Lithium Source For High Performance Li-ion Cells

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Project ID: # ES140

Overview

Timeline

- Start Date: July, 2010
- End Date: June, 2012
- 90% Completed

Barriers

- Low Energy Density
- Cost
- Abuse tolerance limitations

Budget

- Phase II SBIR
- Total Project Funding
    - $1M
- 2011 Funding: $460,000
- 2012 Funding: $220,000

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 and 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_5FeO_4/LiV_3O_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_5FeO_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_3O_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.

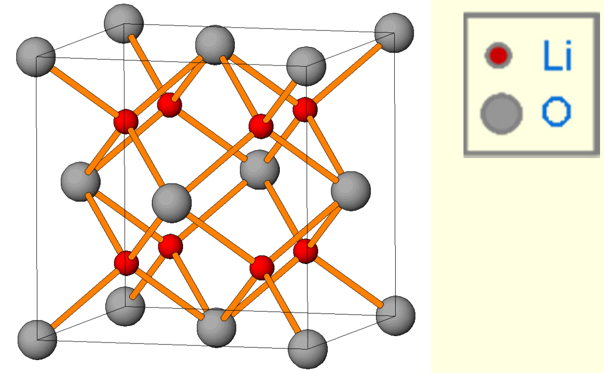
2011 Accomplishments

- Low cost synthesis method developed and scaled for LFO materials.
- Multiple synthesis methods evaluated for LVO materials.
- LFO degradation process characterized by Raman Spectroscopy.
- Improved stability of LFO materials to handling in manufacturing environment.
- Improved material utilization by 20%, achieving greater than 800 mAh/g
- Initiated cell development and evaluation.

Technical Approach

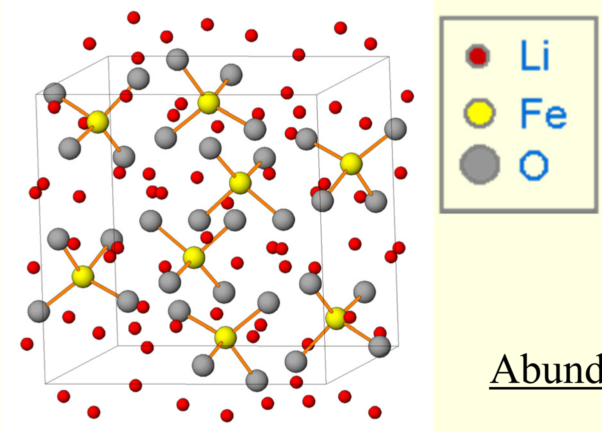
Li_5FeO_4 (LFO) as a pre-lithiation precursor

Li_2O (Fm-3m)
(*a*=4.614 Å)



Li_2O: Li - tetrahedral sites
O - face-centered-cubic sites

Li_5FeO_4 (Pbca)
(*a*=9.218 Å; *b*=9.213 Å; *c*=9.159 Å)



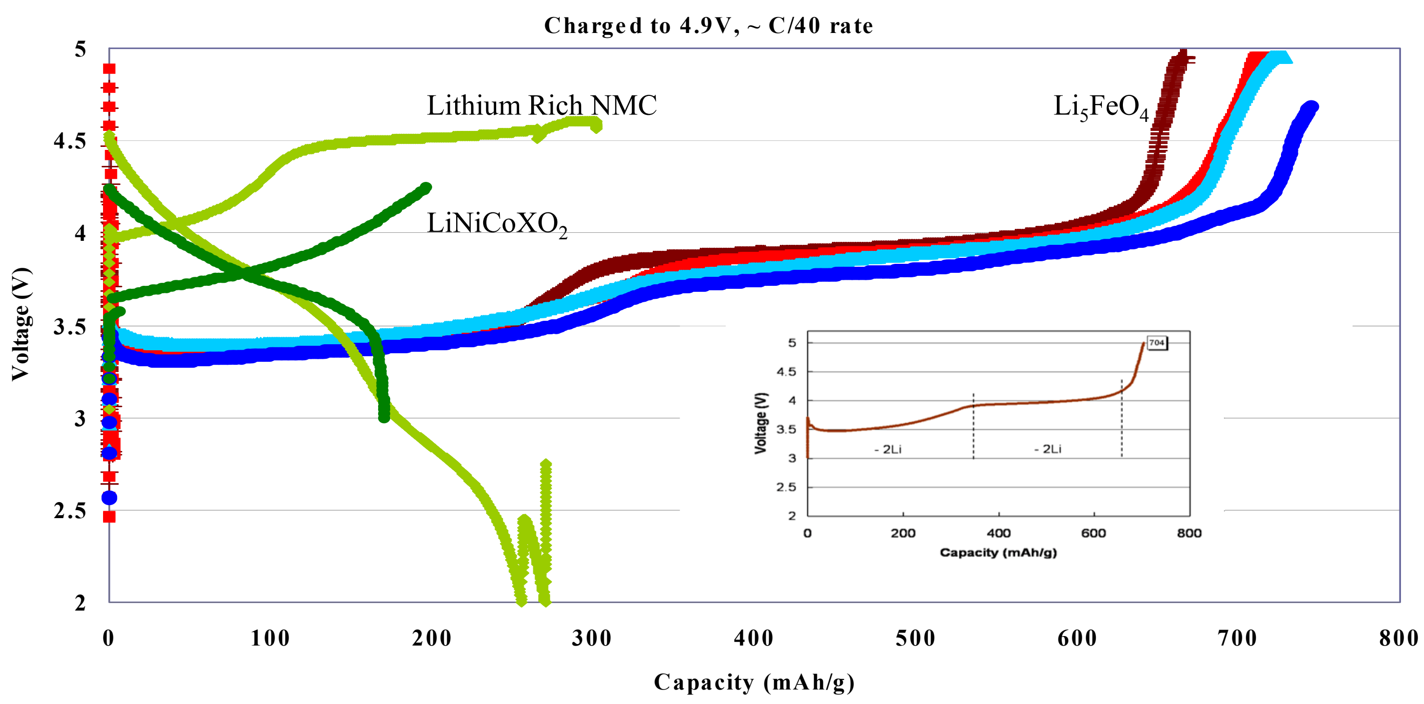
Defect antifluorite structures

- Li_5FeO_4: $5Li_2O \bullet Fe_2O_3$ or $Li_{1.25}Fe_{0.25}\square_{0.5}O$
  5 Li per Fe atom
- Li_6MO_4 (M=Mn, Co):
  $3Li_2O \bullet MO$ or $Li_{1.5}M_{0.25}\square_{0.25}O$
  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 mateirals
- 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_5FeO_4 and LiV_3O_8

Sacrificial Lithium Source Component:

First Charge LFO: $2\ Li_5FeO_4 \rightarrow 5\ Li_2O + Fe_2O_3$ **(first charge)**

$5\ Li_2O \rightarrow 10\ Li^+ + 10\ e^- + 5/2O_2$

(theoretical 867 mAh/g)

Reversible Active Component(s):

"Reversible" LFO: "Fe_2O_3" + Li → "$LiFe_2O_3$" **(rock-salt)**

(theoretical 160 mAh/g)

Charged Cathode LVO: $LiV_3O_8 + 4\ Li \rightarrow Li_5V_3O_8$ **(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.

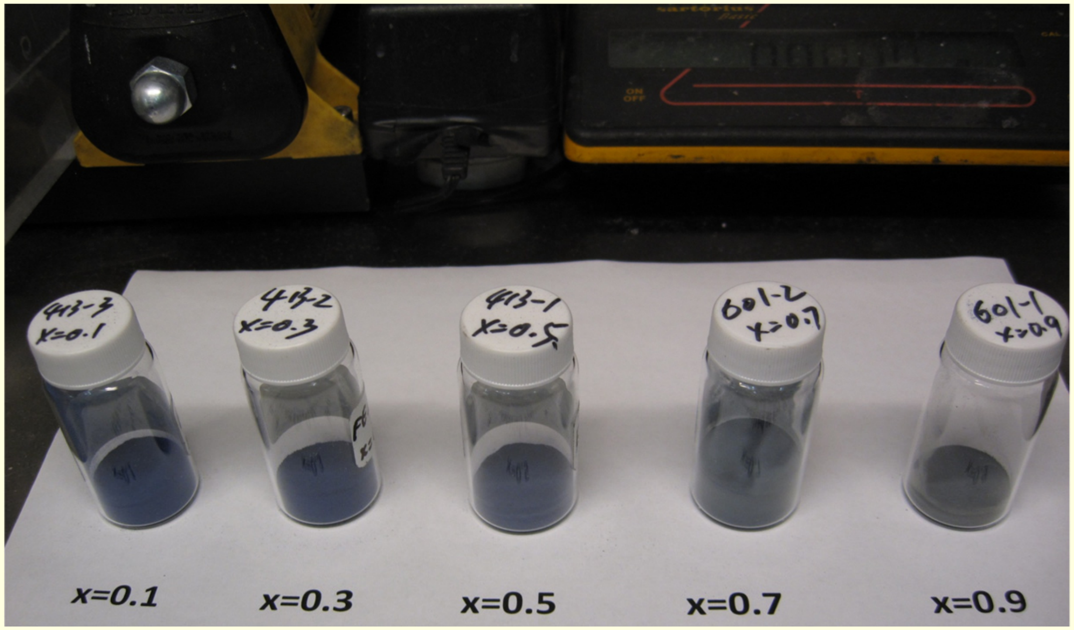
Composite Cathode Designs: For Cell (Li5FeO4+LiV3O8) vs. Carbon Anode (with 5% Irreversible Loss)													
Component Data			Composite Cathode Materials										
Materials	C1, mAh/g	D1, mAh/g	Li5FeO4 wt%	LiV3O8 wt%	C1, mAh/g	D1, mAh/g	Irreversible Loss Anode, %	C2, mAh/g	D2, mAh/g	Average Voltage, V	Wh/kg Cathode	Electrode Density est. g/cc	Wh/L Cathode
Conventional													
LiFePO4	160	155			160	152	5.00%	**152**	**152**	3.5	**532**	3.00	**1596**
Theoretical (5 Li)													
LiV3O8	370	370											
Li5FeO4	860	0	31.17%	68.83%	268	255	5.00%	**255**	**255**	2.8	**713**	4.00	**2852**
Phase I Best Materials													
LiV3O8	310	325											
Li5FeO4	690	0	32.11%	67.89%	222	221	5.00%	**221**	**221**	2.8	**618**	4.00	**2471**
Phase II Best Materials													
LiV3O8	310	325											
Li5FeO4	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



$Li_5Fe_xCo_{(1-x)}O_4$

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.

Phase II:

- Focus on material composition, solid solutions with Li_6CoO_4, 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.

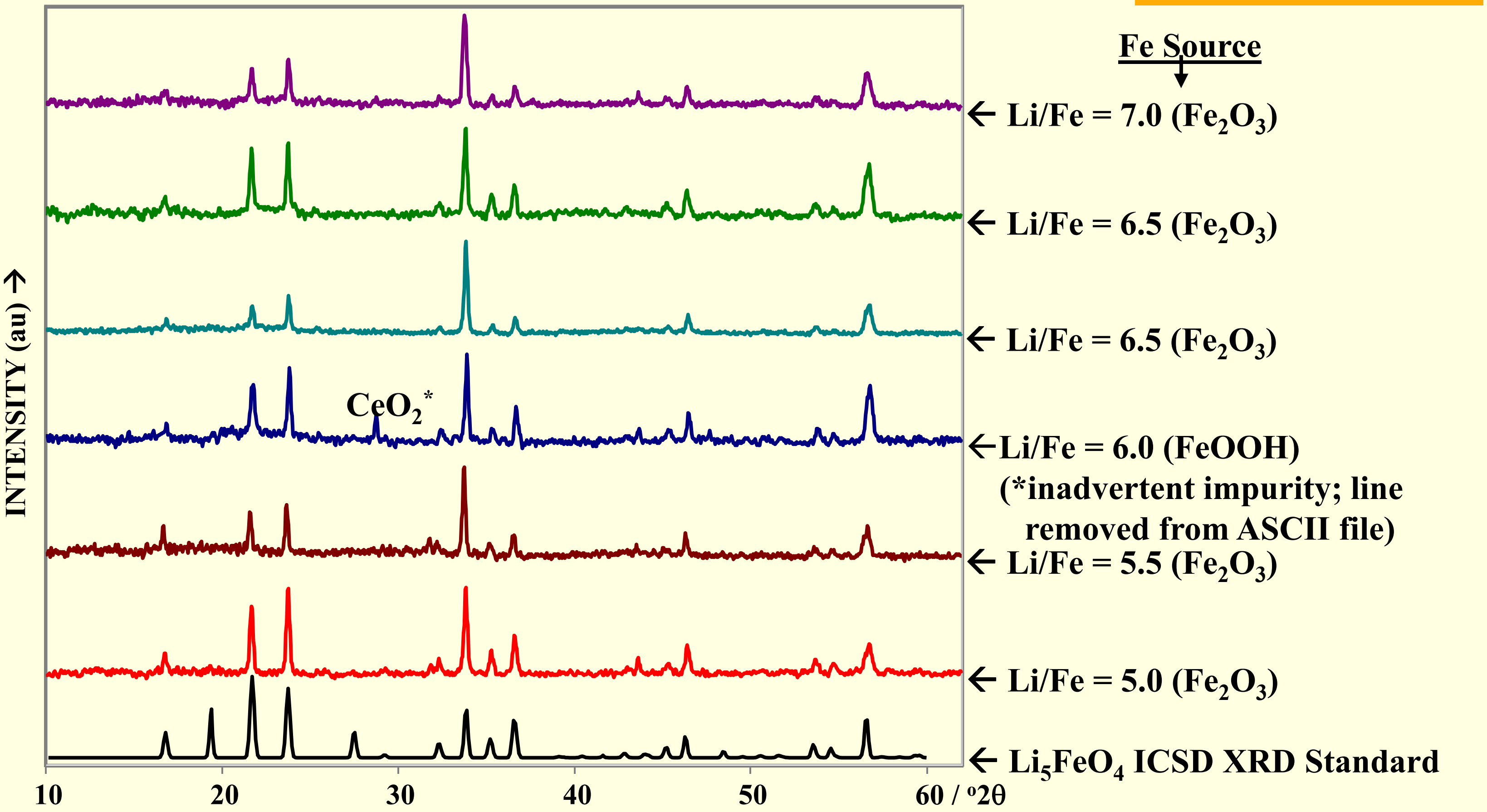
Impact of

Impact of Li/Fe Ratio on $Li_{5+x}FeO_4$ Material

Sample #	Type	Reactants	Notes:	Li/Fe Ratio*
1-25-1	LFO/Li=5.0	Li2CO3+Fe2O3	800^{o}C / ca. 140 hr / Ar	---
1-25-2	LiFeO2	Li2CO3+Fe2O3	800^{o}C / ca. 140 hr / Ar	---
1-26-1	LFO/Li=5.0	LiOH-H2O+Fe2O3	800^{o}C / ca. 140 hr / Ar	5.0
1-26-2	LFO/Li=5.5	LiOH-H2O+Fe2O3	800^{o}C / ca. 140 hr / Ar	5.6
1-28-1	LFO/Li=5.0	LiOH-H2O+Fe2O3	Weighed, not sintered	---
1-28-2	LFO/Li=5.5	LiOH-H2O+Fe2O3	Weighed, not sintered	---
1-39-1	LFO/Li=6.5	LiOH-H2O+Fe2O3	800^{o}C / ca. 25 hr / Ar	6.6
1-40-1	LFO/Li=6.5	LiOH-H2O+Fe2O3	875^{o}C / ca. 25 hr / Ar	6.5
1-42-1	LFO/Li=7.0	LiOH-H2O+Fe2O3	800^{o}C / ca. 25 hr / Ar	7.3
1-44-2	LFO/Li=6.0	LiOH-H2O+FeOOH	850^{o}C / ca. 25 hr / Ar	5.7

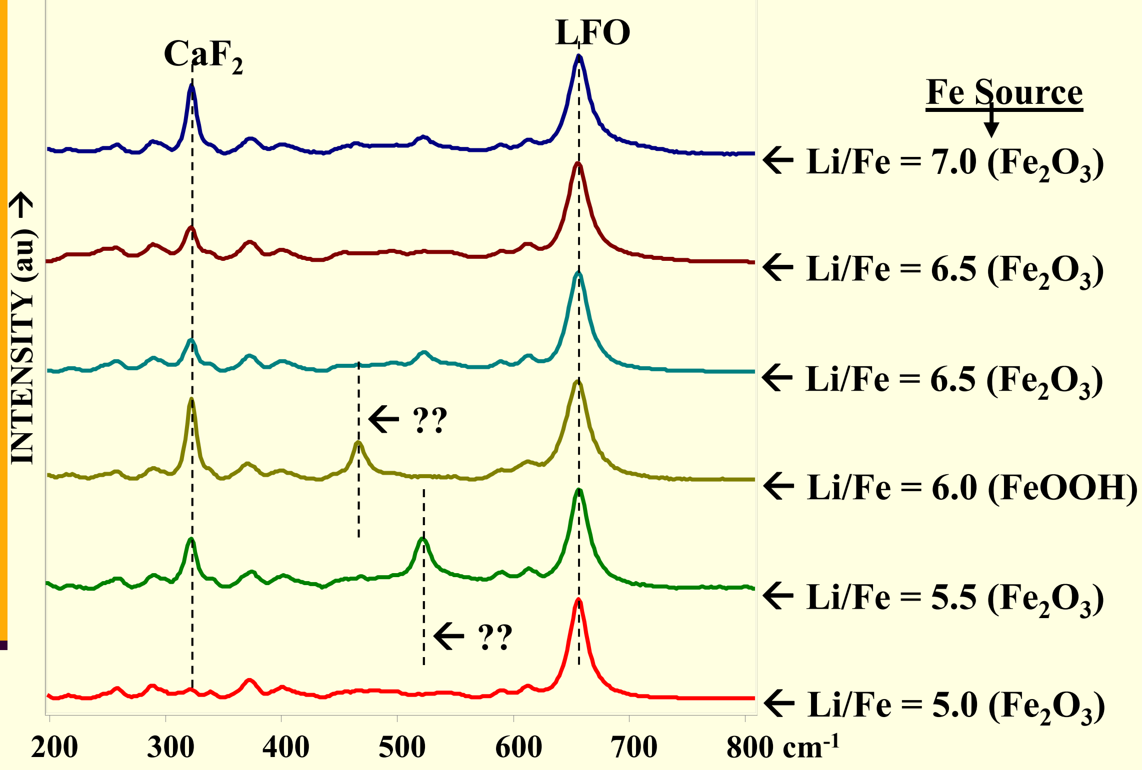
*Li/Fe ratio determined by ICP/OES analysis.

X-Ray Diffraction of LFO Materials with Different Li/Fe Ratios



Key observations: All prominent diffraction lines (Cu-kα) can be indexed to LFO. There are no discernable peak shifts or intensity variations vs. Li/Fe ratio.

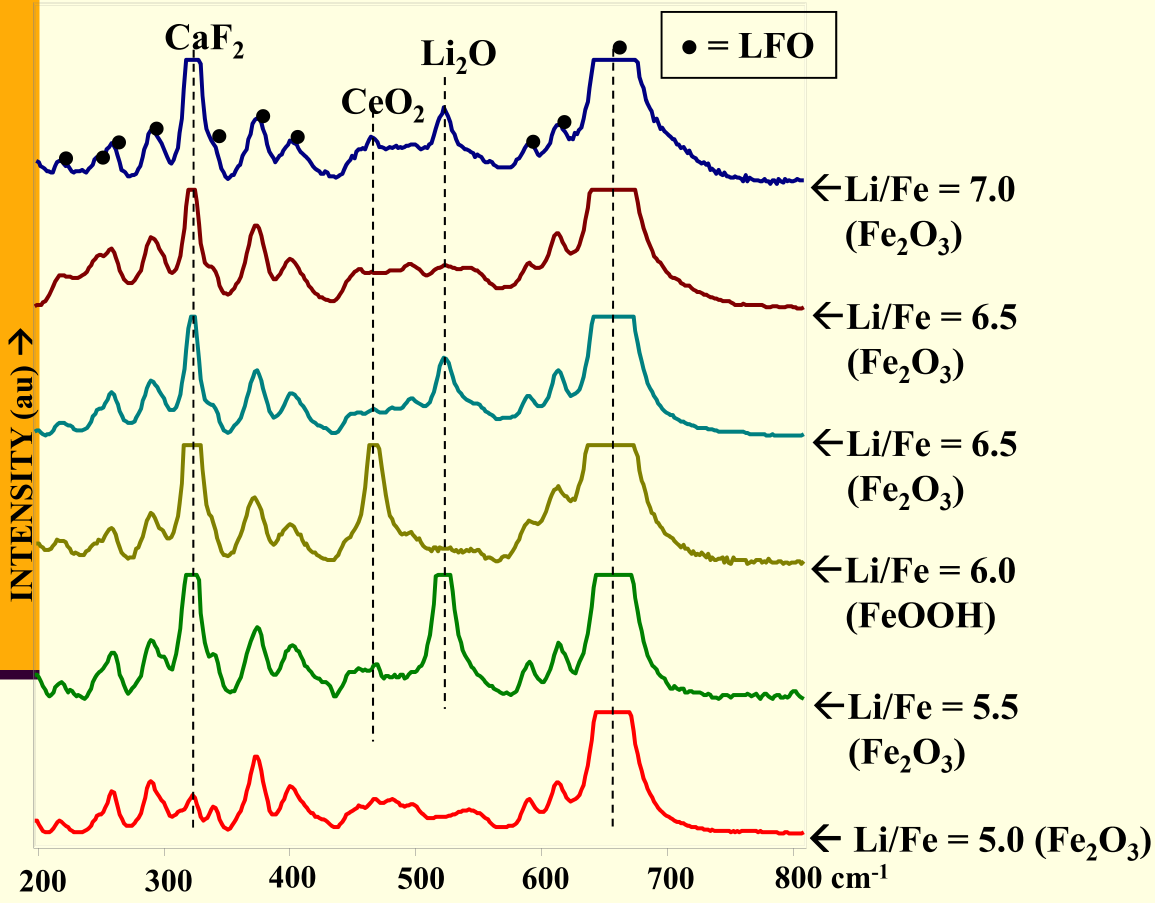
Raman Spectra of LFO Materials with Different Li/Fe Ratios



- A signature Raman band for LFO is found at 656 cm^{-1}.
- The frequency of this band appears to be invariant with respect to Li/Fe ratio.

Spectra recorded using 514 nm excitation at the ANL/CNM. The samples were contained in a sealed cell with a CaF$_2$ window.

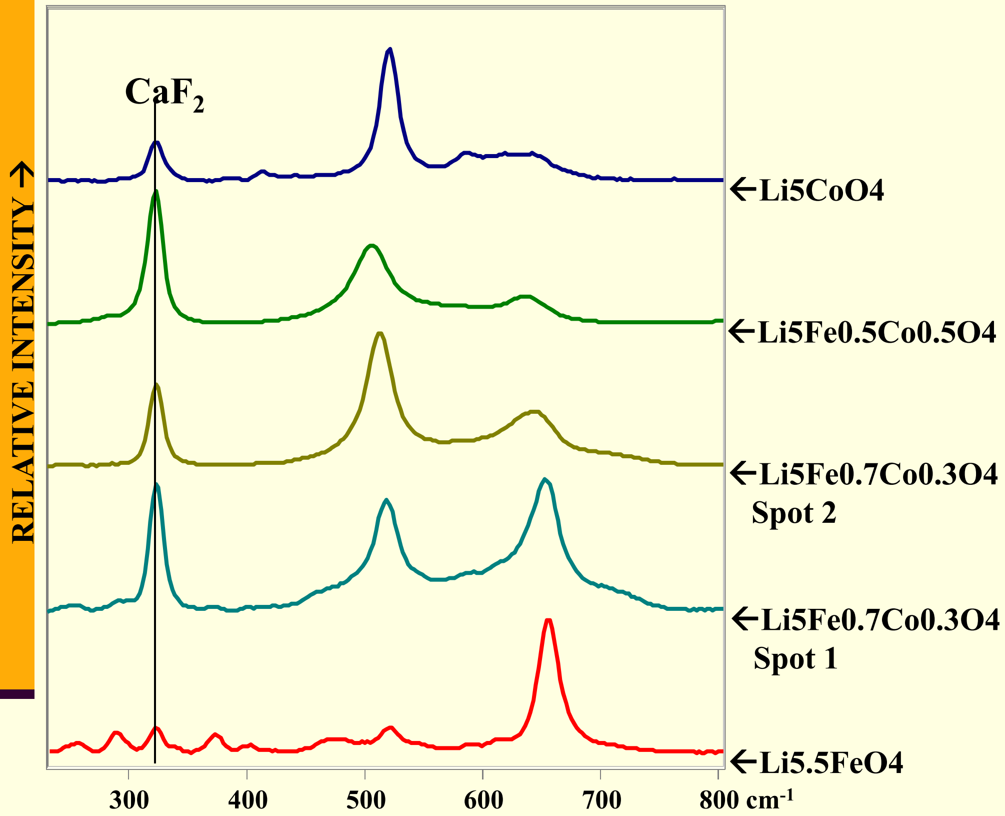
Raman Spectra of LFO Materials with Different Li/Fe Ratios



- ➢ 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_2O 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.

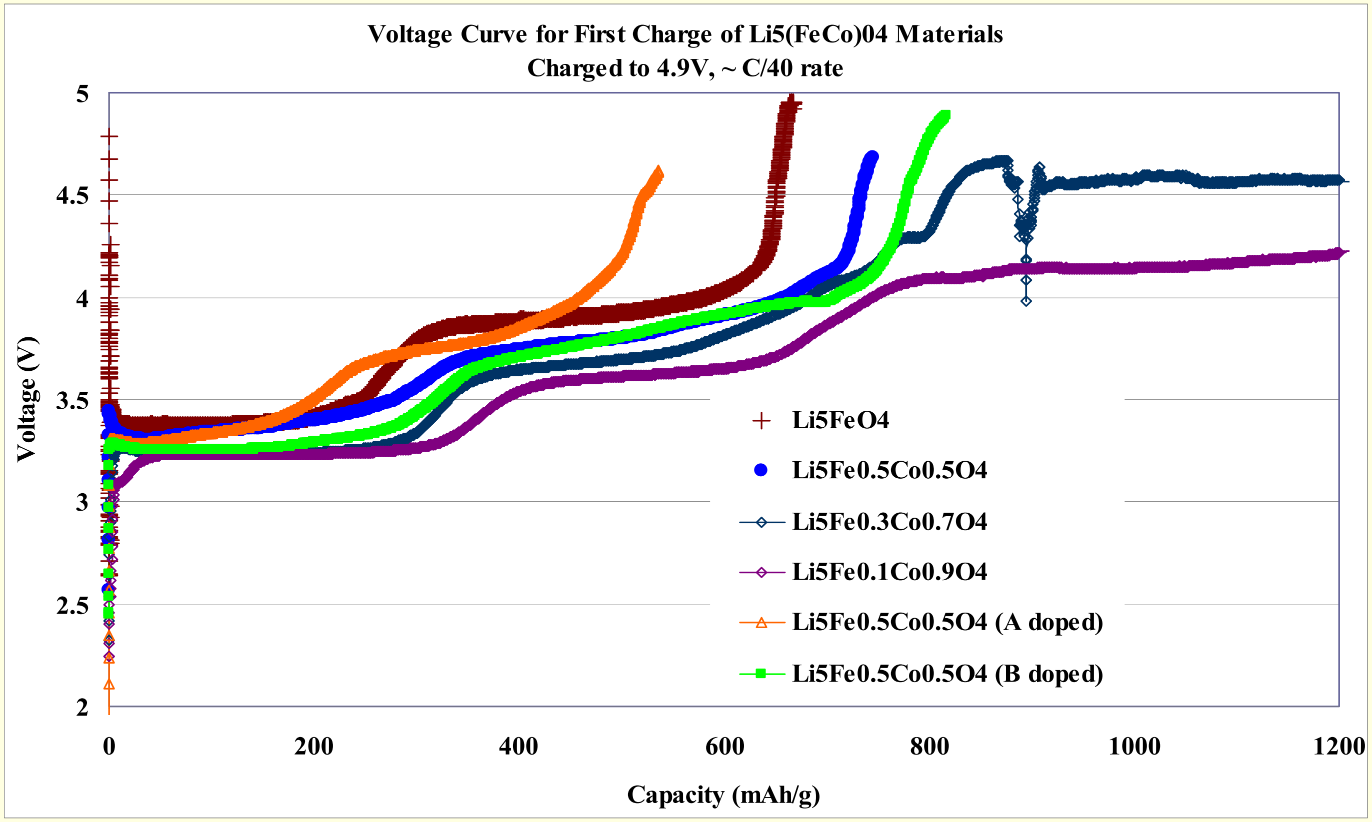
The XRD patterns and Raman spectra provide no definitive indication that any of the excess Li enters the Li_5FeO_4 lattice.

Raman Spectra of Li(FeCo)O Materials with Different Fe/Co Ratios



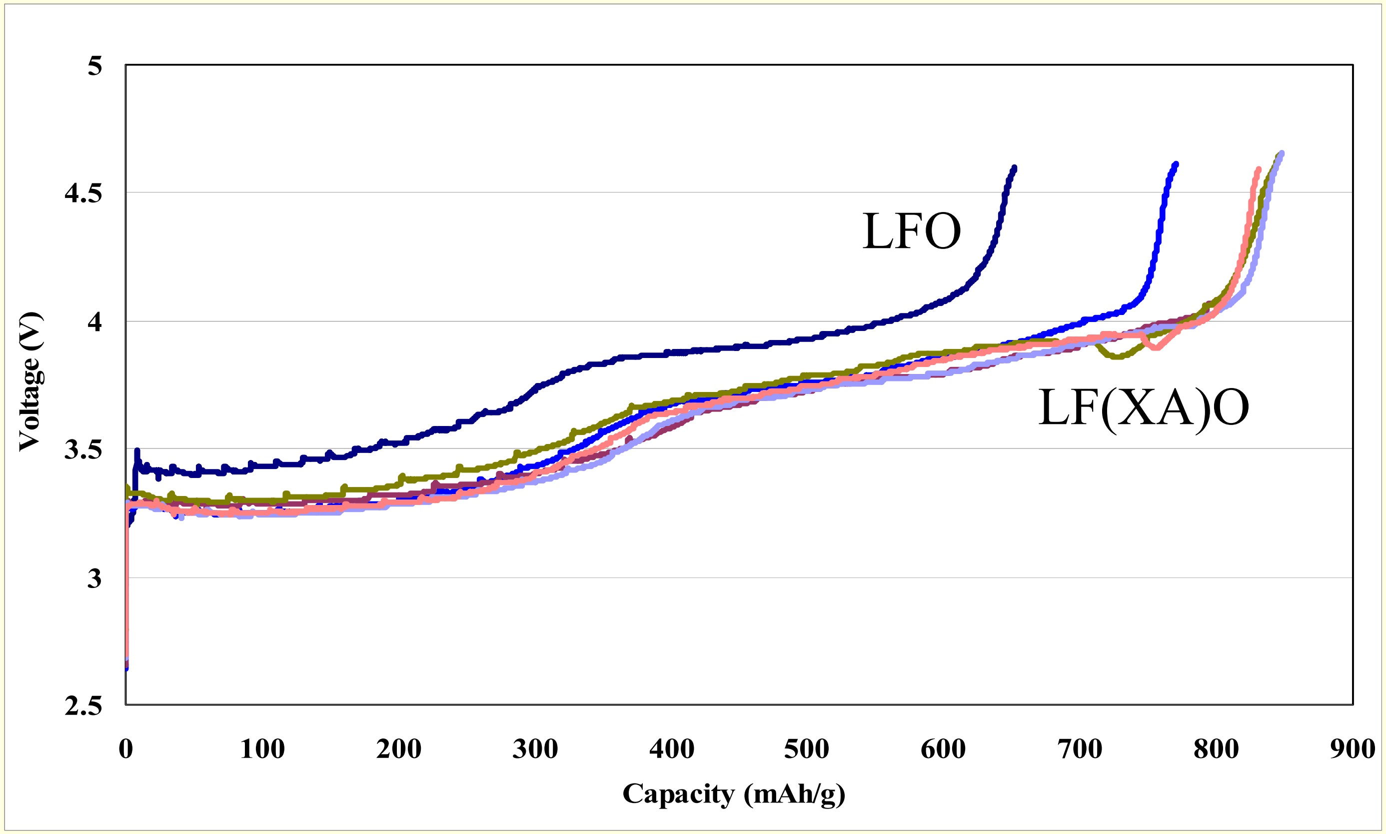
The mixed Fe/Co phases appear to be either an LFO/ LCO solid solution or LFCO crystallites with random amounts of Fe and Co (as if Fe(III) and Co(II) behave in a chemically indistinguishable manner, which is not likely).

First Charge Capacity of $Li_5(FeCo)O_4$ Materials



- Impact of composition on first charge capacity.
- Cobalt content exceeding 50% led to greater instability and/or self discharge
- Pure Li_6CoO_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

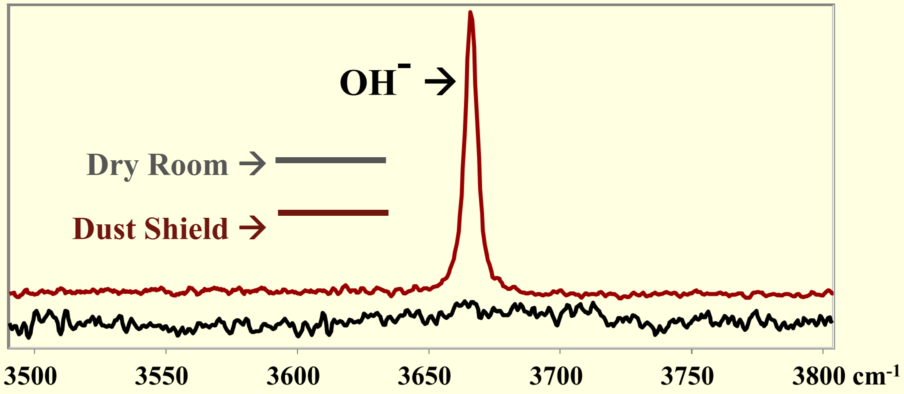


- Optimized dopant compositions exceed 800 mAh/g on first charge

Stability of LFO in Various Environments

<u>Controlled environment test:</u>

- 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.



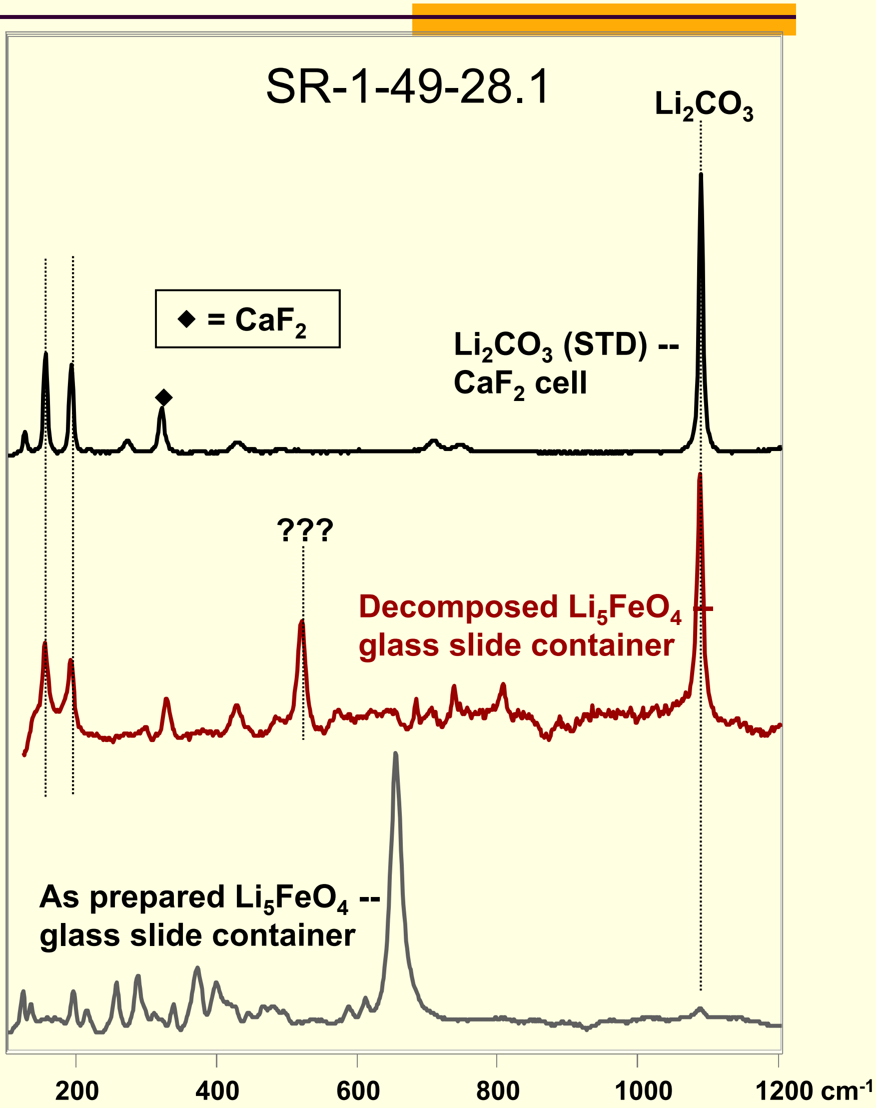
LFO after 5 days in a Plexiglass dust shield with open hand ports.

LFO after 5 days in Dry Room

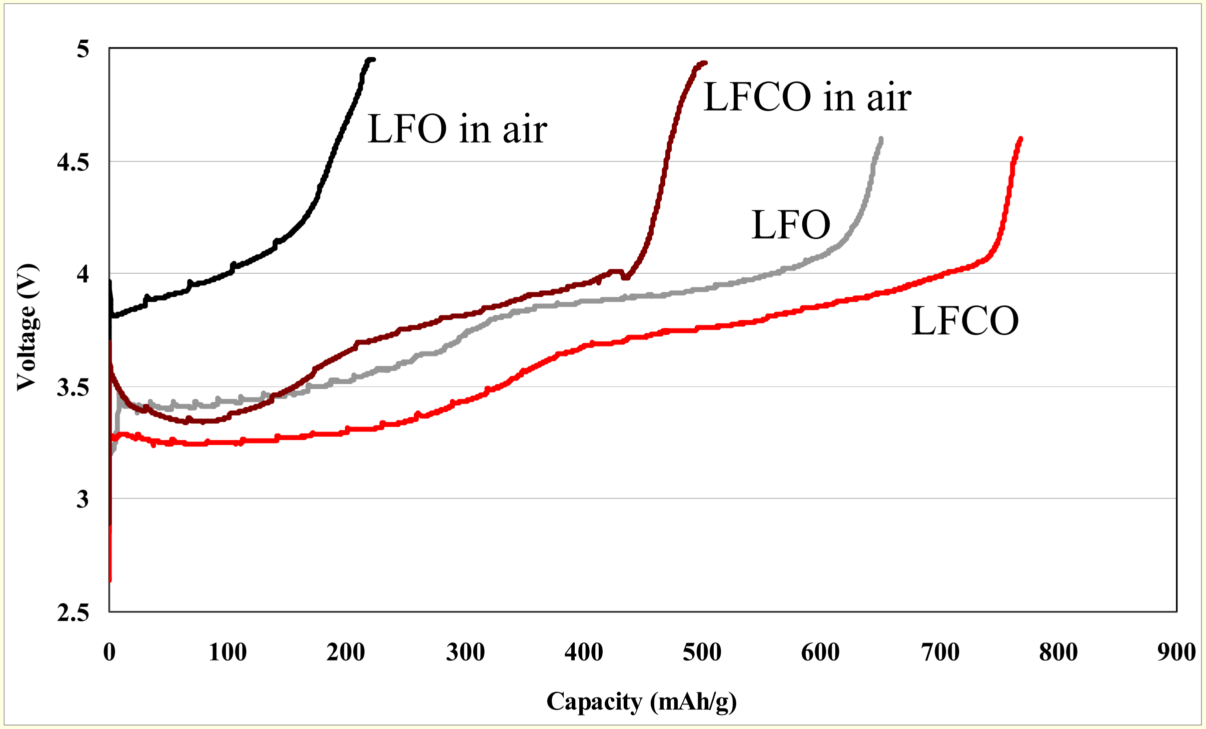
LFO Decomposition Products

When LFO is exposed to ambient laboratory air (presumably containing normal amounts of CO_2 and H_2O), it reacts and the light gray colored LFO turns rust red.

Raman spectroscopy shows clear evidence for formation of Li_2CO_3, as well as Fe-containing phases we have not clearly identified.

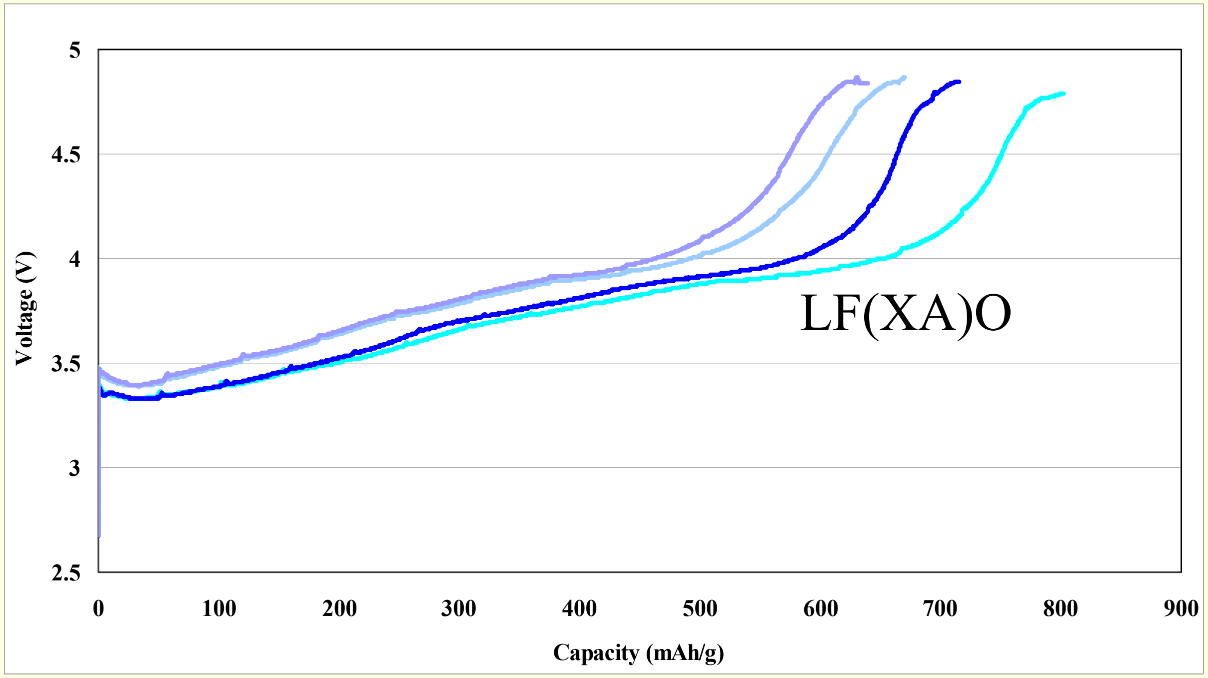


LFO Capacity vs. Atmospheric Exposure Time



- LFO/LFCO materials are stable in dry air or to typical dry room environments and to conventional Li-ion battery slurry solvents which do not impact their capacity.
- LFO/LFCO decomposition and capacity loss from long term moist air exposure affects material capacity. Electrodes were left in air for up to 24 hours before testing.
- Improvement in stability to air will lower cost of material handling/cell manufacture

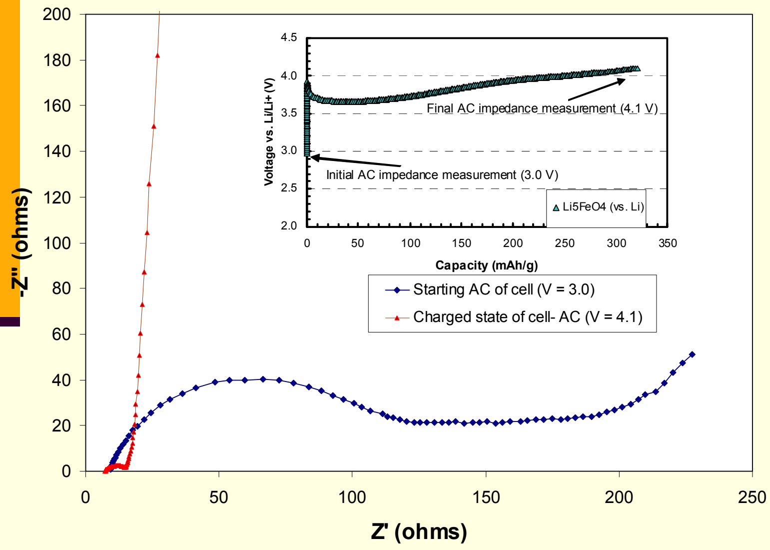
Increased Stability by Doping LFO Materials

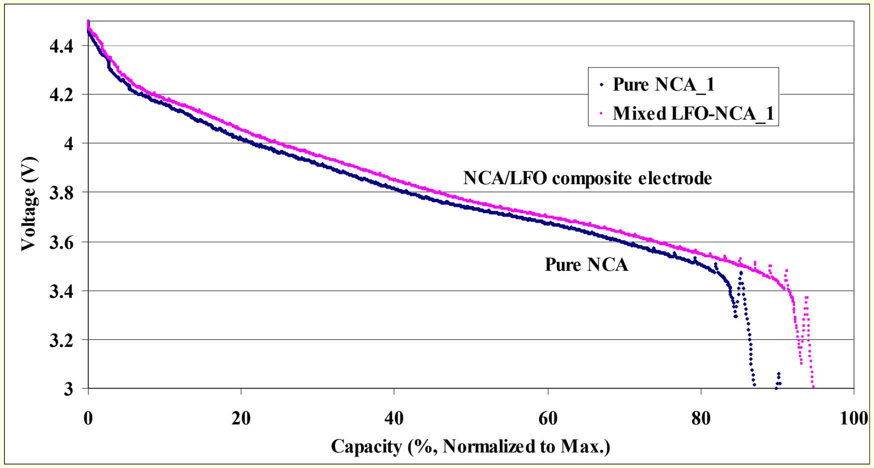


- Doping of LFO materials appears to be an approach that can significantly improve the stability of these materials to moist air over periods of 24 hours.
- Optimization of the capacity and stability is being performed to create materials that are compatible with existing manufacturing methods.

Impedance of Decomposed LFO Cathode Material

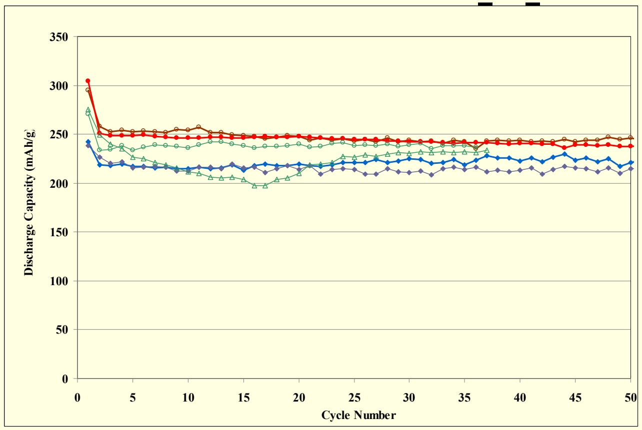
- For some applications LFO may comprise as much as 40% of the mass in the cathode laminate electrode.
- As an inactive component it is important that it should not contribute to any increase in cathode impedance after the initial formation process.
- We have performed numerous experiments and have found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



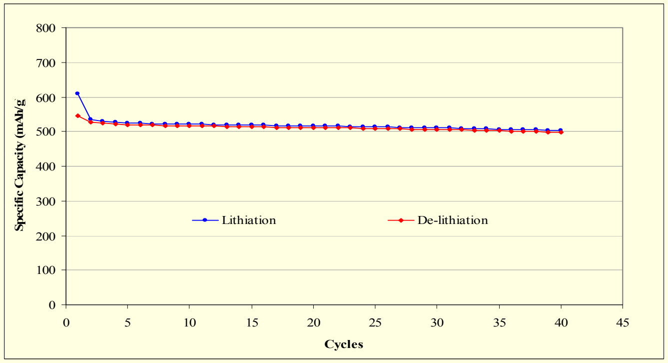


Other Work On Project

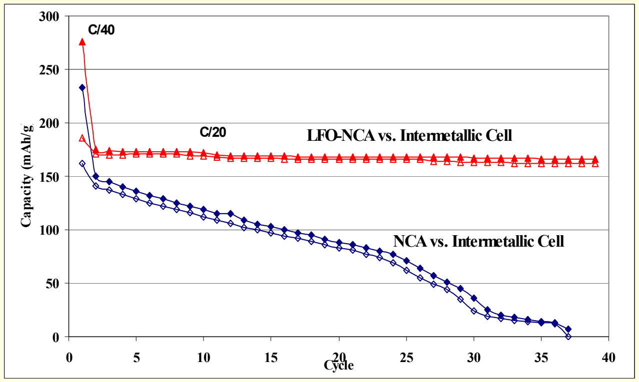
- **Component Materials Development**
  - LiV_3O_8 Rate Capability
  - Intermetallic Anodes
- **Full Cell Design and Development**
  - Charged Cathode/Carbon Anode Cells
  - Intermetallic Anode Cells
  - Recycled cathode cells.



High Capacity LiV_3O_8



Low Cost Intermetallic Anodes



Full Pouch Cells

Future Work

- Further optimization of capacity and stability for LFO materials
- Focus on full cell demonstration for charged cathodes and intermetallic anodes.
- Evaluation of manufacturing methods and impact on cell variation and performance.