

Development of High Energy Cathode Materials

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Project ID#: ES056

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Overview

Timeline

- Start date: Oct. 2010
- End date: Sept.2011
- Percent complete:70%

Budget

- Total project funding
- FY10: 300K (100% DOE)

Barriers addressed

- Low energy/low rate
- High cost
- Cycle life

Partners

- SUNY Binghamton
- ANL
- University of Washington



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Objectives

- Investigate the thermal stability of lithium metal phosphate based cathode.
- Improve the performance of high voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.
- Develop high capacity cathode materials with stable cycling and high rate performances.



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Milestones (FY10-11)

- Synthesize LiMnPO_4 with high performance and investigate their thermal stability. – *Completed*
- Synthesize and optimize the performance of high voltage spinel ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) – *On going*
- Synthesize nano structured vanadium based cathode with high capacity (>300 mAh/g) and rate capability. – *Completed*



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Approach

1. Investigation on the thermal stability of LiMnPO_4

- Synthesize LiMnPO_4 in molten hydrocarbon
- Use electrochemically cycled LiMnPO_4 electrode to replace chemically delithiated sample.
- Investigate thermal stability of LiMnPO_4 using *in-situ* XRD, XPS, SEM-EDAX, TGA-DSC-MS characterizations

2. Synthesis of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

- Starting materials: all low cost (Li_2CO_3 , MnCO_3 , NiO).
- Solid state synthesis: only milling and heating are involved. Easy scale-up.
- Bulk modification: Cr doping
- Surface modification: electrolyte additives, surface coating.
- Investigation of morphology: particle size/morphology, packing density etc.

3. Synthesis of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and LiV_3O_8

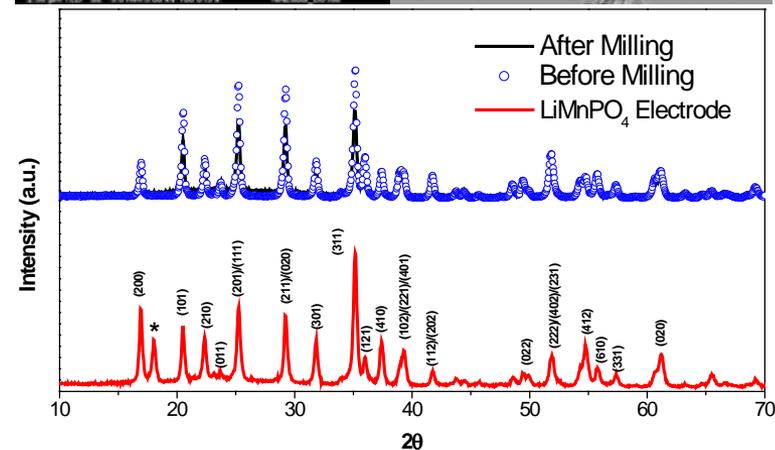
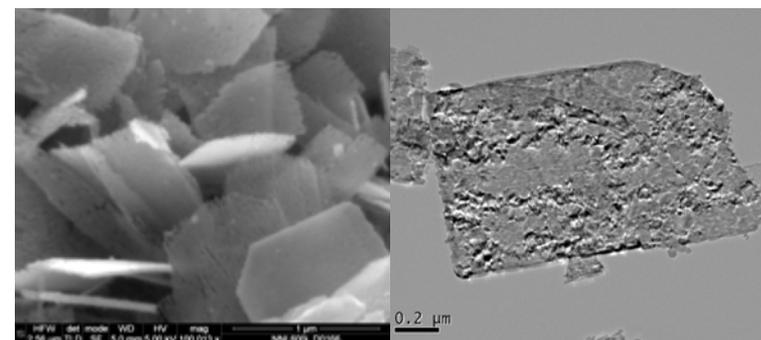
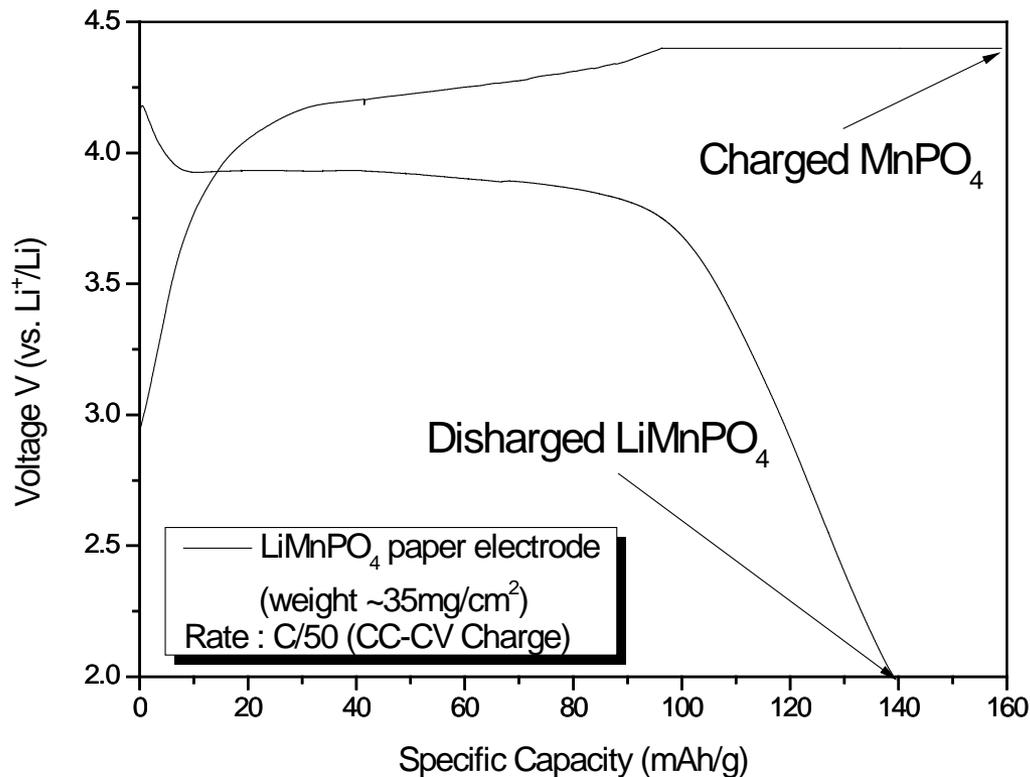
- Two cost-effective solid-state-reaction methods for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$
- Facile solid-state-reaction method for LiV_3O_8



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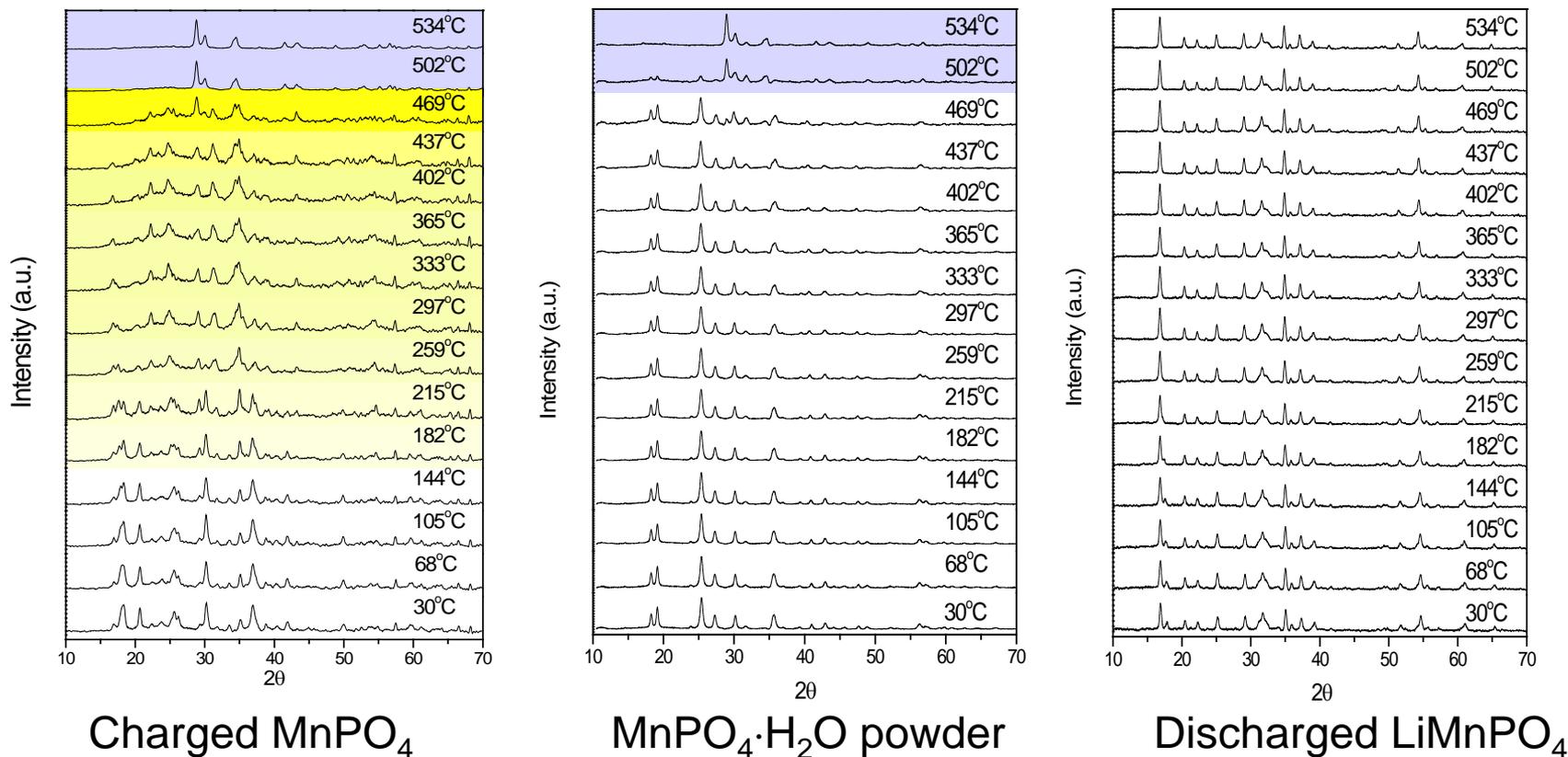
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LiMnPO₄ Electrode for Thermal Stability



- Electrochemically active LiMnPO₄ nanoplates were obtained via molten hydrocarbon approach at 550°C.
- LiMnPO₄ paper electrodes were made for thermal stability study of charged MnPO₄.
- Electrode comprised of LiMnPO₄ : Ketjen black : PTFE = 70 : 22 : 8 wt%.
- Electrodes were collected after electrochemical charge and discharge for stability study.

In-situ XRD on electrochemically cycled LiMnPO_4 and $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ powder as a function of temperature



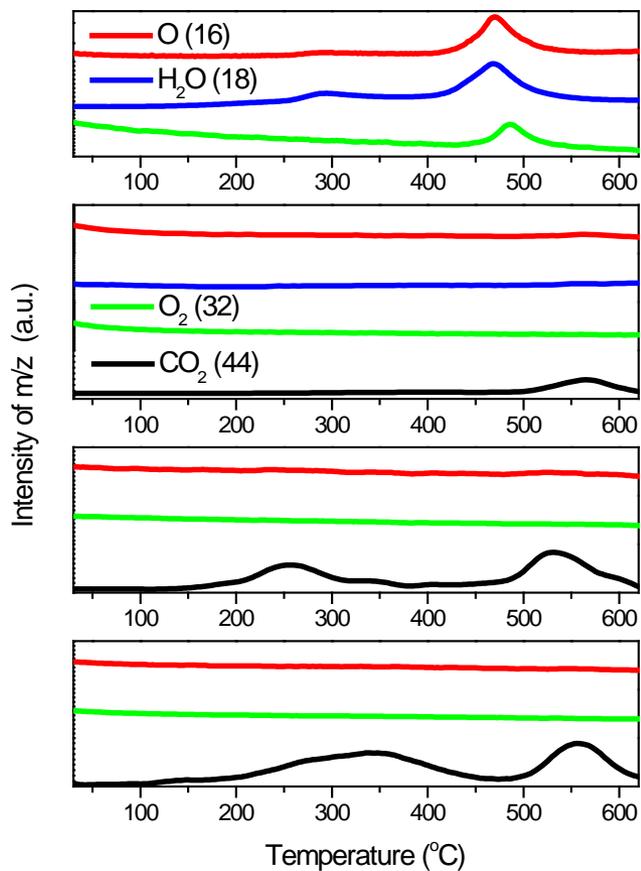
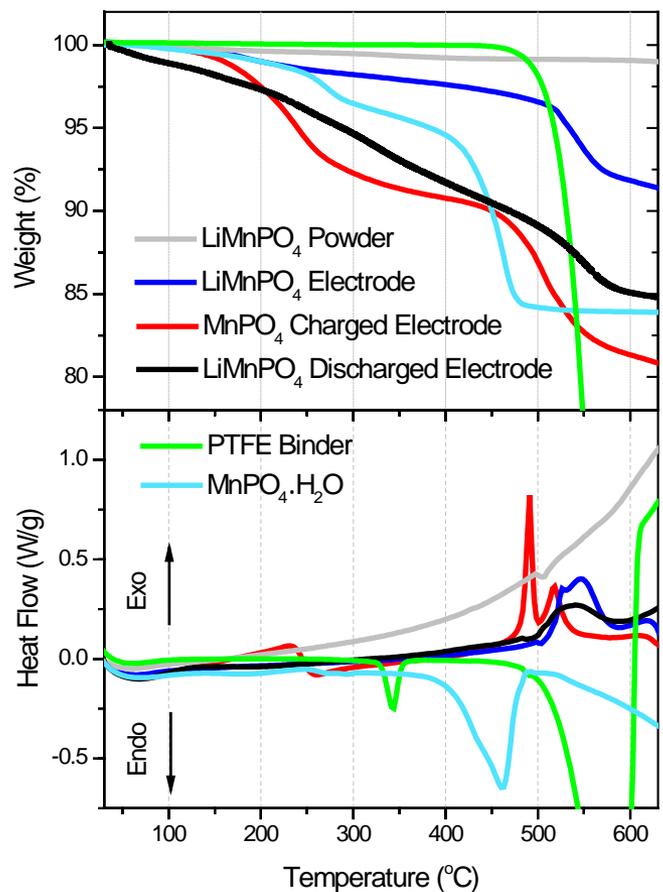
- Charged MnPO_4 electrode undergo structural change (Jahn – Teller Distortion) above 180°C and reduction to $\text{Mn}_2\text{P}_2\text{O}_7$ above 470°C.
- $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ powder undergo reduction to $\text{Mn}_2\text{P}_2\text{O}_7$ above 470°C.
- Discharge LiMnPO_4 electrode was stable up to 534°C.



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TGA-DSC-MS on LiMnPO_4 Electrode



MnPO₄·H₂O

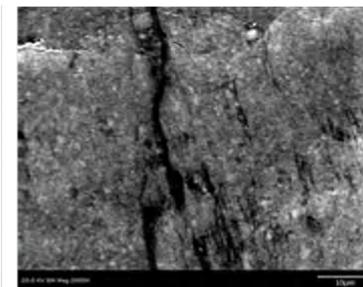
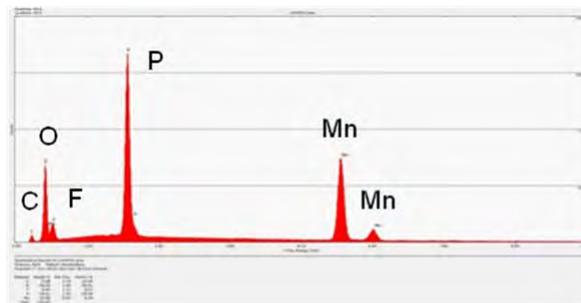
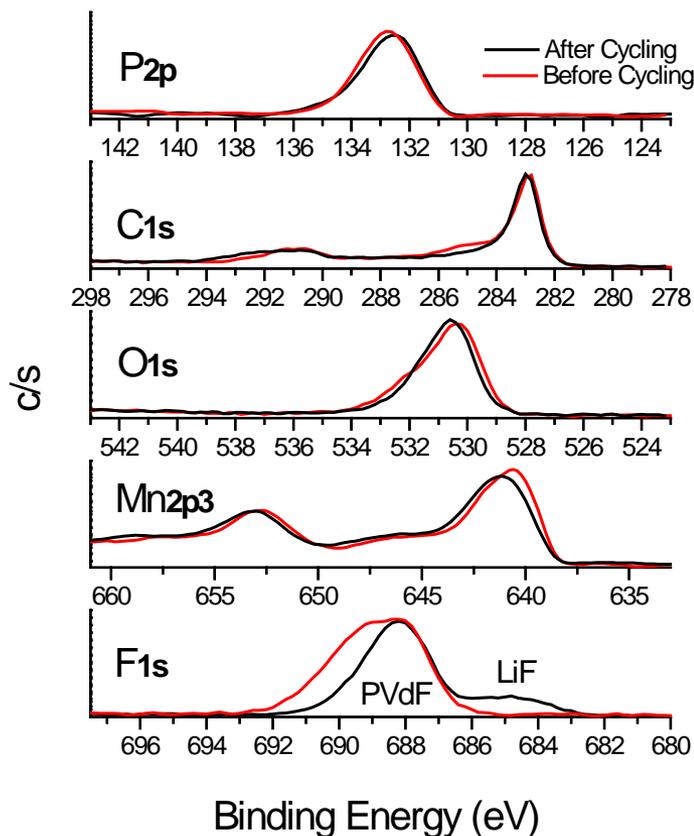
As-prepared
LiMnPO₄ electrode

Charged
MnPO₄ electrode

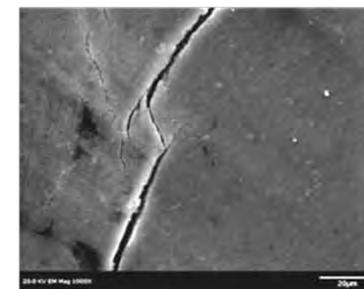
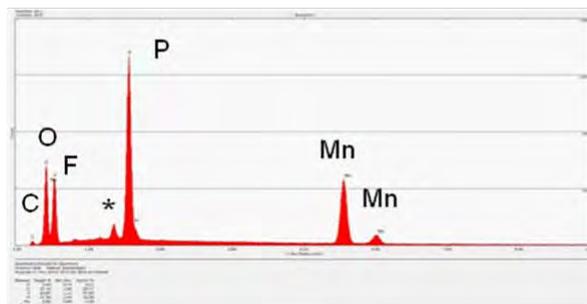
Discharged
LiMnPO₄ electrode

- DSC show sharp exothermic peak at 490°C related to oxygen release during reduction of MnPO₄ to Mn₂P₂O₇.
- No oxygen evolution is observed but most likely to be released as CO₂ (C + O₂ → CO₂).

Surface Chemical Analyses on LiMnPO_4 Electrode



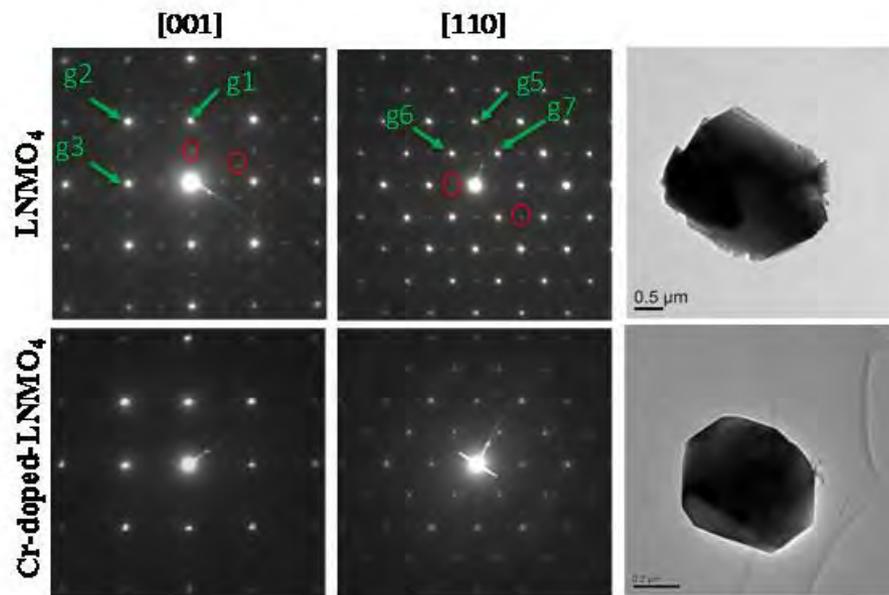
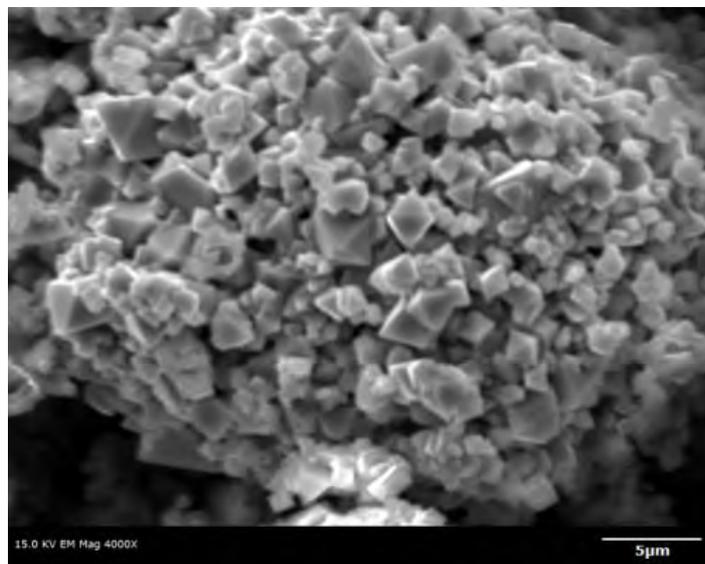
LiMnPO_4 electrode before electrochemical cycling



LiMnPO_4 electrode after 1st cycle (discharged state)

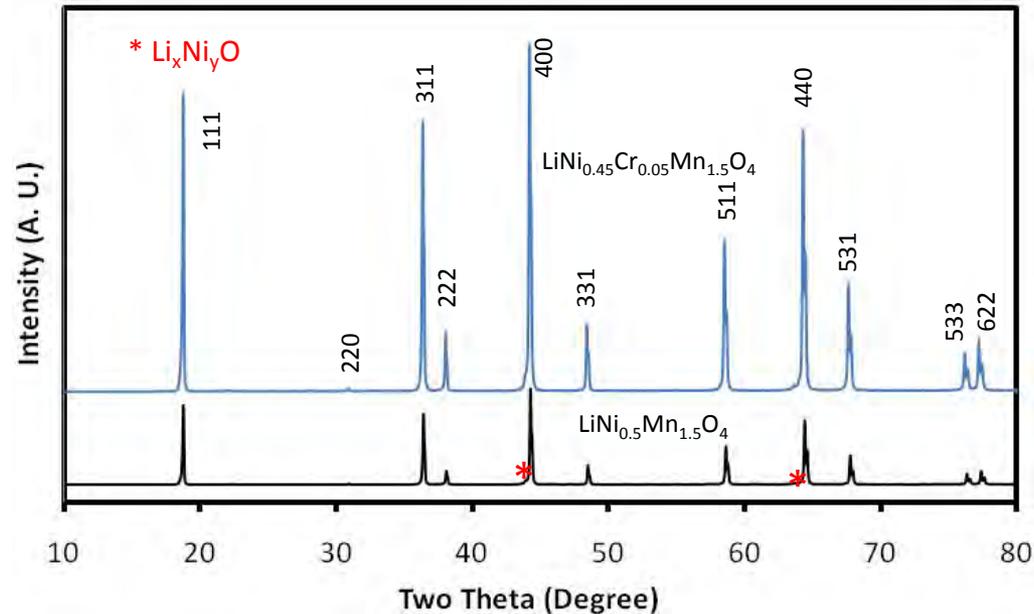
- LiMnPO_4 electrodes before and after electrochemical cycling show increase in F content from both XPS and EDAX.
- This indicates some type of SEI layer formation on the electrode which is responsible for the weight changes below 450°C.

Cr Doping Increased Disorder



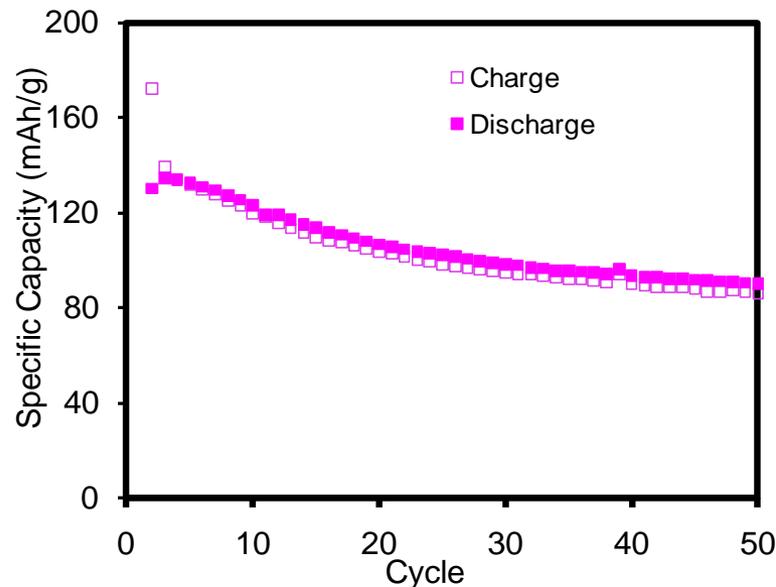
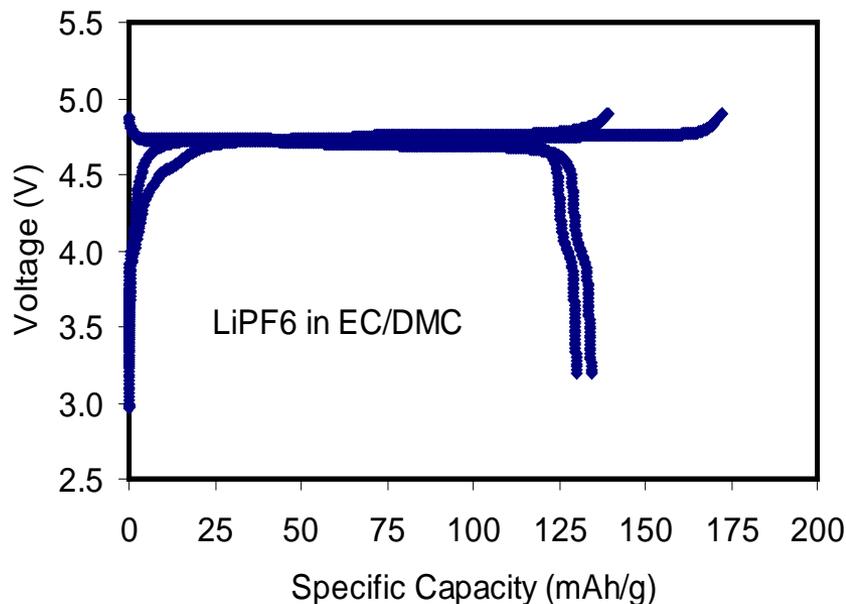
- ✓ As-prepared particles has a large particle size (>2 μm).
- ✓ Micron-sized samples further aggregate into secondary particles beneficial the practical application.
- ✓ LiNi_{0.5}Mn_{1.5}O₄: Mixed phases of disordered and ordered phase (the highlighted reflections are forbidden by Fd $\bar{3}$ m).
- ✓ Cr-doped spinel: The super-lattice pattern is not observable.
- ✓ Cr substitution increases the disordering between Ni and Mn ions (consistent with the volume increase in Cr-doped spinel)

Cr Doping: Reduced Impurity Phase and Increased Disorder



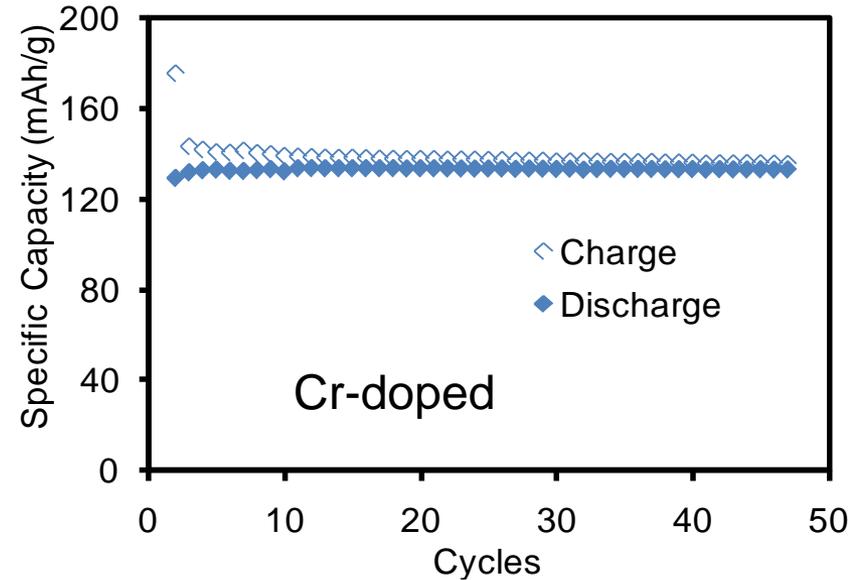
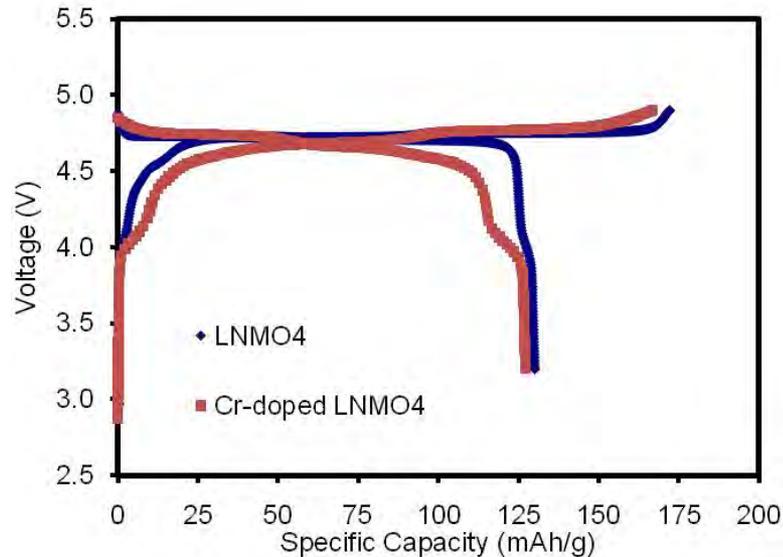
- Both curves can be indexed into $\text{Fd}\bar{3}\text{m}$ (non-stoichiometry disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$)
- Without doping: a small amount of $\text{Li}_x\text{Ni}_y\text{O}$ co-exist.
- After Cr doping: Impurity not detectable.
- Lattice parameter increases after Cr-doping (greater disorder)

Electrochemical Performances of Undoped LNMO₄



- Reversible capacity: 130 mAh/g; 1st cycle efficiency: 75%.
- Mn³⁺ content is minimal as reflected by the short 4.0 V plateau.
- Operation voltage is ~ 4.7 V with small polarization.
- Capacity fading is quick for pure LNMO₄.

Electrochemical Performances of $\text{LiNi}_{0.45}\text{Cr}_{0.05}\text{Mn}_{1.5}\text{O}_4$



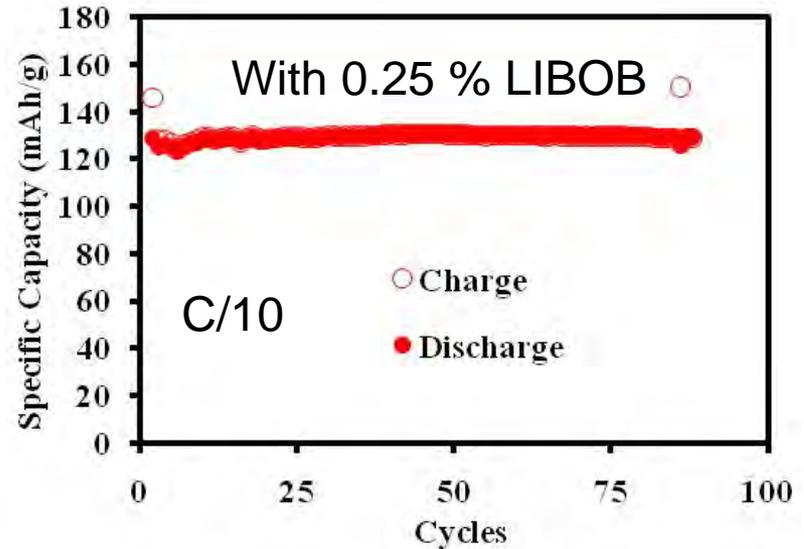
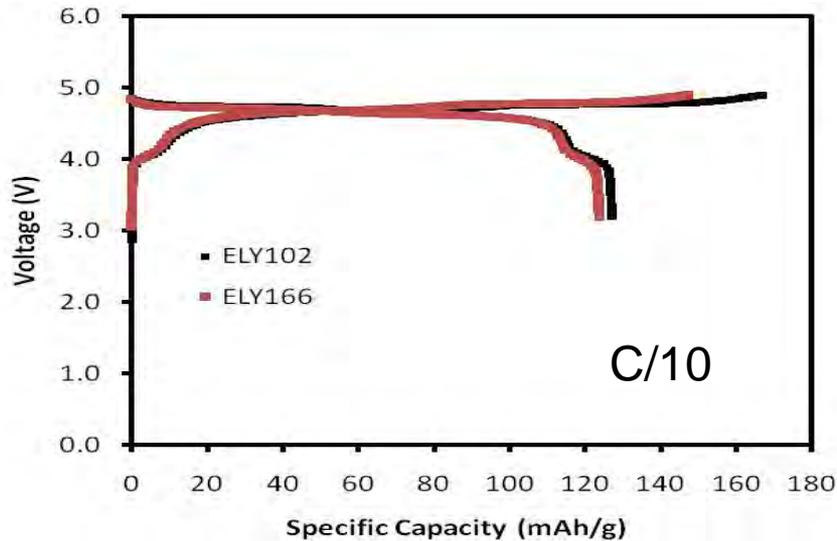
- After Cr-doping:
 - Disordered phase is increased
 - Mn^{3+} content is also increased.
 - The initial capacity is slightly decreased due to Cr-doping
- Very stable cycling is maintained in Cr-doped spinel with reversible capacity at ca. 130 mAh/g.
- The content of disordered phase (Mn^{3+}) is critical for the high performance spinel.



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Electrolyte Additive Improved 1st Cycle Efficiency of $\text{LiNi}_{0.45}\text{Cr}_{0.05}\text{Mn}_{1.5}\text{O}_4$



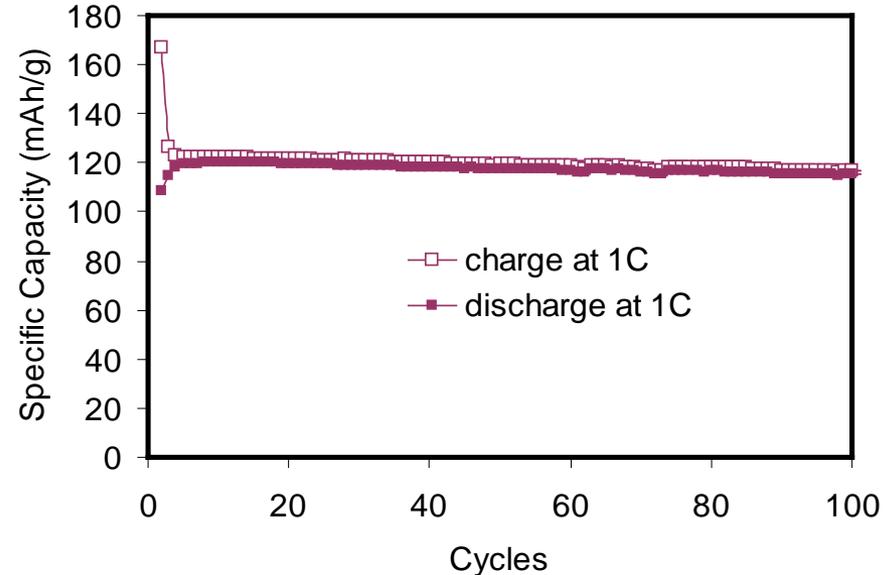
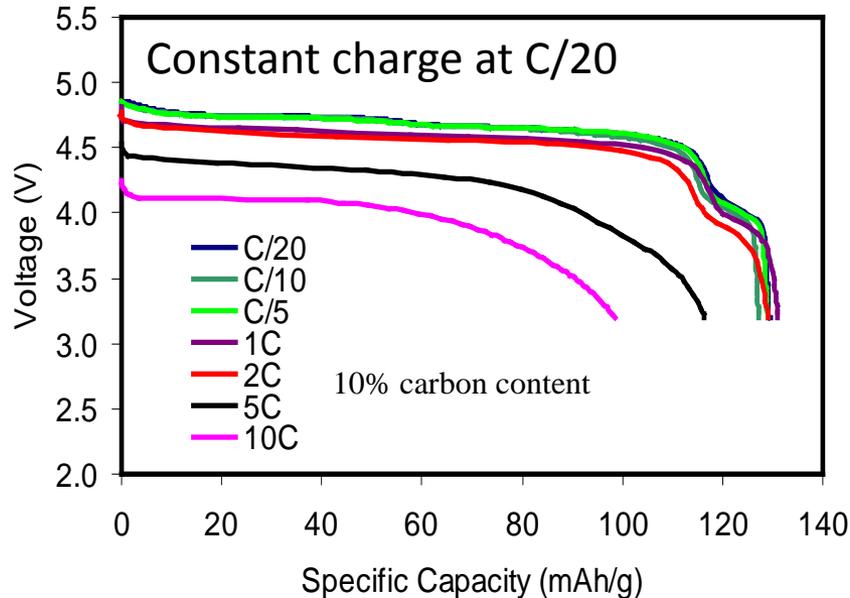
- Without electrolyte additive, 1st cycle efficiency is low (~75%).
- LiBOB additive (0.25%) increased 1st cycle efficiency to 82%.
- Stable cycling almost without capacity fading in the first 80 cycles.
- Electrolyte additive is also important for high voltage spinel.



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Rate Capability of $\text{LiNi}_{0.45}\text{Cr}_{0.05}\text{Mn}_{1.5}\text{O}_4$



- Good rate capability is observed at different rates.
- High voltage spinel does NOT have to go to nano size.
- No need to add a large amount of carbon for good high rate performance.

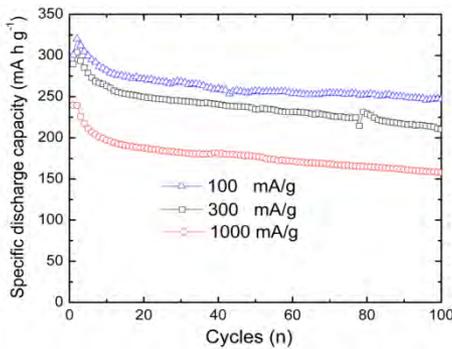
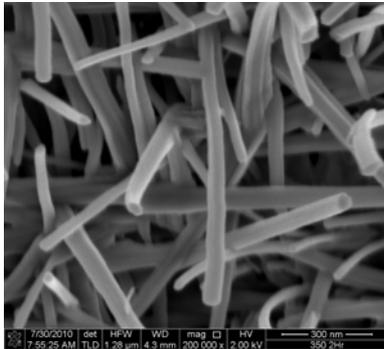


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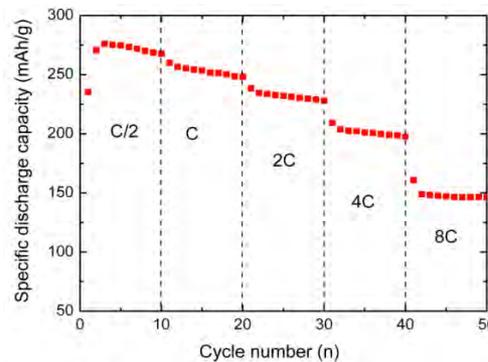
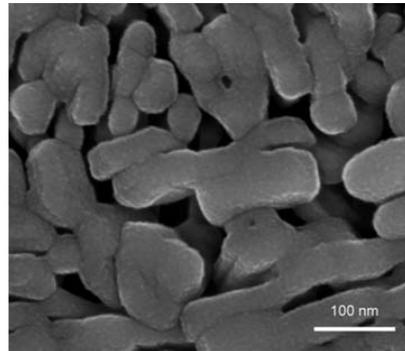
Nano-Engineering Improves Performance of Vanadium Based Cathode Materials

LiV_3O_8 nanorod



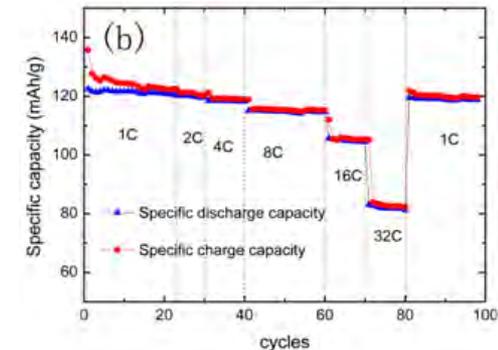
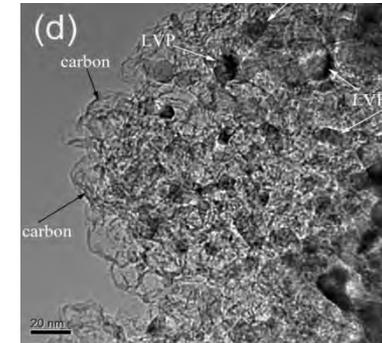
320 mAh/g at C/3

V_2O_5 nanorod



198 mAh/g at 4C

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$ nano particle in carbon matrix



83 mAh/g at 32C rate

Synthesis controls material properties



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Collaboration and Coordination with Other Institutions

Partners:

- SUNY Binghamton (Academic): Magnetic properties of doped LiMnPO_4 .
- ANL (Federal Lab): Provide alternative precursors for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesis.
- University of Washington (Academic): Characterization of vanadium based cathodes.



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Future Work - FY2011/FY2012

- Understand how the disordered content, residual Mn^{3+} and different dopants influence the electrochemical behavior of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.
- Improve the first cycle efficiency and high temperature cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ through surface modification combined with appropriate electrolyte additives.
- Develop spinel/layered cathode composite with improved energy density.

Milestones (FY12)

- Optimization of synthesis approach for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and doped ones. –3/12
- Identification of electrolyte/additive for surface-modification on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. – 6/12
- Synthesis of spinel/layered cathode composite. –9/12



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Summary

1. Improved the performance of high voltage spinel- $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.
 - A facile and cost-effective synthesis approach to prepare high voltage spinel.
 - Cycling performances is significantly improved after Cr-doping.
 - Appropriate electrolyte additives effectively improves the Coulombic efficiency of the first cycle.
2. Investigated the thermal stability of lithium metal phosphate based cathode.
 - Charged MnPO_4 is structurally stable up to 180°C .
 - Oxygen release during reduction occurs at 490°C .
 - Significant amount of SEI layer (~ 10 wt%) is formed during electrochemical charging of LiMnPO_4 cathode.
3. Developed vanadium-based high capacity cathode materials with stable cycling and high rate performances.
 - LiV_3O_8 with High rate performance: 239 mAh g^{-1} at 1000 mA g^{-1} rate and an average capacity fading rate of 0.34% per cycle for 100 cycles.

