A Novel Concept for Energy Storage

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Megatrends ... fuel cost, emission reduction & digitization

Intermittent renewables, smart grid deployment
Opportunities for an advanced energy storage

Grid
Renewable Integration, Power Quality, Smart Grid, T&D Management

Energy Storage
Mechanical, Chemical, Electrical, Electrochemical

Backup Power
Telecom, UPS, Stand Alone Systems

imagination at work

10/19/2010
Application Energy Storage Requirements

<table>
<thead>
<tr>
<th>Application Duration</th>
<th>Application Energy Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 sec</td>
<td>1 kWh</td>
</tr>
<tr>
<td>15 min</td>
<td>10 kWh</td>
</tr>
<tr>
<td>30 min</td>
<td>100 kWh</td>
</tr>
<tr>
<td>1 hour</td>
<td>1 MWh</td>
</tr>
<tr>
<td>5 hrs</td>
<td>10 MWh</td>
</tr>
</tbody>
</table>

- Power Battery
- Dual Battery
- Energy Battery
- Flow Battery

Energy battery: NaMx now...organic flow battery in future
Energy Storage Market

- Global investment in electric power ancillary services systems will reach $6.6 billion by 2019
- Deployment of renewables and smart grid is the strongest driver to push the grid storage market 3 – 5 times by 2016
- The global stationary energy storage business $35 billion by 2020
  - 11 competing technologies
  - Li ion batteries may be ¼ of revenue
  - Compressed air, flywheel and sodium-sulfur batteries follow
- Stationary fuel cells revenue $0.7 – 1.2 billion in 2013
- Stationary energy storage got a boost from transportation energy storage development (market size $19.9 billion in 2012)

Sources: [http://www.pikeresearch.com/category/research/energy-storage](http://www.pikeresearch.com/category/research/energy-storage)
Electrochemical Energy Storage Options

**Secondary batteries**
- Stationary electrode materials
- Mature technology (lead acid, NiCd, NiNH, NaS)
- Emerging technologies (NaMCl₂, Li-ion)
- New chemistries (Li-air, Li-S, Zn-air)

*NGK 34 MW NAS alongside 51 MW Wind Farm*

**Redox flow batteries**
- Flowing electrode materials
- Mature technology (zinc-bromine, all-vanadium)
- Emerging technologies (cerium-zinc, iron-chromium)
- New chemistries (vanadium-bromine, soluble lead)

*VRB (Prudent Energy) PacifiCorp (Moab, Utah) 2 MWh VRB-ESS*

**Regenerative fuel cells**
- Gaseous electrode materials
- Emerging technologies (H₂–O₂ conventional and unitized)
- New chemistries (H₂–Br₂, H₂–H₂O₂, NaBH₄–H₂O₂)

*1kW-prototype Regenerative Fuel Cell System*
Source: [www.apg.jaxa.jp](http://www.apg.jaxa.jp)
Electrochemical Energy Storage Comparison

**Secondary batteries**
- No power-energy separation
- Moderate energy density (50 – 240 Wh/kg)
- High energy efficiency (65 – 90%)
- Degradation mode – electrode
- Linear scalability (small cells)
- Moderate cost
- Mature technology

**Redox flow batteries**
- Power and energy separated
- Low energy density (10 – 50 Wh/kg)
- High energy efficiency (65 – 78%)
- Degradation mode – membrane
- Non-linear scalability (cell stacks)
- Low cost
- Emerging technology

**Regenerative fuel cells**
- Power and energy separated
- High energy density (450 – 500 Wh/kg)
- Low energy efficiency (35 – 50%)
- Degradation mode – catalyst
- Non-linear scalability (cell stacks)
- High cost
- New technology

• Combination of high energy density and efficiency, long cycle life, high DOD, low cost, fire and environmental safety desirable
• Main focus on transportation, more efforts on stationary storage needed
• New concepts wanted
Direct organic fuel cell/flow battery concept

- Feed the hydrogenated organic liquid carrier directly into the fuel cell where it will be electrochemically dehydrogenated to a stable, hydrogen depleted organic compound without ever generating gaseous $\text{H}_2$ to produce power.
- The spent organic carrier may be replenished either mechanically or electrochemically from water splitting.
- Minimize the balance of plant by excluding a catalytic reactor and a heat exchanger.

- High theoretical energy density (up to 1350 Wh/kg)
- Low membrane crossover – high efficiency
- Energy conversion and storage separated - low packaging
- Reversibility (fuel cell $\leftrightarrow$ flow battery)
- Excellent safety, zero carbon emission
Electrocatalysis, transport phenomena and membrane materials basic research aimed to three novel components of an entirely new high-density energy storage system combining the best properties of a fuel cell and a flow battery: organic carriers, electro(de)hydrogenation catalysts, and compatible PEM.

Focus areas:
- C-H bond catalysis/
- Electro(de)hydrogenation catalyst
- Organic fuel
- Low humidity proton exchange membrane

Award DE-SC0001055
Task interactions and program vision

**Challenges and needs**
- Electron level material processes
- Atom- and energy efficient synthesis
- Far from equilibrium processes control
- Electrical energy storage
- Catalysis for energy
- Hydrogen economy
- Solar energy utilization

**Fundamental research**
- **Focus 1**: Selection and synthesis of organic carriers
- **Focus 2**: Discovery of electrodehydrogenation and electrohydrogenation catalysts
- **Focus 3**: Immobilization and characterization of electrocatalysts
- **Focus 4**: Novel proton exchange membrane development
- **Focus 5**: Modeling of interactions among components

**Technology**
- High density energy storage
- Organic fuel cell/flow battery

**Applications**
- Solar energy
- Plug-in hybrids
- Wind energy
- Load leveling

**Program management**
Fuel (organic carrier) focus

Traditional approach
\[ LQH_n \leftrightarrow LQ + n/2 H_2 \]
\( \Delta H \) to be minimized

EFRC approach
\[ LQH_n + n/4 O_2 \leftrightarrow LQ + n/2 H_2O \]
\( \Delta(G_{LQHn} - G_{LQ}) \) to be minimized to maximize cell voltage
Theoretical cell voltage 0.95 – 1.1 V (depends on organic hydrogen carrier)

Organic fuel requirements
• Minimal \( \Delta G \) dehydrogenation of organic carriers via molecular modeling guidance
• Scalable synthesis of aromatic precursors and hydrogenation to saturated carriers (high pressure lab)
• Liquid at ambient conditions, low vapor pressure
Comparison of dehydrogenation energies for model and promising fuels in kcal/mol H₂ by DFT calculation (method B3LYp, basis set 6-311++G**)

Electrooxidation of model fuels on Pt electrode

First dehydrogenation step most critical

Single-bond and multiple-bond model and promising fuels selected based on computational modeling
**C-H bond catalysis focus**

Homogenous C-H bond activation **and** electron transfer

Catalyst requirements

- Catalytic activity in the C-H bond activation and further dehydrogenation of saturated hydrocarbons
- Redox activity in target electrochemical potential windows
- Microscopic reversibility (dehydrogenation/hydrogenation)
- Ability to transfer multiple electrons and protons
- Tunable redox potentials to selected organic fuels

**LHₙ - n e⁻ ⇌ L + n H⁺**

Utilize defined metal centers for catalysis understanding

Rh-based pincer complex

Organic catalyst for electrodehydrogenation

First electrocatalytic oxidation of cycloalkane on a metal complex
Alkane dehydrogenation mechanism

Computational simulation of catalytic cycle

Iridium pincer dihydride primary target for e/chem study


No sacrificial olefin

-2e- -2H+

Yale
**Electrocatalysis focus**

Electrocatalysis for dehydrogenation and hydrogenation

Electrocatalyst requirements

- Fast electron transfer from metal centers through a linker to electrode via study of the transport mechanism and determination of controlling factors
- Fast proton transport to PEM via structured catalyst/support
- Robust catalyst that tolerant to impurities/reaction products
  - design catalyst ligand environment for selectivity
  - use nanosized metal alloys catalysts supported on carbon

\[ 
\text{LH}_n - n \text{ e}^- \iff L + n \text{ H}^+ 
\]

1) IN\textsubscript{3} in hexanes

EtOH, CH\textsubscript{3}Cl Rinse

2) \text{Cu(I)}

CH\textsubscript{3}Cl, DMSO, H\textsubscript{2}O Rinse

**Chronoamperometry of baseline RVC (blue) and functionalized RVC (red)**
Proton exchange membrane focus

Membrane requirements
• Water free PEM (H₂O detrimental to anode chemistry)
• Low fuel and products solubility – mechanical integrity
• Proton conductivity $10^{-3}$ S/cm @ 120 °C
• High oxidative stability at 120 °C
• Thermal stability (> 150 °C)
Direct organic hydride fuel cell testing

Membrane Electrode Assembly (MEA)

- 5 cm² active area
- Anode: 4mg/cm² 60% PtRu/C
- C-cloth anode GDL
- Cathode: 2 mg/cm² 40% Pt/C
- 115 Nafion® membrane

Cyclohexane/air cell

Membrane dehydration, new membranes needed

Fuel Cell Assembly

Tetralin/air cell

Significant current observed for tetralin

Use of liquid hydrocarbon fuel in fuel cell demonstrated

Liquid fuel cells OCV, V
Fuel Theory Exp.
MeOH 1.21 0.73
Decalin 1.10 0.55
Tetralin 1.08 0.66
Conclusions

• Smart grid development and deployment of intermittent renewables require performance and cost effective energy storage

• New concept of high energy density storage system combining a PEM fuel cell and a flow battery suggested

• Energy Frontier Research Center targets major components of this system: organic fuel, electrocatalyst and low humidity PEM
Backup slides
Secondary batteries

<table>
<thead>
<tr>
<th>Type</th>
<th>Cell voltage, V</th>
<th>Energy density, Wh/kg</th>
<th>Demo scale, MW</th>
<th>Major players</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead acid</td>
<td>2.04</td>
<td>30 - 50</td>
<td>20</td>
<td>C&amp;D Battery, Exide Technologies, Hagen Batterie AG, Storage Battery Systems</td>
</tr>
<tr>
<td>NiCd</td>
<td>1.29</td>
<td>50 - 75</td>
<td>27</td>
<td>Saft Batteries, Storage Battery Systems</td>
</tr>
<tr>
<td>NaS</td>
<td>1.78 – 2.07</td>
<td>150 - 240</td>
<td>34</td>
<td>NGK Insulators Ltd.</td>
</tr>
<tr>
<td>Li-ion</td>
<td>3.3 – 4.2</td>
<td>75 - 200</td>
<td>20</td>
<td>A123, Ener1, Altair Nanotechnologies, Saft Batteries</td>
</tr>
<tr>
<td>NaNiCl₂</td>
<td>2.58</td>
<td>135</td>
<td>-</td>
<td>FZ Sonick SA, GE</td>
</tr>
<tr>
<td>LiS</td>
<td>2.2</td>
<td>350</td>
<td>-</td>
<td>SION Power, PolyPlus</td>
</tr>
</tbody>
</table>

Advantages:
- Mature technology
- High round trip efficiency
- High power or high energy
- Modular design

Major technical challenges:
- High cost for advanced batteries
- Linear scalability (kW to MW)
- No deep cycling
- Electrode degradation, short lifetime
- Corrosion (high temperature batteries)
- Safety
Flow batteries

Advantages:
- Separation of energy and power
- Non-linear scalability (kW to MW)
- High round trip efficiency
- Modular design
- Long lifetime
- Low cost

<table>
<thead>
<tr>
<th>Type</th>
<th>Cell voltage, V</th>
<th>Membrane</th>
<th>Energy efficiency, %</th>
<th>Major players</th>
</tr>
</thead>
<tbody>
<tr>
<td>All-vanadium</td>
<td>1.26</td>
<td>PEM</td>
<td>78</td>
<td>Prudent Energy, Sumitomo, VFuel Pt</td>
</tr>
<tr>
<td>Polysulfide-bromine</td>
<td>1.36</td>
<td>Ion-selective</td>
<td>77</td>
<td>Prudent Energy (IP holder)</td>
</tr>
<tr>
<td>Zinc-bromine</td>
<td>1.85</td>
<td>Porous diaphragm</td>
<td>73</td>
<td>ZBB Energy, Premium Power, Primus Power</td>
</tr>
<tr>
<td>Cerium-zinc</td>
<td>2.48</td>
<td>PEM</td>
<td></td>
<td>Plurion</td>
</tr>
<tr>
<td>Iron-chromium</td>
<td>1.18</td>
<td>Ion-selective</td>
<td>66</td>
<td>Deeya Energy</td>
</tr>
<tr>
<td>Soluble lead acid</td>
<td>2.04</td>
<td>No membrane</td>
<td>65</td>
<td>General Atomics</td>
</tr>
</tbody>
</table>

Major technical challenges:
- Low energy density (25 – 70 Wh/kg)
- Corrosion, expensive plumbing
- Environmental issues
Regenerative $\text{H}_2/\text{O}_2$ fuel cells

**Major players:**
- Giner, Proton Energy Systems

**Advantages:**
- High energy density (500 Wh/kg)
- Separation of energy and power
- Long lifetime
- No environmental issues

**Major technical challenges:**
- Dual function oxygen electrode (unitized FC)
- Low roundtrip energy efficiency
- Low energy density storage system
- Cost

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**Conventional design**

- **Electrolyzer**
  - $\text{H}_2$ tank
  - $\text{H}_2$ to $\text{H}_2\text{O}$
- **Fuel cell**
  - $\text{H}_2\text{O}$ to $\text{DC power}$
  - $\text{DC load}$
- **$\text{O}_2$ tank**

**Charge**

**Discharge**

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**Unitized design**

- **Unitized regenerative fuel cell**
  - $\text{H}_2\text{O}$ to $\text{DC power}$
  - $\text{DC load}$
  - $\text{O}_2$ tank
- **$\text{H}_2$ tank**

**Charge**

**Discharge**

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D. Bents et al., NASA Glenn Research Center, 2008
http://gltrs.grc.nasa.gov

F. Mitlitsky et al., LLNL [https://www.llnl.gov/str/Mitlit.html](https://www.llnl.gov/str/Mitlit.html)

F. Barbir et al., IEEE A&E Systems Magazine, 2005
500 Wh/kg with roundtrip efficiency of 34%.
# Electrochemical energy storage systems

<table>
<thead>
<tr>
<th>System</th>
<th>Energy density, Wh/kg</th>
<th>Round trip efficiency, %</th>
<th>Cost, $/kWh</th>
<th>Cycle life</th>
<th>Deep cycling</th>
<th>Scale</th>
<th>Response time</th>
<th>EHS issues</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead acid</td>
<td>41</td>
<td>78</td>
<td>150</td>
<td>short</td>
<td>no</td>
<td>kWh</td>
<td>+</td>
<td>Toxic, corrosive</td>
</tr>
<tr>
<td>Na/S</td>
<td>120</td>
<td>72</td>
<td>450</td>
<td>long</td>
<td>no</td>
<td>MWh</td>
<td></td>
<td>Thermal runaway</td>
</tr>
<tr>
<td>Na/MCl2</td>
<td>135</td>
<td>75</td>
<td>400</td>
<td>moderate</td>
<td>no</td>
<td>kWh</td>
<td></td>
<td>Molten Na</td>
</tr>
<tr>
<td>Li-ion</td>
<td>130</td>
<td>60 - 80</td>
<td>1300</td>
<td>moderate</td>
<td>no</td>
<td>kWh</td>
<td>+</td>
<td>Thermal runaway</td>
</tr>
<tr>
<td>VRB</td>
<td>35</td>
<td>78</td>
<td>800</td>
<td>long</td>
<td>yes</td>
<td>MWh</td>
<td>+</td>
<td>Corrosive, toxic</td>
</tr>
<tr>
<td>ZBB</td>
<td>70</td>
<td>73</td>
<td>500</td>
<td>long</td>
<td>yes</td>
<td>MWh</td>
<td></td>
<td>Toxic, corrosive</td>
</tr>
<tr>
<td>RFC</td>
<td>450</td>
<td>35 - 50</td>
<td>?</td>
<td>long</td>
<td>yes</td>
<td>kWh</td>
<td>+</td>
<td>Flammable</td>
</tr>
</tbody>
</table>

- Solid electrodes – degradation, liquid electrodes – low energy density