Advanced Aqueous Redox Flow Battery

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Redox flow batteries (RFB)

Why RFB?

- High safety
  - Na-S Battery: NGK 2MW system fire in September 21 of 2011.
  - Li-ion Battery: Electrovaya 1.5MW lithium polymer system fire in November of 2012.
  - Lead Acid Battery: Xtreme Power 15MW lead-acid battery fire in August of 2012

Separation of reactive materials
Easy thermal management

Zhenguo Yang, et. al. Chemical Reviews, 111, 2011, 3577
An integrated approach to advance the RFB technology

Novel electrolyte
- L. Li, etc. *AEM* 2011, 394-400
- W. Wang, etc. *EES* 2011, 4068

Flow stack R&D

Advanced electrode
- B. Li, etc. *Nano. Lett.* 2013, 1330-1335
- B. Li, etc. *Nano. Lett.* 2014, 158-165

High performance membrane and transport
- X. Wei, etc. *AEM* 2013, 1215-1220
- Q. Luo, etc. *ChemSusChem* 2013, 268

Non-aqueous RFB
- W. Wang, etc. *ChemComm.* 2012, 6669
- X. Wei, etc. *AM, in press,* 2014
Review of RFB R&D at PNNL

Program start

Fe-V RFB

Paper published

1kW/1kWh DEMO

Fe-V License
Aartha USA
New Chemistry

UET first commercial system

License: UET/ X / Aartha/Wattjoule

Deployment
Major Challenge of the current RFB technology: low energy density

120MWh system, peak power ~15MW.
Each tank holds 1800m$^3$ of electrolyte.
- Large form factor/footprint
- Limited application
High energy density Zn-Polyiodide aqueous RFB

Solubility of ZnI$_2$ is 7M in water → theoretical energy density ~322Wh/L

Identify high solubility redox active species

$$I_2(s) + I^- \leftrightarrow I_3^- \quad K \approx 720 \pm 10(298K)$$

Positive: $3I^- \xrightleftharpoons[Charge]{Discharge} I_3^- + 2e^- (E_0 = 0.536V)$

Negative: $Zn^{2+} + 2e^- \xrightleftharpoons[Charge]{Discharge} Zn (E_0 = -0.7626V)$

Overall: $Zn^{2+} + 3I^- \xrightleftharpoons[Charge]{Discharge} Zn + I_3^- (E_0 = 1.2986V)$

Characteristics of the Zn-I RFB

- Ambipolar electrolyte
  - Both anion and cation are active species.
- Bifunctional electrolyte
  - Active species can act as charge carrier.
- High energy density
- High safety: PH value: 3~4
  - No strong acid
  - No hazardous materials
Electrochemical performance

CV of 0.085 M ZnI\(_2\) on a glassy carbon electrode at the scan rate of 50 mV s\(^{-1}\).

Typical charge-discharge curves at 1.5 M ZnI\(_2\) at a current density of 20 mA cm\(^{-2}\).
Electrochemical performance

Charge/discharge curves for the cell with 5.0 M ZnI$_2$ and Nafion 115 as membranes operated at the current density of 5 mA cm$^{-2}$.

The charge and discharge energy density as a function of the concentration of I$^-$. The inset lists concentration vs. energy density of several current aqueous redox flow battery chemistries for comparison.
Cycling performance

Capacities and energy density of the cell with 3.5 M ZnI$_2$ and Nafion 115 as membranes under the current density of 10 mA cm$^{-2}$.

Efficiencies of the cell with 3.5 M ZnI$_2$ and Nafion 115 as membranes under the current density of 10 mA cm$^{-2}$. 

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Polyiodide species in the catholyte

Raman spectra of catholytes at different state of charges (SOCs) and discharge from 0 to 100% SOC.
Voltage profiles of the flow cell test with different rest time.
Temperature stability of the catholyte

Temperature stability (off-line) of 100% SOC catholytes

<table>
<thead>
<tr>
<th>ZnI₂ (M)</th>
<th>50°C</th>
<th>25°C</th>
<th>0°C</th>
<th>-10°C</th>
<th>-20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>stable</td>
<td>stable</td>
<td>ppt</td>
<td>ppt</td>
<td>ppt</td>
</tr>
<tr>
<td>2.5</td>
<td>stable</td>
<td>stable</td>
<td>ppt</td>
<td>ppt</td>
<td>ppt</td>
</tr>
</tbody>
</table>

NMR and DFT study of the catholyte solution chemistry

\[
\text{[Zn}^{2+} \cdot I^- \cdot 5H_2O]^{+} \leftrightarrow \text{[Zn}^{2+} \cdot I^- \cdot 5H_2O]^{+} + I_2(s)
\]
Stabilize the catholyte through coordination chemistry

Temperature stability with alcohol additives

<table>
<thead>
<tr>
<th>ZnI₂ (M)</th>
<th>Vol% EtOH</th>
<th>50°C</th>
<th>25°C</th>
<th>0°C</th>
<th>-10°C</th>
<th>-20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>25</td>
<td>stable</td>
<td>stable</td>
<td>stable</td>
<td>stable</td>
<td>stable</td>
</tr>
<tr>
<td>25 (EG)</td>
<td>25</td>
<td>stable</td>
<td>stable</td>
<td>stable</td>
<td>stable</td>
<td>stable</td>
</tr>
<tr>
<td>2.5</td>
<td>25</td>
<td>stable</td>
<td>stable</td>
<td>stable</td>
<td>stable</td>
<td>stable</td>
</tr>
</tbody>
</table>
Mitigation of Zinc dendrite growth

Dendrite growth in the flowing electrolyte

Alcohol complexing ameliorate the dendrite growth

Morphologies of zinc dendrites after charge for the cells with 3.5 M ZnI$_2$ operated at the current density of 10 mA cm$^{-2}$ (A) in the static cell and (B) the flow rate of 100 mL min$^{-1}$.

Morphologies of zinc dendrites after charge (A) without EtOH and (B) with EtOH in the electrolytes.
Summary

- High energy density Zn-I RFB (>150Wh/L) has been designed and demonstrated
- Alcohol molecules are found to complex with the Zn ions, which improve the temperature stability and ameliorate Zn dendrite growth.

Future work

- Investigation of the Zn dendrite formation mechanism and development of mitigation methods.
- Improve the kinetics of the polyiodide redox reaction.

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- US Department of Energy’s Office of Electricity Delivery and Reliability – Dr. Imre Gyuk, Energy Storage Program Manager.
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**Effect of the Ethanol and anolyte volume**

Voltage profiles of a flow cell test on a 2.5M ZnI₂ electrolyte with and without ethanol.

Voltage profile of flow cell tests with different anolyte volumes.
Mass spectrometry analysis of catholyte

Mass spectrometry analysis of (a) pristine and (b) EtOH-added catholyte at fully charged condition. The presence of ZnI$_3^-$ and molecular triiodide confirms our NMR and DFT-based analysis.