Advanced Stationary Electrical Energy Storage R&D at PNNL

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Funded by the Energy Storage Systems Program of the U.S. Department Of Energy through Pacific Northwest National Laboratories
EES technologies and PNNL focus

Electrical energy

- **Direct Storage in charges**
  - Electrical charges: Capacitors

- **Indirect storage via energy conversion**
  - Kinetic energy: flywheels
  - Potential energy: pump hydro, compress air
  - Chemical energy: batteries
PNNL strategy in stationary EES R&D

EES R&D at PNNL

Collaboration with industries, universities, etc.

Grid analytics on EES
• Roles of storage in US grids
• Value, locations, targets
• Cost and performance requirements

EES Technologies

Novel redox flow batteries, MWhs
New gen Na-batteries, up to MWhs
Low cost, long life Li-ion, community storage

Materials
➢ Materials synthesis,
➢ Ionic membrane
➢ Mixed conducting electrodes
➢ ...

Crosscutting science

Computer Modeling
• Mass/charge transport
• Electrical fields
• Flow, thermal, ...

Advanced diagnostic study, NMR, TEM, etc.
• Basic chemistry
• Materials structure
• Physical properties

Electrochemical study
• Electrochemical activity
• Reaction kinetics
• Performance/chemistry/structure

Collaboration with industries, universities, etc.

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Grid analytics on energy storage technologies (discussed by Dr. Kintner-Meyer)

- Actual production
- Generation schedule
- Real-time operation
  - Meeting Balance Requirements
  - Arbitrage
  - Infrastructure deferment
    - Located at strategic location in bulk power to reduced congestion
    - In distribution system/home to reduce distribution congestion

Energy storage is an valuable grid assets to provide balance services

- Reliability value
- Economic value
Redox flow battery RD&D

Materials, components, technology RD&D
- Redox electrolytes
- Electrodes-bipolar plate
- Membranes/separators
- Other stack components
- Modeling & Simulation
- Design and prototype

Core team
- PNNL
- Other labs
- Universities
- Industries
- Small business

Demonstration commercialization
- Scale up
- System design/engineering
- Demonstration
- Production

Vertical team
- Battery manufacturers
- Utilities
- ……

Pacific Northwest
NATIONAL LABORATORY
Toward cost reduction and commercialization

Develop cost-effective, optimized components:
- Electrolytes, higher energy capacity and improved stability;
- Electrodes of improved electrochemical activity;
- Membrane/separator of high conductivity, selectivity and stability;

Develop novel cell/stack designs/engineering:
- Increase current density (>50mA.cm⁻²);
- Reduce shunt current;

Demonstration (kWh prototype)

Scale production

Current focus

$\text{Kwh} / \text{hr}$

Year

2010 2011 2012 2013 2014 2015

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Electrolyte development

- Alternative redox couples to all V:
  - Fe$^{3+}$/Fe$^{2+}$ vs. V$^{3+}$/V$^{2+}$, ...

- Supporting electrolytes:
  - Chloride acid
  - Sulfate-chloride mixed acid
    (to be discussed by Dr. Liyu Li)

\[
[\text{VO}_2\text{H}_2\text{O}]^+ \rightarrow \text{VO(OH)}_3 + \text{H}_3\text{O}^+
\]
\[
2\text{VO(OH)}_3 \rightarrow \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}
\]
### Stability of chloride electrolytes

<table>
<thead>
<tr>
<th>V specie</th>
<th>-5°C</th>
<th>25°C</th>
<th>40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sulfate</td>
<td>Chloride</td>
<td>sulfate</td>
</tr>
<tr>
<td><strong>V^{2+}</strong></td>
<td>2M (419 h)</td>
<td>2.3M (&gt;20 d)</td>
<td>2M (30 d)</td>
</tr>
<tr>
<td><strong>V^{3+}</strong></td>
<td>2M (634 h)</td>
<td>2.3M (96 h)</td>
<td>2M (&gt;30 d)</td>
</tr>
<tr>
<td><strong>V^{4+} (VO^{2+})</strong></td>
<td>2M (18 h)</td>
<td>2.3M (&gt;20 d)</td>
<td><strong>2M (95 h)</strong></td>
</tr>
<tr>
<td><strong>V^{5+} (VO_{2}^{+})</strong></td>
<td>2M (&gt;30 d)</td>
<td>2.3M (&gt;20 d)</td>
<td>2M (&gt;30 d)</td>
</tr>
</tbody>
</table>

- Energy capacity up to 2.3M V over 0~50°C (1.7 M and 10~40°C for current sulfate chemistry), due to change in chemistry:
Electrochemical properties of all V chloride system

Chloride system shows higher charging and discharging potential for the same condition.

Positive: \[
[\text{VO}_2 \cdot 3\text{H}_2\text{O}]^+ + 2\text{H}^+ + e \xrightleftharpoons[\text{D}][\text{C}] [\text{VO} \cdot 4\text{H}_2\text{O}]^{2+} \quad E^0 = 1.0 \text{ V}
\]
\[
\text{VO}_2\text{Cl} \cdot 3\text{H}_2\text{O} + 2\text{H}^+ + e \xrightleftharpoons[\text{D}][\text{C}] [\text{VO} \cdot 4\text{H}_2\text{O}]^{2+} + \text{Cl}^- \quad E^0 = 1.0 + \alpha
\]

Negative: \[
\text{V}^{2+} \xrightleftharpoons[\text{D}][\text{C}] \text{V}^{3+} + e \quad E^0 = -0.25 \text{ V}
\]
Performance of all V chloride batteries

<table>
<thead>
<tr>
<th>Chloride</th>
<th>Sulphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>7\textsuperscript{th}</td>
<td>2.05 Ah</td>
</tr>
<tr>
<td>94\textsuperscript{th}</td>
<td>1.95 Ah</td>
</tr>
</tbody>
</table>

- Chloride system shows better and stable performance
- 30% energy density improved; Lower capacity loss
- Negligible, if any, chlorine gas evolution
Electrochemical properties of Fe/V redox couples

- Fe$^{3+}$/Fe$^{2+}$ (positive) vs. V$^{3+}$/V$^{2+}$, $E_o=1.02$ V
- Advantages over Fe/Cr system: no H$_2$ evolution and without catalysts
- Over V/V system: significantly improved chemical compatibility by avoiding high oxidant V$^{5+}$, allowing use of low cost materials, e.g. separator
Battery performance of Fe/V chloride system

On going research on the electrolyte system with higher concentration and improved efficiency
Membrane/separator development

- Develop cost-effective, optimized membranes or separators that can demonstrate high ionic conductivity, selectivity and mechanical/chemical durability through collaboration with universities, among national labs, industries.

- Nafion modification
  - Surface coating (PPR, PANI)
  - Nano-composite doping with SiO₂

- Hydrocarbon membrane:
  - S-Radel and SPEEK
  - Degradation Mechanism

Collaborated with Prof. Mike Hickner of Penn State

- Future focus on optimization of Nafion and searching its low cost alternatives via collaboration with ORNL, SNL, Penn State, DuPont, …
Electrodes/bi-polar plates of improved electrochemical activity

- Improve carbon/graphite electrode activity and current capability by modifying surface chemistry and structure/microstructure.
- Carried out thermal oxidation, doping and nanostructuring.

\[
E = E_0 - [(\eta_{ct})_a + (\eta_c)_a] - [(\eta_{ct})_c + (\eta_c)_c] - iR = iR
\]

**Graph:**
- Cell voltage increasing
- Current increasing
- IR – Ohmic loss or polarization
- \((\eta_{ct})_a + (\eta_{ct})_c\) – activation polarization
- \((\eta_c)_a + (\eta_c)_c\) – concentration polarization
Na-batteries

Electrochemical storage that utilize Na- or Na-containing electrodes and a Na\(^+\) conducting electrolyte, either solid or liquid

Why Na-battery chemistries?

- Li-resources constrains;
- Low cost of raw materials

- Na-beta alumina electrolyte batteries (SBB)
- Na-S or Na-Ni/NaCl
- Na-NaSicon electrolyte batteries
- Na-ion (aqueous or non aqueous electrolyte) batteries

Operating °C

~300

RT
PNNL (supported by DOE-ARPA-E, with Eagle Pitcher (lead)) is developing new generation Na-beta batteries that can meet economic and performance requirements for wide market penetration.

To be discussed by Dr. Vince Sprenkle.
Na-ion battery development

- Search materials and structures that are capable of facile Na\(^+\) insertion/deinsertion, and develop low cost Na-ion batteries

orthorhombic Na\(_4\)Mn\(_9\)O\(_{18}\)

To be discussed by Dr. Jun Liu
Unique Li-ion for community storage

- Long cycle life (>6,000 cycles)
- Low cost (<$250/kWh)
- Low P/E (≤0.5)
- Easy heat management

To be discussed by Dr. Choi
Summary and Future Work

- PNNL has adopted a systematic approach in searching suitable technologies, including novel redox flow batteries, Na-batteries and low cost, long life Li-ion batteries, for distribution and community storage.

- Substantial progress has been achieved in development and optimization of key materials, components, and cell designs, which include new redox flow battery electrolytes, electrodes and electrolytes for planar Na-beta alumina batteries, etc.

- Future work will focus on cell scale up, stack design and engineering, while continuing efforts on materials/components, through collaboration with academia, industries, and among national labs.

Please follow other talks from PNNL for further information.
Acknowledgements

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  Liyu Li, Soowhan Kim, Gordon Xia, Wei Wang, Vijayakumar Murugesan, Dean Matson, Jianlu Zhang, Yuliang Cao, Birgit Schwenzer, Feng Chen, …
Electrical energy storage

Carbon constrained, unsustainable

Clean, sustainable future

THANK YOU FOR YOUR ATTENTION