Ambient Temperature Aqueous Sulfur Batteries for Ultralow Cost Grid Storage

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Sulfur

4 million cubic meters in single sulfur stockpile
16 terawatthours of Li-S batteries
10 years supply for all North American and European light vehicles if all are EVs
3 years Google’s electricity consumption
4 times world’s existing pumped hydroelectric storage capacity

<table>
<thead>
<tr>
<th></th>
<th>US$/kg</th>
<th>kAh/kg</th>
<th>US$/kAh</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO₂</td>
<td>40</td>
<td>0.14</td>
<td>292</td>
</tr>
<tr>
<td>Graphite</td>
<td>12</td>
<td>0.37</td>
<td>32</td>
</tr>
<tr>
<td>Lithium</td>
<td>50</td>
<td>3.86</td>
<td>13</td>
</tr>
<tr>
<td>Zinc</td>
<td>3</td>
<td>0.82</td>
<td>4</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.25</td>
<td>1.67</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Air-breathing aqueous sulfur battery using water, air, and sulfur, and operating at ambient temperature

Li et al., Joule, 1, 306-327 (2017). DOI: 10.1016/j.joule.2017.08.007
Chemical cost of new battery chemistries over 60 years of battery development

Chemical cost = cathode + anode + electrolyte

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Chemical cost = cathode + anode + electrolyte

Assume 25%-50% utilization of full sulfur capacity

Lowest chemical cost of rechargeable battery chemistries currently known

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Air-breathing aqueous sulfur battery

Cathode (oxygen) electrochemistry

\[ \text{Discharge (reduction)} \]
\[ 2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^- \]

\[ \text{Charge (oxidation)} \]

Alkaline working ion \((A^+)^\) can be either \(Li^+\) or \(Na^+\)

\[ E^0 = 1.23 \text{ V} \]

vs. SHE
Air-breathing aqueous sulfur battery

Anode (sulfur) electrochemistry

\[ \text{Charge (reduction)} \]

\[ \text{Discharge (oxidation)} \]

\[ \text{E}^0 = -0.45 \text{ V vs. SHE} \]

\[ \text{Na}_2\text{S}_4, > 3 \text{ M solubility (in 3 M NaOH)} \]

High basicity is required to stabilize it.
Four lab-scale cell designs for various experiments

A. Polarization and efficiency tests (H-cell)
B. Catholyte limited cycling (L-cell)
C. Anolyte limited cycling (low-vol. cell)
D. Air-breathing flow cell

Purpose:
Membrane resistance dominates the overall cell resistance at > 2 mA/cm²

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Lower membrane resistance, higher power density

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Demonstration of ~1000h stability for catholyte and anolyte using non-flowing cells

Li catholyte, 1600h, 96% SOC

Na anolyte, 720h, Na$_2$S$_2$ to Na$_2$S$_4$

\[ \text{Sulfur SOC (\%)} \]

\[ \begin{align*}
\text{Voltage (V vs Pt Pseudo)}
\end{align*} \]

\[ \begin{align*}
\begin{array}{c}
\text{Sulfur Oxidation} \\
\text{Sulfur Reduction}
\end{array}
\end{align*} \]

\[ \begin{align*}
\text{Room Temperature, Air Tight} \\
1 \text{mm Ceramatec NASICON} \\
0.65 \text{ mA/cm}^2
\end{align*} \]

\[ \begin{align*}
1 \text{M Na}_2\text{S}_4 + 3 \text{M NaOH} \\
\text{Stainless Steel electrode}
\end{align*} \]

\[ \begin{align*}
\text{1st Cycle} \\
\text{10th Cycle} \\
\text{20th Cycle} \\
\text{30th Cycle}
\end{align*} \]

\[ O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O \]

\[ \text{Na}_2\text{S}_4 + 2Na^+ + 2e^- \leftrightarrow 2\text{Na}_2\text{S}_2 \]
Lab-scale flow cell prototyping in the air-breathing mode (Li\(^+\) working ion)

\[\text{Li et al., Joule, 1, 306-327 (2017). DOI: 10.1016/j.joule.2017.08.007}\]
Towards higher energy density (for lower cost)
Sodium polysulfide stability limits are defined by *speciation* and *solubility*.

Conventional redox flow batteries use fully soluble electrodes, thus, **constrained by the solubility of the active materials**. For aqueous polysulfide, the upper solubility limit is **5M sulfur** as demonstrated previously.
Reversible precipitation in an 8M sulfur solution during reduction from Na$_2$S$_4$ to Na$_2$S$_2$ ($S_4^{2-}$ to $S_2^{2-}$) (C/21 galvanostatic cycling)

Voltage (V vs Pt Pseudo)

Time (Hr)

(C/21 galvanostatic cycling)

2.5 mL 2M Na$_2$S$_4$ + 3M NaOH Stainless Steel electrode
Room Temperature, Air Tight 1mm Ceramatec NASICON 1.97 mA/cm$^2$

Asymmetric anolyte-anolyte cell
Stable cycling through reversible precipitation

- **Faster dissolution rate** of polysulfide precipitates than in non-aqueous Li-S batteries enabling recovery of capacity from electrically disconnected precipitates.
- **Signs of precipitation** in voltage profile.
- Stable cycling for **>1600 hours**.
- 5M Sulfur: 67 Ah/L → 8M Sulfur: **107 Ah/L** → 10M Sulfur: **134 Ah/L**.
Installed cost comparison between storage technologies – PHS and CAES

At long storage durations, the cost contribution of turbines is “diluted” and system cost drops.

PHS – using water as the working fluid

CAES – using air as the working fluid

Installed Cost (US$/kWh)

Duration E/P (hours)
Installed cost comparison between storage technologies – PHS, CAES, Li-ion, and VRFB

VRFB – decoupled energy and cost but vanadium is expensive

Installed cost at long duration asymptotically approaches energy cost
Installed cost comparison between storage technologies – PHS, CAES, Li-ion, VRFB, and our work

Air-breathing aqueous sulfur battery – ultralow chemical cost

Assume:
- Acidic catholyte, 5 M working ion, and 5 M total sulfur, $S_2^{2-}$ to $S_4^{2-}$ with experimentally determined OCV
Installed cost comparison between storage technologies – PHS, CAES, Li-ion, VRFB, and our work

Overall cost of our battery matches that of PHS or CAES

Assume:
ASR 15 – 100 Ω cm² (peak power 4 – 30 mW/cm²) and membrane cost 10 – 100 $/m²; 1.7 $/kWh energy cost (Na⁺)
Key Takeaways

- We developed an air-breathing aqueous sulfur battery with low chemical cost of storage ~1US$/kWh.
- In a flow battery architecture, the installed cost of this battery technology can compete with that of PHS or CAES, without geographical constraints.
- Future work should be focusing on decreasing the stack power cost by reducing the membrane resistance and cost, streamlining the cell designs, and using less or lower-cost catalyst.