(^{-1}))</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br(^{-})</td>
<td>4</td>
<td>648 ± 2</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>518 ± 1</td>
</tr>
<tr>
<td>Cu(I,II)</td>
<td>“Standard”</td>
<td>150</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>1</td>
<td>23 ± 5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>-47 ± 1</td>
</tr>
</tbody>
</table>

- Cell potential can reach ~700 mV with high concentration
- Cu(I)NH\(_3\) complex limits solubility to 0.6 M
Theoretical energy density was estimated to be double previous TRB chemistries.

Cell potential: ~700 mV

Max solubility: 0.6 M

$$Max \ energy \ density = E_{cell}^0 * c_{max} * F$$

Milestone 1: Quantify thermodynamic energy storage density

"Power and energy capacity tradeoffs in an all-aqueous copper thermally regenerative ammonia battery", Cross, et al., 2022
Power density can be improved at elevated temperatures through lower ohmic losses
Power density is simulated accurately with our model and shows the importance of ohmic losses.

Milestone 2: Preliminary power density assessment using a COMSOL model

Unpublished data
How do the electrolyte composition and operating parameters impact power and energy output?
Increasing ammonia concentration increases power density

0.1 M Cu, 5 M NH₄Br
200 ml min⁻¹, 99% SOC
Nafion 117

“Power and energy capacity tradeoffs in an all-aqueous copper thermally regenerative ammonia battery”, Cross, et al., 2022
Higher copper concentration does not change power and increases energy density

Higher copper concentration does not change power and increases energy density.

“Power and energy capacity tradeoffs in an all-aqueous copper thermally regenerative ammonia battery”, Cross, et al., 2022
Increasing applied current can counteract ammonia crossover

- Evidence of a tradeoff between overpotential and discharge time
- Higher applied currents lead to higher overpotentials and less usable energy
- Higher applied currents decrease discharge time which provides less time for parasitic crossover

0.3 M Cu, 5 M NH₄Br, 1 M NH₃₂
200 ml min⁻¹, 99% SOC
Nafion 117

"Power and energy capacity tradeoffs in an all-aqueous copper thermally regenerative ammonia battery", Cross, et al., 2022
The Cu\textsubscript{aq} - TRAB performs well compared to previous TRAB chemistries

- Large increases in peak power and theoretical energy density

"Power and energy capacity tradeoffs in an all-aqueous copper thermally regenerative ammonia battery", Cross, et al., 2022
Milestone 1: Quantify thermodynamic energy storage density

Milestone 2: Preliminary power density assessment using a COMSOL model

Milestone 3: Identify performance characteristics of suitable membrane types
Membranes are being evaluated for peak and long-term performance.
Resistance data indicates that membranes can increase battery performance

- Charged membranes had lowest resistances
- NF membrane had low resistance, but will likely have high permeability
- Thin Sustainion membrane had best performance
An All-Aqueous Thermally Regenerative Ammonia Battery Chemistry Using Cu(I, II) Redox Reactions

Renaldo Springer,1,2 Nicholas R. Cross,3,4 Serguei N. Lvov,1,2,4 Bruce E. Logan,3,5 Christopher A. Gorski,5 and Derek M. Hall1,2,8,8,9

Power and energy capacity tradeoffs in an all-aqueous copper thermally regenerative ammonia battery

Nicholas R. Cross,a Matthew J. Rau,b Serguei N. Lvov,d,e,f, Christopher A. Gorski,f Bruce E. Logan,b,f, Derek M. Hall1,2,d,
Thank you and please contact us if you have any questions!

Derek Hall
dmh5373@psu.edu

Nicholas Cross
nrc83@psu.edu