

Design and Evaluation of Novel High Capacity Cathode Materials

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ES017

*This presentation does not contain any
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Vehicle Technologies Program

Overview

Timeline

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

Budget

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

Barriers

- Low energy density
- Cost
- Abuse tolerance limitations

Partners

- Lead P.I. — C. S. Johnson
- Collaborators (Argonne):
 - 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) and vanadium (V) oxides. Such low-cost systems will allow a large ramp-up of materials production in order to satisfy demand as it increases.
 - Synthesis of materials, scale-up and spectroscopic and electrochemical data is currently being collected.
 - Validation of the technology in larger cells is under investigation with an industrial partner.
- Iron oxides and vanadium 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 to load 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 Li-rich oxide precursor anti-fluorite materials with ‘charged’, stabilized V-based cathodes in a *Li-ion* full cell is the objective.
 - *New approach*
 - ✓ V-based cathodes have high-capacity, but have not been evaluated in Li-ion cells.
 - ✓ Target materials are low cost Fe and V lithium oxides; these materials are typically thermally stable.
 - Li-rich anti-fluorite Fe based oxides release large quantity of lithium on the initial charge.
 - ✓ This method will be useful for cycling against new high-capacity anodes (for e.g. Si-based) that may have a high-first cycle irreversible capacity loss; the sacrificial lithium source or precursor material is blended into the cathode.



Milestones of FY10

- Synthesis of defect anti-fluorite Li_5FeO_4 materials – done
 - Process reduced from 70 h to 2 h reaction time using nano-powder of Fe_2O_3 starting materials
- Synthesis of Co-substituted Li_5FeO_4 cathode materials – done
 - will be used to determine the effect of Co^{2+} on performance and stability
- Electrochemistry of Li_5FeO_4 materials – done
- Electrochemistry of Co-substituted Li_5FeO_4 cathode materials – done
 - Combination with ‘charged’ cathodes – on-going
- Structural characterization of Li_5FeO_4 and oxidized forms – done
- Structural characterization of Co-substituted Li_5FeO_4 and oxidized forms – on-going
- Cell optimization with V-based ‘charged’ cathodes with Li_5FeO_4 – on-going
 - Significant improvement of V-based electrodes through coating process discovered
 - Types : multi-electron V couples; LiV_3O_8 – 372 mAh/g capacity
 V_2O_5 – 442 mAh/g
- 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-Li₂O content component precursor material that is incorporated in the initial cathode.
- A high ‘lithia/Li₂O’ content material is co-blended or synthesized as a composite with a non-lithium containing ‘charged’ – type positive electrode material.
 - The Li₂O component is electrochemically oxidized out of the structure in an ‘activation’ first charge.
- Examples of high-Li₂O content electroactive materials are Li₅ZO₄ (Z=Fe, Ga), Li₂M'O₃ (M'=Mn, Ti, Zr, Ru), & Li₆MO₄ (M=Co, Mn).
 - The lithium released from the reaction is, in turn, intercalated into the negative electrode (i.e. graphite, intermetallics, Si-C composites, high-capacity TiO₂ (B), Li₄Ti₅O₁₂, etc...).
- The high-energy ‘charged’ containing positive electrode materials such as LiV₃O₈, V₂O₅, MnO₂, or MPO₄ (M=Fe, Mn, Co, Ni: delithiated olivines), and others are subsequently cycled, starting on the first discharge.



Approach (cont'd)

- The system studied in this work project consists of a blend of $\text{Li}_5\text{FeO}_4 \cdot \text{LiV}_3\text{O}_8$ cathode material.
 - In composite 'lithia' notation, the above compound may be rewritten as: $[(5\text{Li}_2\text{O} \cdot \text{Fe}_2\text{O}_3) \cdot (\text{LiV}_3\text{O}_8)]$, 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 V for Li-ion battery technology.



Approach (cont'd)

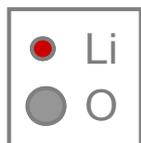
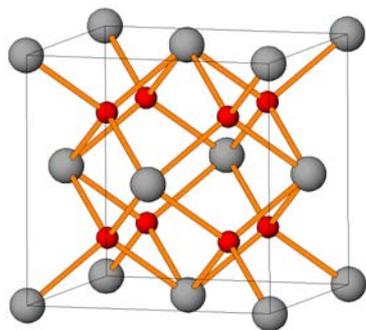
Reaction Design



Background - Anti-fluorite Structures

Li_5FeO_4 as a prelithiation precursor

Li_2O (Fm-3m)
($a=4.614 \text{ \AA}$)

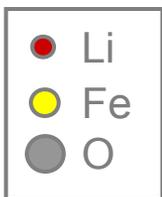
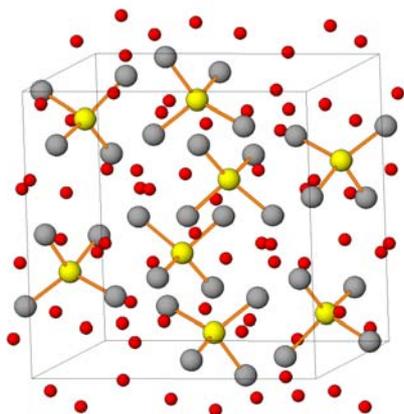


Li_2O : Li - tetrahedral sites
O - face-centered-cubic sites

Defect antifluorite structures

■ Li_5FeO_4 : $5\text{Li}_2\text{O} \bullet \text{Fe}_2\text{O}_3$ or $\text{Li}_{1.25}\text{Fe}_{0.25}\square_{0.5}\text{O}$
5 Li per Fe atom

Li_5FeO_4 (Pbca)
($a=9.218 \text{ \AA}$; $b=9.213 \text{ \AA}$; $c=9.159 \text{ \AA}$)



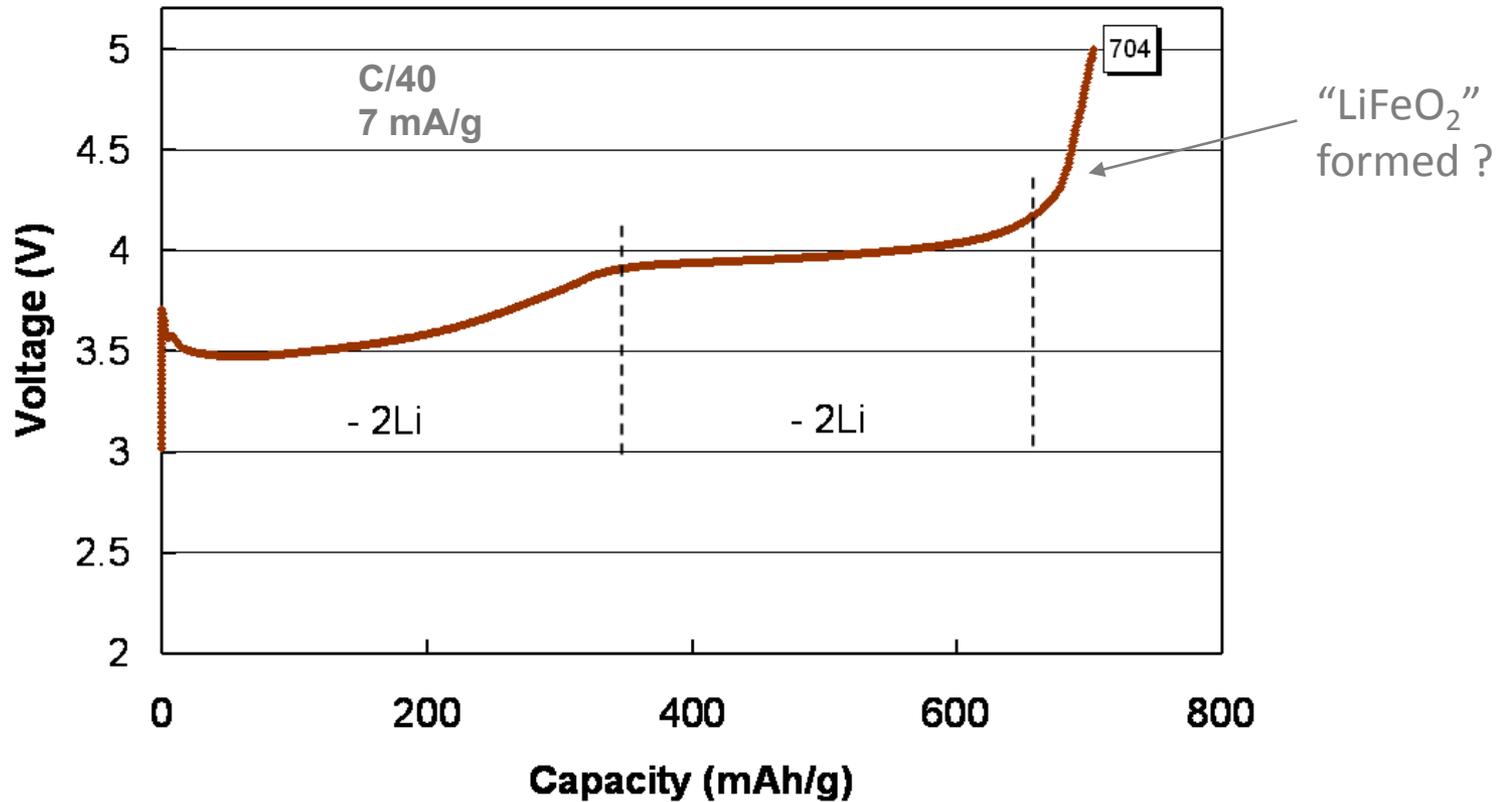
■ Li_6MO_4 (M=Mn, Co):
 $3\text{Li}_2\text{O} \bullet \text{MO}$ or $\text{Li}_{1.5}\text{M}_{0.25}\square_{0.25}\text{O}$
6 Li per M atom

Abundant Li in defect structure ideally provides good Li^+ mobility

- ✓ 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



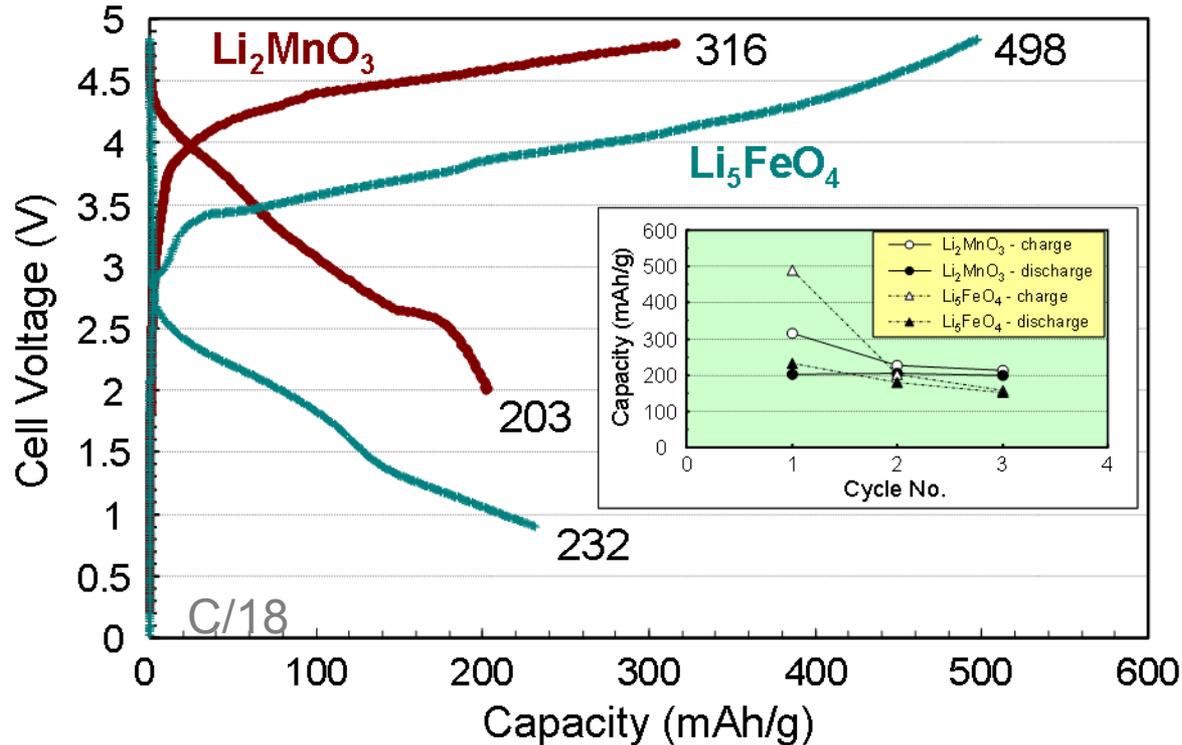
Voltage profile Li/Li₅FeO₄ cell



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



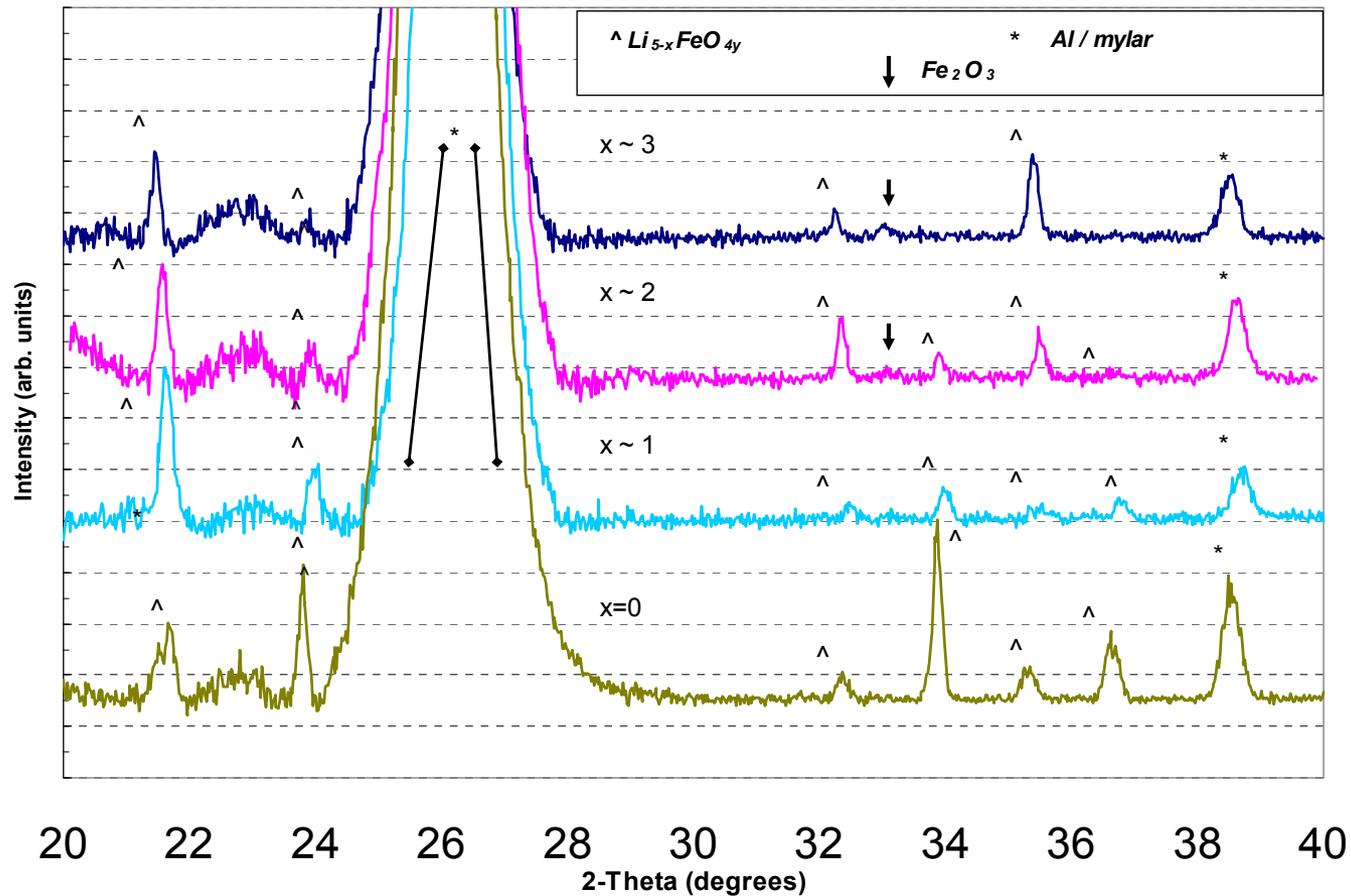
Li_5FeO_4 and Li_2MnO_3 electrodes: full cells



- ✓ Confirms active Li in a Li-ion full cell.
- ✓ The release of Li_2O from Li_5FeO_4 occurs in a lower potential window; thus electrolyte stability is maintained.
- ✓ Li_2MnO_3 and Li_5FeO_4 provide 200 mAh/g during early discharge cycles.
- ✓ Li_5FeO_4 component is suitable for an end-of-discharge indicator when used in combination with higher potential, high-capacity charged cathodes, e.g., LiV_3O_8



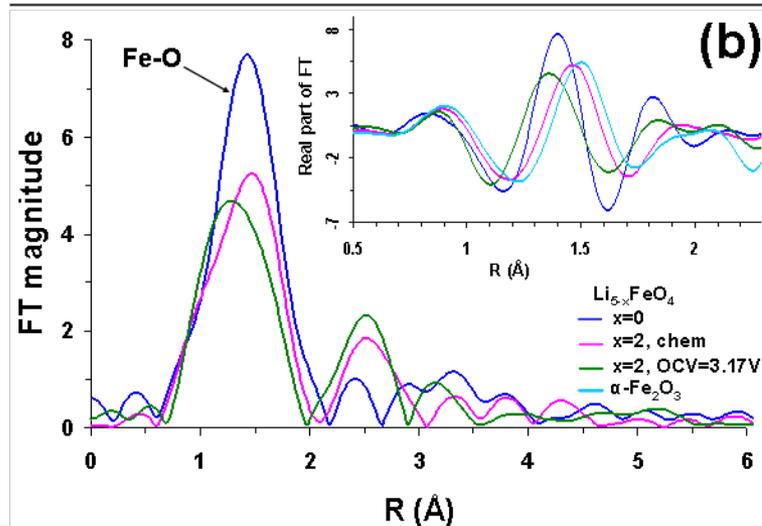
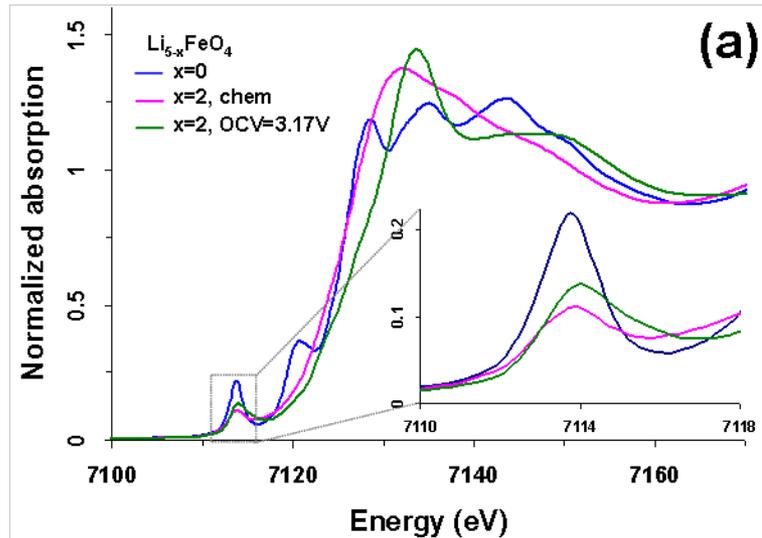
X-ray diffraction of chemically delithiated $\text{Li}_{5-x}\text{FeO}_{4y}$



- ✓ XRD pattern shows evidence of Li_5FeO_4 anti-fluorite structure at $x \sim 3$.
- ✓ The ICP analysis confirms Li/Fe stoichiometry in delithiated samples.
- ✓ Fe_2O_3 was identified with increasing lithium removal (i.e. Li_2O loss).



Fe X-ray absorption results - delithiation of Li_5FeO_4

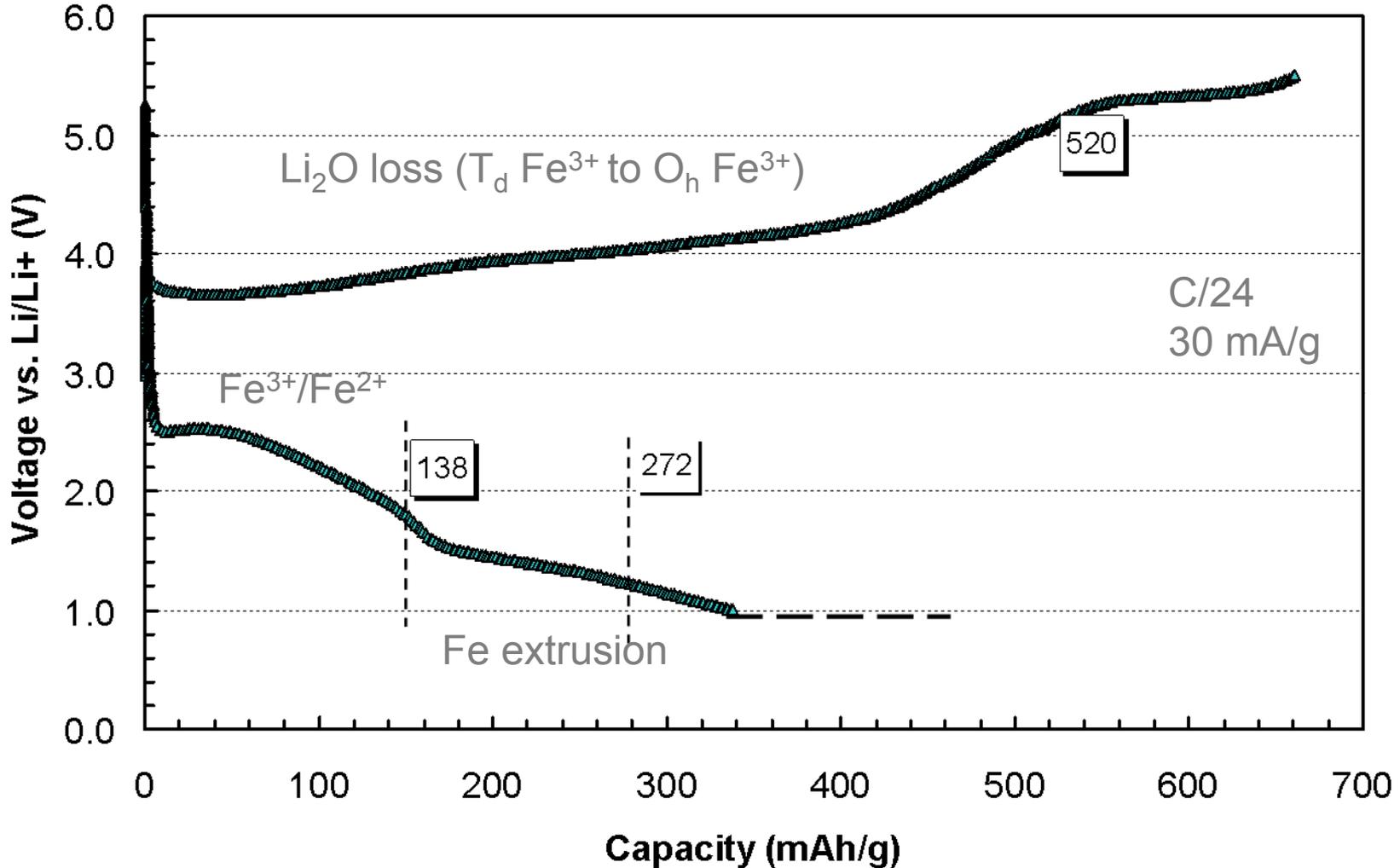


- ✓ Li_5FeO_4 samples chemically delithiated with NO_2BF_4 /acetonitrile solution
- ✓ No apparent change in Fe^{3+} oxidation state
⇒ Li_2O extraction
- ✓ Gradual reduction in pre-edge peak height is consistent with conversion from tetrahedral Fe to octahedral coordination.
- ✓ Evidence of tetrahedral Fe^{4+} in electrochemically oxidized Li_5FeO_4

* M. Balasubramanian, S. Pol (APS)



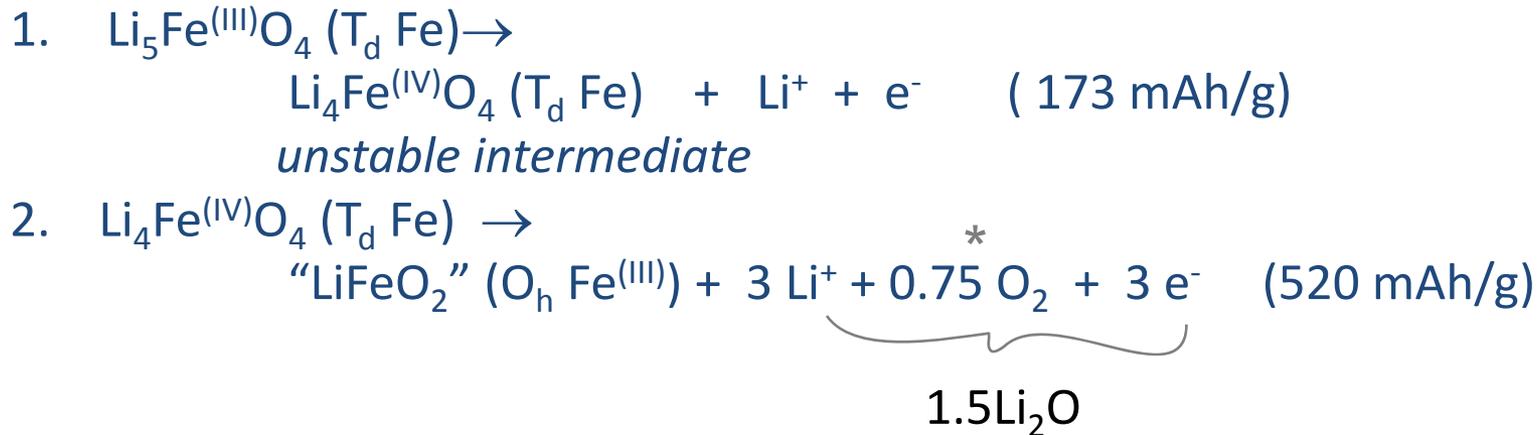
Voltage profile Li/Li₅FeO₄ cell with discharge step



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



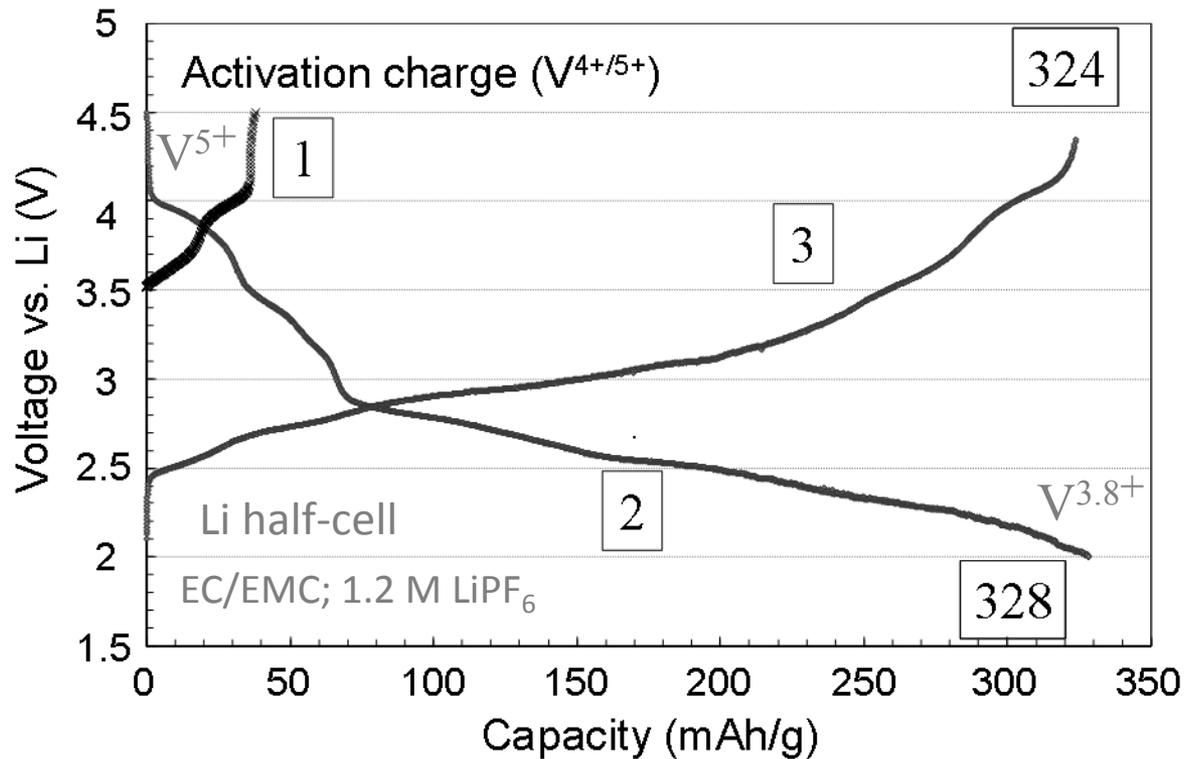
Proposed reaction mechanism



- * This an oxygen loss process; however, if Li_2O can reform with LiFeO_2 to form nanoscopic Li_5FeO_4 , then this material has potential in Li-air applications



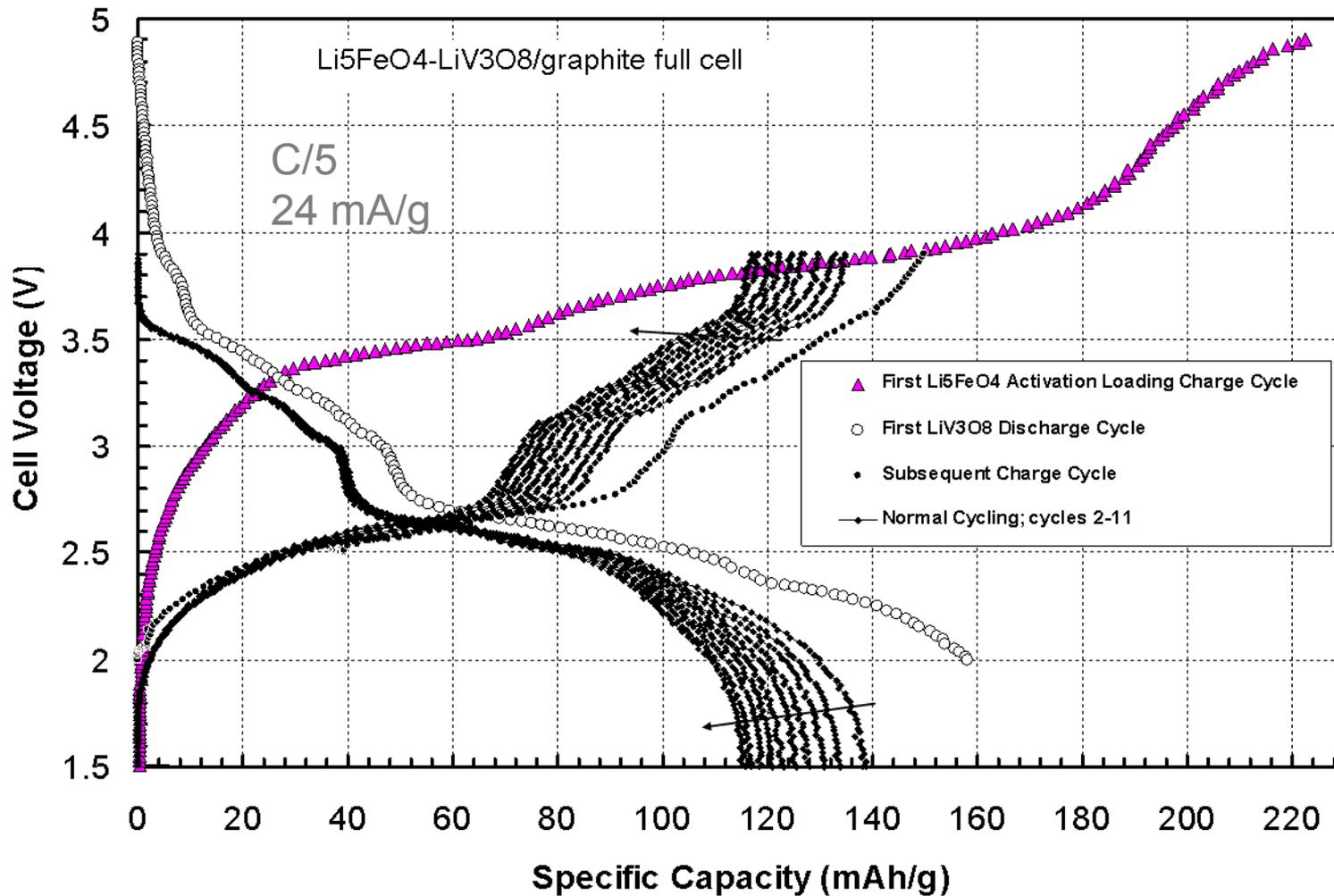
'Charged' electrode: activation charge/discharge cycles: $\text{Li}_{1.2}\text{V}_3\text{O}_8$



- ✓ 0.2 Li^+ can be extracted during an initial charge ($\text{V}^{4+} \rightarrow \text{V}^{5+}$).
- ✓ It is difficult to extract Li_2O from $\text{Li}_{1.2}\text{V}_3\text{O}_8 (\text{Li}_2\text{O} \bullet 3\text{Li}_{0.133}\text{V}_2\text{O}_5)$ below 5.0 V.
- ✓ $\text{Li}_{1.2}\text{V}_3\text{O}_8$ can deliver 328 mAh/g between 4 and 2 V (3.5 Li inserted).



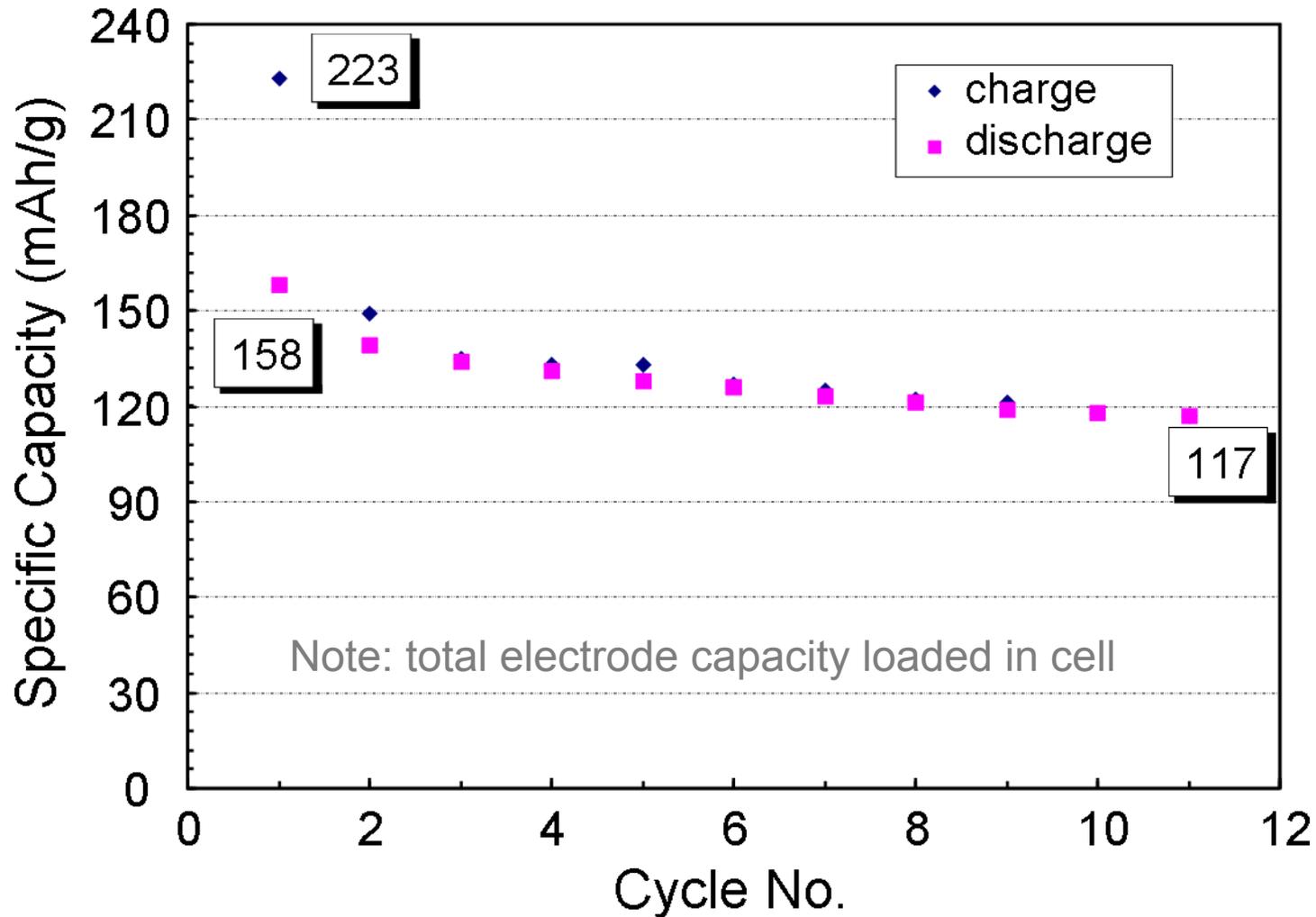
Voltage profiles of C/Li₅FeO₄•LiV₃O₈ cell



✓ Li₅FeO₄/LiV₃O₈ ratio needs to be optimized;
e.g. 30wt.% Li₅FeO₄ would lead to > 200 mAh/g for a C/LiV₃O₈ cell



Capacity vs. cycle number for C/Li₅FeO₄•LiV₃O₈ cell



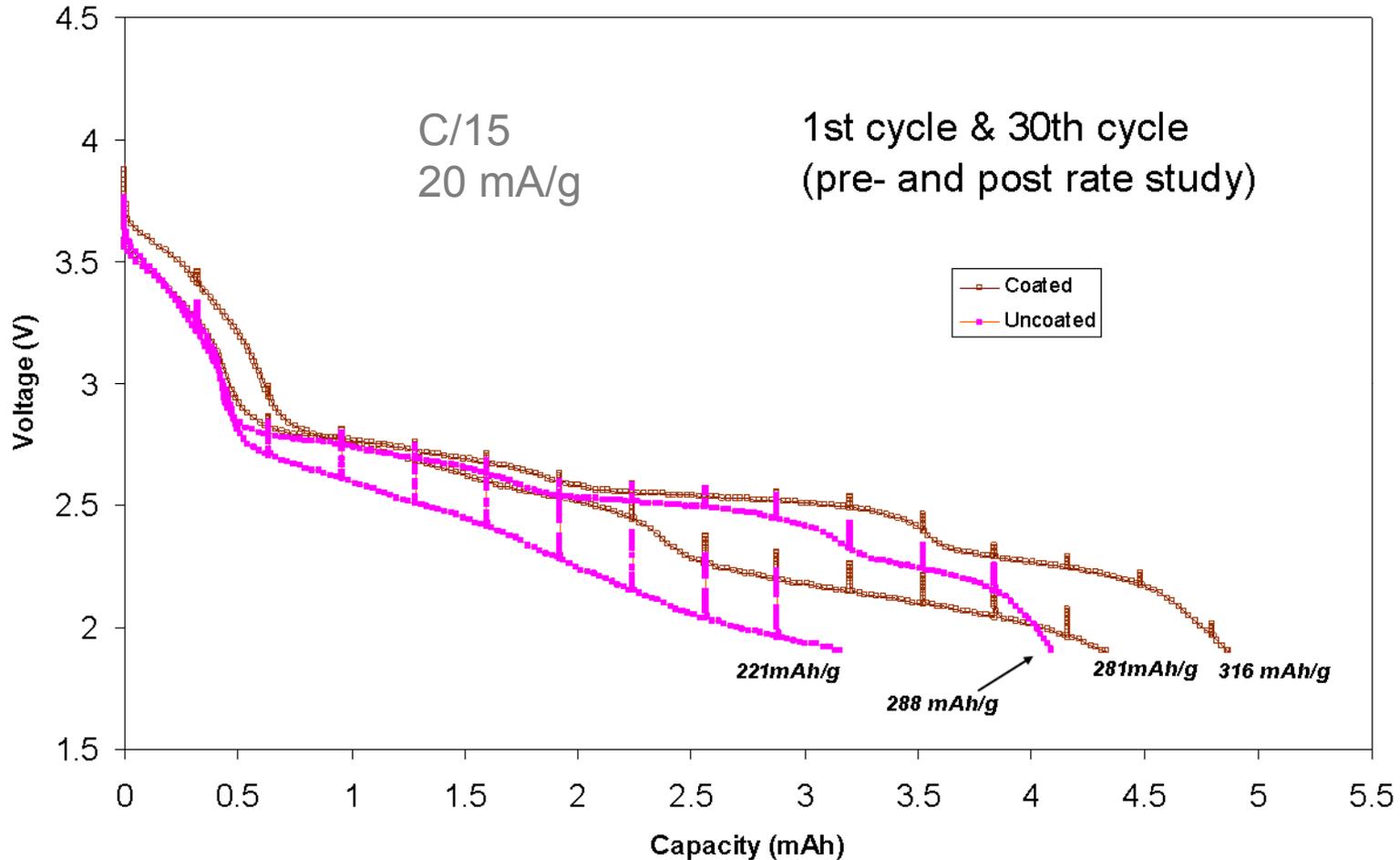
✓ Excellent coulombic efficiency, but some fade occurs in uncoated LiV₃O₈.



Voltage profiles of Li/LiV₃O₈ cells

LiV₃O₈ vs. Al₂O₃-(5wt%) coated LiV₃O₈

Coated Material made by colloidal method

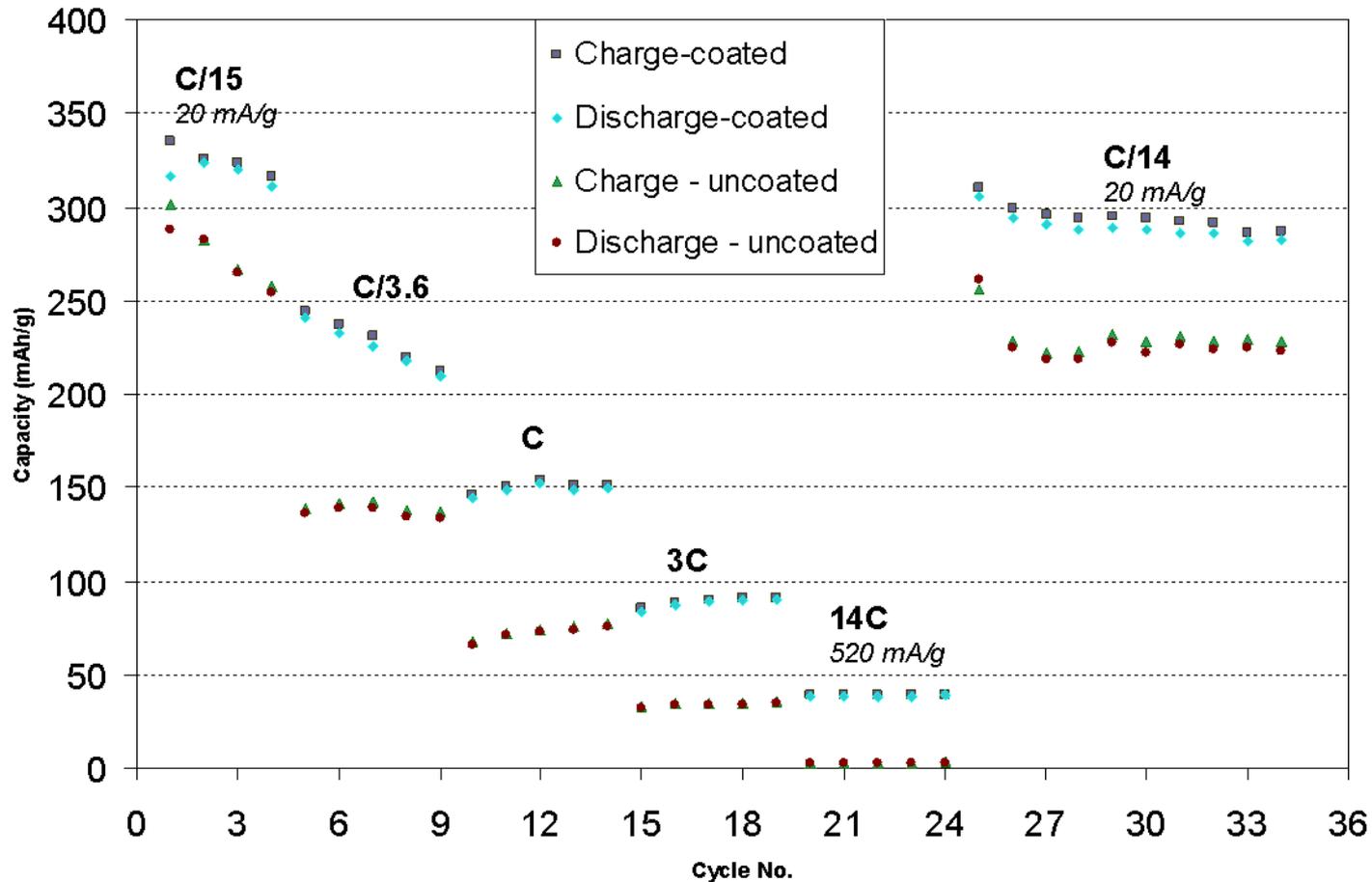


✓ Impedance of coated LiV₃O₈ electrodes is lower than the uncoated type.



Rate study of LiV_3O_8 at various C rates

RATE STUDY - LiV_3O_8 vs. Al_2O_3 (5 Wt%) coated LiV_3O_8

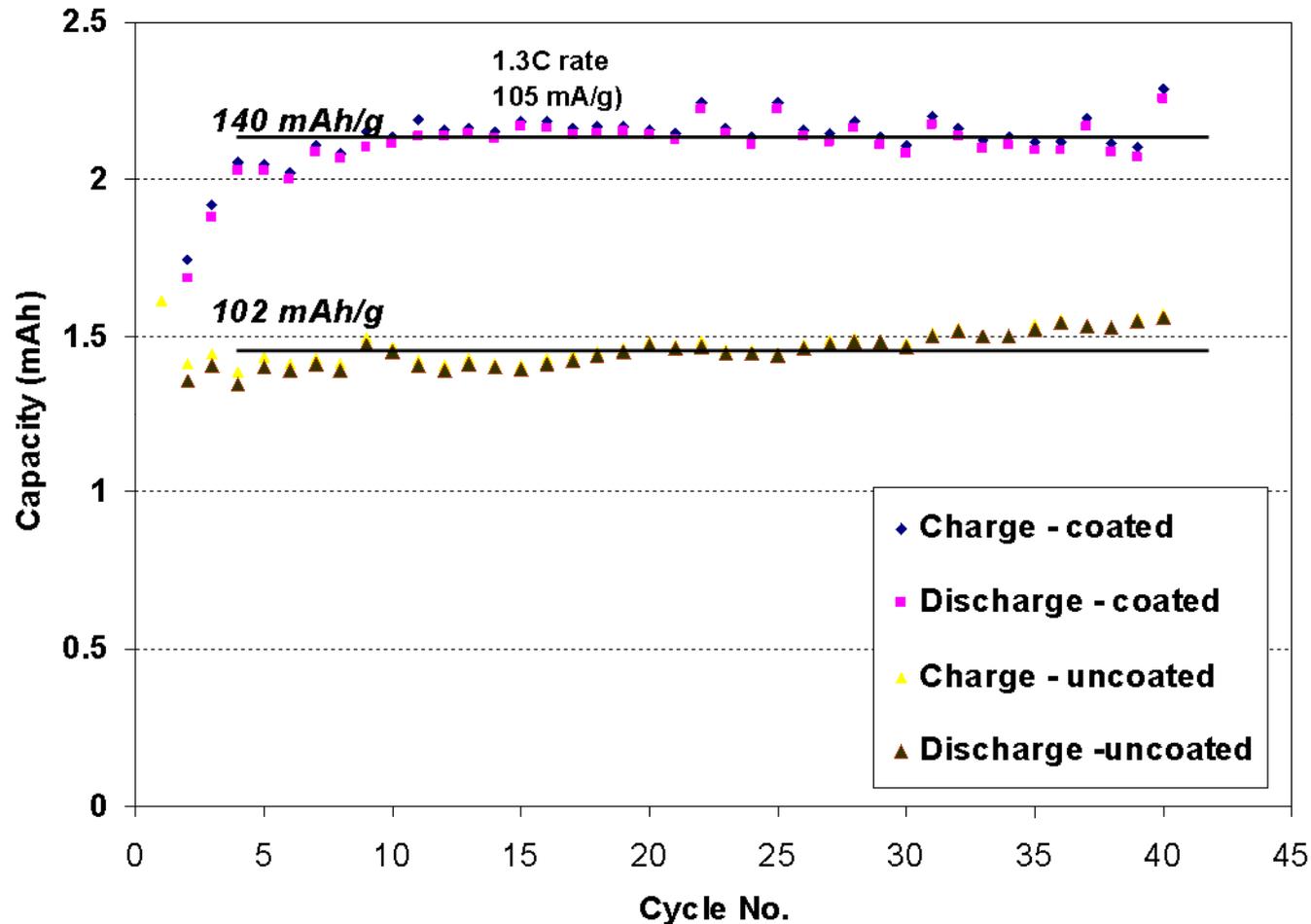


✓ Coated LiV_3O_8 electrodes have $\sim 2x$ the capacity compared to uncoated electrodes at high-rates.



Long-term cycling of LiV_3O_8 at 1.3C rate

Continued cycling LiV_3O_8 vs. Al_2O_3 -coated (5wt.%) coated LiV_3O_8



✓ Vanadium was not detected (EDS) on the Li anode; there is no dissolution of LiV_3O_8 in EC/EMC, LiPF_6 electrolyte.



Model - Li-ion configuration cell calculations

Example - Si/C composite anode

- 1200 mAh/g first cycle, 900 mAh/g reversible capacity...

...a 30% irreversible loss

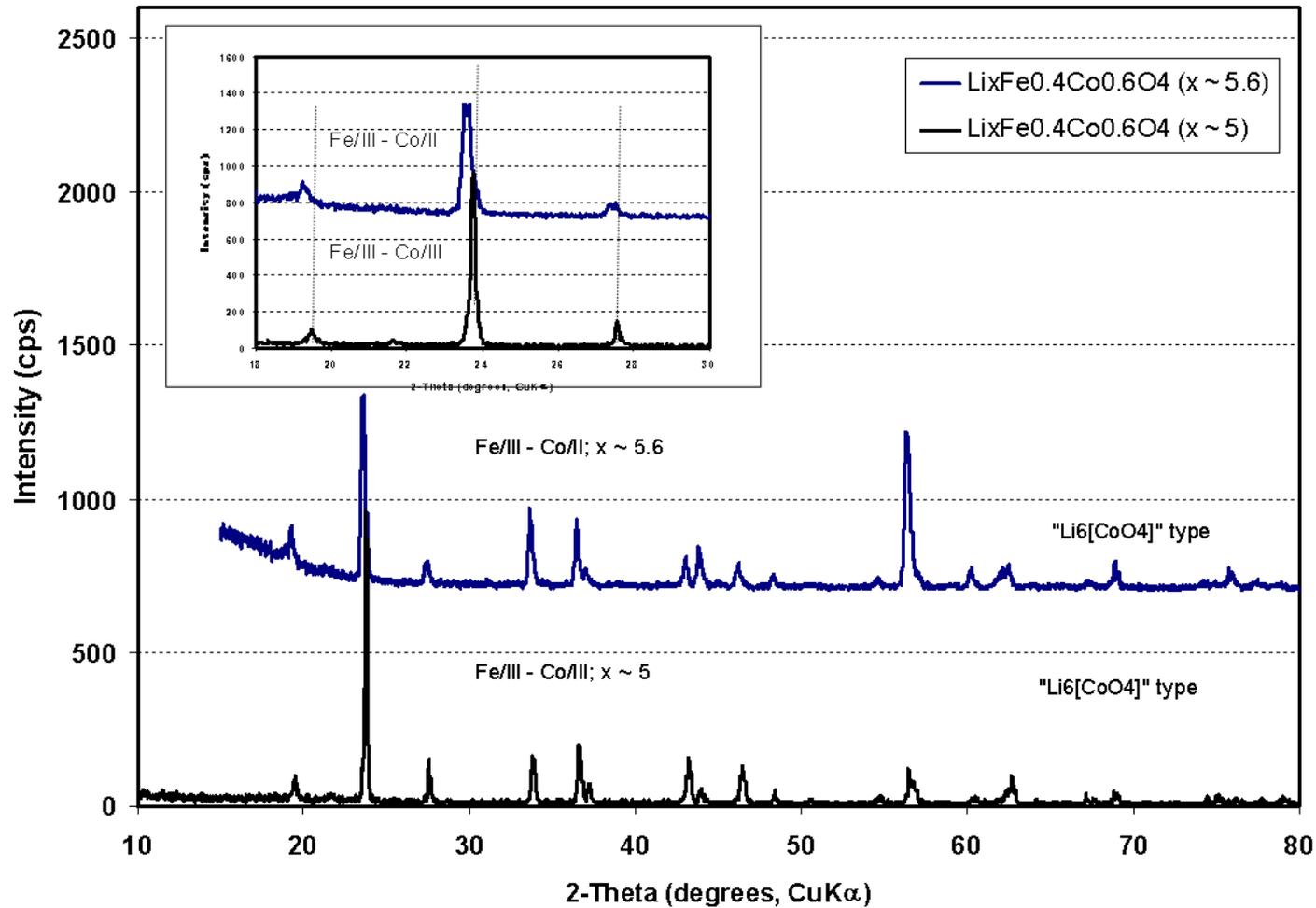
- Neg. loading : **2** mg/cm², yields ~ 1.7 mAh/cm² (after cycling break-in) - > this is a very thin-high specific energy electrode...

...paired with a 30%Li₅FeO₄/70%LiV₃O₈ cathode (w:w)

- Pos. loading : **6.3** mg/cm², yields ~ 1.7 mAh/cm² (after cycling break-in)
- This overall lower negative and positive electrode weights translate into about ~ 1-fold increase in energy density.



Cobalt-substitution into Li_5FeO_4

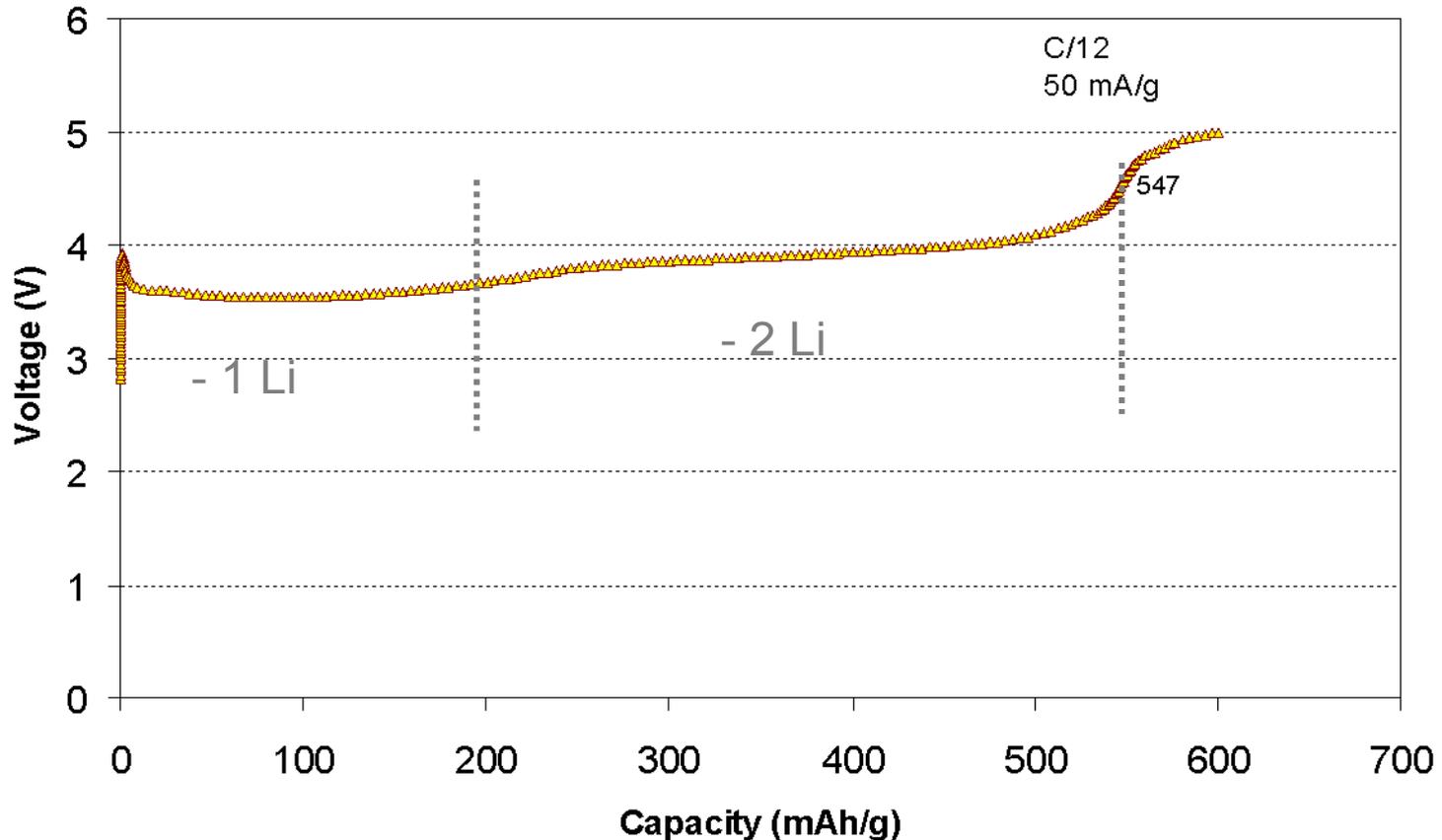


- ✓ Single phase materials synthesized – Co(II) shows larger lattice parameters which may result in a better Li^+ conductivity compared to Li_5FeO_4 .



Li/Co-substituted Li_5FeO_4 voltage profile

$\text{Li}_x\text{Fe}_{0.4}\text{Co}_{0.6}\text{O}_4$ first charge - activation



- ✓ Co oxidation state change is being studied by in-situ XAS.
- ✓ Co-substituted material shows better release of lithium at higher rates.



Collaborations

- **Partners:**

- Industry partner - work-for-others program with a SBIR Company
 - Phase I project titled “Technical Evaluation and Testing of Pre-lithiation Cathodes for Li-ion Batteries” : investigation involves the use of Li_5FeO_4 precursor to load advanced anodes
- Government Laboratory Partners -
 - ES021 ABR project – “Li metal electrodes” (P.I. Dr. Jack Vaughey)
 - 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 $\text{Li}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_4$ will be synthesized, characterized and evaluated; attempts to make pure Li_6CoO_4 , and Li_6MnO_4 will be undertaken.
 - the conditions of release of Li_2O will be better understood and optimized for maximal capacity
- Other charged cathodes such as V_2O_5 , 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 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 LiV_3O_8 identified and tested as a new chemistry for Li-ion cells.
 - Mechanism of lithium removal determined as Li_2O loss; but Fe^{4+} observed in electrochemically charged samples.
 - Cycling yields about 125 mAh/g total electrode.
 - Calculations shows that > 200 mAh/g could be achieved based on blended ratios.
 - This may be a good system for high-capacity advanced anodes such as Si/C.
 - Synthesis has been optimized and cobalt substitutions have been initiated and testing begun.
 - LiV_3O_8 optimization is underway and initial samples have been evaluated.
 - 1.3 C rate (coated LiV_3O_8) = 140 mAh/g in liquid electrolyte

Acknowledgment

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

