NATIONAL ENERGY TECHNOLOGY LABORATORY

Next Generation Energy Storage Materials

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Office of Research & Development

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U.S. DEPARTMENT OF ENERGY

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

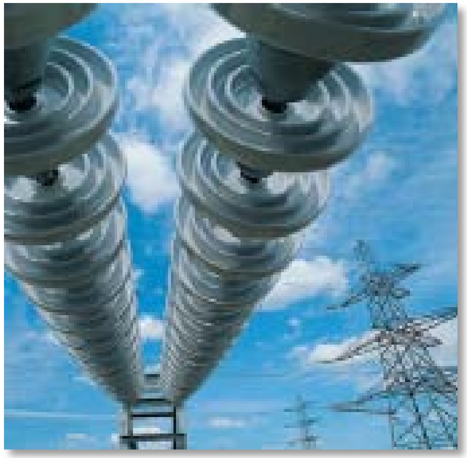
- **Timeline**
  - Start: Oct. 1, 2009
  - Finish: Sept. 30, 2010
  - 70% complete
- **Budget**
  - Total FY10 project funding
    - $150K
  - Funding received in FY10
    - $145K
- **Materials**
  - $Na_xFe(PO_4)_yF_z$
  - $Mg_xMo_6S_8$
  - $Na_xTi_2O_4$
- **Challenges**
  - Grid-scale energy storage
  - 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

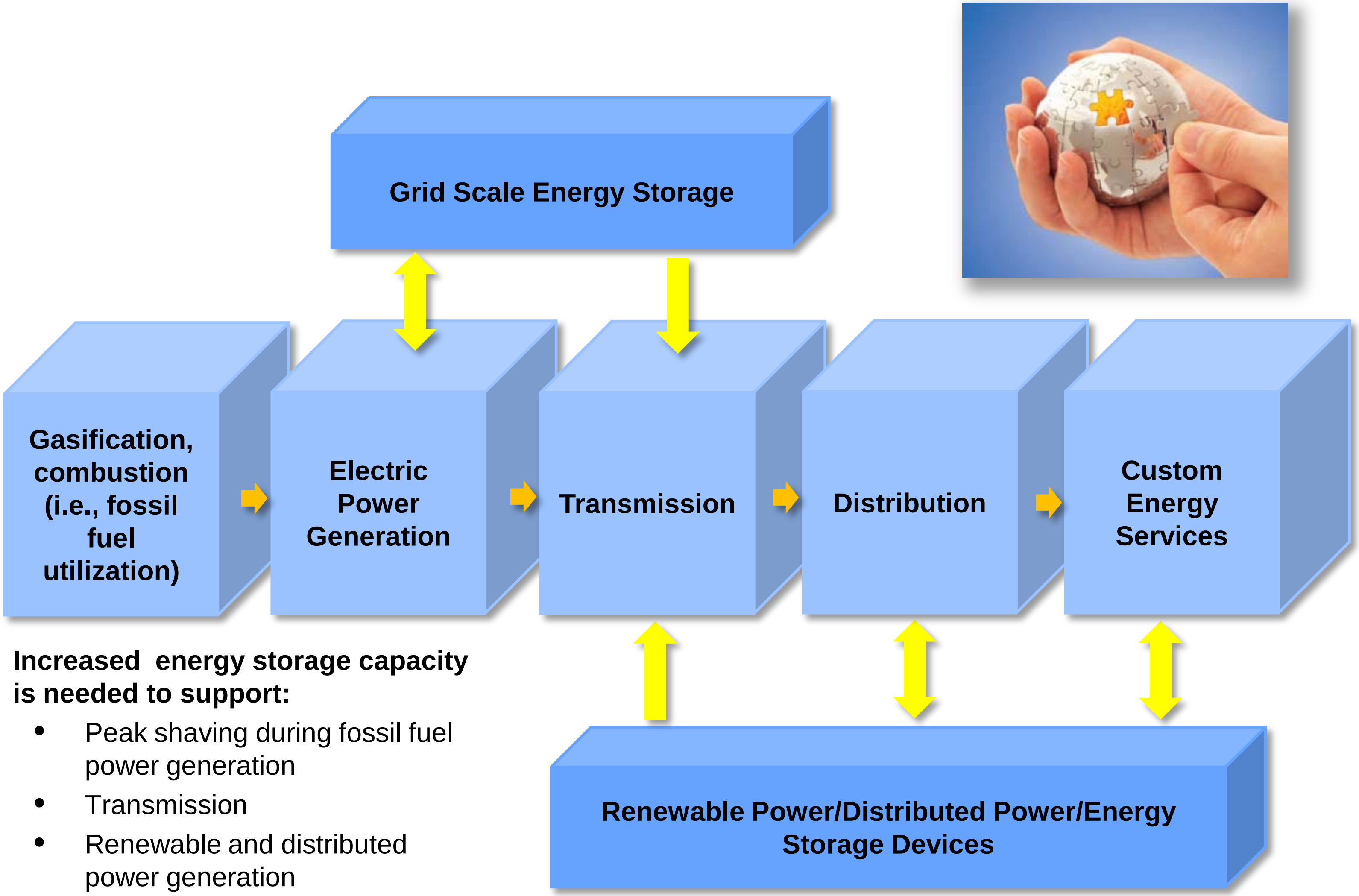
Addressing the Challenge of Grid Scale Energy Storage

- **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.
Source photo: www.oe.energy.gov/SmartGridIntroduction.htm.

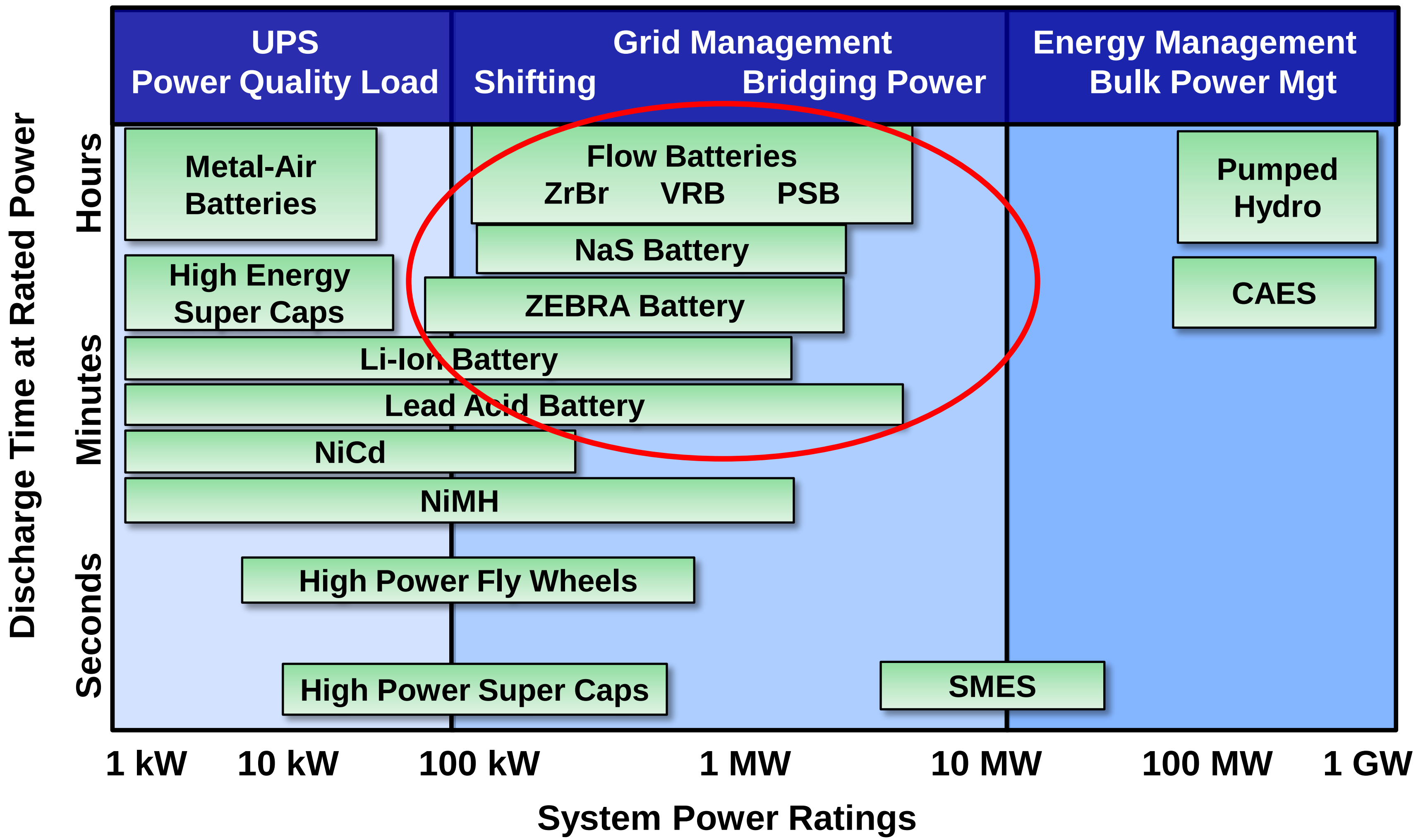
Fossil Energy and The Modern Grid



- **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.
Source Photo: www.oe.energy.gov/SmartGridIntroduction.htm.

Energy Storage Technologies



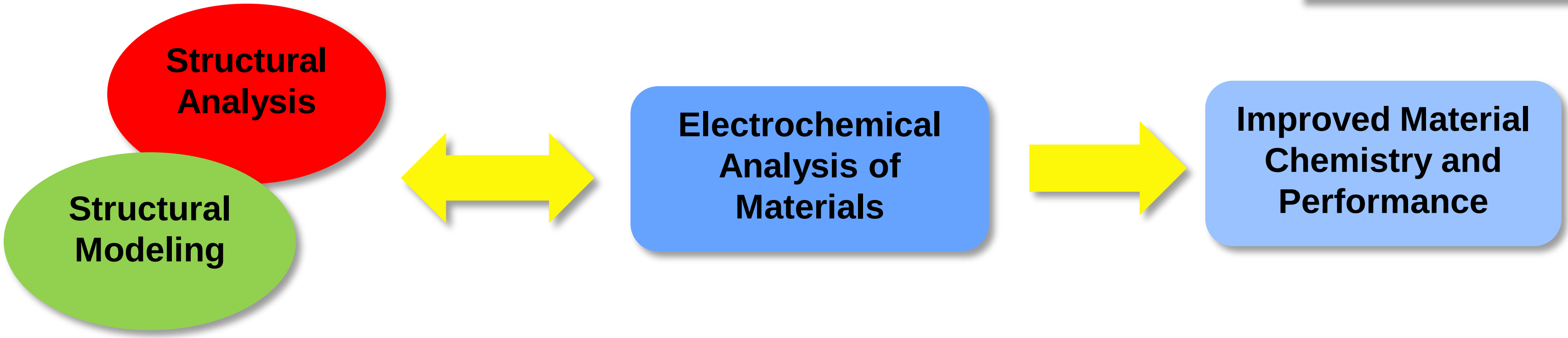
- ***Large stationary grid scale battery technologies have power and energy capacity ratings that support <u>fossil energy</u> power production applications…***

Source: Figure adapted from EPRI report, "Integrated Distributed Generation and Energy Storage Concepts," (2003) Product ID 1004455.

Project Goals

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

- **Improve the efficiency of <u>fossil fuel</u> utilization**
- **Reduce greenhouse gases**
- **Reduce the need for spinning reserve**
- **Increase the use of renewables**

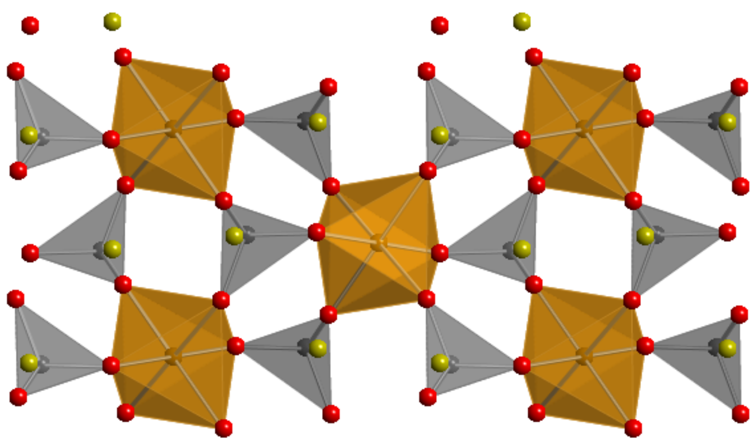


Source photos: www.oe.energy.gov/SmartGridIntroduction.htm.

Objectives and Materials Focus

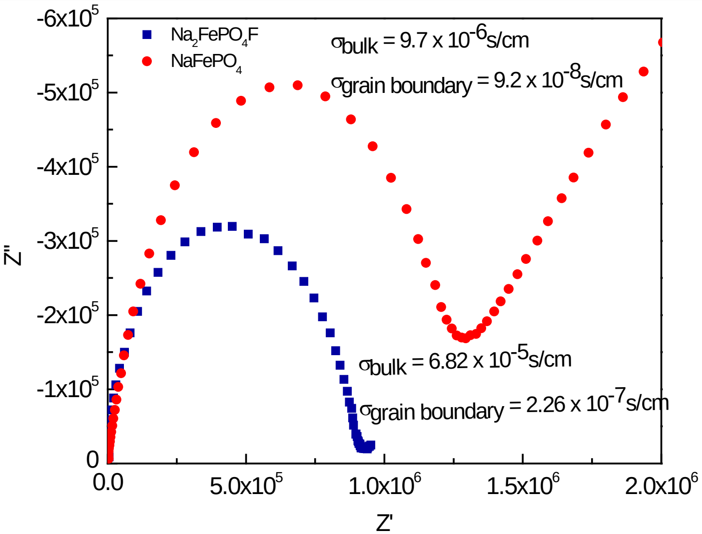
- **Objectives:** Develop low cost energy storage materials. Assess the effect of intercalation material structure on the stability of cathode electrode materials. Examine performance relative to structure, particle size and morphology
- **Approach:** Synthesize novel alternative chemistry intercalation materials at the nanoscale and characterize performance

Structure, Particle Size and Morphology from Experiment



$NaFePO_4$ Crystalline Structure

Electrochemical Performance from Experiment



Source: CrystalMaker® V 2.2.3 CrystalMaker Software, Ltd, Oxford, England.

Materials Focus

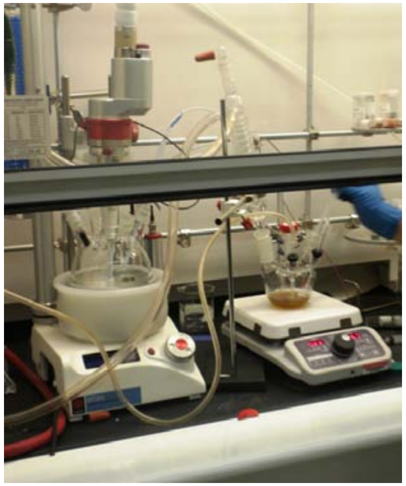
- **Intercalation chemistry** for low cost, high performance cathode electrode materials:
  - **Phosphates** ($Na_xFe_y(PO_4)_yF_z$)
    - Phase: Olivine, maricite, etc.
      - $NaFePO_4 \rightarrow xNa + xe^- + xFePO_4 + (1\text{-}x)\ NaFePO_4$
      - E = 3.48 V
  - **Sulfides** ($Mg_xMo_6S_8$)
    - Phase: Chevrel
    - Issues with regenerability
  - **Layered** ($Na_xTi_2O_4$)
    - Phase: Spinel

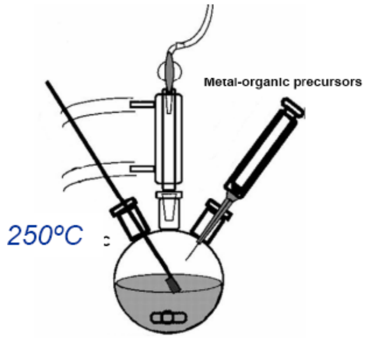
Synthesized Materials

Material	No. of Preparations	Preparation Method	Analytical
$NaFePO_4$	3	**Microwave**, thermolysis	XRD, BET, FE-SEM, EDX, TEM
$NaFePO_4F$	3	Microwave, thermolysis	-
Na_2FePO_4F	16	Microwave, thermolysis, **solid-state**	XRD, BET, FE-SEM, EDX, TEM
$Na_3Fe_2(PO_4)_2F_3$	18	Microwave, thermolysis, **solid-state**	XRD, BET

Data shown is for preparation methods given in bold.

Nanoscale Synthesis

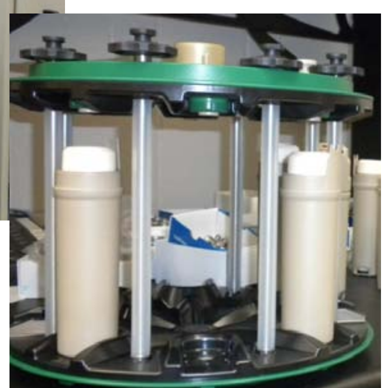




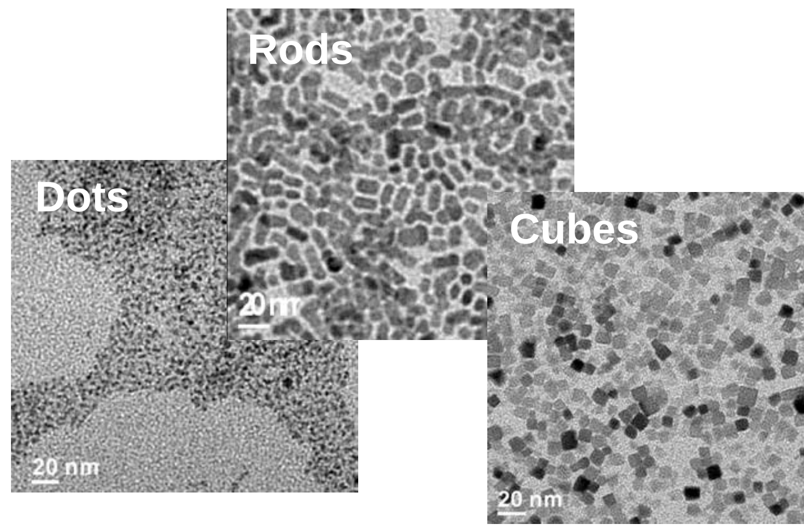
Thermolysis

NETL Material Synthesis Capability

- Controlled particle shapes and surface properties: nano-particles, nano-wires and nano-belts
- Techniques:
  - Thermolysis, microwave assisted thermoloysis
  - Hydrothermal
  - Sol-gel

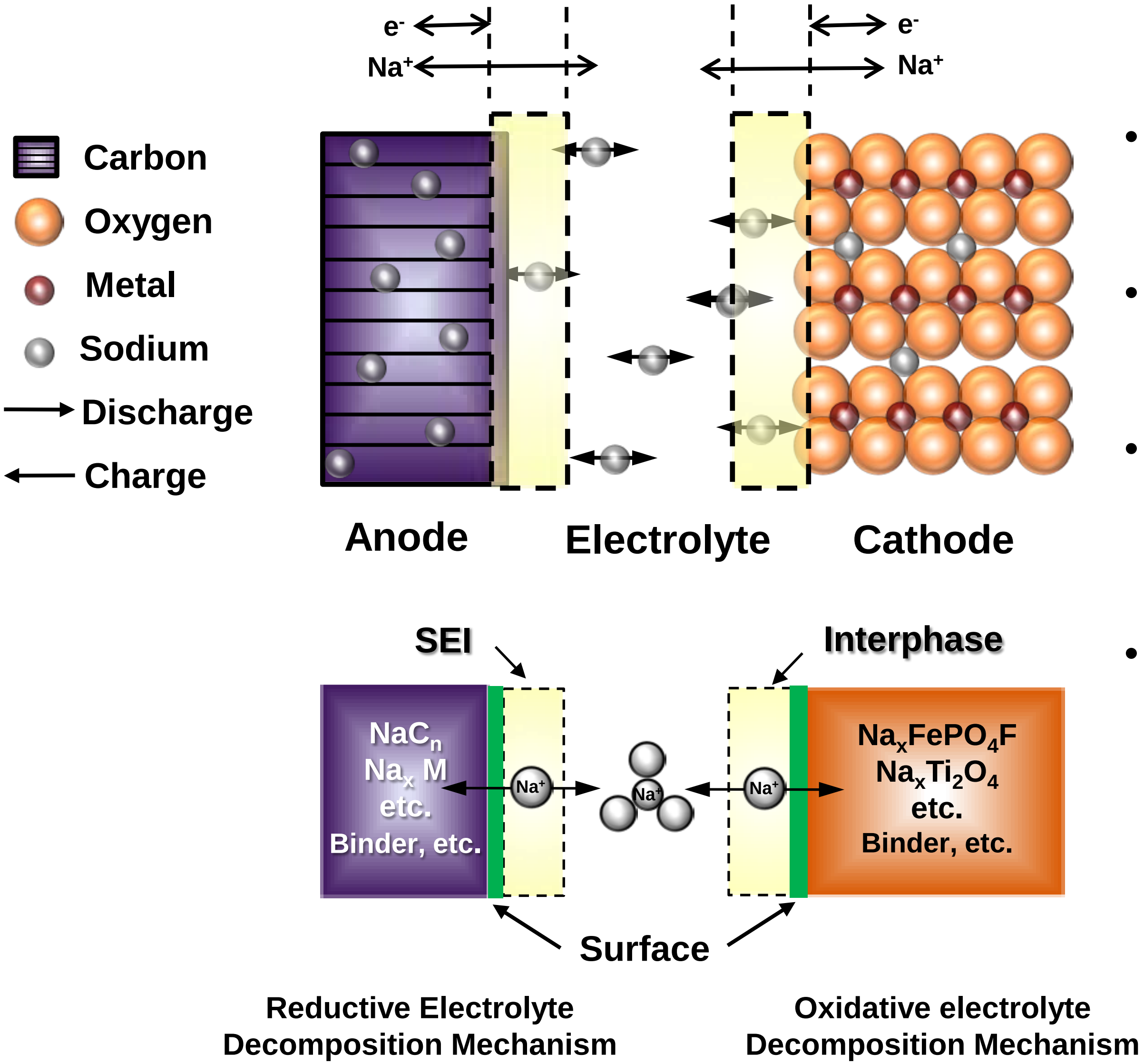


Microwave Synthesis



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

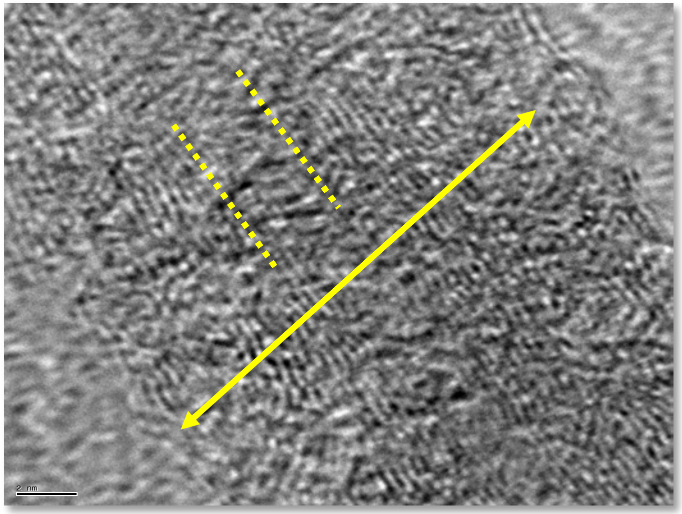
Source: Figure adapted from Basic Energy Needs for Electrical Energy Storage, Report to Basic Energy Sciences Workshop on Electrical Energy Storage, April 2-4, 2007.

Intercalation Energy Storage

Na Ion Materials

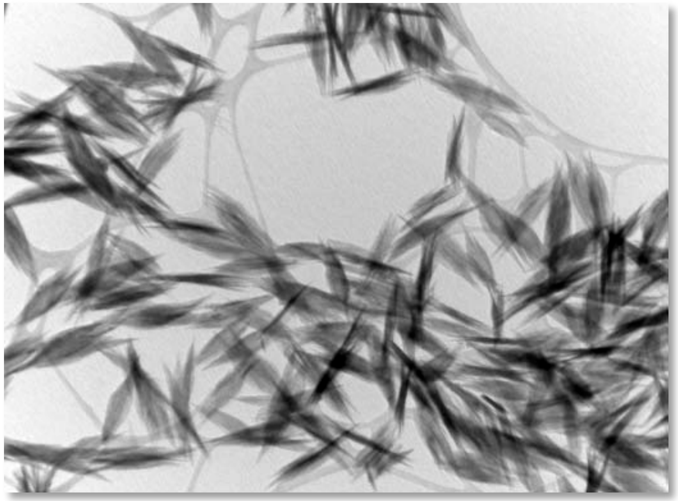
Nano-sized sodium iron phosphate materials have shorter electron and ion diffusion path lengths. Shorter diffusion path lengths improve the charge/discharge kinetics

2 nm



HR TEM of Synthesized $NaFePO_4$ shows Atomic Fringes which Indicate that Nanorods Have a Crystalline Core with an Amorphous Shell

1000 nm

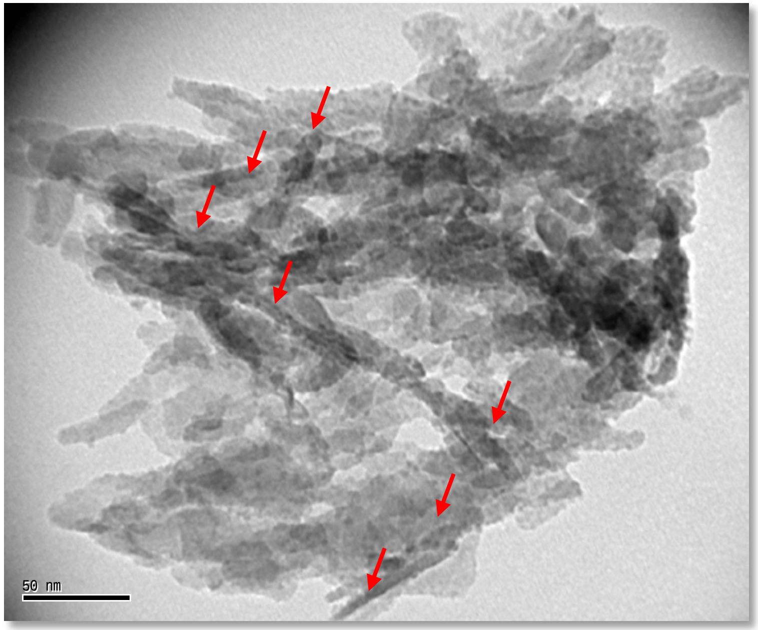


TEM of Synthesized $NaFePO_4$ Indicates Bundled Nanorods with High Aspect Ratio (1:50)

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

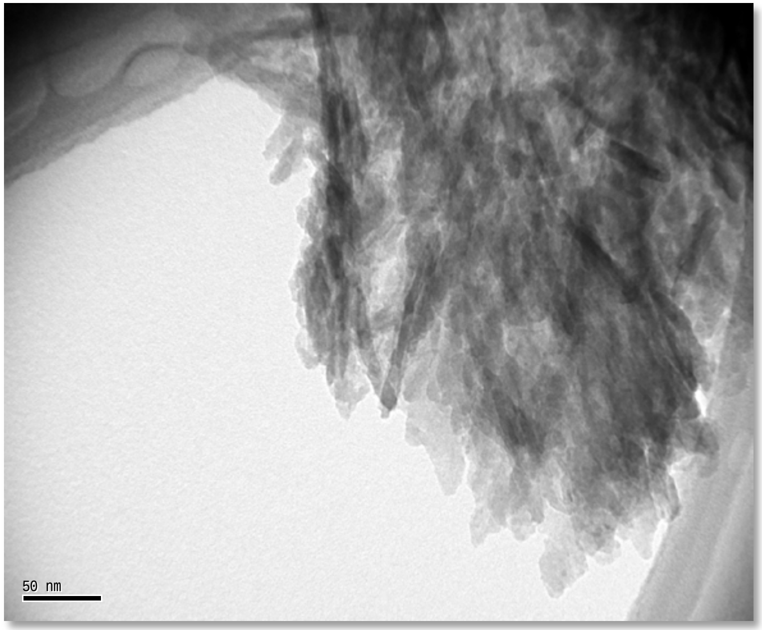
Na Ion Materials



TEM of Microwave Synthesized $NaFePO_4$ Nanomaterial

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

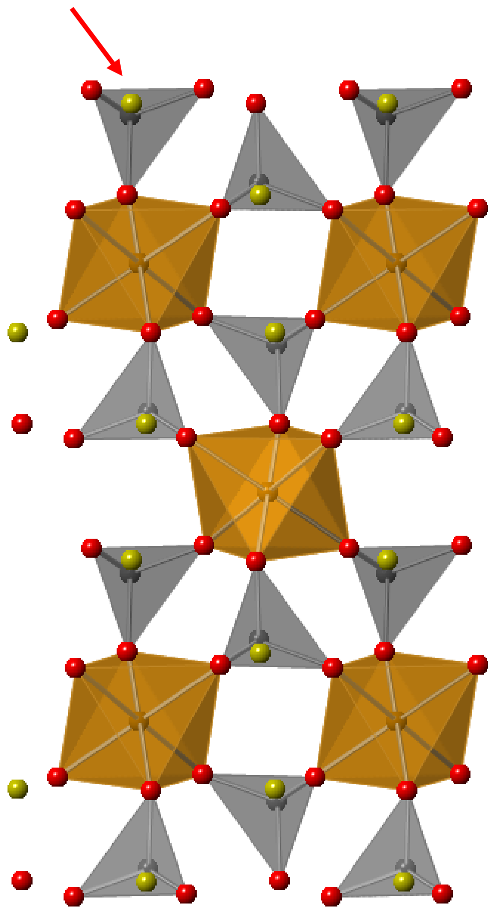
- Most as synthesized $NaFePO_4$ nanorods are crystalline with an amorphous shell as indicated from XRD results



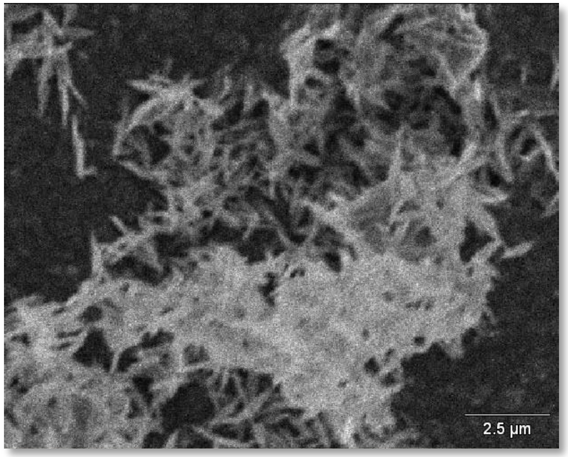
TEM of Microwave Synthesized $NaFePO_4$ Nanomaterial

Next Generation Energy Storage Materials

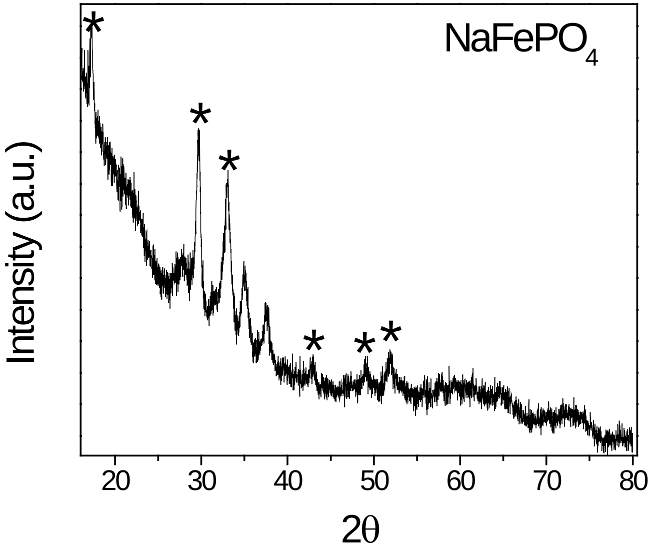
Na Ion Materials



$NaFePO_4$ XRD Crystal Structure [100] Direction



FE-SEM Photomicrograph of Microwave Synthesized $NaFePO_4$

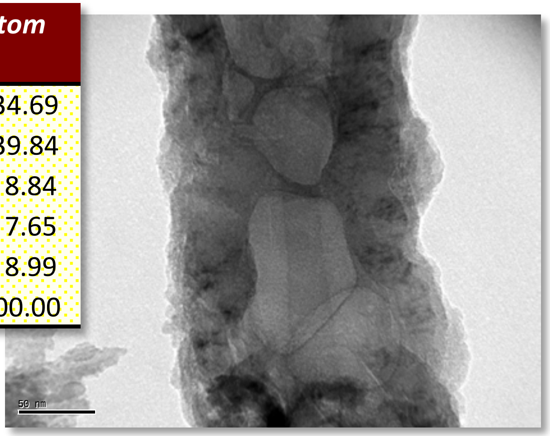


$NaFePO_4$ XRD Powder Diffraction

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

Element	*Weight %*	*Atom %*
C	20.87	34.69
O	31.93	39.84
Na	10.18	8.84
P	11.87	7.65
Fe	25.15	8.99
Total	100.00	100.00

EDX Analysis

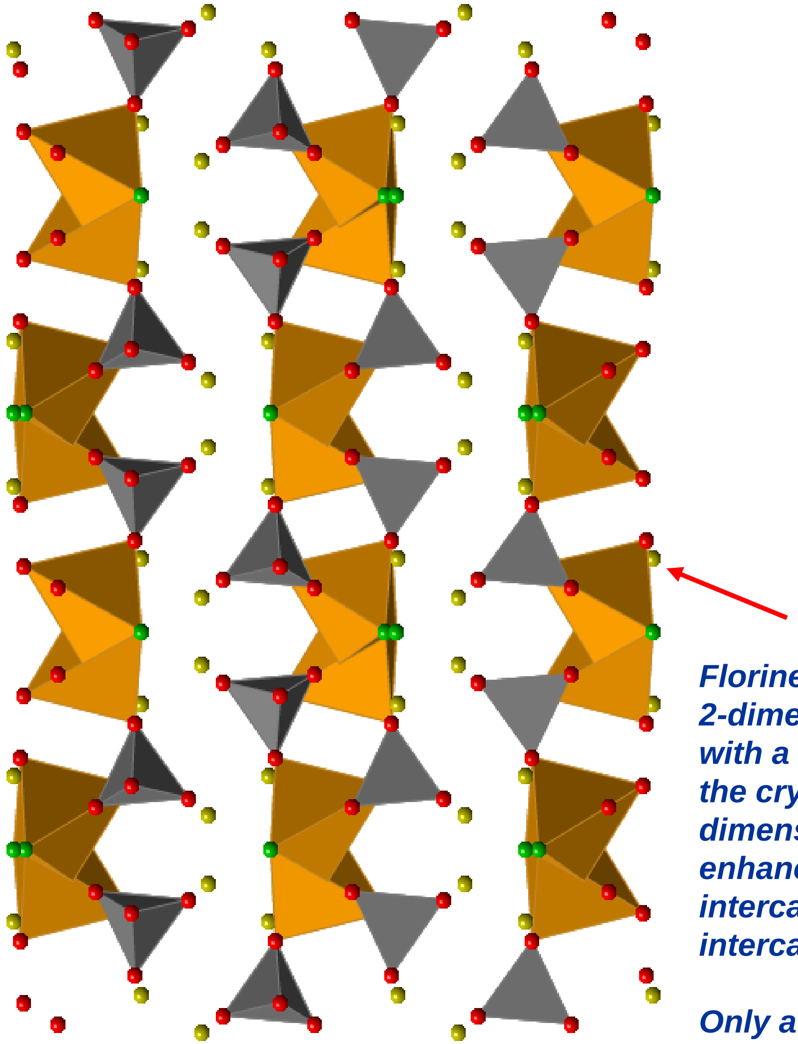


TEM of $NaFePO_4$ Showing Nanorod Structure

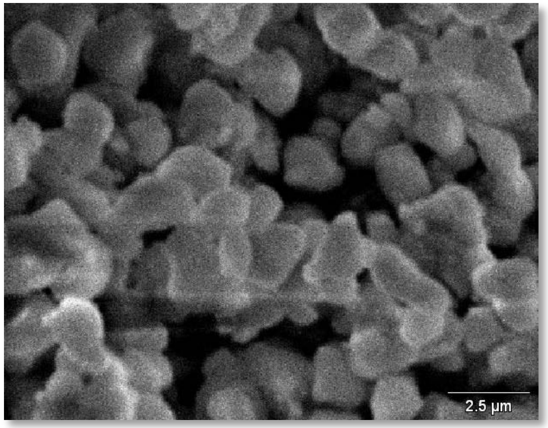
Image Source: CrystalMaker® V 2.2.3 CrystalMaker Software, Ltd, Oxford, England.

Next Generation Energy Storage Materials

Na_2 Ion Materials



Na_2FePO_4F Crystal Structure [100] Direction

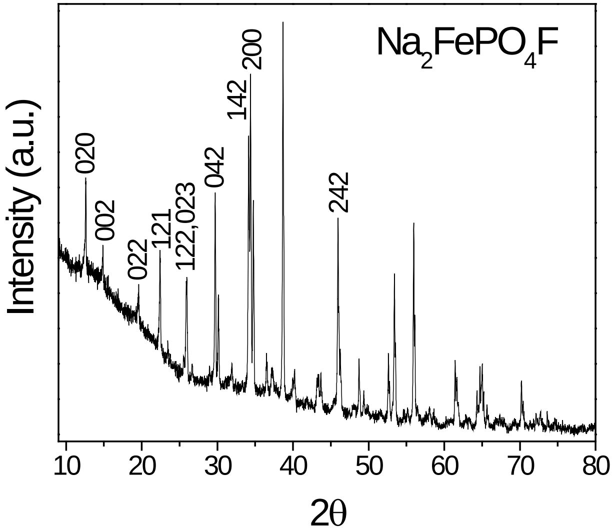


FE-SEM Photomicrograph of Na_2FePO_4 F

Solid state synthesis produced multi-faceted crystals with micron sized dimension

Florine 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

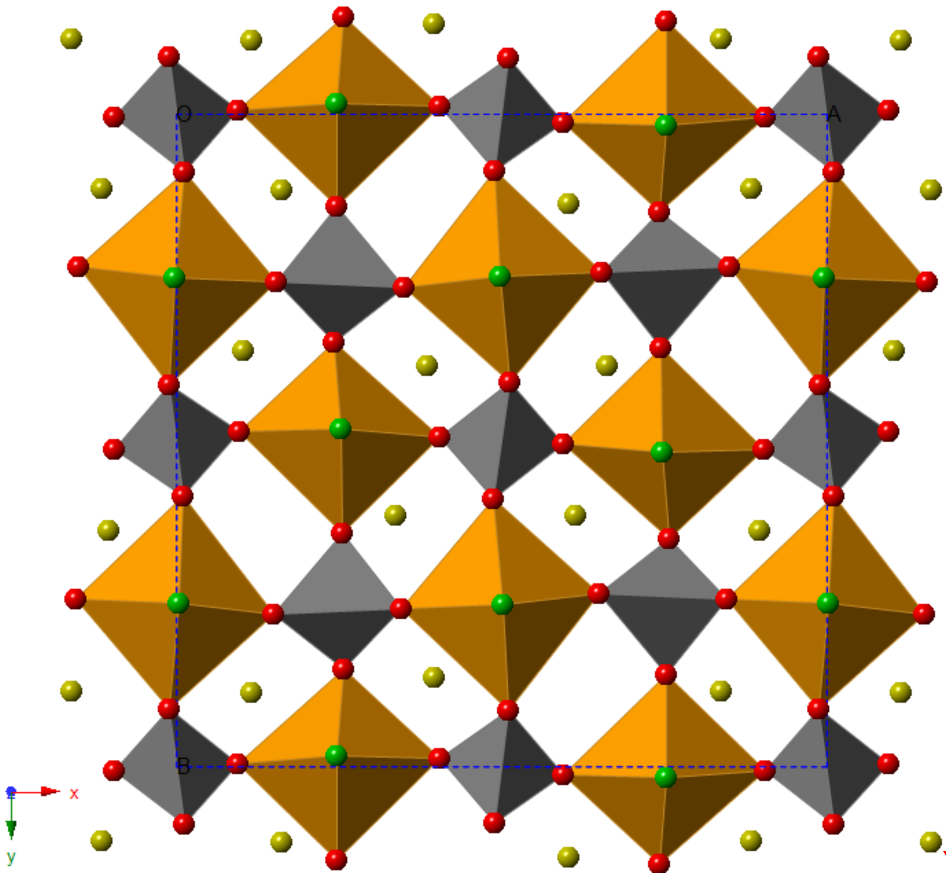


Na_2FePO_4F XRD Powder Diffraction

Image Source: CrystalMaker® V 2.2.3 CrystalMaker Software, Ltd, Oxford, England.

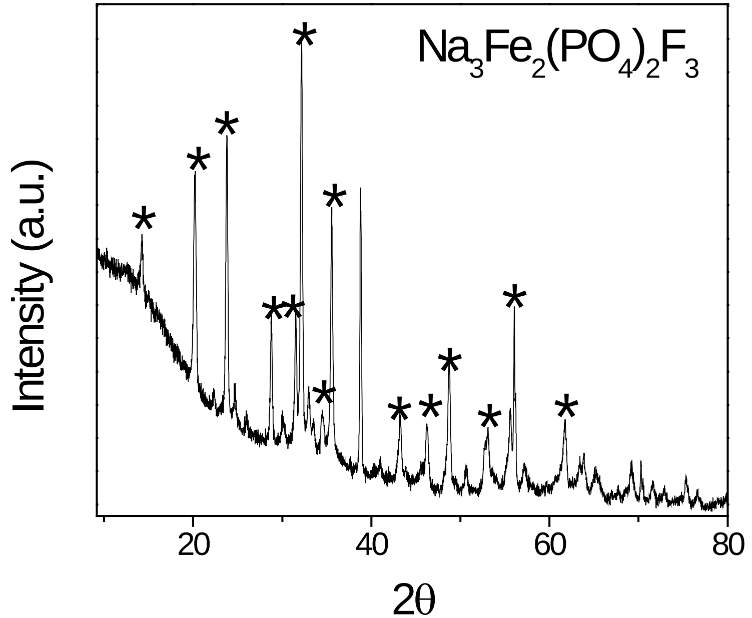
Next Generation Energy Storage Materials

Na_3 Ion Materials



Na

$Na_3Fe_2(PO_4)_2F_3$ Crystal Structure [001] Direction



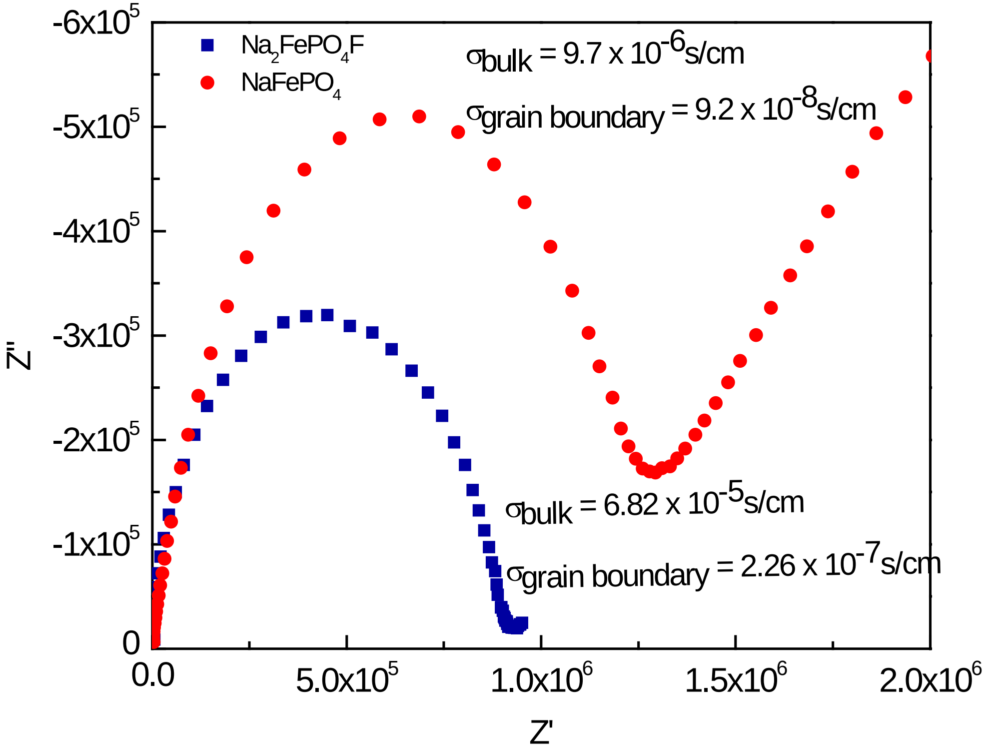
$Na_3Fe_2(PO_4)_2F_3$ XRD powder diffraction

Florine 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.

Image Source: CrystalMaker® V 2.2.3 CrystalMaker Software, Ltd, Oxford, England.

Energy Storage Materials Performance

Na and Na_2 Ion Materials



Na_2FePO_4F and $NaFePO_4$ Impedance Measurements

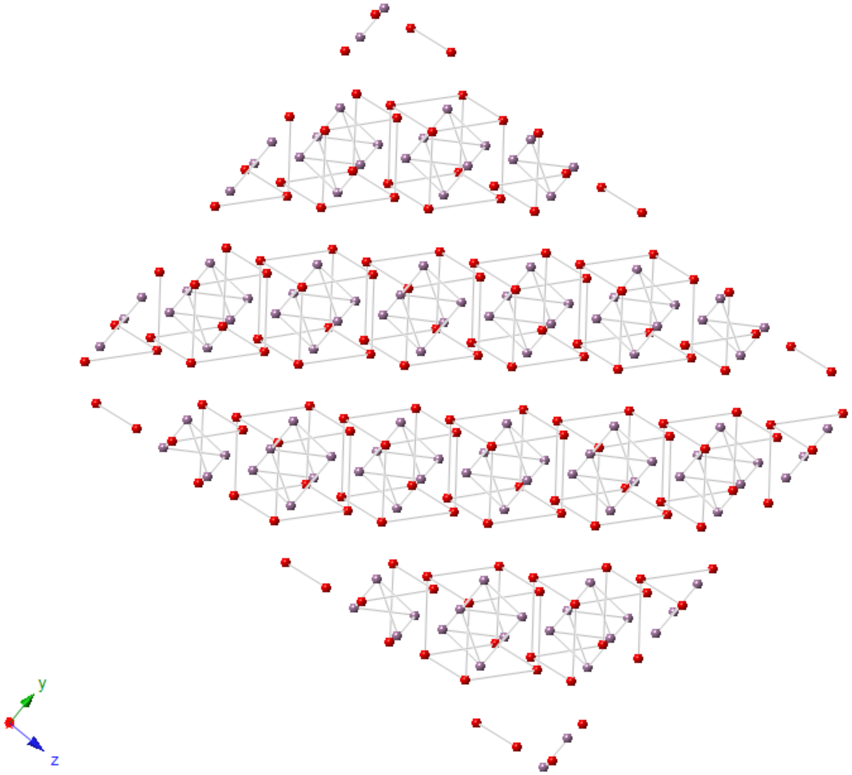
- **Na_2FePO_4F is more conductive than $NaFePO_4$**
- **Cathode conductivity could potentially be improved with F addition and by reducing particle size**
- **$\sigma_{LiFePO_4} = 10^{-10} \sim 10^{-9}$ s/cm**[1]
  - $LiFePO_4$ has a lower conductivity than $NaFePO_4$

[1]http://en.wikipedia.org/wiki/Lithium_iron_phosphate

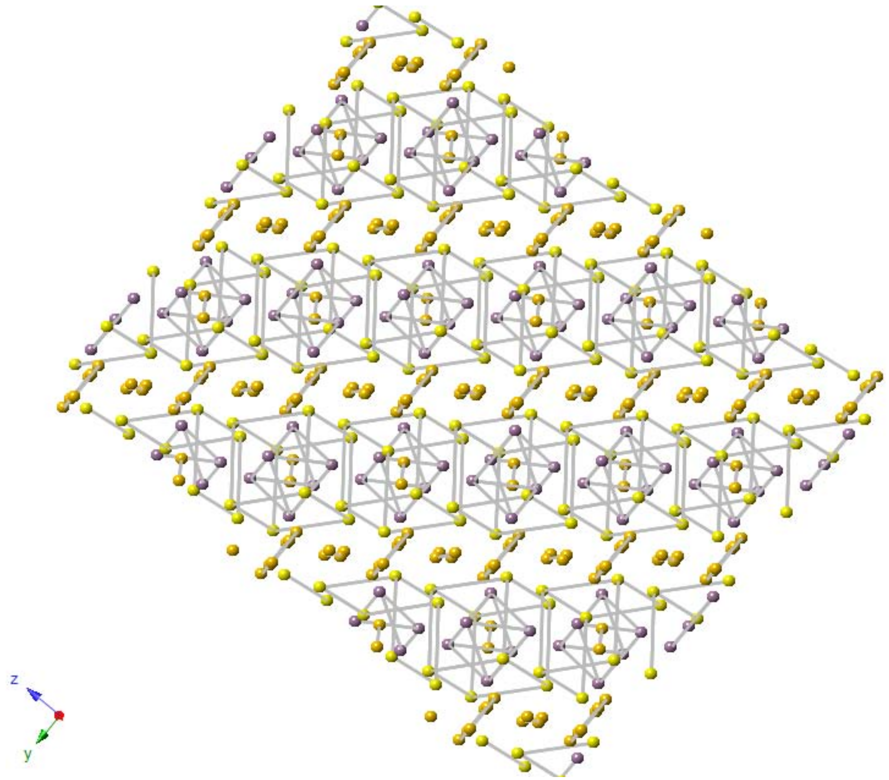
Next Generation Energy Storage Materials

Mg Ion Materials

- **Chevrel Phases:** $Mg_xMo_6S_8$



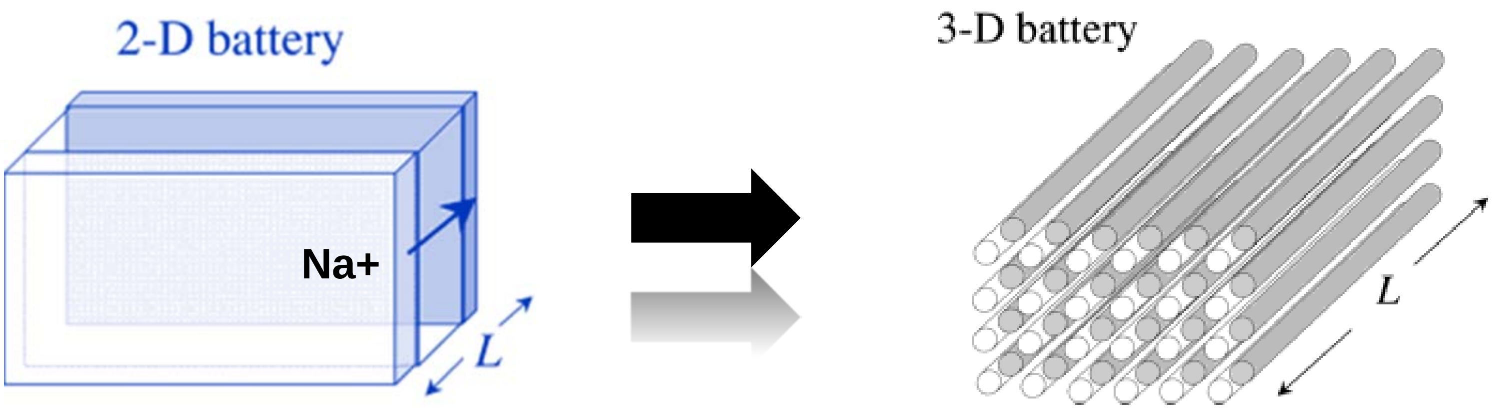
Mo_6S_8 Crystal Structure <u>without</u> Mg Intercalation

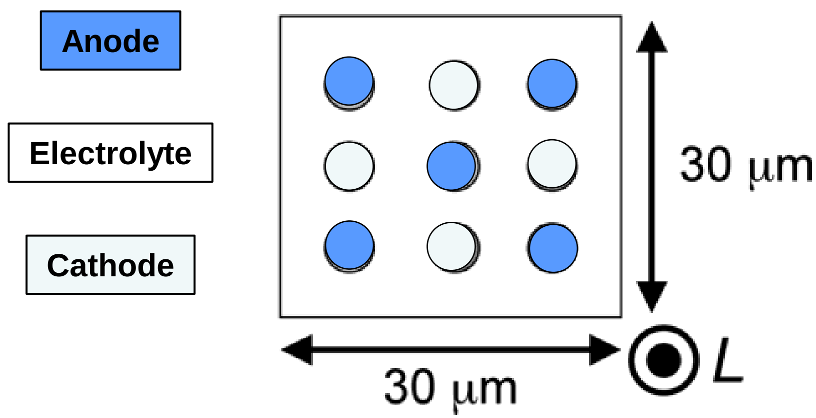


$Mg_2Mo_6S_8$ Crystal Structure <u>with</u> Mg Intercalation

Image Source: CrystalMaker® V 2.2.3 CrystalMaker Software, Ltd, Oxford, England.

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***

Source: J.W. Long, B. Dunn, D.R. Rolison, H.S. White, *Chem. Rev.* 104 (2004) 4463.

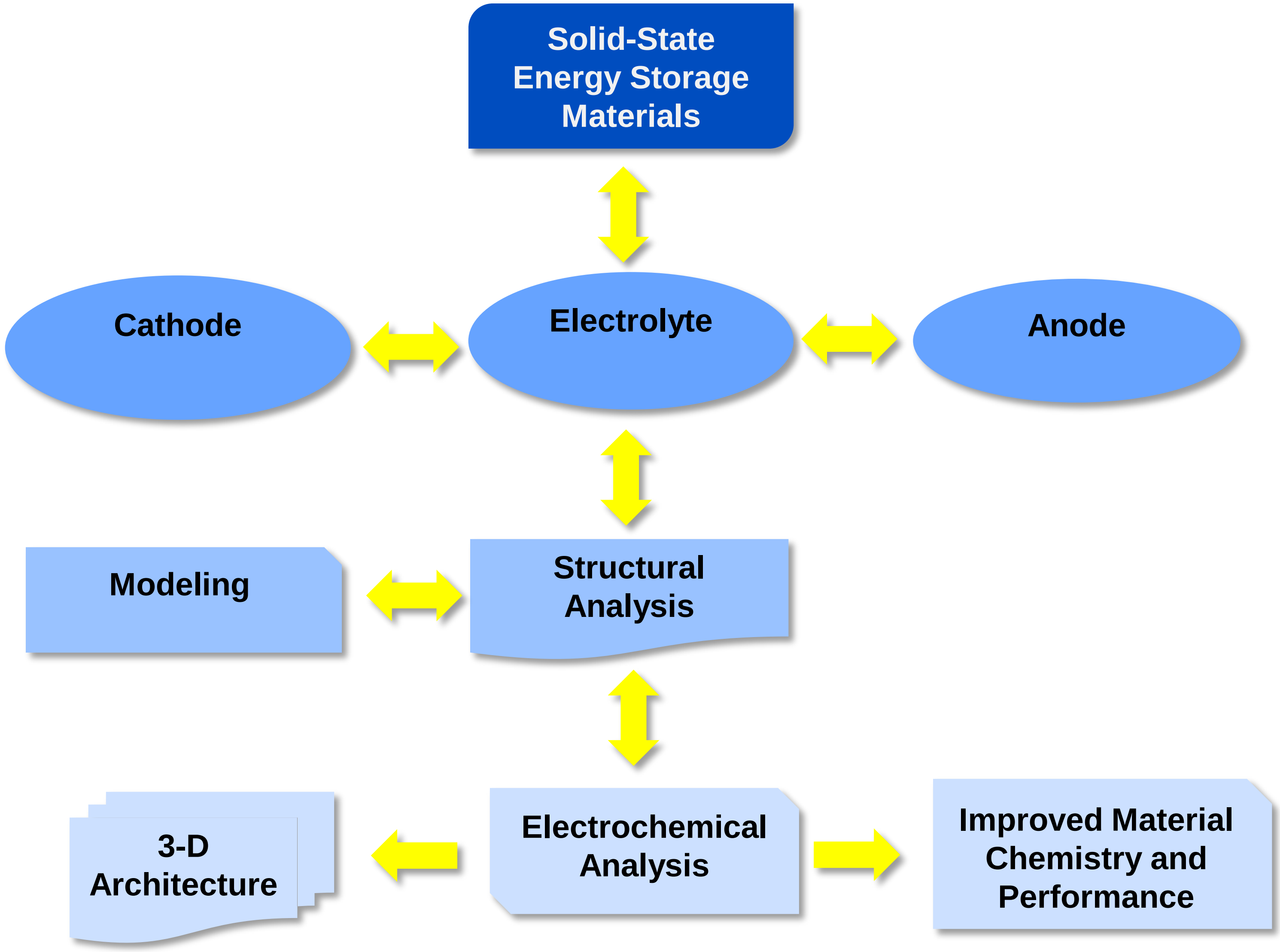
Conclusions

- **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_2FePO_4F 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

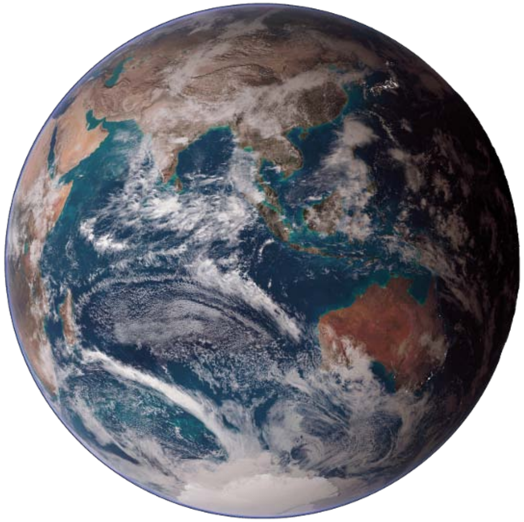


Acknowledgements

- **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 21st 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