Batteries on the Grid: Opportunities, Challenges, and New Technologies

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Today’s Presentation

1. The case for batteries on the electric grid.

2. Incumbent technologies: sodium-sulfur and lithium ion.

Energy Storage on the Grid:

• There are many situations in which energy storage provides value to an entity that operates or uses the electric grid.
  – Power generators: smooth the generative capacity of volatile renewables such as solar or wind.
  – Grid operators: regulate the balance of generation and load in real time without using fossil fuel peaker plant capacity.
  – Customers: avoid peak demand rates through energy arbitrage.
The Challenge for Renewables is Volatility

- Solar power generation operates on a diurnal basis.
- On cloudy days, the power generation fluctuates at up to 90%/minute.\textsuperscript{1}
- Many grids require generators to smooth to $\leq 10\%$/minute.\textsuperscript{2}
The Challenge for Renewables is Volatility

- Wind power suffers from short-term volatility similar to solar.
- Wind is also unreliable from one day to the next.
- The cost of balancing this volatility can be a large fraction of the retail spot price.
Grid Generation and Load Is Balanced In Real Time

- Generation and load must be balanced in real time. If they are not, then the increase/decrease in frequency and voltage can damage grid infrastructure.
- Today, generation is regulated by rapidly ramping conventional power plants (typically natural gas).
- It is widely believed that regulatory services can be performed more cheaply using energy storage.
The Motivation for Energy Storage

• Power generators: Stored energy can be discharged or charged on-demand to balance out the volatility of renewable energy generation.

• Grid operators: It can also be used to balance generation and load in real time (regulatory services).

• Electricity customers: Use storage to perform energy arbitrage to avoid peak demand rates and to avoid curtailment.
Energy Storage Options

- Nearly 99% of energy storage deployed on grids worldwide is pumped hydropower.\(^7\)
  - Limited siting options.
  - High capital cost and difficult permitting/regulation.
- Energy storage systems using batteries can be sited locally with a wide range in system capacity.

![Worldwide installed storage capacity for electrical energy](image)

Ref. 7

Seneca Pumped Storage Station, Pennsylvania (US Army Corps of Engineers)
Examples of Grid Battery Systems
Incumbent Technology 1: Sodium-Sulfur

- NaS batteries account for the vast majority of all batteries installed on electric grids worldwide (>400 MW installed power).
- New installations (100 MW/year) limited by single manufacturer (NGK Insulator).
- Operated at 350° C (molten sodium and sulfur electrodes with a solid Al$_2$O$_3$ electrolyte).
- Good system-level energy density of ~150 Wh/L.
- Risk of catastrophic fire/explosion.
- Slow ionic conduction in the solid electrolyte results in poor rate capability: 4-6 hour charge or discharge.

**Electrochemistry:**

- Cathode: $S_x + 2 \text{e}^- + 2 \text{Na}^+ = \text{Na}_2S_x$ ($V^0 = 2$ V vs. Na$^+$/Na; $x = 4$)
- Anode: $2 \text{Na}^+ + 2 \text{e}^- = 2 \text{Na}$ ($V = 0$ V)
- Total: $S_x + 2 \text{Na} = \text{Na}_2S_x$ ($V = 2$ V)
- Electrolyte: beta-Al$_2$O$_3$(Na$^+$)

![Ref. 7](image.png)
Incumbent Technology 2: Lithium-Ion

- Li-ion is on track to become the dominant grid battery technology.
- It offers higher energy and power density than any other commercialized battery technology.
- Most new battery installations on first world grids are Li-ion.
- System-level cost is falling rapidly and has reached parity with sodium-sulfur.
- Fire/explosion safety hazard is being accepted due to the high performance and ROI.

Electrochemistry:
- Cathode: $\text{Li}_{1-x}\text{MO}_2 + e^- + \text{Li}^+ = \text{LiMO}_2$
- Anode: $\text{C}_6 + e^- + \text{Li}^+ = \text{C}_6\text{Li}$
- Total: $\text{Li}_{1-x}\text{MO}_2 + \text{C}_6\text{Li} = \text{C}_6 + \text{LiMO}_2$
- Electrolyte = organic solvents (Li$^+$ salt)
A New Technology: the Prussian Blue Battery

- Under development by Alveo Energy (Stanford spin out).
- Both electrodes based on Prussian Blue, a common pigment.
- Benefits: 5-10x longer cycle life at very a low price.
- Detriments: bigger/heavier than Li-ion, but smaller/lighter than lead acid.
Introduction to Prussian Blues

- General chemical formula: $A_xP_y[R(CN)_6]_z\cdot nH_2O$
  - $A =$ alkali cations, alkali earth cations, $NH_4^+$
  - $P =$ transition metal cation
  - $R =$ transition metal hexacyanometalate complex

Examples:
Prussian Blue (Ferric ferrocyanide)
- $A =$ K$^+$, Na$^+$, $NH_4^+$
- $P =$ Fe$^{3+/2+}$
- $R =$ Fe$^{3+/2+}$

Copper hexacyanoferrate (CuHCF) cathode
- $A =$ K$^+$, Na$^+$, $NH_4^+$
- $P =$ Cu$^{2+}$
- $R =$ Fe$^{3+/2+}$

Metal hexacyanomanganate (M-HCMn) anode
- $A =$ K$^+$ or Na$^+$
- $P =$ M$^{2+}$
- $R =$ Mn$^{3+/2+/1+}$
The A Sites Accommodate Hydrated Inserted Ions

<table>
<thead>
<tr>
<th></th>
<th>Crystal Ionic Radius</th>
<th>Hydrated Ionic Radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>1.12 Å</td>
<td>2.76 Å</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.52 Å</td>
<td>1.88 Å</td>
</tr>
</tbody>
</table>

Prussian Blue analogues:
A Site: $R_A = 2.5$ Å
Electrodes and Reaction Mechanisms:

• Single-phase insertion reaction of Na\(^+\) into the framework crystal structure.

• Cathode: Fe\(^{III}/Fe^{II}\) redox couple.

\[
Cu_{1.5}Fe^{III}(CN)_6 + n \cdot (Na^+ + e^-) \xrightarrow{0.9V} Na_nCu_{1.5}[Fe^{III}(CN)_6]_{1-n}[Fe^{II}(CN)_6]_n
\]

• Anode: Mn\(^{II}/Mn^{I}\) couple.

  – A = alkali cation; M\(^{2+}\) = transition metal.

\[
A_2M[Mn^{II}(CN)_6] + n \cdot (Na^+ + e^-) \xrightarrow{-0.7V} Na_nA_2M[Mn^{II}(CN)_6]_{1-n}[Mn^{I}(CN)_6]_n
\]
Structure and Morphology

- Synthesized by aqueous reaction of transition metal precursors:
  - Cathode example: aqueous copper sulfate + aqueous sodium ferricyanide = cathode.
  - Room temperature synthesis in a few minutes.
- Polydisperse nanoparticles of 100-300 nm.
Test Cell Design and Operation

- Flooded and pouch cells.
  - Flooded cells include a reference electrode that allows failure analysis of individual electrodes.
  - Pouch cells represent prototypes for the cells to be used in battery packs and modules.
Prussian Blue Electrodes Have High Cycling Efficiency

- Single-phase insertion reactions at +0.9 V and -0.7 V vs. SHE gives 1.6 V average cell voltage.

- 65 mAh/g = ½ of common Li-ion electrodes.
Cathode Lifetime

- No capacity loss observed for cathode-limited cells operated for six months at continuous 1 hour charge/discharge cycling (95% depth of discharge).
- Projected cathode lifetime of 100,000 cycles demonstrated at 20C (3 minute charge/discharge).

**Baseline Cell Data:**
- The cathode is stable during normal cycling in a cell containing baseline electrolyte and a carbon anode.
  - Zero loss observed during over six months of cycling and 2300 cycles.
- 0.05%/month loss observed for this cell.
- Average capacity change of many cathode cells operated for several months is zero.
  - >95% capacity utilization during cycling.

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**Cycle Life of CuHCF Cathode in 1 M Na+ (1C CCCV)**

![Graph showing cycle life of CuHCF cathode in 1 M Na+ (1C CCCV)](image)

**Cycle Life of CuHCF/Na⁺ at 20C**

- Zero loss 5000 cycles
- Potential cutoffs increased
- ~75 days
- <5% loss 22000 more cycles
Anode Lifetime

- Projected anode lifetime of >5 years/20,000 cycles at 98% depth of discharge.
- Zero capacity loss observed after 800 cycles/10 weeks of continuous cycling (1 hour charge/discharge).
Long Cycle Life Due to Near-Zero Strain

- 1% strain is observed during 100% DOD cycling.
- Negative strain during charge insertion due to contraction of the M-CN bond as M is reduced.
- No phase changes or structural damage allows for thousands of full cycles.

Cathode (400) Peak Position vs. Charge State

Cathode Lattice Parameter vs. Charge State
# Projected Cell Performance

<table>
<thead>
<tr>
<th>Metric:</th>
<th>Prussian Blue Battery:</th>
<th>Sodium Sulfur</th>
<th>Li-Ion</th>
<th>Lead Acid:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Useful Energy Density (Wh/L)</td>
<td>60</td>
<td>150</td>
<td>250</td>
<td>20 (20% DOD)</td>
</tr>
<tr>
<td>Maximum sustained C rate</td>
<td>10-20</td>
<td>1/4</td>
<td>4</td>
<td>1/3 (charge) 2 (discharge)</td>
</tr>
<tr>
<td>Power Density (W/L)</td>
<td>500-1000</td>
<td>40</td>
<td>1000</td>
<td>~100</td>
</tr>
<tr>
<td>Energy Efficiency</td>
<td>&gt;98% at 1C;</td>
<td>80-90%</td>
<td>&gt;90%</td>
<td>50-80%</td>
</tr>
<tr>
<td>Cycle Life</td>
<td>&gt;20,000 (&gt;90% DOD)</td>
<td>5000 (80% DOD)</td>
<td>&gt;5000 (80% DOD)</td>
<td>2000 (20% DOD)</td>
</tr>
<tr>
<td>Calendar Life</td>
<td>5-10 years</td>
<td>10 years</td>
<td>5-10 years (Room T)</td>
<td>2-5 years (20% DOD)</td>
</tr>
<tr>
<td>Cell Price/Useful Energy ($)</td>
<td>&lt;200</td>
<td>~1000</td>
<td>300</td>
<td>&gt;600</td>
</tr>
</tbody>
</table>
Final Comments

- Energy storage is being deployed in increasing quantities in support of volatile renewables and for other grid applications.

- Incumbent technologies likely to enjoy widespread installation include sodium-sulfur and Li-ion.

- The Prussian Blue battery is a new technology that will offer lifetime and price advantages over the incumbents.

- We are in the midst of an energy storage renaissance!
Acknowledgements
References

Thank you.