Sealed Recombinant Flow Batteries

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Problem

• All-iron hybrid flow batteries operate using the following reactions:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Electrode</th>
<th>Reaction</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>negative</td>
<td>Fe$^{3+}$ + 2e$^-$ $\rightleftharpoons$ Fe$^{2+}$</td>
<td>-0.44</td>
<td></td>
</tr>
<tr>
<td>positive</td>
<td>Fe$^{3+}$ + e$^-$ $\rightleftharpoons$ Fe$^{2+}$</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>overall</td>
<td>3Fe$^{2+}$ $\rightleftharpoons$ Fe$^{3+}$ + 2Fe$^{2+}$</td>
<td>1.21</td>
<td></td>
</tr>
</tbody>
</table>

• During battery charging, the $H_2$ side reaction (Equation 1) can lead to electrolyte instability

$$2H^+ + 2e^- \rightarrow H_2$$  (1)

• The increase in pH promotes formation of hydroxide precipitates that hinder battery performance

Solution

• A capillary-action galvanic reactor (CGR) can carry out Equation 2 passively

$$2Fe^{3+} + H_2 \rightarrow 2Fe^{2+} + 2H^+$$  (2)

• In-tank (no footprint)

• Self-regulating (no control system)

• Low-cost

CGR Electrochemistry in Pressurized Vessels

• A three-electrode apparatus was used to investigate $H_2$ oxidation

• Faster kinetics at higher $H_2$ partial pressures

Three-electrode apparatus

• In the two-electrode apparatus, $H_2$ was added into the system and then the pressure drop was recorded; the rate was then given by $i_{H_2} = -\frac{nFV_{H_2}}{\delta P/\delta t}/RT$

• Mixed-potential consistent with Evans diagram

Average current density of 8 mA/cm$^2$ for electrode with 6 cm$^2$ catalyzed area

Two-electrode apparatus

Battery Cycling with Recombination

• Conventionally, hydrogen is allowed to vent to the atmosphere

• Alternatively, fuel cells, PBRs, or other complex systems are used to balance the electrolyte

• In the proposed system, the reservoir headspace volumes are connected and recombination occurs within the positive electrolyte reservoir

Pressure was monitored during continuous cycling at $\pm$ 20 mA/cm$^2$ at room-temperature

The hydrogen pressure was controlled passively through Equation 2, maintaining the essential chemical balance of battery reactants

Conclusions and Future Work

• The $H_2$-Fe$^{3+}$ recombination reaction was successfully carried out under passive, room-temperature conditions using a novel electrochemical reactor

• Promising method for maintaining electrolyte stability in aqueous flow batteries; offers significant advantages compared to fuel cells, packed-bed reactors, or rebalancing with external reactants

• Future work will include reactor optimization and larger-scale demonstration

Acknowledgements

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