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Design and Evaluation of Novel High Capacity Cathode Materials

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Annual Merit Review

DOE Vehicle Technologies Program

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Vehicle Technologies Program

Overview

Timeline

- Start date: FY08
- End date: On-going
- Percent complete:

  On-going

Budget

- Total project funding
  - 100% DOE
- FY08: $400K
- FY09: $300K
- FY10: $400K

Barriers

- Barriers addressed:

  - Low energy

  - Cost

  - Abuse tolerance

Partners

- Co-investigators (Argonne):

  - S.-H. Kang

  - M. Balasubramanian

    (Advanced Photon Source (APS))

  - S. Pol (APS)

  - J. Vaughey

Objectives

- Design and develop novel high capacity cathodes to meet the USABC's energy requirement for a 40-mile range PHEV
  - *Improve the structural and morphological design, composition and performance of low cost Mn-based and Fe-based cathodes*

Milestones (FY08-09)

- Synthesize, discover and evaluate novel high capacity cathodes – *on going*

- Initial technical target: >200 mAh/g for 100 cycles between 4.5 and 2.0 V without compromising power

- Evaluate promising cathode materials in Li-ion cell configuration against graphite, metal or intermetallic anodes
  – *on going*

- Determine structural and electrochemical properties, e.g., by *in situ* techniques at the Advanced Photon Source at Argonne
  – *on going*

Approach

- Our approach is exploratory with a longer term outlook. The primary goal is to propose and evaluate new practical avenues to advance cathode materials rather than provide optimized solutions or performance.

- Basic concepts: 1) Use high potential (>4 V) electrochemical reactions to design new high capacity cathode materials, 2) use surplus lithium in precursor electrode structures to load carbon (graphite), metal- or metal-alloy anode substrates, and 3) include a charged component in the cathode to accommodate the surplus lithium during discharge.

- Specifically, extend the concept of using Li_2MnO_3 ($Li_2O \bullet MnO_2$) or structurally integrated $xLi_2MnO_3 \bullet (1-x)LiMO_2$ precursors (BATT Review 2008) as a source of surplus lithium to antifluorite Li_5FeO_4 ($5Li_2O \bullet Fe_2O_3$) and Li_6MO_4 ($3Li_2O \bullet MO$, M=Mn, Ni, Co) structures.

- Alternative approach to using stabilized lithium metal powder (SLMP^{TM}, FMC Corporation) for lithiating anode materials.

Recap FY08: Electrochemical Activation of Li_2MnO_3

$$Li_2MnO_3\ (Li_2O{\bullet}MnO_2) \xrightarrow{4.5\text{-}4.8\ V} MnO_2 + 2\ Li + 1/2O_2\ (459\ mAh/g)$$

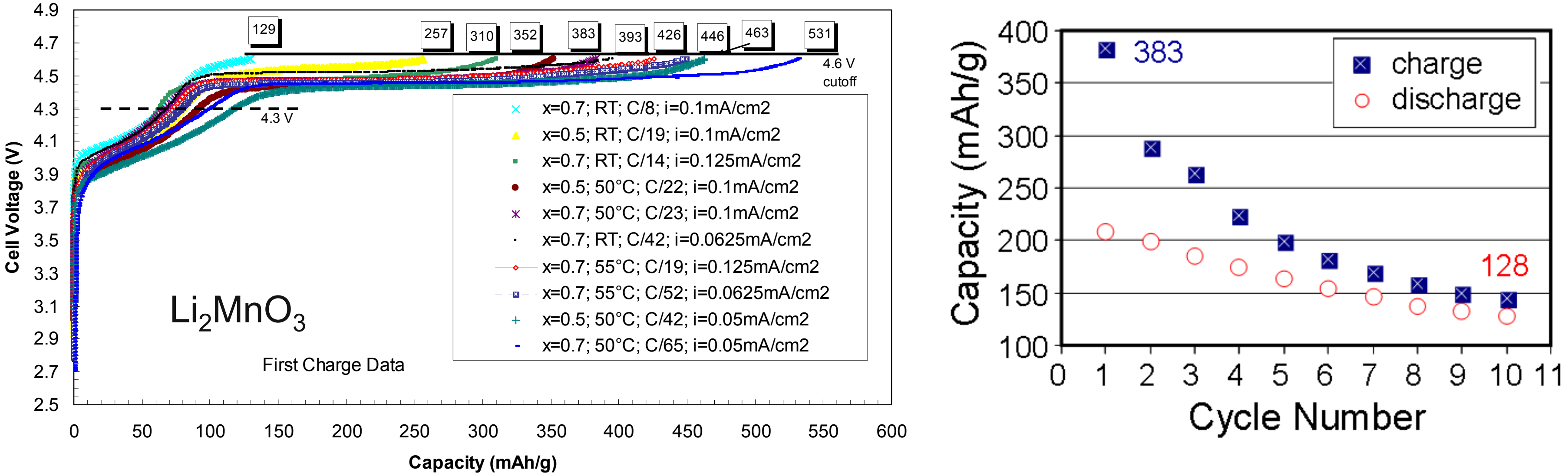
- Net loss is Li_2O
- Two Li^+ ions removed during electrochemical activation (charge)
- One Li^+ ion reinserted into residual MnO_2 component:

$$Li + MnO_2 \rightarrow LiMnO_2\ \ (229\ mAh/g,\ mass\ of\ parent\ electrode)$$

- Use surplus Li to load anode: C_6, metals or even bare substrate (Li metal)
- Complementary to lithium metal project (Vaughey and Dees)
- Use Li_2MnO_3 (or $xLi_2MnO_3{\bullet}(1-x)LiMO_2$, M=Mn, Ni, Co) precursor in combination with high capacity charged cathodes, particularly where two-electron transfer reactions are possible, e.g., V_2O_5 (442 mAh/g), $Li_{1.2}V_3O_8$ (372 mAh/g)
- $Li_{1.2}V_3O_8$ preferred 'test' cathode - greater structural stability than V_2O_5

Li_2MnO_3 Precursor Electrodes

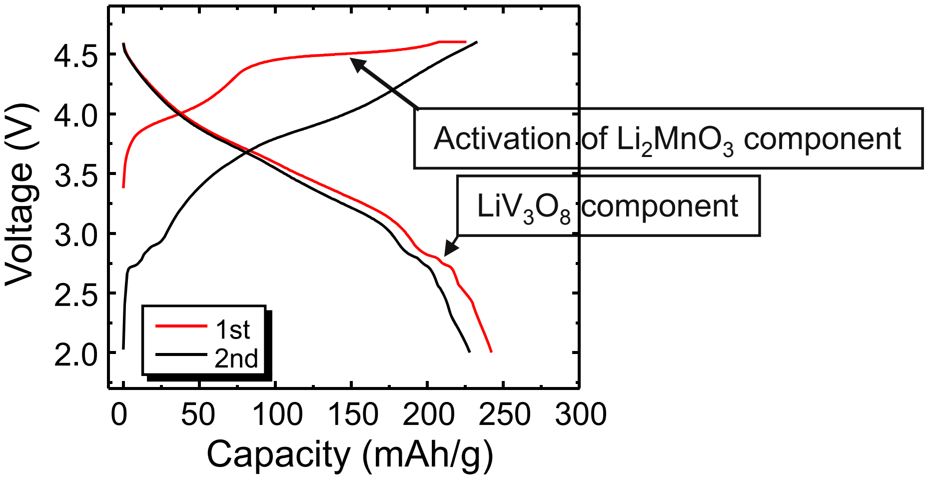
Li/Li_2MnO_3 half-cell

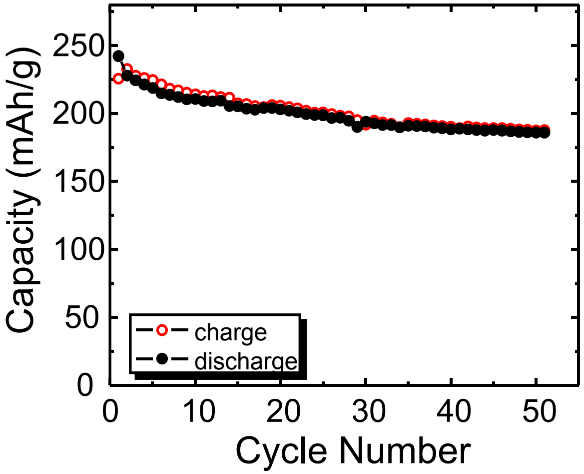


- Electrochemical activation of Li_2MnO_3 by Li_2O removal at 4.5-5.0 V is a function of temperature and current rate
- Essentially all the Li can be removed at 50 °C at slow rates (C/42)
- MnO_2 component from activated Li_2MnO_3 does not operate effectively as a rechargeable electrode

$0.5Li_2MnO_3 \cdot 0.5LiMO_2$ Precursors

$(M=Ni_{0.44}Co_{0.25}Mn_{0.31})$



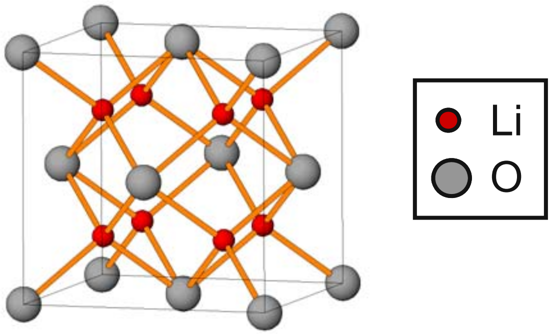


- $0.5Li_2MnO_3 \cdot 0.5LiMO_2$ precursors provide more stable electrodes
- $Li_{1.2}V_3O_8$ used as charged cathode: provides end-of-discharge indicator
- ~200 mAh/g (average) obtained for 50 cycles, 4.6 - 2.0 V, 0.05 mA/cm^2
- Similar data for V_2O_5 (Manthiram et al., Electrochem Comm. 2008)
- Half cell data: Surplus Li at anode ⇒ need validation in full cells
- FY09: Emphasis placed on Li_5FeO_4: higher Li_2O content

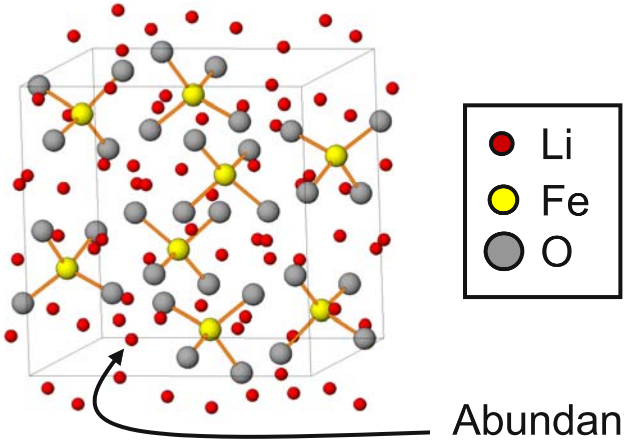
Alternative High-Li_2O Content Precursors

Antifluorite structures

Li_2O (Fm-3m)
(*a*=4.614 Å)



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



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

Defect 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

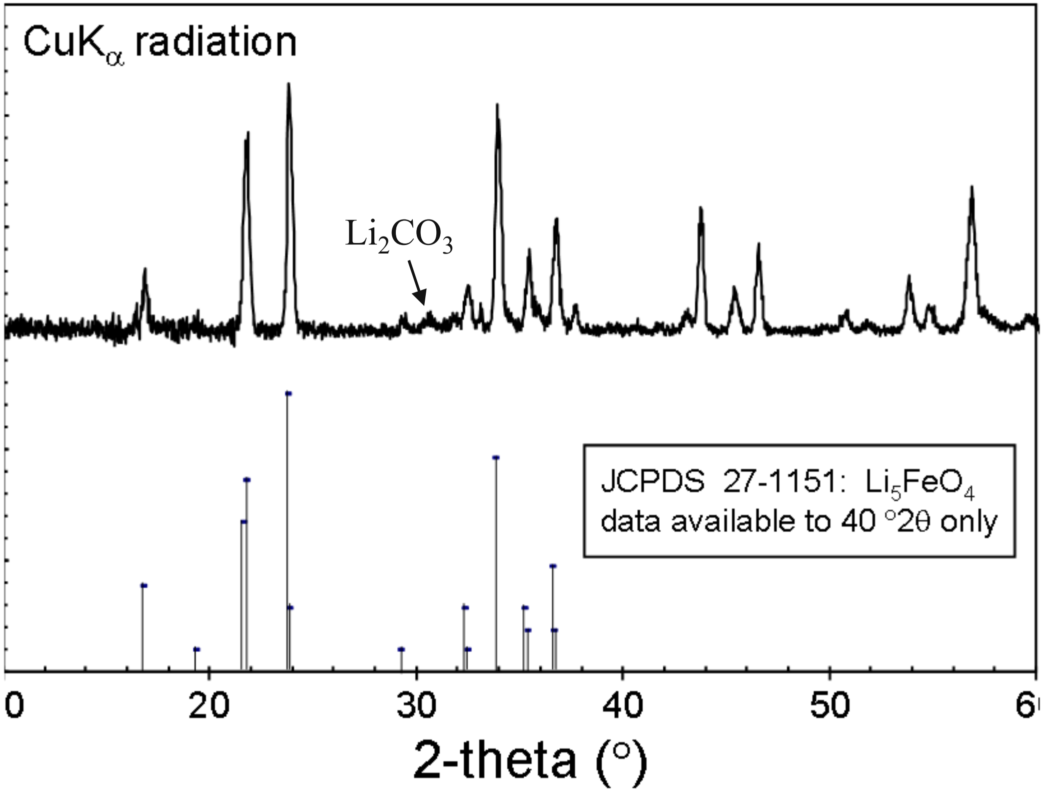
- Li_6MO_4 (M=Mn, Co, Ni):
  $3Li_2O{\bullet}MO$ or $Li_{1.5}M_{0.25}\square_{0.25}O$
  6 Li per M atom

cf: Layered Li_2MnO_3 (Li_2O:MnO_2)
2 Li per Mn atom

Abundant Li in defect structure provides good Li^+ mobility

Synthesis and X-ray pattern of Li_5FeO_4

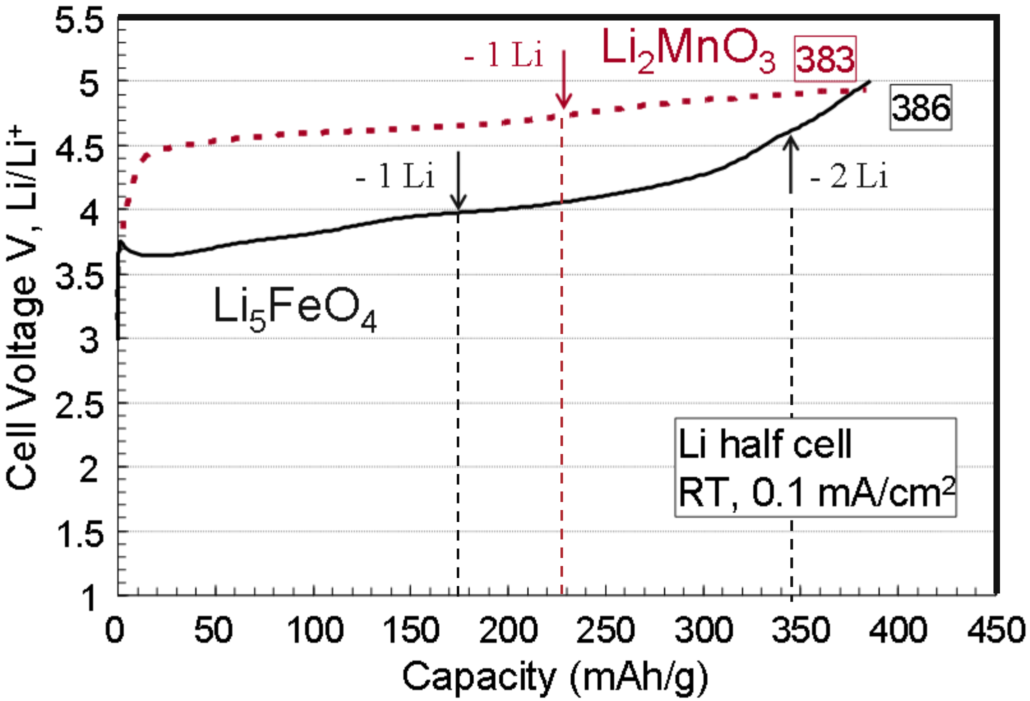
$$10\ LiOH \cdot H_2O + Fe_2O_3 \rightarrow 2\ Li_5FeO_4 + 15\ H_2O$$



- Slurry with methanol
- 800-850 °C under N_2/72h
- Single phase product

- Hygroscopic (kept in N_2)
- Metastable in dry air, forming Li_2CO_3
- XRD pattern is of Li_5FeO_4 after standing 8 hr in air

Electrochemical Activation of Li_5FeO_4 vs. Li_2MnO_3

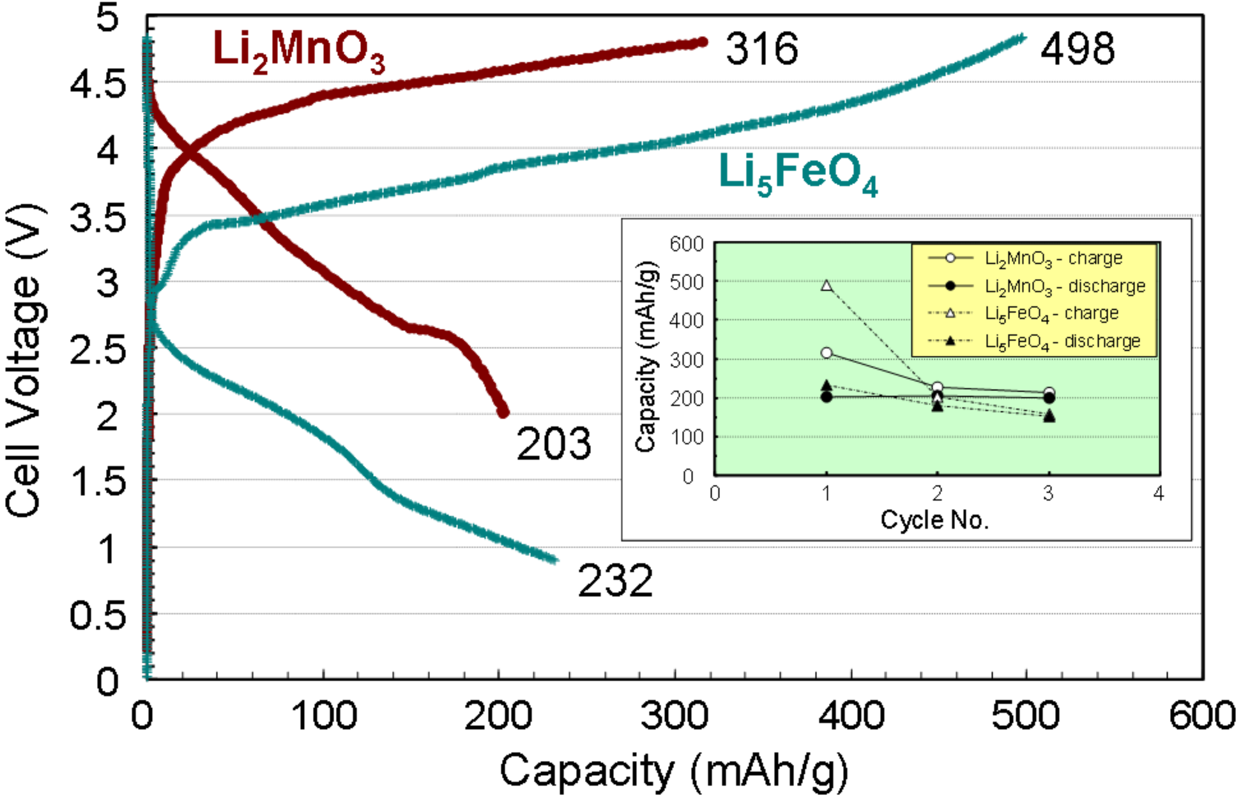


- Lithium extraction from Li_5FeO_4 easier than from Li_2MnO_3 (lower voltage)
- One Li_2O unit per Li_5FeO_4 is extracted below 4.5 V at 0.1 mA/cm^2
  - Li extraction with Fe $^{3+/4+}$ oxidation as per literature reports?*
  - Li_2O extraction?

* Imanishi et al., J. Power Sources. 146, 21 (2005)

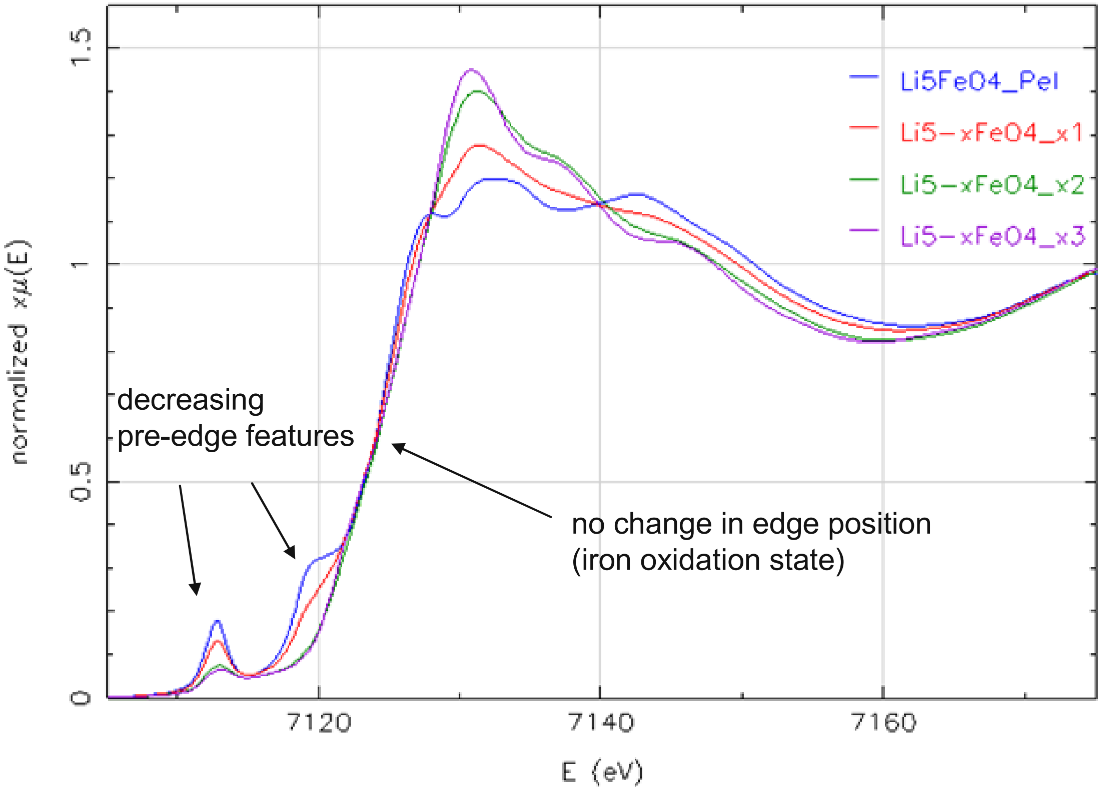
Li_2MnO_3 and Li_5FeO_4 Electrodes: Full Cell Data

(Graphite anode)



- Li_2MnO_3 and Li_5FeO_4 provide 200 mAh/g during early discharge cycles
- Li_5FeO_4 component suitable for end-of-discharge indicator when used in combination with higher potential, high capacity charged cathodes, e.g., $Li_{1.2}V_3O_8$

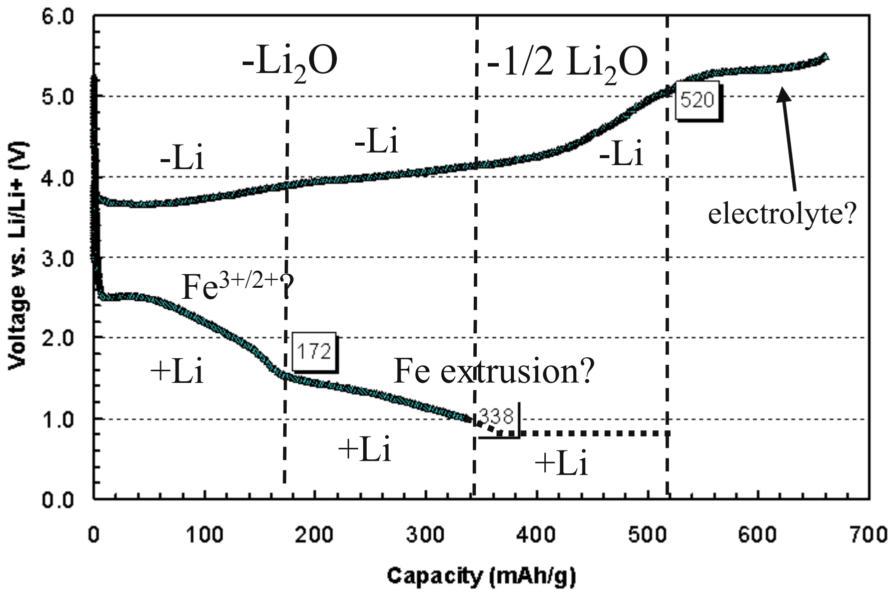
XANES Data: Delithiation of $Li_{5-x}FeO_4$



- Li_5FeO_4 samples chemically delithiated with NO_2BF_4/acetonitrile solution
- No apparent change in Fe^{3+} oxidation state $\Rightarrow$ Li_2O extraction
- Gradual reduction in pre-edge peak height is consistent with conversion from tetrahedral Fe to octahedral coordination.
- EXAFS shows evidence of formation of edge-shared Fe-octahedra with increasing x.

Activation Charge/Discharge Cycles: Li_5FeO_4

Li/Li_5FeO_4 ($5Li_2O \bullet Fe_2O_3$) half-cell

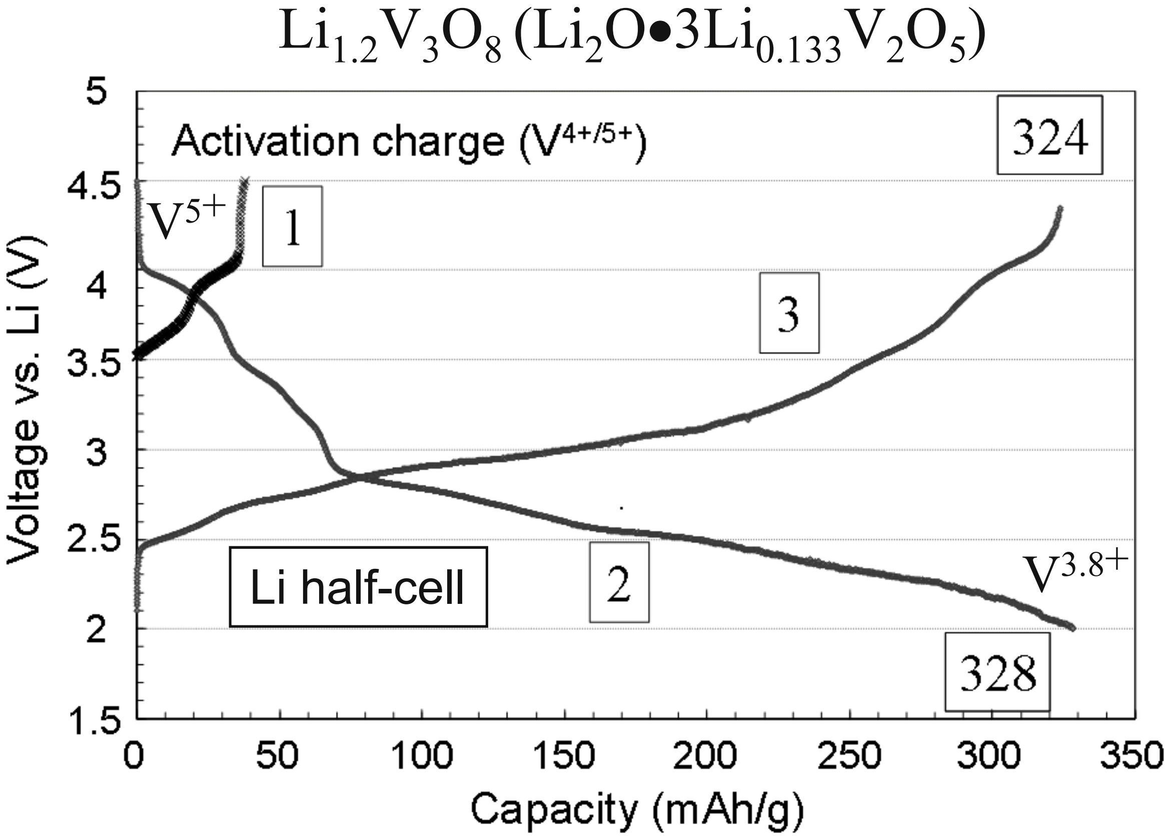


Proposed reaction

1. $Li_5FeO_4 \rightarrow$ "$Li_2O \bullet FeO_{1.5}$" ($Li_2O \bullet 0.5Fe_2O_3$) + 3 Li^+ + 0.75 O_2 + 3 e^- (520 mAh/g)
2. Li + "$Li_2O \bullet FeO_{1.5}$" + e^- $\rightarrow$ "$Li_2O \bullet LiFeO_{1.5}$" ($2Li_2O \bullet Li_2Fe_2O_3$) (173 mAh/g)
3. 2 Li + "$Li_2O \bullet LiFeO_{1.5}$" + e^- $\rightarrow$ "2.5 Li_2O + Fe" (346 mAh/g)

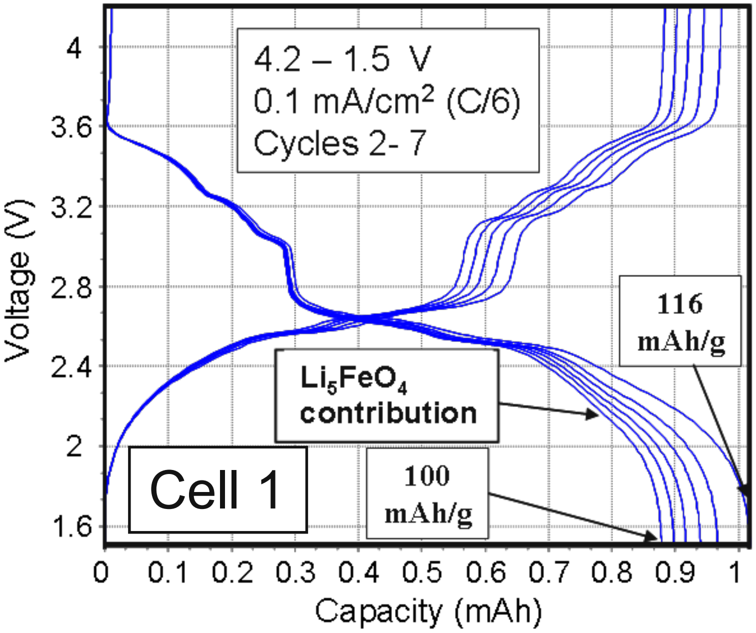
Notes: i) In practice, it is difficult to extract >3 Li from structure (>0.1 mA/cm^2)
ii) Li + Li_5FeO_4 $\rightarrow$ Li_6FeO_4 should be possible (cf: Li_6MO_4, M=Mn, Co, Ni)

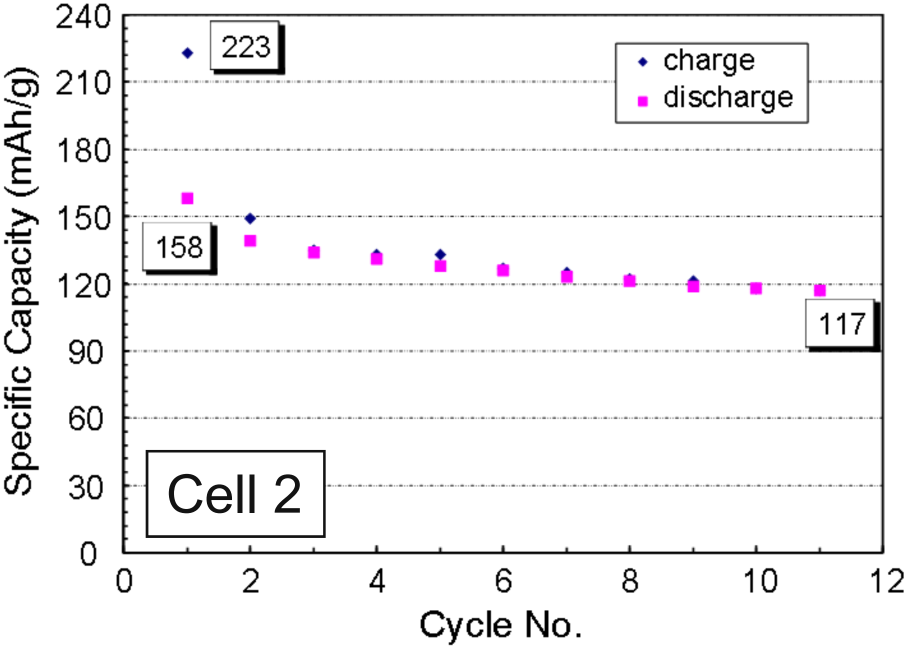
Activation Charge/Discharge Cycles: $Li_{1.2}V_3O_8$



- 0.2 Li^+ can be extracted during an initial charge ($V^{4+} \rightarrow V^{5+}$)
- It is difficult to extract Li_2O from $Li_{1.2}V_3O_8$ ($Li_2O{\bullet}3Li_{0.133}V_2O_5$) below 5.0 V
- $Li_{1.2}V_3O_8$ can deliver 328 mAh/g between 4 and 2 V (3.5 Li inserted)

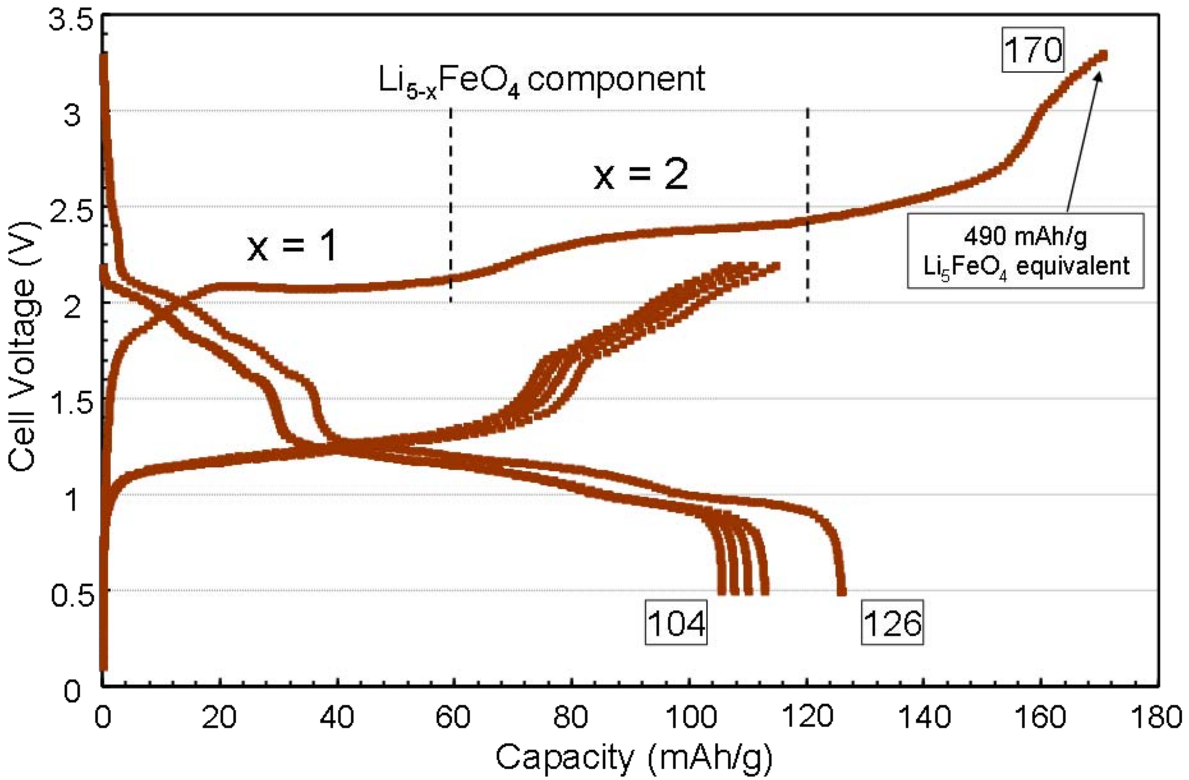
C_6/Li_5FeO_4-$Li_{1.2}V_3O_8$ Li-Ion Cells





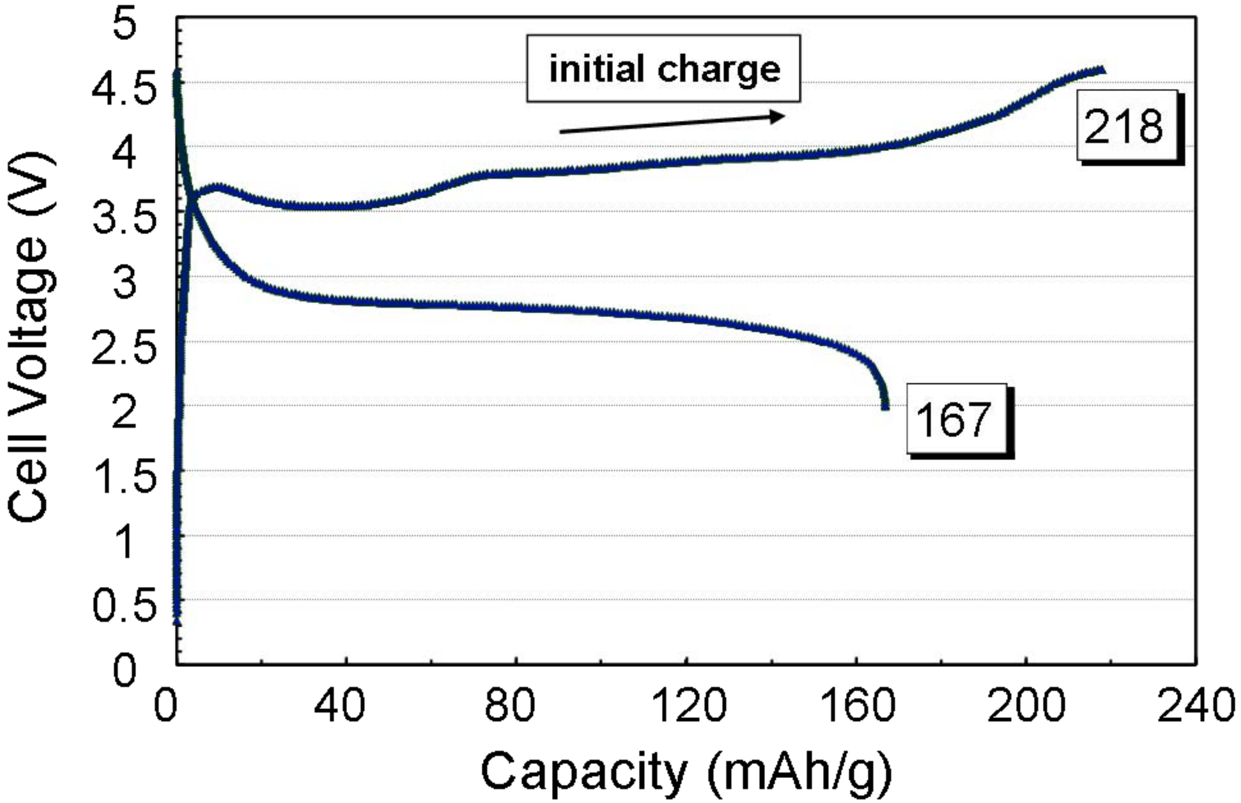
- 1:1 Li_5FeO_4:$Li_{1.2}V_3O_8$ ratio used (electrode balance not optimized)
- Capacities based on mass of parent electrode before activation (Li_2O loss)
- 120 cycles at C/2 rate achieved: 80 mAh/g (~240 mAh/g LiV_3O_8 component only)
- >99% coulombic efficiency
- Devise methods to exploit Fe redox couple more effectively – in progress

$Li_4Ti_5O_{12}/Li_5FeO_4$-$Li_{1.2}V_3O_8$ Li-Ion Cell



- Excellent demonstration of functionality of Li_5FeO_4 precursor
- Capacities based on mass of parent electrode before activation (Li_2O loss)
- Confirms 3-step process for lithium removal and the difficulty of removing >3 Li per Li_5FeO_4 unit (520 mAh/g)

Li_5FeO_4-MnO_2/C_6 Li-Ion Cell – preliminary data



- Initial tests show better overall utilization than $Li_{1.2}V_3O_8$ charged cathode
- Cell chemistry (Li-Fe-Mn-O) appealing; capacity improvement required

Future Work - FY2009/FY2010

- Exploit and evaluate properties of Li-rich antifluorite structures.
  - electrochemical behavior
  - chemical and thermal stability in charged and discharged states
  - structural properties by XRD, XAS and other spectroscopic methods

- Extend studies of Li_5FeO_4 to Li_6MO_4 (M=Mn, Ni, Co) compounds
  - probe two-electron redox behavior of $Ni^{2+/4+}$ and $Co^{2+/4+}$ couples

    e.g., Li_6NiO_4 offers 328 mAh/g (without Li_2O removal)

- Optimize electrode balancing and available capacity
  - devise methods to extract more Li than currently possible
  - attempt to improve the electrochemical properties of the composite electrodes (antifluorite precursor + charged component) by manipulating the redox behavior of the precursor cations (Fe, Mn, Ni, Co) and the cycling stability of the activated electrode materials

Summary

- Li_2MnO_3-based electrodes can be used as a precursor to either offset irreversible capacity loss effects at the anode or for providing excess lithium that can react, after an initial charge to high potentials (>4.5 V), with a charged component in the parent electrode.
- Work in FY ’09 was extended to evaluate other precursors with a high lithium content such as Li_5FeO_4. Work in 2008/09 focused predominantly on evaluating Li_5FeO_4 precursors with LiV_3O_8 and MnO_2 charged cathodes in lithium half cells and against graphite and $Li_4Ti_5O_{12}$ anodes.
- This approach has opened the door to the possibility of fabricating new electrode materials, whereby electrochemically active cathodes are created or modified *in situ* at moderate to high potentials during the initial charge reaction.

Acknowledgment

Support for this work from DOE-EERE, Office of Vehicle Technologies is gratefully acknowledged - David Howell