Next Generation Energy Storage Materials

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Outline

- Overview
- Milestones
- Background
- Goals & Objectives
  - Materials
  - Nanoscale Synthesis
  - Intercalation Energy Storage
  - Next Generation Energy Storage Materials
    - Na, Na$_2$ and Na$_3$ Ion Materials
    - Na Ion Performance
    - Mg Ion Materials
- Conclusions
- Future Plans

Source photos: www.oe.energy.gov/SmartGridIntroduction.htm
Overview

• **Timeline**
  – Start: Oct. 1, 2009
  – Finish: Sept. 30, 2010
  – 70% complete

• **Budget**
  – Total FY10 project funding
    • $150K
  – Funding received in FY10
    • $145K

• **Materials**
  – $Na_xFe(PO_4)_yF_z$
  – $Mg_xMo_6S_8$
  – $Na_xTi_2O_4$

• **Challenges**
  – Grid-scale energy storage
  – Low manufacturing costs
  – Use of abundant, low cost materials
  – Long cycle life
  – Solid-state material designs

• **Collaborators**
  – Discussions with potential RUA partners
Milestones

- **FY09**
  - N/A

- **FY10**
  - Complete procurement of an automated battery testing system
  - Complete synthesis of a series of nanoscale cathode electrode materials
  - Complete an initial series of performance tests on the synthesized nanoscale cathode electrode materials
Addressing the Challenge of Grid Scale Energy Storage

- U.S. generating capacity: 1,088 GW
  - 85% of U.S. power generation utilizes fossil resources
- U.S. storage capacity: 22 GW (pumped hydro)
- Today’s grid connects electricity where it is needed and large stationary grid energy storage adds electricity when it is needed\(^1\)
- New Needs\(^1\):
  - Distributed power
  - PEV, PEHV
  - Renewable peak shaving
  - Power quality and grid management

\(^1\)Adapted from M. Johnson, D. Danielson and I. Gyuk, Grid-Scale Energy Storage, ARPA-E, www.arpa-e.energy.gov.
Increased energy storage capacity is needed to support:

- Peak shaving during fossil fuel power generation
- Transmission
- Renewable and distributed power generation
- Customer focus on energy services

Source: Figure adapted from J. Makansi, Energy Storage, [www.energystoragecouncil.org](http://www.energystoragecouncil.org).

Source Photo: [www.oe.energy.gov/SmartGridIntroduction.htm](http://www.oe.energy.gov/SmartGridIntroduction.htm).
> Large stationary grid scale battery technologies have power and energy capacity ratings that support fossil energy power production applications…

Project Goals

Addressing the Gaps in Grid-Scale Energy Storage Solutions for Fossil Fuel Power Production to...

• Improve the efficiency of fossil fuel utilization
• Reduce greenhouse gases
• Reduce the need for spinning reserve
• Increase the use of renewables

Objectives and Materials Focus

- **Objectives**: Develop low cost energy storage materials. Assess the effect of intercalation material structure on the stability of cathode electrode materials. Examine performance relative to structure, particle size and morphology.

- **Approach**: Synthesize novel alternative chemistry intercalation materials at the nanoscale and characterize performance.

**Structure, Particle Size and Morphology from Experiment**

**Electrochemical Performance from Experiment**

NaFePO₄ Crystalline Structure

Materials Focus

• **Intercalation chemistry** for low cost, high performance cathode electrode materials:

  – **Phosphates** \((\text{Na}_x\text{Fe}_y(\text{PO}_4)_y\text{F}_z)\)
    - Phase: Olivine, maricite, etc.
      - \(\text{NaFePO}_4 \rightarrow x\text{Na} + x\text{e}^- + x\text{FePO}_4 + (1-x)\ \text{NaFePO}_4\)
      - \(E = 3.48\ \text{V}\)
  
  – **Sulfides** \((\text{Mg}_x\text{Mo}_6\text{S}_8)\)
    - Phase: Chevrel
    - Issues with regenerability
  
  – **Layered** \((\text{Na}_x\text{Ti}_2\text{O}_4)\)
    - Phase: Spinel
## Synthesized Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>No. of Preparations</th>
<th>Preparation Method</th>
<th>Analytical</th>
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<tr>
<td>NaFePO₄</td>
<td>3</td>
<td>Microwave, thermolysis</td>
<td>XRD, BET, FE-SEM, EDX, TEM</td>
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<tr>
<td>NaFePO₄F</td>
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<tr>
<td>Na₂FePO₄F</td>
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<td>XRD, BET, FE-SEM, EDX, TEM</td>
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<tr>
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<td>Microwave, thermolysis, solid-state</td>
<td>XRD, BET</td>
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</tbody>
</table>
Nanoscale Synthesis

NETL Material Synthesis Capability

- Controlled particle shapes and surface properties: nano-particles, nano-wires and nano-belts

- Techniques:
  - Thermolysis, microwave assisted thermolysis
  - Hydrothermal
  - Sol-gel

Microwave Synthesis

Shape Selectivity of Nanoparticles using NETL Developed Synthetic Methods
Intercalation Energy Storage

- **Electrical energy** is stored chemically in the cathode electrode.
- **Na-ions migrate** between cathode and anode during charge/discharge cycles.
- **Na-ion guests** reside in cathode and anode hosts via intercalation mechanisms.
- **Secondary architecture** is critical for low cost and high performance.

Nano-sized sodium iron phosphate materials have shorter electron and ion diffusion path lengths. Shorter diffusion path lengths improve the charge/discharge kinetics.

Nano-sized sodium iron phosphate particles provide an elegant means of studying the mechanism of sodium intercalation in new materials may hold the key to grid-scale energy storage batteries.
Intercalation Energy Storage

Na Ion Materials

- A closer look at the nanobundles indicates that the nanorods are interconnected to form chains with 10 to 20 nm widths

- Most as synthesized NaFePO$_4$ nanorods are crystalline with an amorphous shell as indicated from XRD results
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**Na Ion Materials**

Maricite is a relatively closed framework with no layered or channeled pathways for Na$^+$ intercalation which can result in irreversible redox behavior.

NaFePO$_4$ XRD Crystal Structure [100] Direction

FE-SEM Photomicrograph of Microwave Synthesized NaFePO$_4$

EDX Analysis

<table>
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<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atom %</th>
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<tr>
<td>O</td>
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<td>Na</td>
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<td>P</td>
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<tr>
<td>Fe</td>
<td>25.15</td>
<td>8.99</td>
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<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
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</table>

NaFePO$_4$ XRD Powder Diffraction

TEM of NaFePO$_4$ Showing Nanorod Structure

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**Na₂ Ion Materials**

**Na₂FePO₄F**

Fluorine addition produces 2-dimensional channels with a layered structure in the crystalline lattice. 2-dimensional channels enhance the Na⁺ intercalation and de-intercalation mechanism.

Only a 4% decrease in the unit cell volume which limits deterioration.

Solid state synthesis produced multifaceted crystals with micron sized dimension.

**FE-SEM Photomicrograph of Na₂FePO₄F**

**Na₂FePO₄F XRD Powder Diffraction**

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*Na₃ Ion Materials*

Fluorine addition produces 2-dimensional channels without a layered structure in the crystalline lattice. 2-dimensional channels enhance the Na⁺ intercalation and de-intercalation mechanism. Higher concentration of Na⁺ per unit cell leads to increased energy density.
Energy Storage Materials Performance

**Na and Na$_2$ Ion Materials**

- **Na$_2$FePO$_4$F** is more conductive than NaFePO$_4$
- Cathode conductivity could potentially be improved with F addition and by reducing particle size
- $\sigma_{\text{LiFePO}_4} = 10^{-10} \sim 10^{-9}$ s/cm$^1$
  - LiFePO$_4$ has a lower conductivity than NaFePO$_4$

*http://en.wikipedia.org/wiki/Lithium_iron_phosphate*
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Mg Ion Materials

- **Chevrel Phases**: $\text{Mg}_x\text{Mo}_6\text{S}_8$
3-D Energy Storage Material Architecture

3-D energy storage architecture increases the contact area between cathode, electrolyte and anode materials allowing the discharge characteristics of the battery to be tailored to the material characteristics.

Conclusions

• Sodium iron phosphate was synthesized as cathode electrode energy storage materials using microwave, thermolysis and solid-state synthesis techniques
• As synthesized materials were characterized using TEM, XRD, EDX and BET surface area
• Microwave synthesized NaFePO$_4$ nanocrystals were shown by TEM to exhibit tubular geometry
• Impedance testing of nano-sized NaFePO$_4$ and Na$_2$FePO$_4$F revealed that NaFePO$_4$ possesses greater internal resistance
• Sodium iron phosphate represents a potentially low cost, environmentally benign, energy storage material for use on the modern grid
Future Plans

• Cathode electrode materials
  – Continue on series with sodium iron phosphates
    • Na, Na$_2$ and Na$_3$
      – Effect of dopants? Nanoscale architecture?
  – Novel intercalation materials
    • Spinel and chevrel phases
      – Na, Mg

• Electrolyte material development
  – Solid-state, solvent (aqueous, organic)

• Anode material development

• 3-D secondary battery architectures

• Computational modeling of structure

• Long term cycle testing
Energy Storage Materials Development

Solid-State Energy Storage Materials

- Cathode
- Electrolyte
- Anode

Modeling

Structural Analysis

Electrochemical Analysis

3-D Architecture

Improved Material Chemistry and Performance
Acknowledgements

• TEM Analysis
  – Dr. Xueyang Song, WVU

• Impedance Analysis
  – Prof. Xingbo Liu, WVU

• NETL
  – Dr. Charles Taylor
  – Dr. Cynthia Powell
Sound Strategies for Meeting Future Fossil Energy Needs

- Fossil energy will meet the majority of the world’s energy demand well into the 21\textsuperscript{st} century
- We must continue to pursue technologies that balance energy security, cost, and environmental stewardship
- NETL is working to meet these challenges through publicly funded R&D that pursues high-risk, long-range solutions
- Our facilities and knowledge-base are available for collaborations with domestic and international partners
National Energy Technology Laboratory

- Designated as 15th National Laboratory in 1999
- Only DOE national lab dedicated to fossil energy
  - Fossil fuels provide 85% of U.S. energy supply
- One lab, one management structure, five locations
  - Government owned and operated
  - 3 R&D locations
- Roughly 1,200 employees, both federal and support-contractor
- Research spans fundamental science to technology demonstrations
Contact Information

Fossil Energy website: www.fe.doe.gov

NETL website: www.netl.doe.gov