Design and Evaluation of Novel High Capacity Cathode Materials

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Project ID: ES017

Overview

Timeline

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

  - project on-going

Budget

- Total project funding

  - 100% DOE
- FY10: $300K
- FY11: $300K

Barriers

- Low energy density
- Cost
- Abuse tolerance limitations

Partners

- Lead P.I. – C. S. Johnson
- Collaborators (Argonne):
  - P. Kumta (Univ. or Pittsburgh)
  - S.-H. Kang, K. Gallagher, J. Vaughey, M. M. Thackeray (all of CSE)

  - M. Balasubramanian, S. Pol, N. Karan

  (Advanced Photon Source (all of APS))

Relevance

- New cathode materials are required to improve the energy density of Li-ion cells for transportation technologies.
- The cathode system in this project directly addresses the barriers to PHEVs and longer term EVs, which are low-energy density, cost and abuse tolerance limitations
- In this work, we are studying new novel cathode systems that utilize low-cost and abundant iron (Fe), vanadium (V) oxides, and Mn oxides. Such low-cost systems will allow a large ramp-up of materials production in order to satisfy demand as it increases.
- Iron oxides, vanadium oxides, and manganese oxides are amongst the most stable of transition metal oxides and will provide large abuse tolerance.
- This work provides an alternative route to high-energy density cells consisting of Ni and Co-based oxides by utilizing, instead, a pre-lithiation lithium-iron oxide source that is implemented to load lithium in advanced anode systems.

Objectives

Design and develop novel high capacity and high-energy cathode materials that are **low cost, with high-thermal stability** for PHEVs

- The implementation of layered transition metal oxides to Li batteries is well established, but this work is a novel designed approach to new high-energy Li-ion battery systems.
- Demonstrate the viability of this approach in a full battery system
  - Continue optimizing synthetic conditions to produce materials with the most favorable properties, such as surface area, tap density, phase purity, cost and safety
  - Continue the search for high-capacity charged cathodes with high-energy to combine with the Li_5FeO_4 (LFO) anti-fluourite pre-lithiation material
- Perform both physical property and electrochemical property measurements to understand cathode materials
  - Cycle the blended cathode material in Li half cells and show at least 40 cycles above 200 mAh/g
  - Conduct power rate tests and demonstrate a capacity of 150 mAh/g at C/1 rate
  - Cycle the blended cathode material with a high-performance Si anode
  - Evaluate the cathodes before and after cycling using microscopy methods

Milestones of FY11

- Synthesis of defect anti-fluorite (LFO) materials – done
  - Process was examined using Fe_3O_4 and Li salt – not preferred
  - LiOH hydrate is the preferred Li salt, Fe_2O_3 (hematite) is the preferred iron compd.
  - Effect of different contents of Li/Fe ratios initiated
- Synthesis of Co-substituted and Mn-substituted LFO cathode materials – on-going
  - The whole series was synthesized – i.e. from Li_5CoO_4 to (LFO); some with Mn
  - The effect of Co and Mn on performance and stability was checked –on-going
- Electrochemistry of LFO materials – done
  - Impedance of LFO - done
- Electrochemistry of Co- & Mn- -substituted LFO cathode materials – on-going
  - Combination with ‘charged’ cathodes – on-going
- Cell optimization with Mn-based ‘charged’, EMD –fines, α-MnO_2, λ-MnO_2 cathodes with LFO –on-going
  - Significant improvement of Mn-based electrodes, in particular α-MnO_2, through optimization efforts
  - Types : one electron Mn redox used
- Receipt of state-of-art Si-Carbon composite powder received and electrodes made - done
- Evaluation of cathode materials thermal stability – initiated
- Modeling/calculations of cathode-anode material balance and performance parameters - initiated

Approach

- ***This approach is new***. It is the implementation of an enabling technology that utilizes high-capacity (high energy) ‘charged’ cathodes in a ***Li-Ion*** cell configuration. The lithiation of a negative electrode occurs from a high-Li_2O content component precursor material that is incorporated in the initial cathode.

- A high ‘lithia/Li_2O’ content material is co-blended or synthesized as a composite with a non-lithium containing ‘charged’ – type positive electrode material.
  - The Li_2O component is electrochemically oxidized out of the structure in an ‘activation’ first charge.
- Examples of high-Li_2O content electroactive materials are Li_5ZO_4 (Z=Fe, Ga), $Li_2M'O_3$ (M’=Mn, Ti, Zr, Ru, Rh), & Li_6MO_4 (M=Co, Mn).
  - The lithium released from the reaction is, in turn, intercalated into the negative electrode (i.e. graphite, graphene composites, intermetallics, Si-C composites, high-capacity TiO_2 (B bronze), TiO_2 nanotubes, $Li_4Ti_5O_{12}$, etc…).
- The high-energy ‘charged’ containing positive electrode materials such as LiV_3O_8, V_2O_5, or MPO_4 (M=Fe, Mn, Co, Ni: delithiated olivines), and others such as, EMD-f, α-MnO_2, and λ-MnO_2 are subsequently cycled, starting on the first discharge.
  - Mn is preferred over V because of toxicity issues

Approach (cont'd)

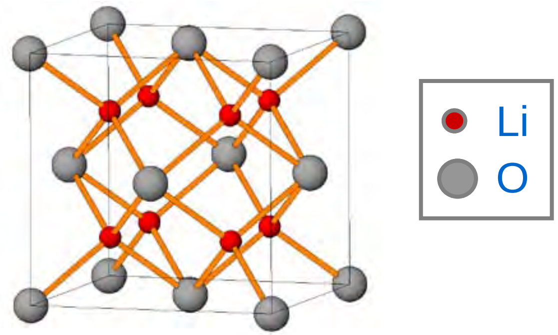
- The system studied in this work project consists of a blend of LFO▪MnO_2 cathode materials.
  - In composite 'lithia' notation, the above compound may be rewritten as: [$(5Li_2O$▪$Fe_2O_3)$•(MnO_2)] , in order to help show the large amount of sacrificial lithium that the lithia-component precursor can yield.

- This strategy is expected to :
  1. Allow the use of ultra-high capacity anodes such as Si-C nanocomposites to be used, despite their large first cycle irreversible capacity.
  2. Enable the use of traditional battery materials in Li-ion cell configuration.
  3. Introduce stable iron oxides into Li-ion cell chemistry, which may be expected to improve the thermal stability of the battery.
  4. Utilize inexpensive and abundant Fe and Mn for Li-ion battery technology.

Background – Anti-fluorite Structures (Recap)

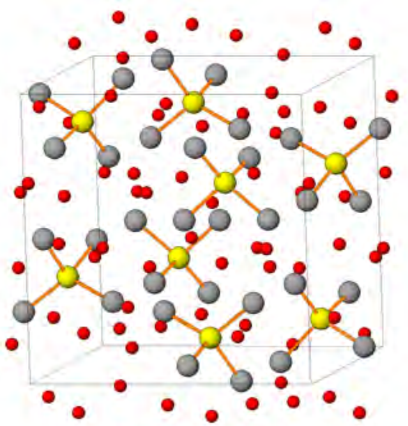
Li_5FeO_4 (LFO) as a prelithiation precursor

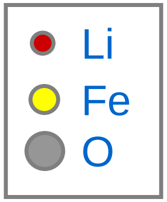
Li_2O (Fm-3m)
(*a*=4.614 Å)



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)





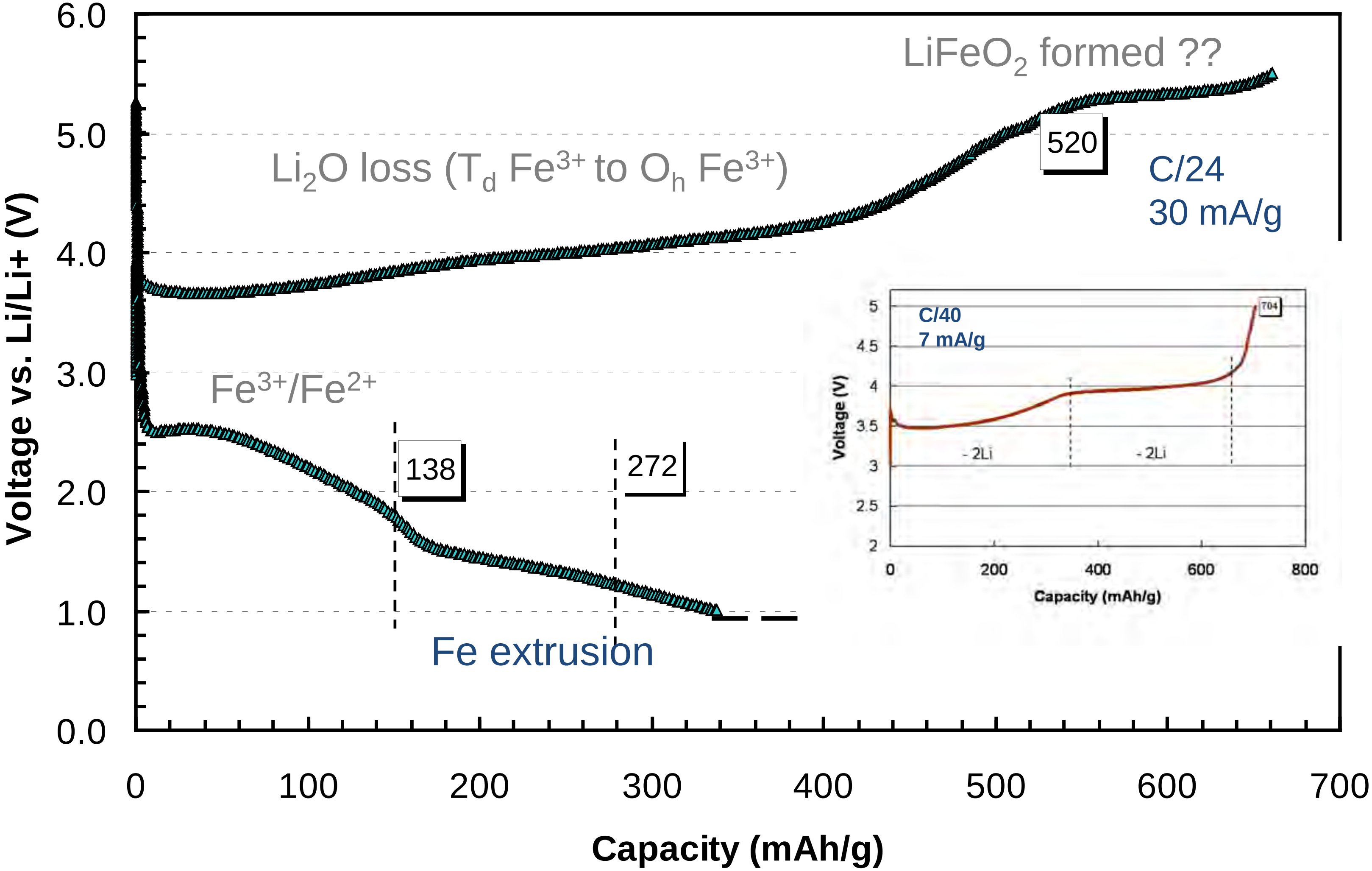
Defect antifluorite structures

- 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

<u>Abundant Li in defect structure ideally provides good Li^+ mobility</u>

✓Synthesis has been optimized; 2h synthesis in N_2 to produce Li_5FeO_4
✓Related antifluorite materials have been synthesized :
Co substitutions into Li_5FeO_4 completed

Voltage profile Li/LFO cell with discharge step



✓Ideal reaction : $2Li_5FeO_4 \rightarrow 5Li_2O + Fe_2O_3$

✓Large irreversible capacity loss on first charge due to oxygen loss effect

C. S. Johnson, et al., *Chem. Mat.* 22, (2010) 1263

Proposed reaction mechanism

1. $Li_5Fe^{(III)}O_4$ (T_d Fe)$\rightarrow$

   $Li_4Fe^{(IV)}O_4$ (T_d Fe) + Li^+ + e^- (173 mAh/g)

   unstable intermediate

2. $Li_4Fe^{(IV)}O_4$ (T_d Fe) $\rightarrow$

   *, ^^

   "$LiFeO_2$" (O_h $Fe^{(III)}$) + 3 Li^+ + 0.75 O_2 + 3 e^- (520 mAh/g)

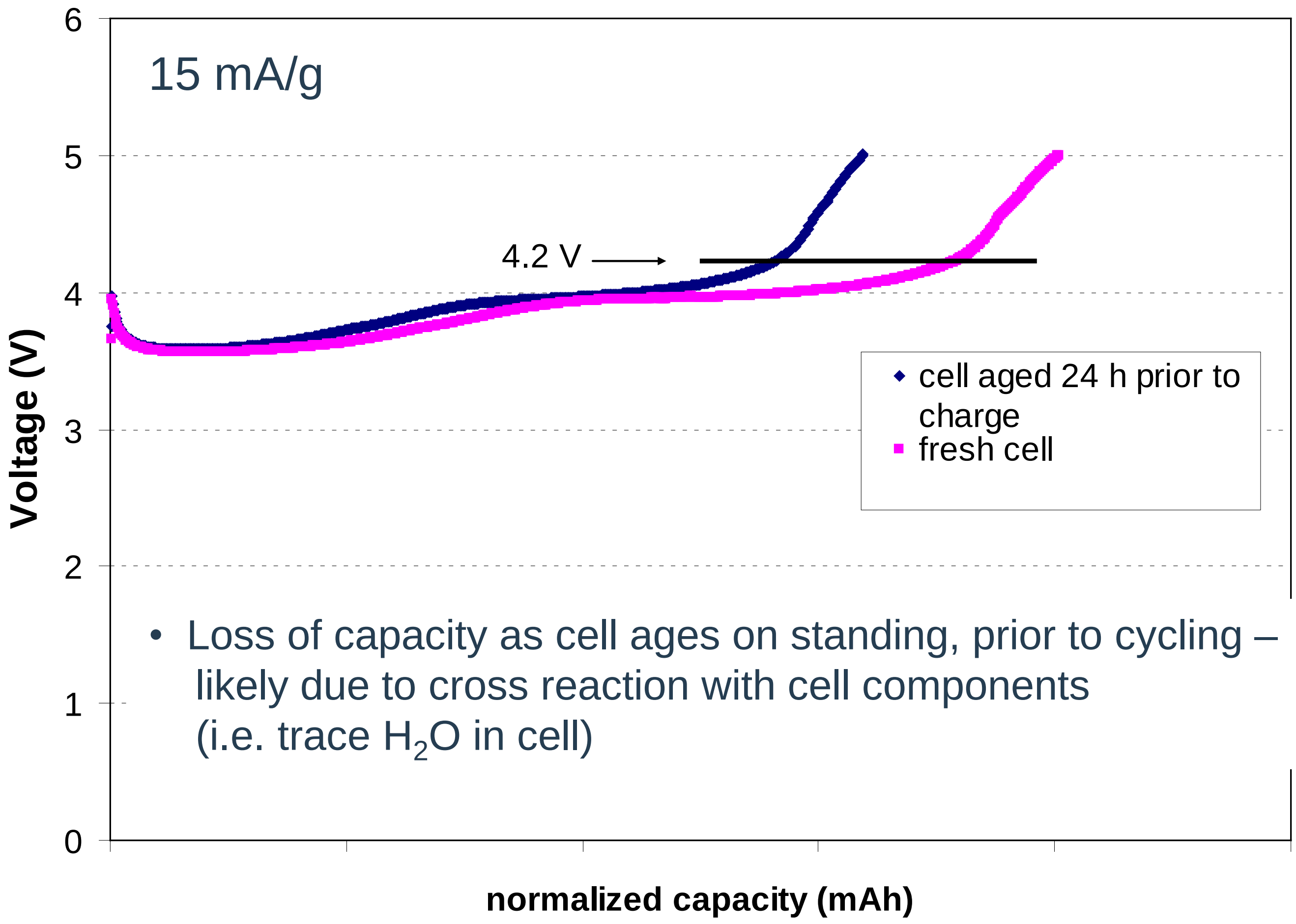
   (3 Li^+ + 0.75 O_2 + 3 e^- =) $1.5Li_2O$

^^ $O^{2-} \rightarrow 1/2O_2 + 2\ e^-$

* This is an oxygen loss process; however, if Li_2O can reform with $LiFeO_2$ to form nanoscopic Li_5FeO_4, then this material has potential to be reversible.

^^ Need to capture O_2 loss within the lattice or with a sacrificial O_2 binding material, then reverse the process on discharge to form O^{2-} anions that go back into the lattice. A typical O_2 binding material are metallic porphryins. Ceria (CeO_2) would work as well to make the reaction $O^{2-} \rightarrow 1/2O_2 + 2\ e^-$ reversible.

Li/LFO cell aging



- Loss of capacity as cell ages on standing, prior to cycling – likely due to cross reaction with cell components (i.e. trace H_2O in cell)

- Coating LFO can increase stability of material in air

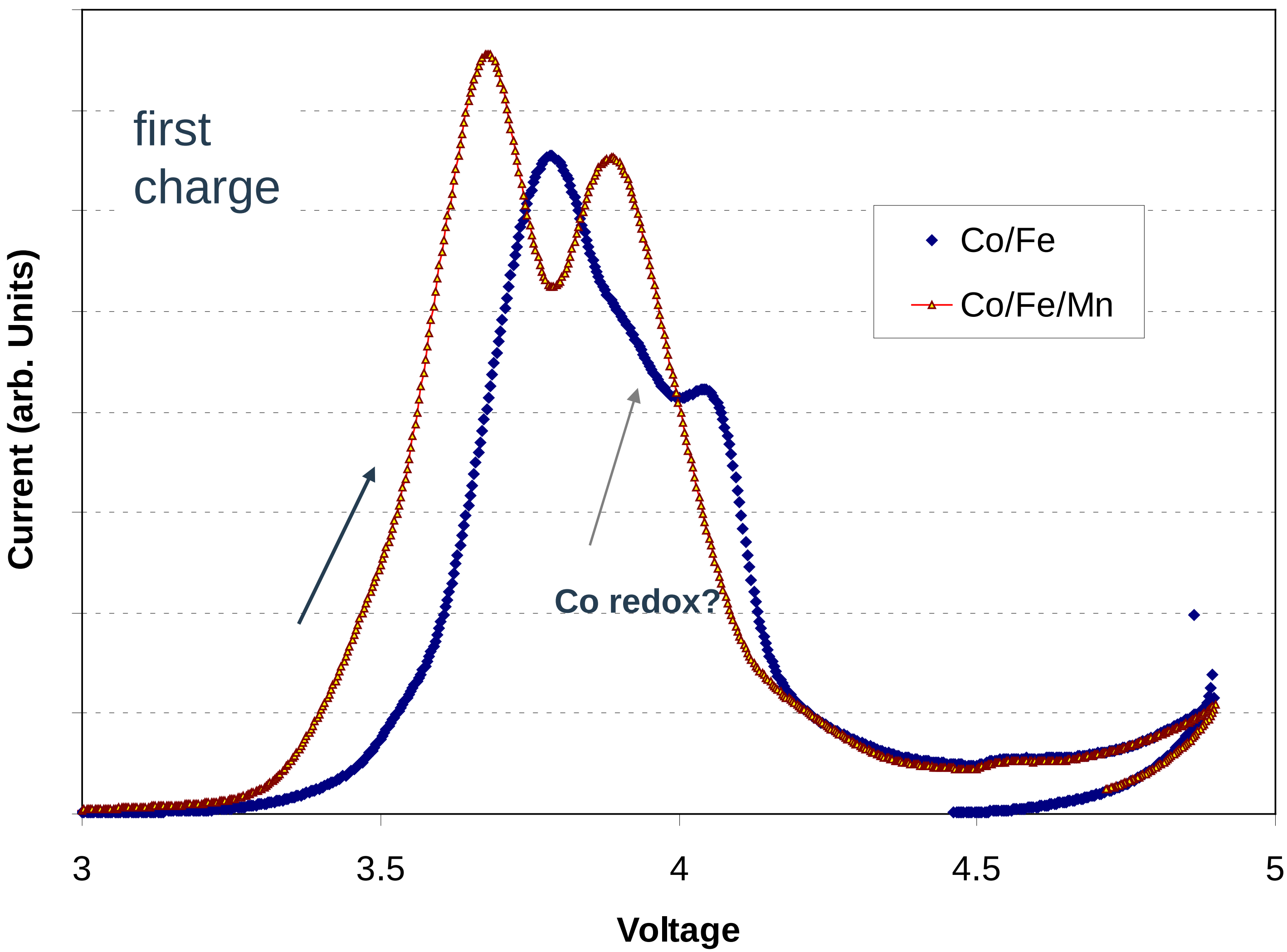
Cobalt-substitution into LFO

Samples synthesized

- ✓LFO
- ✓$Li_5Fe_{0.9}Co_{0.1}O_4$
- ✓$Li_5Fe_{0.8}Co_{0.2}O_4$
- ✓$Li_5Fe_{0.7}Co_{0.3}O_4$
- ✓$Li_5Fe_{0.6}Co_{0.4}O_4$
- ✓$Li_5Fe_{0.5}Co_{0.5}O_4$
- ✓$Li_5Fe_{0.4}Co_{0.6}O_4$
- ✓$Li_5Fe_{0.3}Co_{0.7}O_4$
- ✓$Li_5Fe_{0.2}Co_{0.8}O_4$
- ✓$Li_5Fe_{0.1}Co_{0.9}O_4$
- ✓Li_5CoO_4

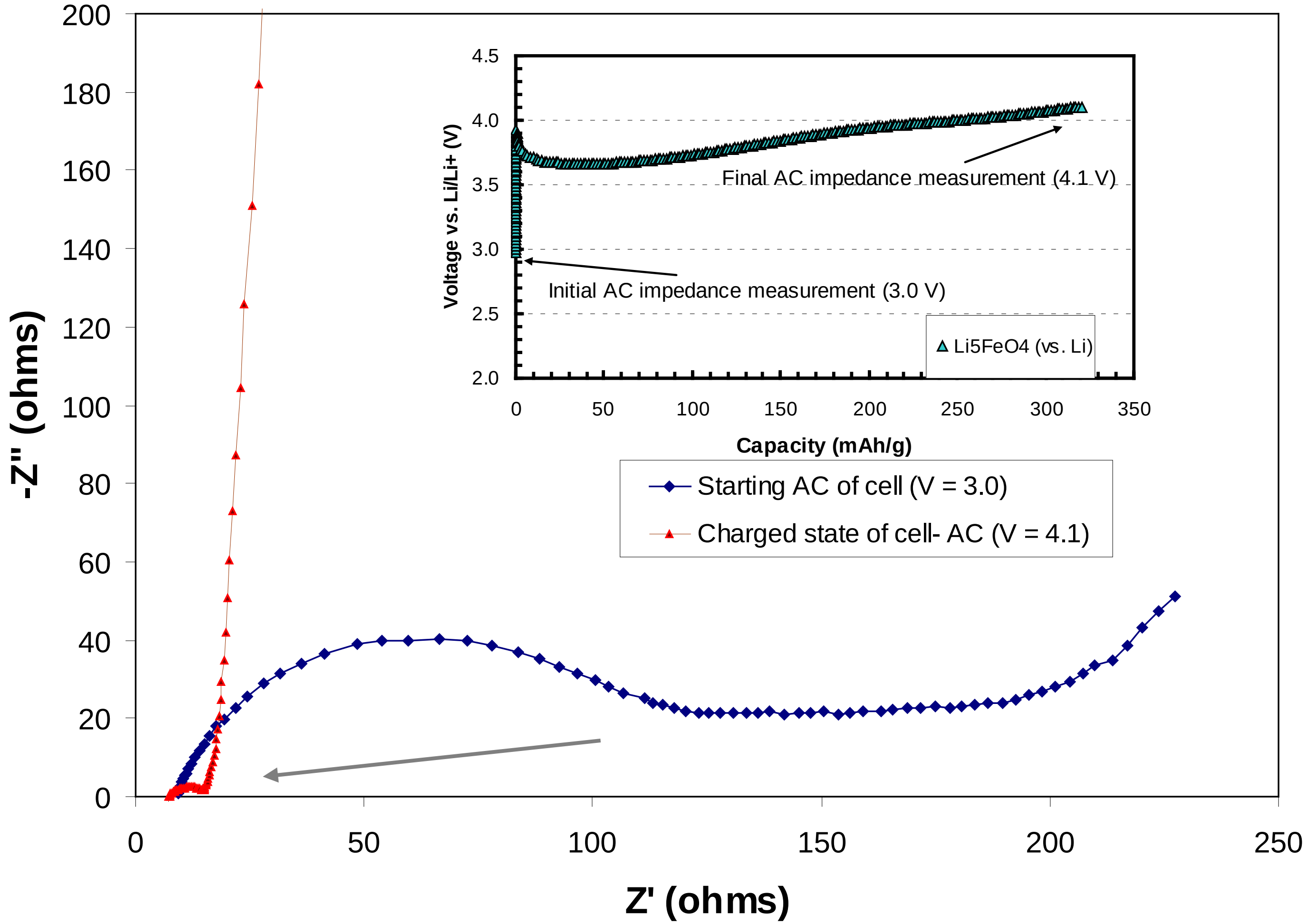
- In all cases single phase materials were synthesized, and will be tested in the upcoming months.

Cyclic Voltammetry : LFO derivatives



- $Li_5Fe/Co/MnO_4$ anti-fluorites show various redox processes during loss of Li_2O

Cell Impedance



- As lithia (Li_2O) is removed from LFO, the impedance drops significantly.

Reaction Design

$$[1]\quad Li_5FeO_4 + Si\text{-}C \xrightarrow{3.0 - 4.3\ V} Li_4Si\text{-}C + \text{“}LiFeO_2\text{”} + O_2$$

$$[2]\quad Li_4Si\text{-}C + \alpha\text{-}MnO_2 \underset{}{\overset{\sim 2.7\ V}{\rightleftharpoons}} Si\text{-}C + \alpha\text{-}LiMnO_2$$

-Specific energy (Wh/kg) can be increased because thinner laminates such as for Si-C composite anodes can be used in the full cell.

-The benefits of increase in energy density are evident…-> next

Model – Li-ion configuration cell calculations

Example – Si/C composite anode (Kumta, J. Power Sources, 194 (2009) 1043)
- 1200 mAh/g first cycle, 900 mAh/g reversible capacity…
…a 30% irreversible loss

•Neg. loading : ***2*** mg/cm^2, yields ~ 1.7 mAh/cm^2 (after cycling break-in) - > this is a very thin-high specific energy electrode…

…paired with a 30%Li_5FeO_4/70%MnO_2 cathode (w:w)

•Pos. loading : ***6.3*** mg/cm^2, yields ~ 1.7 mAh/cm^2 (after cycling break-in)

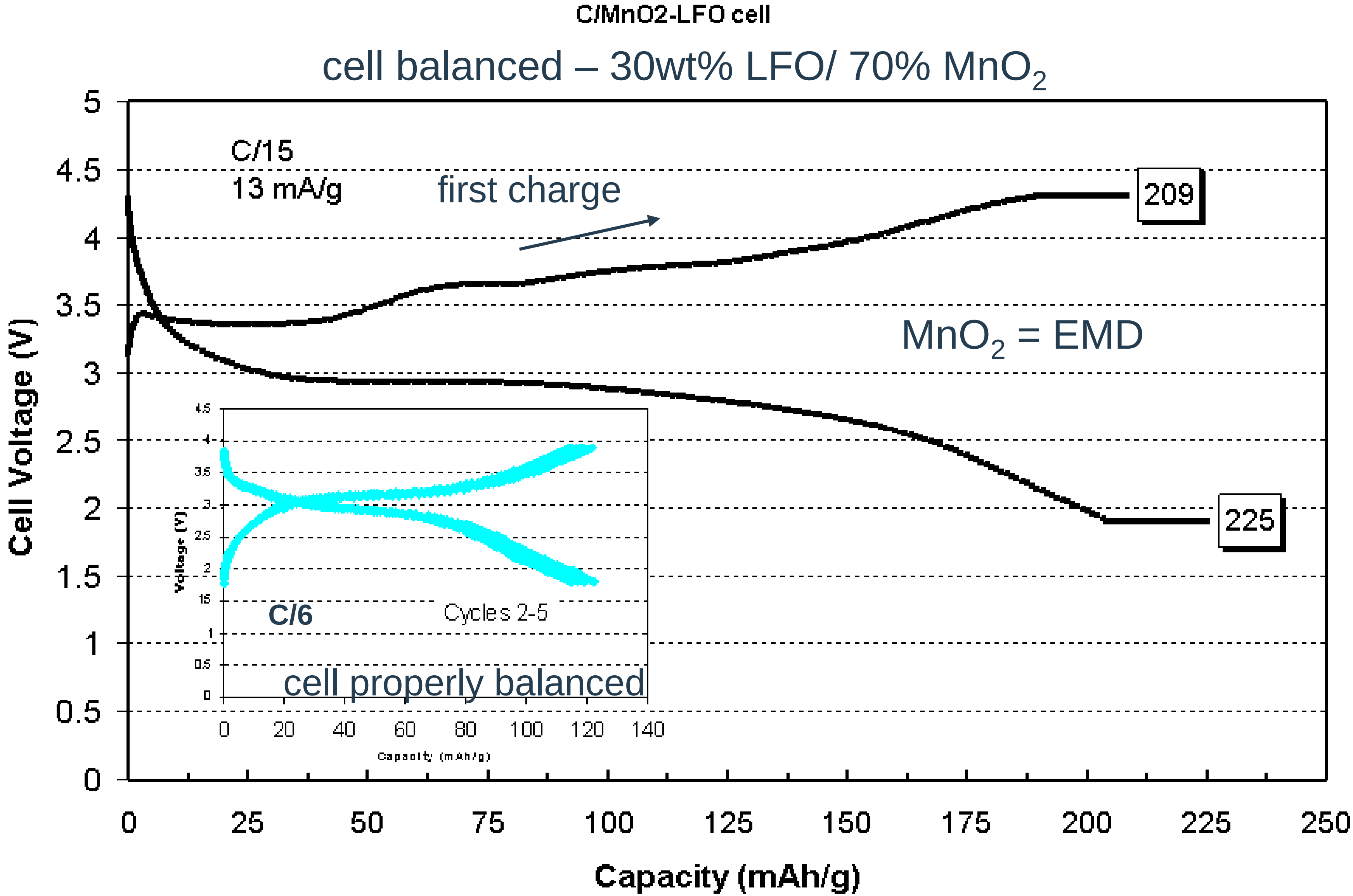
• This overall lower negative and positive electrode weights translate into about ~ **1-fold** increase in energy density (Wh/kg).

Energy Densities of Li/MnO_2 Cells

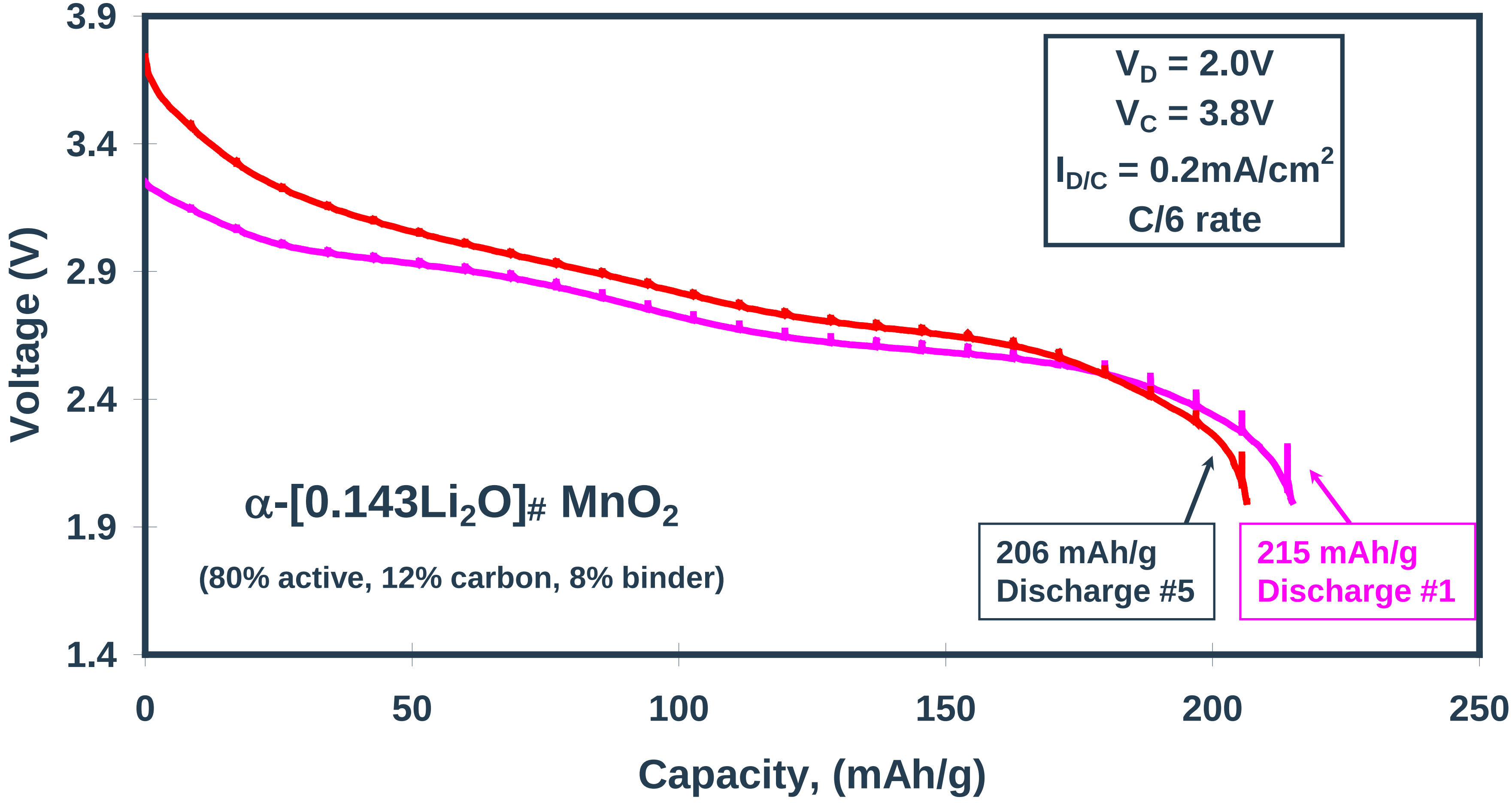
Structure Type	Average Discharge Voltage (V)	x range	Theory Capacity (mAh/g)	Practical Capacity (mAh/g)	% Electrode Utilization	Li per Mn	Energy Density Wh/kg
$Li_xMn_2O_4$ spinel	4	$0 \leq x \leq 1$	148	110-120	81%	0.4	480
Li_xMnO_2	2.8 (3)	$0 \leq x \leq 1$	308	160-180	58%	0.6	504 ↑

- Objective – increase this capacity (> 200 mAh/g) and cell energy density – use improved α-MnO_2 as charged cathode

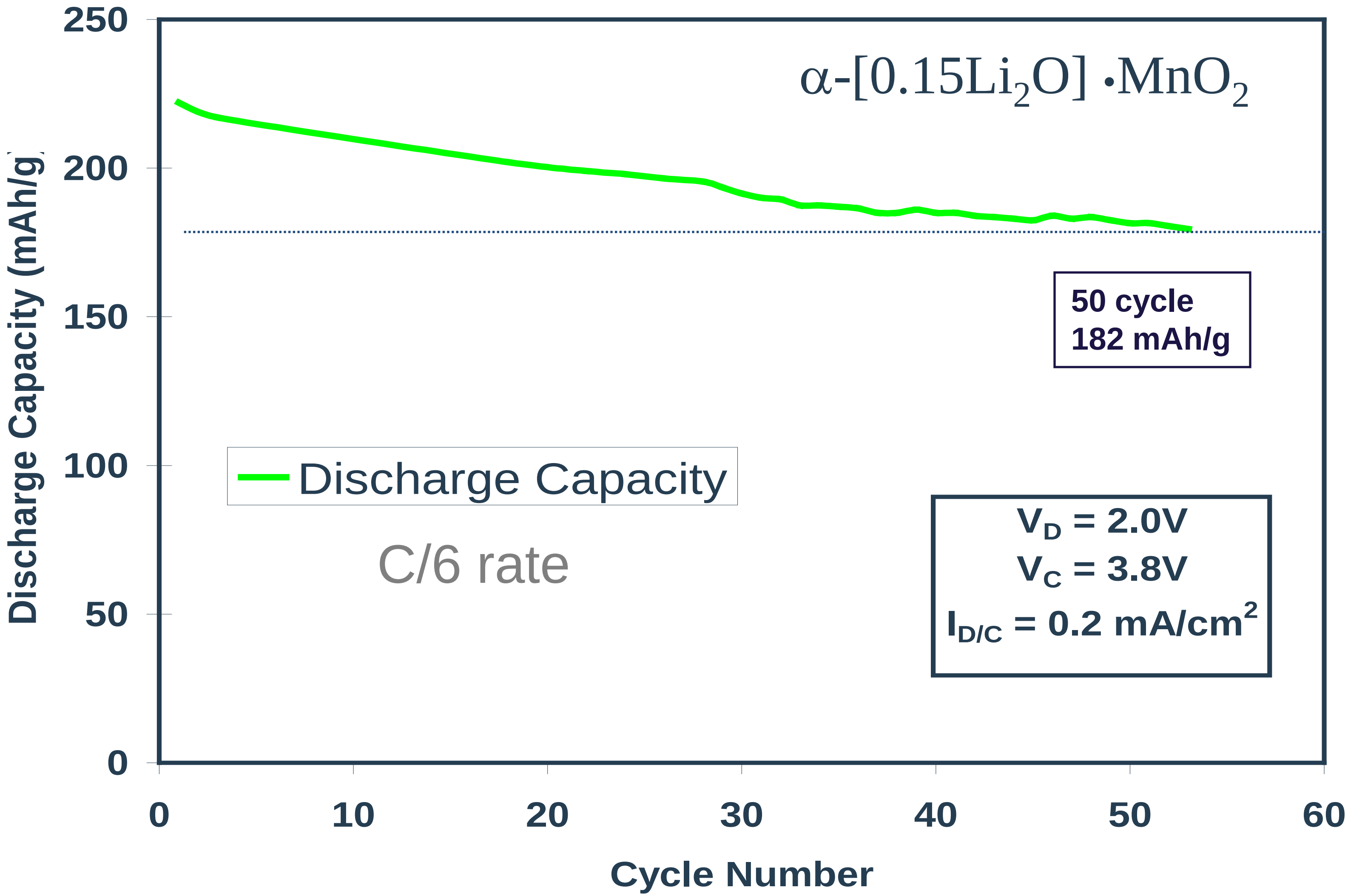
Voltage profile : full cell C/MnO_2-LFO



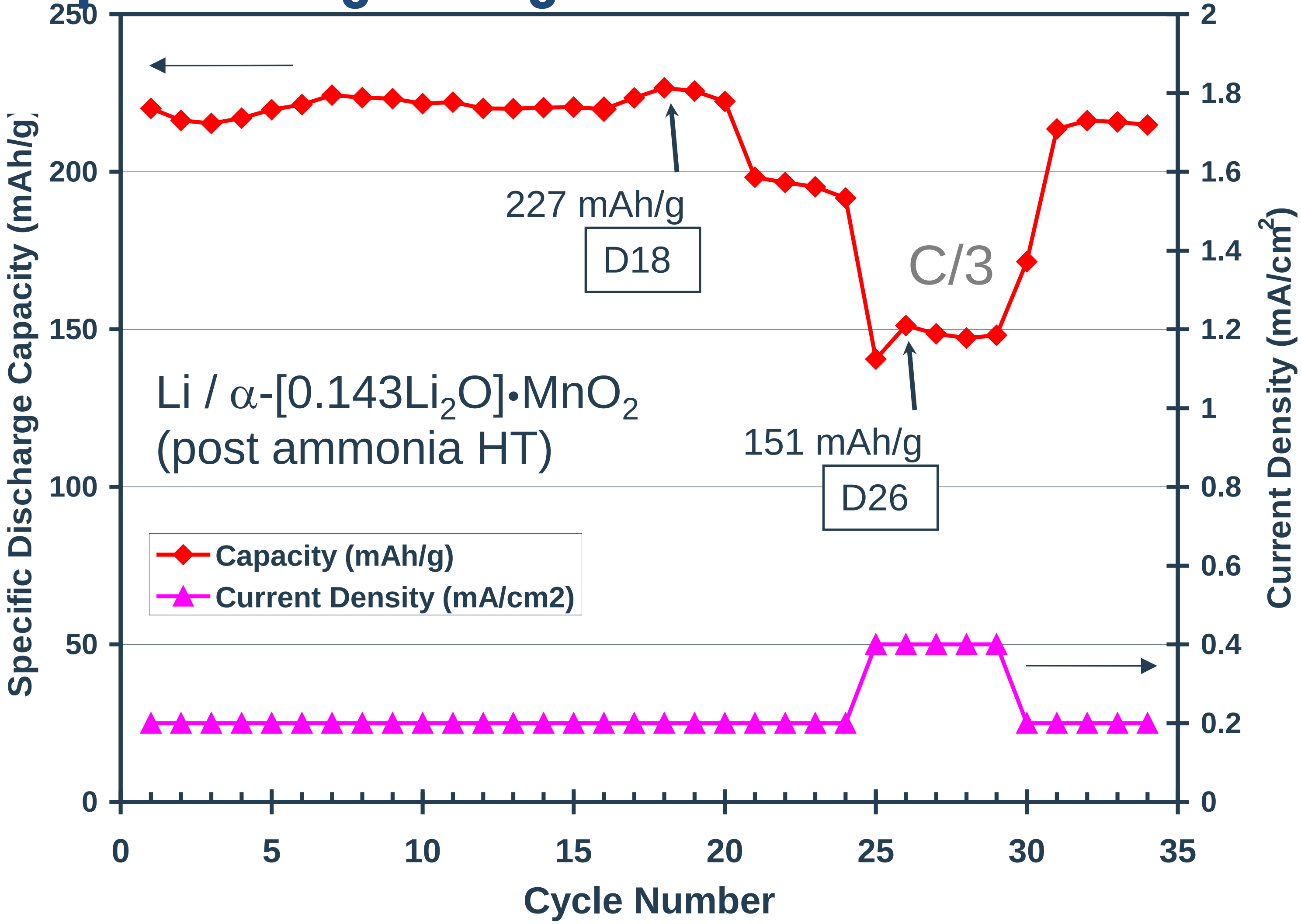
Electrochemical Activity of Lithia-doped (Stabilized) α-MnO_2 Material is promising for LFO-MnO_2 charged cathode



Capacity Fade of Lithia-stabilized α-MnO_2 Cathode Material must be Improved



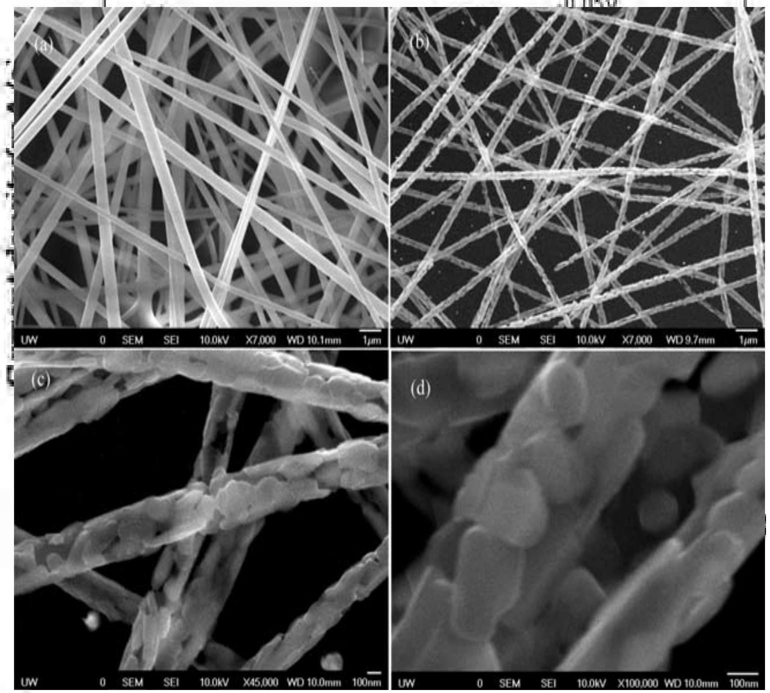
Cycling Behavior of Lithia-stabilized/ Ammonia-treated α-MnO_2 Cathode Material - promising charged cathode material

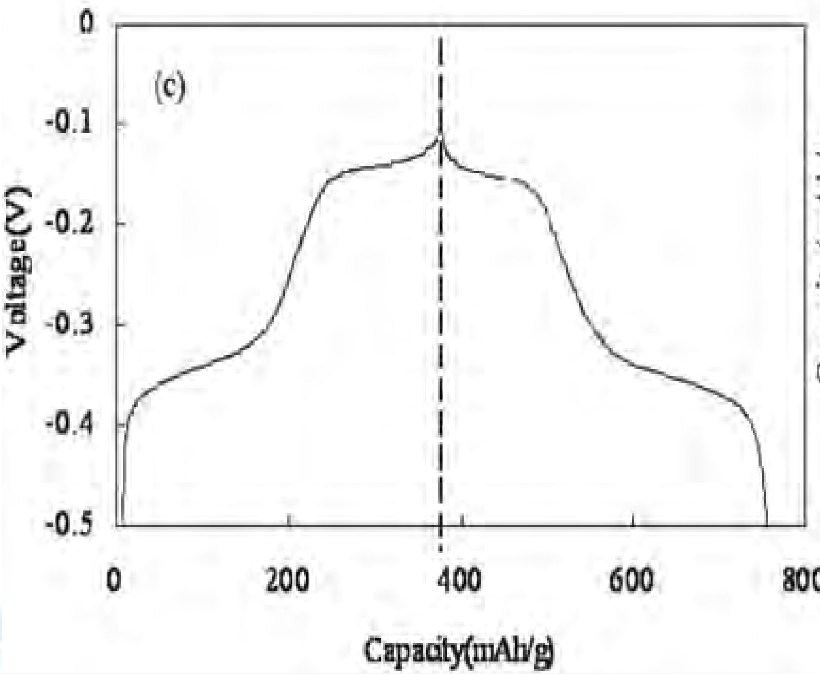


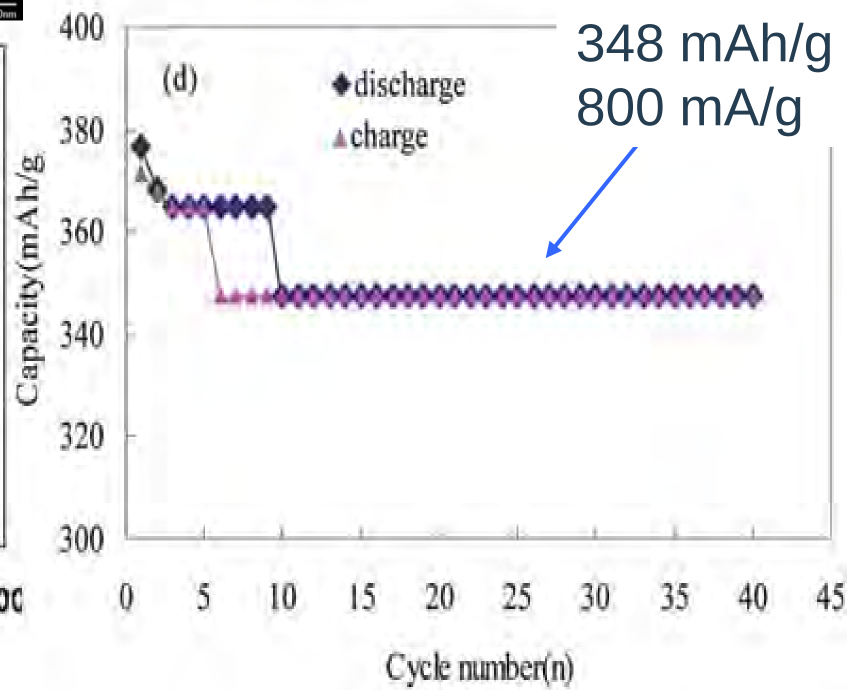
Future: revisit V_2O_5

Electrospun V_2O_5 fibers

(ref: D. Yu, et al. Energy and Environmental Science, 4 (2011) 858)







348 mAh/g @ 800 mA/g

Collaborations

- **Partners:**
  - Industry partner - work-for-others program with a SBIR Company
    - Phase II project titled "Technical Evaluation and Testing of Pre-lithiation Cathodes for Li-ion Batteries" : investigation involves the use of LFO precursor to load advanced anodes
  - Government – University Laboratory Partners -
    - BATT project – "Si-Carbon nanocomposite anodes" (P.I. P. Kumta)
    - ES028 ABR project – "Materials screening" (P.I. Dr. Wenquan Lu)
    - The Center of Nanoscale Materials (CNM) at Argonne is used to analyze materials.
      - Scientists: Dr. David Gozstola and Dr. Vic Maroni
    - The Advanced Photon Source (APS) at Argonne is used to analyze materials.
      - Scientists: Drs. Mali Balasubramanian, Swati V. Pol, and N. Karan.

Future work

•New variable Fe/Co ratios for $Li_xFe_{1-y}Co_yO_4$ will be characterized and evaluated

- the conditions of release of Li_2O will be better understood and optimized for maximal capacity

•Other charged cathodes such as V_2O_5 (electrospun fibers), MnO_2 (various forms) and delithiated olivines MPO_4 (M=Fe, Mn, Co, Ni) will be evaluated in new blended cells.

– the most promising cathodes will be improved by coatings or other methods

•Prelithiation precursor cathode system LFO-charged cathode will be tested against high-capacity, high-energy anodes.

•Advanced analytical methods (SEM, TEM) and diagnostic tools @APS & CNM (Raman) will be used to characterize new materials and will provide guidance for the project.

•Collaborations with other ABR teams will continue.

- Li-metal project (Vaughey, Dees), and material screening (Lu)

Summary & Conclusions

- Li_5FeO_4 and MnO_2 (EMD and α-MnO_2) identified and tested as a new chemistry for Li-ion cells ; low cost, environmentally friendly and stable systems
  - Mechanism of lithium removal from LFO determined as Li_2O loss
    - Cycling yields about 128 mAh/g total electrode; 220 mAh/g first cycle
    - Calculations shows that > 200 mAh/g could be achieved based on optimized/blended ratios.
      - This may be a good system for high-capacity advanced anodes such as Si/Carbon composites.
  - Electrochemical and stability properties have been measured.
    - Impedance decreases 15x on charge
    - LFO ages quickly in cell
  - Synthesis has been optimized and cobalt substitutions have been initiated and testing begun.
  - MnO_2 optimization is underway and initial samples have been evaluated.
    - Alpha-MnO_2 synthesized and studied as a charged cathode
      - Lithia-doping into MnO_2 key to improved Li cathode performance