NOVEL REDOX FLOW BATTERIES
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What is a redox flow battery?

- Stores energy in reduced and oxidized species in solution
- Solution is pumped through cell during charge/discharge

Positive: $A^n \rightarrow A^{n+1} + e^-$
Negative: $C^{n+1} + e^- \rightarrow C^n$

charge $\rightarrow$
discharge $\leftarrow$

Figure taken from C. Ponce De Leon et al. / J. Power Sources 160 (2006) 716-732
Experimental Flow-Through Cell

- Tokai Graphite
- Felt
- 50 μm Nafion
- Felt
- Tokai Graphite

Cell Flanges
Advantages of flow batteries

• High current and voltage efficiency
  • High usage of active materials
  • Stable voltage throughout charge and discharge
• Long useful life (> 20 years with maintenance)
  • No phase change in electrodes
  • Simple replacement of materials
• Modularity and scalability
  • Energy capacity is a function of the size of tanks
  • Power capacity is a function of the number of cells
## Redox Flow Batteries vs. Alternatives

<table>
<thead>
<tr>
<th></th>
<th>RFB</th>
<th>Primary Battery</th>
<th>Secondary Battery</th>
<th>Fuel Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rechargeable</td>
<td>✔</td>
<td>✗</td>
<td>✔</td>
<td>✗</td>
</tr>
<tr>
<td>Separate sizing of power and energy (capacity)</td>
<td>✔</td>
<td>✗</td>
<td>✗</td>
<td>?</td>
</tr>
<tr>
<td>No phase change on cycling</td>
<td>✔</td>
<td>✗</td>
<td>✗</td>
<td>✔</td>
</tr>
<tr>
<td>Simple outer sphere redox reactions</td>
<td>✔</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
</tr>
<tr>
<td>High energy density</td>
<td>✗</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
</tbody>
</table>

- **Cost (inexpensive materials)**: Fe, Sn...
- **Stability (cycle life)**: Accelerated Testing
- **Corrosion resistance**: Electrolyte
- **Energy density**: n=2... Solubility
- **Solution stability**: Single solution RFB, separator, membrane
Examples of flow battery chemistries

- **All-Vanadium**
  
  \[
  \begin{align*}
  \text{VO}^{2+} + \text{H}_2\text{O} & \rightarrow \text{VO}^{2+} + 2\text{H}^+ + e^- & E^0 = +1.0 \text{ V vs. SHE} \\
  \text{V}^{3+} + e^- & \rightarrow \text{V}^{2+} & E^0 = -0.26 \text{ V vs. SHE}
  \end{align*}
  \]

- **Tin-Bromine**
  
  \[
  \begin{align*}
  2\text{Br}^- & \rightarrow \text{Br}_2 + 2e^- & E^0 = +1.09 \text{ V vs. SHE} \\
  \text{Sn}^{4+} + 2e^- & \rightarrow \text{Sn}^{2+} & E^0 = +0.15 \text{ V vs. SHE}
  \end{align*}
  \]

- **Alkaline Iron-Cobalt (TEA)**
  
  \[
  \begin{align*}
  \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + e^- & E^0 = -0.76 \text{ V vs. SHE} \\
  \text{Co}^{3+} + e^- & \rightarrow \text{Co}^{2+} & E^0 = +0.25 \text{ V vs. SHE}
  \end{align*}
  \]

- **Nitrobenzene-Bromine**
  
  \[
  \begin{align*}
  2\text{Br}_3^- & \rightarrow 3\text{Br}_2 + 2e^- & E^0 = +1.10 \text{ V vs. SHE} \\
  \text{NB} + e^- & \rightarrow \text{NB}^- & E^0 = -0.90 \text{ V vs. SHE}
  \end{align*}
  \]
General Challenges and Motivation

- Cost is the primary driving factor
  - High capital costs (> $300/kWh or > $1000/kW)
  - Long payout (10+ years)
  - Polymer membranes for separators ($1000/m²)
  - Pumps and other system equipment

- Focus of research efforts
  - Cheaper materials
  - Higher energy density (most flow batteries < 100 Wh/L)
  - Better energy efficiency (most flow batteries ~ 80%)
Motivation and Goals

State-of-the-art RFBs suffer from capacity fading due to species crossover. Our goal was to develop a low-cost, gas-free, crossover-free technology in strongly alkaline electrolyte.

![Graph showing battery capacity fading over cycles]

Drawing of an all vanadium system with Nafion N117 membrane based on reference [1].

\[ A \rightleftharpoons B + e^- \]

\[ X + e^- \rightleftharpoons Y \]

\[ B \rightarrow Y \]

\[ B + Y = \text{deactivation} \]

Complexes of Fe and Co as Redox Species

(L) is an organic ligand. The maximum solubility of the Co/Fe system is $\approx 0.45$ M.
**Co/Fe: The Alkaline Redox Flow Battery**

- **Example: Half-Cells and Net Cell Reaction**

\[
\begin{align*}
[Fe(TEA)(OH)] + e^- & \rightarrow [Fe(TEA)(OH)]^2^+ \quad E = 1.05 \text{ } V \\
[Co(mTEA)(H_2O)] + e^- & \rightarrow [Co(mTEA)(H_2O)]^- \quad E = 0.04 \text{ } V
\end{align*}
\]

**Discharge:**

\[
C / 0.9 \text{ M } [Fe(TEA)(OH)]^{2^+}, 4 \text{ M } OH^- // 4 \text{ M } OH^-, 0.45 \text{ M } [Co(TEA)(OH)] \text{ } / \text{ C}
\]

\[E_{cell} = 1.00 \text{ } V\]

\[\text{mTEA = } \quad \text{TEA = }\]
Co/Fe: The Alkaline Redox Flow Battery

**Cell Performance**

**Battery Cycling**

- 50 μm thick Nafion membrane
- Carbon felt electrodes: (4.5 x 4.5 x 0.5) cm
- 10 mA/cm²
- Flow rate: 2 mL/min
- Voltage efficiency: 86.8 % in 10 cycles

**Battery Capacity, %**

- Charge Efficiency: 95%
- Volume: 50 mL
- Concentration: 50 mM
- Atmosphere: Argon
- Pump: Peristaltic
- Tubing: Norprene
Co/Fe: The Alkaline Redox Flow Battery
Sn/\text{Br}_2\text{ Redox Flow Battery}

Cell configuration

 Separator

C / HBr (2 M), NaBr (4 M) // HBr (2 M), NaBr (4 M), Sn^{4+} / C

Half-cell charge/discharge reactions

Positive electrode: \text{Br}_2 + 2\text{e}^- \rightleftharpoons \text{Br}^-

Negative electrode: \text{SnBr}_6^{2-} + 2\text{e}^- \rightleftharpoons \text{SnBr}_4^{2-}

Advantages

1. No cross contamination problem
2. High capacity per unit concentration (2\text{e}^-\text{ electrons transfer})
Understanding the mechanism should offer guidance for solving the large irreversibility.
Scanning electrochemical microscopy (SECM) - Mechanistic study of Sn(IV)/Sn(II) reduction-

The short-lived Sn(III) intermediate, Sn(III)Br₆³⁻, was detected at small $d$

Br$_2$/Nitrobenzene Redox Flow Battery

Redox active liquids for low-cost, high-energy-density flow batteries

- A bromine (Br$_2$) / nitrobenzene (NB) flow battery could achieve energy densities comparable to Li-ion batteries.

$\Delta E = 2.0 \text{ V}$

Negative: NB + e$^- \rightarrow$ NB$^-$

Positive: 2Br$_3^-$ $\rightarrow$ 3Br$_2$ + 2e$^-$

charge $\rightarrow$

$\leftarrow$ discharge
Advantages of Br$_2$/NB RFB

• High energy density $\rightarrow$ lower cost, smaller footprint
  • Vanadium RFB: 25-35 Wh/L
  • RFB with redox liquids (theoretical): $\sim$ 200 Wh/L

• Simple chemistry $\rightarrow$ new cell designs
  • Low-cost membrane or membrane-free

![Diagram of cell design]

**Solvent:** nitrobenzene

**Anode and cathode:** porous carbon

**Separator:** low-cost polymer
Research Challenges

- Low solution conductivity → low power density
  - We can have lower $/kWh, but can we achieve lower $/kW?
- Energy density is limited by solubility of electrolyte salt
- Br\(^{-}/\)Br\(_2\) reaction is not reversible in nonaqueous solvents

Can we uncover the reaction mechanisms and make the reactions more reversible?

**Reaction 1:** \(3\text{Br}_2 + 2e^- \leftrightarrow 2\text{Br}_3^-\)

**Reaction 2:** \(\text{Br}_3^- + 2e^- \leftrightarrow 3\text{Br}^-\)

![Graph showing electrochemical reactions with current (\(\mu\)A) vs. potential (V vs. Ag QRE).]

- 10 mM TEA-Br
- 0.1 M TEA-BF\(_4\)
- Pt WE (radius = 1 mm)
- Ag wire quasi-reference
- scan rate = 20 mV/s
Acknowledgment

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