Battery Materials and Issues for Grid Applications

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Energy Storage is Clearly a Critical Component
What Path? Electrochemical or Other
If Electrochemical, what are the options present and future...
Although all have similar list of key performance criteria
Distinctly different priorities
Ultra Low lifetime cost Electrochemical Systems for Grid:

Key Requirements:
a. Low Lifetime Cost (25 yr)
b. Charge / discharge efficiency = $

c. Green

Many Options:
• Redox Flow: Vanadium, Zn/Br, others
  Very low cost / scalability → Large applications
• Na/S or FeCl₂, NiCl₄ (Zebra) (latter safer in failure mode):
  high energy/ Good for localized apps.
• Hybrid ultracapacitors
• Li, Mg and Ca non-aqueous
• Li aqueous
• Regenerative fuel cell
• Symmetric and Asymmetric Supercapacitors

• Which one to choose? depends on application
• For this talk we focus on batteries..
Introduction

Batteries and the grid
We should not hope or look for a single solution, much depends on application

- We will take a look at 3 different options from the materials perspective

Wh $\rightarrow$ kWh $\rightarrow$ MWh

Modified Li-ion

Molten Sodium

Redox Flow
Batteries: Lithium and Lithium-ion

Intercalation Electrodes (micron size powder):
- +: LiCoO$_2$, LiMn$_2$O$_4$, etc.
- -: Graphite (LiC$_6$)

• *grid will require alternative approaches...*
The Electrochemical Design of Li Battery Technology

- Wide array of materials departing from today's SOA for portable power

Why Window Shift:
Increase potential of electrode
- Safety: reduced H₂ with H₂O/fire
- Low T Performance: Little SEI
- Fast Charge: No Li plating
- Long Life: Focus electrolytes on one voltage extreme relative to SHE
- Voltage more important than capacity
For high rate applications (usually current density limited)
Positive electrodes:
- Path: low cost but high performance: example - phosphates
- Anion stability towards oxidation: inductive polyanion or fluorides
- Material safety = polyanion
- New inductive effect polyanion compounds in 4-5V range

Negative electrode
- lower V than Li$_4$Ti$_5$O$_{12}$: 1-1.2V
- higher capacity than LTO

Electrolytes
- Low Cost
- High V stability
- Low flammability
- No vapor pressure
- SHUTTLES

Positive electrodes:
- LiCaCoF$_6$
- Li(Co,Ni)PO$_4$
- (Li)[Mn$_{1.5}$Ni$_{0.5}$]O$_4$
- LiMnPO$_4$
- LiMn$_2$O$_4$
- Li(Co,Ni,Me)O$_2$
- LiFePO$_4$
- Li$_x$MnO$_2$, VO$_x$
- NiF$_2$, CuF$_2$, BiF$_3$
- S
- TiS$_2$
- Li$_4$Ti$_5$O$_{12}$
- Conv. oxides
- MoO$_2$

Li alloys
- LiC$_x$
- Li metal
Paths towards ultra low cost: General Materials: NEEDS

More extreme focus on cost:

**Electrolytes:**
- low cost salts
- alkali aqueous electrolytes advantages
  - If alternative guest cation → new electrolytes

**Guest Cation:**
- Move away from Li$^+$ ??
  - supply / price / plating efficiency
- low cost polyvalent
  - Mg$^{2+}$ / Ca$^{2+}$
- very low cost monovalent
  - Na$^+$ and K$^+$

**Electrodes:**
- If alt. guest → new insertion electrodes

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More graphs and images are shown, including voltage vs. capacity plots and chemical structures of various compounds such as LiCaCoF$_6$, Li(Co,Ni)PO$_4$, (Li)[Mn$_{1.5}$Ni$_{0.5}$]O$_4$, LiMnPO$_4$, LiMn$_2$O$_4$, Li(Co,Ni,Me)O$_2$, LiFePO$_4$, Li$_x$MnO$_2$, VO$_x$, NiF$_2$, CuF$_2$, BiF$_3$, S, TiS$_2$, Li$_4$Ti$_5$O$_{12}$, Conv. oxides, MoO$_2$.

- Li alloys
- LiC$_x$
- Li metal
- Mg, Na
- Ca, K

Aqueous Window

Li-ion 1990–today

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6V
5V
4V
3V
2V
1V
0V
Long life = Low Lifetime Cost

Challenge: Electromechanical destruction
- Route to eliminate one primary source of failure
- Identify new pos. and neg. zero or quasi zero expansion electrodes

Example: Li_4Ti_5O_{12}:
- 5 years @4C
- 1,000,000 cycles

HYR050 (2x3 bicell (AS/LTO)-MR=4.2)
started 9/02

cycle 1.4-2.8v at 1A
Feb-07

G. Amatucci ONR Capacitor Review 2007
Long life = Low Lifetime Cost

Surface Science: Electrode/electrolyte interface

- Development of interphase to assist low cost electrolytes @ High V
- Electrode passivation (coated electrodes)
- Very effective, but fundamentally flawed
- Entire electronic conductive network must be coated uniformly
  1. New approaches towards in-situ formed inorganic interphases,
  2. Capability to model and predict effectiveness
  3. Stabilization of aqueous electrolytes at V extremes

Internally connected electrode networks

“SEI”
High energy Cathodes: Electrochemical Conversion Processes

**Intercalation**

\[ \text{MeX}_2 \xrightarrow{\text{Discharge}} \text{LiMeX}_2 \xrightarrow{\text{Charge}} \text{MeX}_2 \]

1\(e^-\) transfer 
\(<0.3\text{ mAh/g}\)

**Conversion**

\[ \text{MeX}^{z_3} \xrightarrow{\text{Discharge}} 3\text{Li}_2\text{X} + \text{Me} \xrightarrow{\text{Charge}} \text{MeX}^{z_3} \]

3\(e^-\) transfer 
\(>700\text{ mAh/g}\)
Electrons and Li ions: The Macroscopic Journey is Just the Beginning...
Enabling Insulating Fluorides:

The $\text{MeF}_x$ Nanocomposite
- enable transport in insulating MeFs
- reduce volume wrt discrete nano

Mixed Conducting Matrix (MCM)
- High $\sigma_i$
- High $\sigma_e$
- Mixed conductor

$\text{MeF}_x$ nanodomains

Nanocomposite enabled MeF$_2$

- Nanocomposites have enabled theoretical a variety of MeF$_x$.
- As with dichalcogenides, polarization needs to be addressed.

Examples from Badway et al. Rutgers
Batteries, Moving Towards Larger Applications...
The Problem with High Energy Batteries:
- Limited electrode thickness (transport) = very large area cells for >kWh
- Relatively complex designs
- Except for a few exceptions, Li systems have been goals
  - Debatable reserves of Li supply
- Relatively expensive
  - salts/electrolytes
  - highly engineered electrodes
- Can be difficult to control in series
- Aqueous cells lower cost, but lifetime cost is questionable
Molten Sodium Technology:

Why??

Low Cost, High Energy, and Abundance of Na
Sodium Sulfur Molten Salts

\[ 2Na + 3S \rightarrow Na_2S_3 = 2.08 \text{ V} \]

- \(300^\circ\text{C}\)
- 89% efficient, very high pulse power
- Very inexpensive materials

Hitachi uses 4 2MW NaS systems (NGK)
Tokyo 8 MW system
Both have 58MWh energy
Peak shaving, etc

Very attractive system, work continues in this spirit with the Na metal chlorides...
Positive electrode: \( \text{MeCl}_x \), typically \( \text{NiCl}_2 \)
Electrolyte: \( B^{''} \) alumina and \( \text{NaAlCl}_4 \)
Negative electrode: Na metal
Operating Temperature: 250 - 350°C

Positive electrode Reaction:
\[
\text{NiCl}_2 + 2 \text{Na}^+ + 2e^- \rightarrow \text{Ni} + 2 \text{NaCl}
\]

Negative electrode:
\[
\text{Na} \rightarrow \text{Na}^+ + e^-
\]

Net Reaction:
\[
\text{NiCl}_2 + 2\text{Na} \rightarrow 2\text{NaCl} + \text{Ni} (2.58V)
\]
Zebra:

- Similar energy density as NaS (790 vs. 760 Wh/kg theoretical)
- Overcharge resistant relative to Na/S
- Safety in failure mode
- No need for cooling / independent of ambient temperatures
- 20-100 kWh future MWh?
- No self discharge = efficiency
- No gassing
- 100% coulombic efficiency
- 2.58V, 120-150 Wh/kg, 340 Wh/L
- Very long calendar life (15 years) approx 2000 cycles
- No Na in assembled state
- Very robust in series configuration
- Current collectors are in thermodynamic equilibrium
1. Cost Reduction

- Construction and materials
  - cell fabrication costs
  - much of the complicated B" alumina electrolyte costs have been addressed
  - FeCl₂ → Much lower cost and toxicity than NiCl₂
  - for similar Wh (728 vs 790 Wh/kg)
    - must address: overcharge to Fe³⁺ → dissolves and attacks B" alumina
    - current collector disadvantages
- Improved Performance = smaller cells = lower cost
  - CoCl₂, CuCl₂, SbCl₃, MoClₓ etc. → must be insoluble in electrolyte
  - container corrosion
2. Reduce operation temperature and improved power

Secondary electrolyte melts @ 160°C, Na melts @ 97°C but..
Higher temperature needed to improve kinetics of positive electrode and electrolyte

→ Power needs to be improved
   Address positive electrode kinetics
   · control grain size → S
   · mass transport improvement with iodine and bromine

Pore design
→ Completely new options in Ionic Liquids
→ Alternative solid state electrolytes, Nasicons, etc.
→ Na alloys (Huggins)
Batteries, Moving Towards Even Larger Applications...
### Redox Flow Cells

**Traditional Batteries:**
**Positive attributes:**
- very efficient recharge cycle
- can be very low cost materials
- non mechanical system
- instantaneous power delivery

**Negative attributes**
- inefficient design for large scaling
- challenges for scaling (safety, cost, performance)
- difficult charging protocols

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**Rechargeable Fuel Cells:**
**Positive attributes:**
- efficient tank vs. reactor design = high energy density
- easy to scale
- “green”

**Serious negative attributes:**
- expensive catalysts
- complicated systems, large amount of hydrogen storage
- poor recharging efficiency = $$$ and wasted energy
- slow switching time

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**The Hybrid Approach:**
Redox Flow Cells
Redox Flow Cells: Fundamentally Attractive to Large Applications

- Reserve tank scalability of fuel cell but...
- Higher efficiency, instantaneous power, low cost, cycle life
- Reconfigurable Parallel / Series cell, Scalable energy = tank
- Low level needs: improved membranes, improved catalysts, corr. Res.
- High level grand challenge: New green, reversible, stable chemistries,
  - Can We Hybridize with traditional battery approaches?
Positive Attributes (most relate to ease of scaling to high energy):

- Very Low \$/Wh over lifetime for large Wh applications
- Very high charge/discharge efficiencies
- Long lifetimes
- High current (approach 1000 mA/cm²)
- No cell balancing issues
- Tolerance to overcharge/overdischarge (and also under charge/discharge)
- Power conditioning very easy (DC/DC) conversion = # cells
- Charging configuration can be different from discharge (parallel vs series)
- Instantaneous recharging possible if needed
- Power and energy designed separately
  - power = number of cells and size
  - energy = concentration and volume of catholyte and anolyte

Negative Attributes:

- Requires plumbing / flow pumps
- Best if applied to largest applications >>kW
## Present Redox Flow Cell Chemistries

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Positive Electrode</th>
<th>Negative Electrode</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Bromine – Polysulfide</td>
<td>$\text{Br}^{3-} + 2\text{e}^- \rightarrow 3\text{Br}^-$</td>
<td>$2\text{S}_2^{2-} \rightarrow \text{S}_4^{2-} + 2\text{e}^-$</td>
<td>1.54</td>
</tr>
<tr>
<td>b. Vanadium – Vanadium</td>
<td>$\text{VO}_2^{+} + 2\text{H}^+ + \text{e}^- \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}$</td>
<td>$\text{V}^{2+} \rightarrow \text{V}^{3+} + \text{e}^-$</td>
<td>1.3</td>
</tr>
<tr>
<td>c. Vanadium – Bromine</td>
<td>$\text{ClBr}_2^{2-} + 2\text{e}^- \rightarrow 2\text{Br}^- + \text{Cl}^-$</td>
<td>$\text{VBr}_2 + \text{Br}^- \rightarrow \text{VBr}_3 + \text{e}^-$</td>
<td>1.0</td>
</tr>
<tr>
<td>d. Iron – Chromium</td>
<td>$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$</td>
<td>$\text{Cr}^{2+} \rightarrow \text{Cr}^{3+} + \text{e}^-$</td>
<td>1.03</td>
</tr>
<tr>
<td>e. Zinc – Bromine</td>
<td>$\text{Br}^{3-} + 3\text{e}^- \rightarrow 3\text{Br}^-$</td>
<td>$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$</td>
<td>1.75</td>
</tr>
<tr>
<td>f. Zinc – Cerium</td>
<td>$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$</td>
<td>$\text{Ce}^{3+} \rightarrow \text{Ce}^{4+} + \text{e}^-$</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>
Catholyte and anolyte
- reversible reactions
- all reactants and products are preferably soluble
- wide voltage window
- high concentrations in liquid
- Need high energy
- Need less cost and toxicity

Membrane
- prevent transfer of redox species → needs to be improved
  - but maintain rate
- cation (typical H⁺ or Na⁺) transport and water

Electrodes
- carbon and carbon composite
- electrode design and materials to further improve power density
Batteries offer solutions from < kWh to > MWh
Materials are key to the success

Which System, Which Materials?

Primary decision is dictated by cost, scalability and environmental responsibility
Next generation room to elevated temperature batteries could compete with molten Na
Redox flow has a large number of advantages of very large applications
New hybridized chemistries will most likely be developed

The practical challenge:
Little resources are available to focus on electrochemical energy storage for grid
  Cannot rely on trickle down research from HEV, this is distinctly different in needs
  Need to focus research and resources on this issue
Distinct progress has been made, great progress will be realized in the future...

Thank You!!