Lithium Source For High Performance Li-ion Cells

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5-13-2013

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Project ID: # ES140
Overview

Timeline
• Start Date: July, 2010
• End Date: June, 2012
• Completed

Barriers
• Low Energy Density
• Cost
• Abuse tolerance limitations

Budget
• Phase II SBIR
• Total Project Funding
  • $1M
• 2012 Funding: $160,000

Partners
• Argonne National Laboratory
Relevance

- New cathode and anode electrodes are required to improve the energy density of Li-ion cells for transportation technologies.
- The cost of Li-ion systems for transportation applications needs to be reduced.
- The safety of Li-ion systems utilizing high energy density cells needs to be improved.
- In this work we are developing Li-ion cells utilizing promising high capacity cathode materials comprising low cost, abundant iron, vanadium or manganese oxides and a safe non-lithium anode.
- The work provides an alternative route to high-energy density cells consisting of Ni and Co based oxide by utilizing, instead, a pre-lithiation lithium iron oxide source that is implemented to load lithium in advanced anode systems.
Need for Lithium Source for Li-ion Cells

- Enable use of high capacity, low cost, charged cathodes without a lithium metal electrode.
  - Ex. Li$_5$FeO$_4$/LiV$_3$O$_8$ Cathode
  - Improved performance, safety, cost.

- Enable use of anode systems with large irreversible capacity losses (intermetallics).
  - Ex. LFO containing cathode vs. Silicon anode.
  - Improved energy density, cycle life, performance.

- Method to enable use of partially charged cathodes.
  - Ex. Li$_5$FeO$_4$/Recycled Cathode
  - Low cost, environmentally friendly.
Project Objectives

- Li-ion materials development and study.
  - Lithium Iron Oxide (lithium source)
    - Develop and scale best synthesis methods.
    - Study delithiation and degradation mechanisms of LiFeO materials.
    - Improve stability of LiFeO materials
    - Maximize utilization in Li-ion cells.
  - Lithium Vanadium Oxide
    - Improve cycle life and stability of LiV$_3$O$_8$ cathode.
- Develop three different Li-ion cell types incorporating LFO materials as a lithium source.
  - Develop optimized electrodes and cell designs
  - Build and evaluate cells based on optimized cell designs.
2012 Accomplishments

- LFO degradation process characterized by Raman Spectroscopy.
- Investigated new compositional approach to improving stability.
- Improved material utilization by additional 5%, achieving greater than 850 mAh/g
- Scaled synthesis to ~1kg batch sizes
- Full cell development and evaluation.
**Technical Approach**

**Li₅FeO₄ (LFO) as a pre-lithiation precursor**

- **Li₂O**: Li - tetrahedral sites
  O - face-centered-cubic sites

- **Defect antifluorite structures**
  - Li₅FeO₄: 5Li₂O•Fe₂O₃ or Li₁.₂₅Fe₀.₂₅O
    - 5 Li per Fe atom
  - Li₆MO₄ (M=Mn, Co): 3Li₂O•MO or Li₁.₅M₀.₂₅O
    - 6 Li per M atom

*Abundant Li in defect structure ideally provides good Li⁺ mobility*
Technical Approach

Voltage Curve First Charge for LFO based Cathodes

- LFO fully charged by ~ 4.2V vs. Lithium metal at double the energy density of other high capacity cathode materials
- Lithium released during first charge of LFO in cathode electrode can be used as partial or only source of Lithium for Li-ion cells.
Electrochemistry of Composite Cathode Containing Li$_5$FeO$_4$ and LiV$_3$O$_8$

Sacrificial Lithium Source Component:

First Charge LFO: \[2 \text{Li}_5\text{FeO}_4 \rightarrow 5 \text{Li}_2\text{O} + \text{Fe}_2\text{O}_3\] (first charge)
\[5 \text{Li}_2\text{O} \rightarrow 10 \text{Li}^+ + 10 \text{e}^- + 5/2\text{O}_2\]
(theoretical 867 mAh/g)

Reversible Active Component(s):

“Reversible” LFO: “Fe$_2$O$_3$” + Li → “LiFe$_2$O$_3$” (rock-salt)
(theoretical 160 mAh/g)

Charged Cathode LVO: LiV$_3$O$_8$ + 4 Li → Li$_5$V$_3$O$_8$ (rock-salt)
(theoretical 372 mAh/g)
Cell Designs Utilizing Mixed LFO/LVO Cathodes

Example designs and comparison of LFO/LVO composite cathodes based on different performance parameters compared to typical LFP cathode.

| Composite Cathode Designs: For Cell (Li$_5$FeO$_4$+LiV$_3$O$_8$) vs. Carbon Anode (with 5% Irreversible Loss) |
|---|---|---|---|---|---|---|---|---|---|
| Component Data | Composite Cathode Materials |
| Materials | C1, mAh/g | D1, mAh/g | Li$_5$FeO$_4$ wt% | LiV$_3$O$_8$ wt% | C1, mAh/g | D1, mAh/g | Irreversible Loss Anode, % | C2, mAh/g | D2, mAh/g | Average Voltage, V | Wh/kg Cathode | Electrode Density est. g/cc | Wh/L Cathode |
| Conventional | | | | | | | | | | | | |
| LiFePO$_4$ | 160 | 155 | 160 | 152 | 5.00% | 152 | 152 | 3.5 | 532 | 3.00 | 1596 |
| Theoretical (5 Li) | | | | | | | | | | | | |
| LiV$_3$O$_8$ | 370 | 370 |
| Li$_5$FeO$_4$ | 860 | 0 | 31.17% | 68.83% | 268 | 255 | 5.00% | 255 | 255 | 2.8 | 713 | 4.00 | 2852 |
| Phase I Best Materials | | | | | | | | | | | | |
| LiV$_3$O$_8$ | 310 | 325 |
| Li$_5$FeO$_4$ | 690 | 0 | 32.11% | 67.89% | 222 | 221 | 5.00% | 221 | 221 | 2.8 | 618 | 4.00 | 2471 |
| Phase II Best Materials | | | | | | | | | | | | |
| LiV$_3$O$_8$ | 310 | 325 |
| Li$_5$FeO$_4$ | 800 | 0 | 28.97% | 71.03% | 232 | 231 | 5.00% | 231 | 231 | 2.8 | 646 | 4.00 | 2585 |

- Potential to achieve higher energy density (Wh/kg and Wh/L) at lower voltage for increased stability.
- Phase II materials improvements have increased energy densities achievable at cell level.
Key Barriers to Address

- Maximize utilization of Lithium from LFO material.
- Impact of LFO on cathode performance including impedance and cycling.
- Stability of LFO to manufacturing conditions.
Maximize Utilization of Lithium on First Charge

Phase I investigated impact of synthesis method, charge profile, temperature and electrode formulation on utilization of LFO cathode. Maximum capacity achieved was ~ 690 mAh/g at lab scale.

Li₅FeₓCoₙ₋ₓO₄

Phase II:
- Focus on material composition, solid solutions with Li₆CoO₄, and doping of material to increase utilization.
- Developed two stage mixing and firing method for synthesis of LFO material reducing synthesis time from 72hrs to ~ 6 hrs and reducing synthesis cost.
LFO lattice has very low ($C_1$) symmetry. Hundreds of Raman-allowed bands are predicted.

- Bands appearing in all the spectra shown to the left that are most probably attributable to LFO are indicated by a (●).

- Li$_2$O is detected in varying amounts in several of the samples. It appears to be present as a separate second phase—detected in some places, not in others.

The XRD patterns and Raman spectra provide no definitive indication that any of the excess Li enters the Li$_5$FeO$_4$ lattice.
The mixed Fe/Co phases appear to be either an LFO/ LCO solid solution or LFCO crystallites with random amounts of Fe and Co (as if Fe(III) and Co(II) behave in a chemically indistinguishable manner, which is not likely).

Raman Spectra of Li(FeCo)O Materials with Different Fe/Co Ratios
First Charge Capacity of \( \text{Li}_5(\text{FeCo})\text{O}_4 \) Materials

- Impact of composition on first charge capacity.
- Cobalt content exceeding 50% led to greater instability and/or self discharge.
- Pure \( \text{Li}_6\text{CoO}_4 \) was found to be difficult to process into electrodes.
- Dopants can have significant impact on material utilization.
Optimization of Capacity Utilization for LFO Based Materials

- Optimized dopant compositions exceed 800 mAh/g on first charge
Stability of LFO in Various Environments

Controlled environment test:
- Gauge the rate of decomposition of LFO in two types of atmospheres.
- After five days we detected OH- (see right inset) and CO$_3^{2-}$ in the exposed dust shield sample but no OH- and no additional CO$_3^{2-}$ in the exposed dry room sample.

LFO after 5 days in a Plexiglass dust shield with open hand ports.

LFO after 5 days in Dry Room
When LFO is exposed to ambient laboratory air (presumably containing normal amounts of CO₂ and H₂O), it reacts and the light gray colored LFO turns rust red.

Raman spectroscopy shows clear evidence for formation of Li₂CO₃, as well as Fe-containing phases we have not clearly identified.
Increased Stability by Doping LFO Materials

- Doping element “Z” discovered that has “inactivating” effect on stoichiometric LFO material.
- Tuning of doping amount appears to greatly improve stability in air.
- Optimization could lead to higher capacity with stability.
Impedance of Decomposed LFO Cathode Material

- For some applications LFO may comprise as much as 40% of the mass in the cathode laminate electrode.
- As an inactive component it is important that it should not contribute to any increase in cathode impedance after the initial formation process.
- We have performed numerous experiments and have found that the charged LFO material has low impedance and no negative impact on the active material performance.
Other Work On Project

- Component Materials Development
  - LiV₃O₈ Rate Capability
  - Intermetallic Anodes
- Full Cell Design and Development
  - Charged Cathode/Carbon Anode Cells
  - Intermetallic Anode Cells
  - Recycled cathode cells.

![Graph: High Capacity LiV₃O₈](image1)

![Graph: Low Cost Intermetallic Anodes](image2)

![Graph: Full Pouch Cells w/ Intermetallic Anode](image3)
Future Work

- Further optimization of capacity and stability for LFO materials
- Transfer to production for evaluation of compatibility with existing manufacturing processes.
- Evaluation of manufacturing methods and impact on cell variation and performance.