Hidden in Plain Sight:
Understanding and Exploiting Systematic Couples to Improve Batteries

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A Cultural Bridge
Obligatory Battery Reactor Slide

These design have become implicit compromises. What are the terms of the negotiation?
The Original Negotiation

Optimized for Energy Density

Optimized for Power Density

http://maplesoft.com
The Hidden Metric in Ragone

Energy Density

Power Density  Safety

More Energy @ Unlimited Rate

\[
\frac{\Delta E}{C_p \times m} = \Delta T
\]

Less Mass

V. Srivansan, GigaOM, 2012
Many Negotiations

In any triangle pick two out of three
The Unfortunate Tetrahedron

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

Pick Your Corners

EVs are in the middle

Energy Density

(Ragone Space)

(Utility Space)
A “Stat Mech” Perspective

Initial Conditions

# of bonds in a battery dedicated to storing energy vs. # of bonds dedicated to maintaining structure

$/bond for both kinds of bonds

“how much change (entropy) can you tolerate?”

Operating Conditions

Degree of mixing of these bonds over cycles

“how much nano do you want (to pay for?)”

“how much nanostructure can/should be maintained cycle to cycle?”
“All happy families are alike; each unhappy family is unhappy in its own way”

“If you look for perfection, you'll never be content”

“Anything is better than lies and deceit!”
Underexplored Space

Capital Cost

(Utility Space)
1% of the literature

Amortization/Operating Cost
(Cycle life and Safety)

Power Density

Energy Density

(EVs are in the middle)

(Portable Space)
99% of the literature

(Pick Your Corners)
Grid Scale Batteries: Living Forever by Dying Everyday

Tolerating Failure to minimize Capital Cost and Operating Cost
<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>
</tr>
<tr>
<td>Lion (“Weekly”)</td>
<td>$320.00</td>
<td>500</td>
<td>$0.64</td>
<td>Tesla</td>
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<tr>
<td>V Redox</td>
<td>$1,000.00</td>
<td>5000</td>
<td>$0.20</td>
<td>PNNL</td>
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<tr>
<td>Lion (“Daily”)</td>
<td>$430.00</td>
<td>3600</td>
<td>$0.12</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>
</tr>
<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>
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</tbody>
</table>
How To Proceed?

Start cheap, add money to meet goals

Capital Cost

Amortization/Operating Cost (Cycle life and Safety)

Power Density

Energy Density

Our Approach

Powerwall Approach
Three Ways to Die (gross estimate)

• 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
The Zinc (Alkaline) Electrode

Overall:
\[ \text{Zn} + 4\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} + 2\text{e}^- \]

Possible:
\[ \text{Zn(OH)}_4^{2-} \rightarrow \text{ZnO} + 2\text{OH}^- + \text{H}_2\text{O} \]

<table>
<thead>
<tr>
<th>Element</th>
<th>Potential (V)</th>
</tr>
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<tbody>
<tr>
<td>F</td>
<td>2.74</td>
</tr>
<tr>
<td>Au</td>
<td>1.43</td>
</tr>
<tr>
<td>Cl</td>
<td>1.36</td>
</tr>
<tr>
<td>Ag</td>
<td>0.80</td>
</tr>
<tr>
<td>Cu</td>
<td>0.34</td>
</tr>
<tr>
<td>H (SHE)</td>
<td>0.00</td>
</tr>
<tr>
<td>Pb</td>
<td>-0.13</td>
</tr>
<tr>
<td>Zn</td>
<td>-0.76</td>
</tr>
<tr>
<td>Al</td>
<td>-1.66</td>
</tr>
<tr>
<td>Na</td>
<td>-2.71</td>
</tr>
<tr>
<td>Li</td>
<td>-3.05</td>
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</tbody>
</table>

Cannot Reprocess In Water
Battery Cross Section

Flow of 0.61 mZnO 8.9 M KOH(aq)

Zinc plating on Nickel

Sintered NiOOH

2mm

1 Frame Every 5 Minutes

Zinc plating on Nickel

Ito et al. JOPS 2010
Where Angels Fear to Tread

Potential range where we operate

Limiting Current

Potential at which limiting current is reached

Onset of Diffusion Limited Aggregation

Current Density (A/m²)

Potential (V)
Rough and/or Predictable?

At onset Potential of DLA -> Length scale of aggregate ~ Length of Separation in Battery

Well Beyond Potential of DLA -> Length scale of aggregate << Length of Separation in Battery
Good Dendrites?

The OCV of the battery seems to reflect the dominant facets of zinc
Works in Wearables!

There’s a catch

• We cannot regenerate this structure at this potential given the traditional alkaline MnO$_2$ cathode
  • We can cycle ~500 times against MnO$_2$ before this “turns” to dust
• NiOOH works well!
  • At a system cost of $450/kWhr it is too expensive
• What systems can we use this trick with?
  • High rate or structure free

DoD = Depth of Discharge

<table>
<thead>
<tr>
<th>Fresh Plate 0% DoD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industry Standard Cycling</td>
</tr>
<tr>
<td>30% DoD</td>
</tr>
</tbody>
</table>

? 50% DoD

100% DoD

DoD = Depth of Discharge

1000 Wh/L

10 Wh/L

Conversion

Strain Free

Plate Metal

Conversion - Volume Change

Surface Capacitive

1,000,000
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?
Listening To Batteries

A Universal, Low Cost Diagnostic/Characterization Tool for All (closed) Batteries
State Estimation
Why Does This Happen?

100% SOC
Why does this happen?
It’s Repeatable!
Because of how ZnO Forms

Bhadra et. al. JMCA 2015
Mechanics and Batteries

**Stress-strain**
- Cannarella et. al. *JOPS* 2014

**Acoustic emission**
- Rhodes et. al. *JECS* 2010

**Large-scale delamination**
- Sood et. al. *IEEE* 2013
Is there a global connection?

- Is there a way to study the electrochemical & mechanical behavior of all closed batteries, regardless of chemistry and geometry?
- Can we detect the subtle changes that occur in a battery during cycling?

Thoughts about closed batteries during cycling:

- Density distribution must shift
- Modulus distribution will change as well
Basic Acoustics

Sound speed:
\[ c = \sqrt{\frac{K + \frac{4}{3}G}{\rho}} \]
Longitudinal/Shear Modulus
Density

Acoustic impedance:
\[ Z = \rho \cdot c \]

Hypothesis:
Cycling will affect the behavior of sound traveling through a battery.
Simulation of pulse through a cell

1D continuity equations*

\[ p_t + B \cdot u_x = 0 \]
\[ u_t + \frac{1}{\rho} \cdot p_x = 0 \]

* solved in Clawpack

*Constant SOC*
*assuming only density changes
Experimental Setup

- Pulse/Receive (Reflection)
- Receive (Transmission)
- Battery Cycler
- Ultrasonic Pulser/Receiver
LCO Prismatic

LCO Prismatic Cell, C/2.5 cycling

*experimental data

Hsieh et. al. E&ES 2015
LCO Prismatic

Pulse Echo

Through Signal

Thickness 5mm
~8 layers
NCA 18650

Hsieh et. al. E&ES 2015
Alkaline Brand Comparison

(a) Duracell Brand AA Alkaline Battery

(b) CVS Brand AA Alkaline Battery

Hsieh et al. EES 2015
Summary

- Honest assessment of coupling and compromise informs good design
- We can contrast batteries to understand how to move around the unfortunate Tetrahedron
- We exploit traits common to almost all batteries to use acoustics as, potentially, a new “universal” diagnostic.
Thanks!
Thanks!