Materials Design for Grid-Scale Energy Storage

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Energy Storage: Enable Renewable Penetration

- Smooth fluctuations: seconds-to-minutes-to-hours
- Peak shifting: hours-to-days
Grid Scale Energy Storage

Low-cost:
- Initial cost: <$100/kWh
- Life time cost: <$0.025/kWh cycle

Scalable (~MW-GW/plant) to TW

Life: 20-30 Years

Cycle life: > 5000 cycles

Round trip energy efficiency: >90%

Energy density: affecting cost
## Existing Storage Technologies Are Not Adequate


<table>
<thead>
<tr>
<th>Technology</th>
<th>Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressed Air</td>
<td>440 MW</td>
</tr>
<tr>
<td>Sodium-Sulfur</td>
<td>316 MW</td>
</tr>
<tr>
<td>Lead Acid</td>
<td>35 MW</td>
</tr>
<tr>
<td>Flywheels</td>
<td>&lt;25 MW</td>
</tr>
<tr>
<td>Lithium Ion</td>
<td>20 MW</td>
</tr>
<tr>
<td>Flow Batteries</td>
<td>&lt;3 MW</td>
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</table>


- **Pumped hydroelectric power:**
  - Scalable, low-cost, long life.
  - Location dependent, low energy density, low energy efficiency.
Existing Electrochemical Energy Storage

Not yet scalable:
World annual Li-battery production: 40GW for 1 hr.
Need 30 years to get to 1TW scale.

Battery Basics

1) Low-cost abundant materials
   - Electrode
   - Electrolyte
   - Separators

2) 500 cycles need to go to 50,000 cycles
2) Scalable processing to make batteries

(Courtesy of Venkat Srinivasan)
Prussian Blue: Open Framework

Ferric ferrocyanide hydrate:
$\text{KFe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6 \cdot n\text{H}_2\text{O}$
Open Framework Allows Fast Ion Transport

Prussian Blue analogue:
Channel radius: $R_c = 1.6 \text{ Å}$

LiCoO$_2$:
Channel radius: $R_c = 0.43 \text{ Å}$

<table>
<thead>
<tr>
<th></th>
<th>Crystal Ionic Radius</th>
</tr>
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<tbody>
<tr>
<td>Li$^+$</td>
<td>0.59-0.73 Å</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.12 Å</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.52 Å</td>
</tr>
</tbody>
</table>

A Family of Prussian Blue-Like Materials

- Open Framework Crystal Structure: APR(CN)$_6$·nH$_2$O
  - P and R = Transition Metals, A = Alkali Ions

Examples:
- Prussian Blue:
  P=Fe$^{3+}$  R=Fe$^{2+}$

- Copper Hexacyanoferrate (CuHCF):
  P=Cu$^{2+}$  R=Fe$^{3+}$

- Nickel Hexacyanoferrate (NiHCF):
  P=Ni$^{2+}$  R=Fe$^{3+}$
Synthesis of Prussian Blue Analogues

Room-temperature aqueous chemical reaction of transition metal salts. Result: spontaneous precipitation of solid product.

Example: Prussian Blue

\[ \text{K}^+ + \text{Fe}^{3+} + \text{Fe}^{II} (\text{CN})_6^{4-} \rightarrow \text{KFe}^{III} \text{Fe}^{II} (\text{CN})_6 \]

General synthesis:

\[ A^+ + P^{2+} + R^{III} (\text{CN})_6^{3-} \rightarrow APR(\text{CN})_6 \]

A = K\(^+\), Na\(^+\)

P = Fe, Cu, Ni, Co, Mn, Zn…

R = Fe, Cr, Mn…

Copper Hexacyanoferrate As Ultrafast Positive Electrodes

1 M K⁺ Aqueous Electrolyte:

Copper Hexacyanoferrate As Ultrafast Positive Electrodes

1 M K⁺ aqueous electrolyte:

Also Work Well in Na⁺ Electrolyte
Rate Capability of Copper Hexacyanoferrate

Ultralong Cycle Life of Copper Hexacyanoferroferrate

(Yi Cui Group, Nature Communication, 2:550 (2011))
Near Zero Strain: Stable Open Framework

CuHCF 400 Peak vs. Charge State

Reason for strain: $2 \cdot \Delta r_{\text{Fe-C}} = 0.1 \, \text{Å}$

$\Delta a_0 = 0.1 \, \text{Å} \quad \text{Strain} = 0.1\%$

Tuning the Voltage: Cu, Ni HCF and Their Solid Solution

CuHCF Open Framework: Effects of $A^+$ ions

What About Negative Electrodes?

Need negative electrodes with potential ~0V versus H₂/H⁺
What About Hybrid Negative Electrodes?

Potential vs. SHE / V vs. time

(+) CuHCF

(-) PPy/AC

(-) Activate Carbon (AC)
Hybrid Negative Electrodes

[\text{[K^+] = 1M, pH = 1, 1 C}]

(+) CuHCF

(-) 10\% PPy/AC

NaBH_4

Open Framework Battery: Full Cell Potential Profile

([K⁺]=1M, pH=1, 10°C)

CuHCF- PPy/C Full Battery: Cycle Life

([K\(^+\])=1M, pH=1, 10 C)

Manganese (II) Hexacyanomanganate (III)
Mn$^{\text{III}}$—C≡N—Mn$^{\text{II}}$

M. Pasta, Y. Cui (unpublished results)
CV Mn$^{II}$HCMn$^{III}$, NaClO$_4$ sat. pH=7, 2 mV/s

$j / \text{mAcm}^{-2}$

Potential vs. SHE / V

Mn$^I$-Mn$^{II}$

Mn$^{II}$- Mn$^{III}$
Mn$^{II}$—N≡C—Mn$^{III/II}$

M. Pasta, Y. Cui (unpublished results)
What About Divalent Ion Batteries?

$M^+$ and $e^-$
$M^{2+}$ and $2e^-$

R. Wang, Y. Cui (unpublished results)
Summary

- Single valent aqueous batteries: Na⁺, K⁺
- Divalent aqueous batteries: Mg²⁺

- Potentially low cost and scalable
- High power
- High energy efficient