Living Forever By Dying Everyday

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Group Hypothesis

- Capital Cost
- Energy Density
- Power Density
- Amortization/Operating Cost (Cycle life and Safety)

(Utility Space) 1% of the literature

EVs are in the middle

(Ragone/Portable Space) 99% of the literature
A Brief History of Batteries

~1800
Low Surface Area
Low Rate

~1960
Higher Surface Area
Porous Electrode

~1990-2017
Wound Structures
3D Architectures

~1980-2017
Flow Batteries
“Decouple” Energy and Power

Decoupling Energy and Power

Hierarchical Architectures
Much Has Changed

~1800
- Zinc Silver
- Nickel Iron

~1960
- Lead Acid
- Nickel Cadmium
- Nickel Metal Hydride
- Lithium Ion
- Many Varieties

~1980
- Iron Chromium
- Zinc Bromine
- Vanadium Redox
- Quinone (Organic)

We Have Gotten Much Better At Chemistry And Manufacturing
Some Things Haven’t Changed

What Do All Of These Designs Prioritize?

1) The Oxidant and The Reductant May Never Touch
2) Maximize Shelf Life
3) Balance Energy and Power
4) Make It Rechargeable

*Are These Rules Inviolable? Is This Order Critical?*
Some Things Haven’t Changed

Are These Rules Inviolable? Is This Order Critical?

What if?
1) The Oxidant and The Reductant May Never Touch
2) Maximize Shelf Life
3) Balance Energy and Power
4) Make It Rechargeable
Why?

Maximize Shelf Life

In 1800 batteries were primary power

The Oxidant and The Reducant May Never Touch

*We’ll lose energy as heat*  (yes)

*We’ll destroy the battery*  (maybe)

*Something Horrible Will Happen*

*(can we be more specific?)*
Why Do Batteries Die?

- **Corrosion**
  - The active components oxidize/reduce in a vicious spiral to completion

- **Passivation**
  - The active components oxidize/reduce in a fashion which creates an overly protective coating (electrochemistry is prevented)

- **Too Few/ Too Many Connections**
  - The active components move in untenable ways
What Have We Done?

- Corrosion (Rare)
  - The active components oxidize/reduce in a vicious spiral to completion

- Passivation
  - The active components oxidize/reduce in a fashion which creates an overly protective coating (electrochemistry is prevented)

- Too Few/ Too Many Connections (Rare)
  - The active components move in untenable ways

Batteries Die This Way Because We Designed Them To Die This Way
## Does Shelf Life Matter For Grid?

<table>
<thead>
<tr>
<th>System</th>
<th>$/kWhr</th>
<th>Cycle Life @ 80% DOD</th>
<th>LCOE $/kWhr-Cycle</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead Acid</td>
<td>$250.00</td>
<td>300</td>
<td>$0.83</td>
<td>Exide</td>
</tr>
<tr>
<td>Nickel Zinc</td>
<td>$350.00</td>
<td>500</td>
<td>$0.70</td>
<td>EEI</td>
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<tr>
<td>Lion (&quot;Weekly&quot;)</td>
<td>$320.00</td>
<td>500</td>
<td>$0.64</td>
<td>Tesla</td>
</tr>
<tr>
<td>V Redox</td>
<td>$500.00</td>
<td>5000</td>
<td>$0.10</td>
<td>PNNL</td>
</tr>
<tr>
<td>Lion (&quot;Daily&quot;)</td>
<td>$250.00</td>
<td>2500</td>
<td>$0.10</td>
<td>Tesla</td>
</tr>
<tr>
<td>Nickel Zinc/Modified</td>
<td>$500.00</td>
<td>5000</td>
<td>$0.10</td>
<td>CUNY</td>
</tr>
<tr>
<td>Na-Ion</td>
<td>$250.00</td>
<td>3000</td>
<td>$0.08</td>
<td>CMU/Aquion</td>
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<tr>
<td>NaS</td>
<td>$400.00</td>
<td>5000</td>
<td>$0.08</td>
<td>Difficult</td>
</tr>
<tr>
<td>NaMCl</td>
<td>$400.00</td>
<td>5000</td>
<td>$0.08</td>
<td>GE</td>
</tr>
<tr>
<td>ZnMnO2/Modified</td>
<td>$100.00</td>
<td>2000</td>
<td>$0.05</td>
<td>CUNY/Princeton</td>
</tr>
<tr>
<td>Our Target</td>
<td>$50.00</td>
<td>5000</td>
<td>$0.01</td>
<td>Crazy?</td>
</tr>
</tbody>
</table>
Bounding $/kW and $/kWh

• Rather than find a physical metric, let’s bound our cycle/cost space by competing technology
  • So a battery (to grid) can cost $100/kWhr for 15 hours, $200/kwhr for 7.5 hours, etc.
  • *Carbon cost is 0 and gas price passed directly to consumer*
Without knowing anything else about the battery, as Tesla held the power density constant we can see a tradeoff between cycle life, cost and energy density.

<table>
<thead>
<tr>
<th>Weekly System</th>
<th>Daily System</th>
</tr>
</thead>
<tbody>
<tr>
<td>$/kWh</td>
<td>$350</td>
</tr>
<tr>
<td>$/kW</td>
<td>$1000</td>
</tr>
<tr>
<td>Cycle Life</td>
<td>520</td>
</tr>
<tr>
<td>$/kWhr-cycle</td>
<td>$0.67</td>
</tr>
</tbody>
</table>

These Are The Best Possible Numbers: If we utilize the shelf life, we lose money
What About Short Circuits?

Zinc plating on Nickel

Flow of 0.61 mZnO 8.9 M KOH(aq)

Sintered NiOOH 2mm

Zinc plating on Nickel

Ito et. al. JOPS 2010

1 Frame Every 5 Minutes
Despite the Shorts, This Battery Works

Positive: \[2\text{NiOOH} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{Ni(OH)}_2 + \text{OH}^-\] 1.1 V

Negative: \[\text{Zn} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 + 2\text{e}^-\] -0.76 V

Total: \[\text{Zn} + 2\text{H}_2\text{O} + 2\text{NiOOH} \rightarrow 2\text{Ni(OH)}_2 + \text{Zn(OH)}_2\] 1.86 V
Minimum Viable Flow

Separations Is Hard

Do We Need It?

Pumps Will Break

More $$ Than Budgeted

Can We Be this Casual?
For Example

Example: Zinc-Bromine Redox Flow Battery

- Reactor
- Anolyte
- Catholyte
- Pump
- Generator
- Charge
- Load
- Discharge
A Thought Experiment

We generally design batteries so that the BOP protects the active materials.

If the cheapest stuff in the cell are the reactants, and they are reversible, why are we using relatively expensive BOP to protect them?

Can we use the active materials to protect the balance of plant?
Zn Br$_2$ Is A Hint

- **Simple Reaction (1.8 V nominal)**
  - Zn (s) ↔ Zn$^{2+}$ (aq) + 2e$^{-}$ @ negative
  - Br$^{2+}$ (aq) + 2e$^{-}$ ↔ Br (l) @ positive

- **“Simple” Side Reactions**
  - 2H$^+$ (aq) + Zn (s) → H$_2$(g) + Zn$^{2+}$ (aq)
  - Br$_2$ (l) + H$_2$ (g) → 2Br$^{2+}$ (aq) + 2H$^+$ (aq)
  - Br$_2$ (l) + Zn (s) → 2Br$^{2+}$ (aq) + Zn$^{2+}$ (aq)

*When the “Shorts”, It Returns To Discharged State*
Zn Br$_2$ Is Cheating

- Bromine is a liquid at room temperature
  - Not electronically conducting
  - Doesn't traditionally "short"
- Bromine is 3x as dense as water
- Bromine is sparingly miscible in water
- There is an inherent ability to "demix" the battery
Zn Br$_2$ Is Cheap

- Zn is $2 \text{ kA/h}$
- Br$_2$ is $3 \text{ kA/h}$
- Assume 1.8, ~60% RTE
- ZnBr$_2$ on a fuel basis is ~$10/\text{kWh}$
- *Can we minimize balance of plant to the same numbers?*
Zn Br$_2$ As A Test Case

Maximize Shelf Life

*Not For Grid Scale Applications (Time Is Money Lost)*

The Oxidant and The Reductant May Never Touch

*We’ll lose energy as heat*  (yes)

*We’ll destroy the battery*  (no! well yes! but no!)

*Something Horrible Will Happen*  (no!)
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Standard Flow Battery “Parasitics” Are A ~30% RT Tax
Can We Make a Vague Cell?

We don’t want the cell to self discharge, but if it does, we can start over without crippling the cell.

\[
\begin{align*}
\text{ZnBr}_2 (aq) & \text{ ZnBr}_2 (aq) \\
\text{Zn (s)} & \text{Br}_2 (l)
\end{align*}
\]
We Can Make a Vague Cell

1 cm

Biswa E&ES 2016

Schematic

[Diagram showing a schematic of a cell with labels for Zn electrode, Zn\(^{2+}\), Br\(^{-}\), Carbon Cloth, and 2M ZnBr\(_2\) electrolyte.]

C/2 Rate
80 mAh/g BrC

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td>2000</td>
<td>1.5</td>
</tr>
<tr>
<td>4000</td>
<td>1.0</td>
</tr>
<tr>
<td>6000</td>
<td>0.5</td>
</tr>
<tr>
<td>8000</td>
<td>0.0</td>
</tr>
<tr>
<td>10000</td>
<td>1.0</td>
</tr>
<tr>
<td>12000</td>
<td>1.5</td>
</tr>
</tbody>
</table>

1 s video = 1 hr exp
Passive Flow $\text{ZnBr}_2$

Carbon Cloth
Zn electrode

2M $\text{ZnBr}_2$
electrolyte

Carbon Foam
$\text{Br}_2$ electrode

Carbon Foam = Graphite + C-Black + PVDF

Biswa E&ES 2016
Best Performance to Date

No Degradation Over 1000 Cycles/8000 hours of operation

Lab BOM of $100/kWh

Biswa E&ES 2016
Room For Improvement

Ohmic Loss Is Significant

Zinc dendrites that are formed get eaten away by Br$_2$(l) in the vicinity of the C-foam electrode

Some loss due to gas generation ~ insignificant (< 0.5% of capacity)

H$_2$ gas generated needs to be captured

Potential RTE → 85%
Carbon Seems Stable Time
Anything is Better Than Lies and Deceit!

- This battery has self discharge issues
  - Which, in its current form, can make arbitrage difficult
- This battery has poor power density
  - Which means it has to be really cheap per unit energy
- This battery uses uncomplexed bromine
  - Which can be a safety issue
    → relatively little data in closed systems
- Takeaway: Right now this is a pretty crummy battery…. BUT ITS REALLY CHEAP AND MIGHT
Three Ways to Die Reset

- Corrosion
  - Corrosion returns the battery to its discharged state
- Passivation
  - Nothing Passivates
- Too Few/Too Many Connections
  - These can reset themselves
Plus, Cheap!

Estimated Cost of Our Cell Now

Where we can go if there’s little carbon degradation and we can make bigger cells
Summary

- Abuse, degradation and safety are all relative
- If one can take intrinsic behaviors that are “bad” and judo flip them for good, all the better
- We trade efficiency, energy density, and power density for cost and lifetime, and hopefully safety
Thanks!
Thanks!