Materials – The Technology Barrier to Advanced Batteries
The LiFePO4 Story: What’s Next?

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Types of Energy Storage

- **Pumped Hydro** (potential energy to electrical energy)
  - By far the largest by storage, gigawatts
  - Highly efficient, 70%
  - Limited new sites
- **Batteries** (chemical energy to electrical energy)
  - By far the most flexible and common
  - Portable and stationary
  - Milli Watts to Mega watts
  - Very fast switch on and off
  - Supercapacitors (surface charge rather than bulk chemical reaction)
- **Fly Wheels** (kinetic energy to electrical energy)
  - Very few, one near Albany for power smoothing
  - Hazardous – not likely for mobile applications

Types of Electric Vehicles

- **HEV - Hybrid Electric Vehicle** - no power from your home
  - Toyota Prius – 2 drive trains
  - BAE hybrid buses – all electric drive
- **Stop-start**
  - Engine stops when car stops – Mercedes
  - Most probable long-term solution – no range anxiety
- **PHEV - Plugin HEV** - charge them at night from your home off-peak
  - GM Volt - All-electric drive with Internal Combustion Engine to recharge, 40 miles
- **EV - All electric** - charge them when needed
  - Nissan Leaf – limited range – 80-100 mile range
  - Fleet vehicles – taxis and buses in China
Does BMW have the Answer?

- PHEV - Plugin HEV - charge them at night from your home off-peak $$$
  - Most probable long-term solution – no range anxiety
- EV - All electric - charge them when needed
  - BMW 3 – limited range – 80-100 mile range
  - Range-extender - $2500
    - Diesel engine + Generator

An Intercalation-based Lithium Battery Cell
1970s Technology

Structure Retention

xLi + TiS₂ gives LiₓTiS₂

Li in aluminum carbon (Sn or Si)

Redox Intercalation Cathodes for Lithium Ion Batteries
Dominate the Battery Storage Market

First Generation (1977):
Layered Sulphides.
TiS₂ - LiAl - Exxon
One Lithium to transition metal ratio - 480 Wh/kg (240 Ah/kg)

First Commercial Success (1991):
Layered Oxides.
LiCoO₂ - LiC₆ - SONY
0.5 Li to Co cycling - 480 Wh/kg

Today - 2013:
Mixed layered oxides and LiMn₂O₄ spinel
Li/NiMnCoAlO₂ – electronics, etc
LiFePO₄ & LiMnPO₄?
Power tools, HEV buses, utilities
NECCES goals:
• Develop a fundamental understanding of how key electrode reactions occur, and how they can be controlled.
• What are the intrinsic limitations to intercalation reactions?
  • Model compound – LiFePO_4
    • Major technical impediments to success (= should not work well)
    • But highest rate, large commercial applications

Characteristics of LiFePO_4 Electrochemistry
• Electrochemical behavior of ordered Olivine
  • Electronic insulator
    • Extrinsic conductor added, Fe_2P + C (>650°C)
    • Two-phase reaction: LiFePO_4 + FePO_4 – slow kinetics
    • Plateaus in cycling curves
  • One-dimensional tunnels = easily blocked
  • Inconsistent with actual behavior
    • Highest rates, 100% utilization, voltage gap

Phase Diagram of LiFePO_4-FePO_4
• High rate capability typical of single-phase reaction
  • Li_xFePO_4 for 0 ≤ x ≤ 1 (as in LixTiS_2)
  • Actual: Li_0.3FePO_4 phase to two phases to Li_1FePO_4 phase
    • (α and β 0-3%)
• High rate capability typical of single-phase reaction
  • Li$_x$FePO$_4$ for 0<x<1 (as in Li$_x$TiS$_2$)
  • Actual: Li$_{1-\beta}$FePO$_4$ phase to two phases to Li$_{1-\alpha}$FePO$_4$ (α and β 0-3%)
• Developed model
  • Metastable single phase (kinetic state)
  • Initial single phase expected to stay in reacting cell
  • Two-phase on relaxation (thermodynamic state)

NECCES developed model to explain behavior

How to Test the Single-Phase Model?
• Single phase model applicable to nano-size materials (< 100 nm)
  • Difficult to observe directly (all expts see equilibrium two-phases)
  • Can substitution of some of the Fe or Li give evidence? (adding defects)
    • Substituted aliovalent vanadium, V$^{3+}$, into the structure (theory says no)
      • 550°C single phase - solubility f(T)
        • 10% on Fe site
        • Charge compensation by Fe vacancies
        • 700°C + Li$_x$V$_3$(PO$_4$)$_2$ + Fe$_2$P
  • Micron-size materials
    • Probably nucleation/growth reaction mechanism
    • Not effective in batteries

Performance Enhanced by Vanadium Substitution, V$^{3+}$Fe
(Chem Mater. 23, 4733, 2011)
Vanadium Substitution increases Single-Phase Regions
(Chem. Mater. 25, 85, 2013)

• Vanadium has significant impact on phase diagram
  • Increases single phase regions to around 15% at each end
  • Lowers temperature for complete solid solution

Potential Gap reduced by Vanadium Substitution

Single-Phase Metastable Model predicts a potential gap

- Voltage gap
  - For pure LiFePO4
    - 23 mV
  - For LiFe0.85V0.1PO4
    - 8 mV
  - Thermodynamic solid solution
    - 0 mV

What’s Next: ED of LiFePO4 too low

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<th>Wh/L actual</th>
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What about other Phosphates?
Need 2e per Redox Center for > 700 Wh/kg

- VOPO₄ is one possibility, ....
- Pyrophosphates do not appear to be feasible for more than 1 Li (> 5 V)
- What other systems?
- Ceder study not encouraging.
  (Chemistry of Materials, 23, 3495, 2011)

VOPO₄ can be cycled over the two lithium despite significant reversible lattice changes

Zehua Chen

Conversion reactions: e.g. FeF₂
(Wang et al, JACS_133_18828_2011)

- **Goal**: Understand reaction mechanisms in conversion electrodes
  - What is the origin of large hysteresis?
  - Why are some systems reversible while others are not?
  - FeF₂: Interconnected Fe 2-3 nm particles allow reversibility
Still Opportunities to Improve Intercalation Batteries
Li-Ion will outperform Li-O₂ and Li-S volumetrically

- LiFePO₄ shows direction to go
  - Single-phase reaction mechanism – metastable or thermodynamic
  - 2 electron redox couples desirable in phosphates
    - E.g. VOPO₄ may achieve 350 Wh/kg

- Electrolyte Challenge – >4.8 V will allow 1 electron reaction in oxides
  - > 1 kWh/kg and 2.9 kWh/liter theoretical
  - > 350 Wh/kg and 1 kWh/liter actual cells
LiFePO₄ shows direction to go  
- Single-phase reaction mechanism – metastable or thermodynamic  
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Electrolyte Challenge – >4.8 V will allow 1 electron reaction in oxides  
- > 1 kWh/kg and 2.5 kWh/liter theoretical  
- > 350 Wh/kg and 1 kWh/liter actual cells  

Anode Challenge – make pure Li work  
- Will significantly improve today’s intercalation cells  
- Essential for beyond Li-ion  
  - Li₂O₂ and Li/S cannot attain close to 1 kWh/liter in full cells  
  - Li/S can exceed 350 Wh/kg, unlikely that Li₂O₂ will
Is Characterization and Theory up to the Challenge?

Russ Chianelli - Exxon
1976

[Image of graph and text]

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