Development of High Energy Cathode for Li-ion Batteries

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Project ID#: ES056

Overview

Timeline

- Start date: Oct. 2009
- End date: Sept.2010
- Percent complete:70%

Barriers addressed

- High cost of cathode
- Low energy/low rate
- Safety

Budget

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

Partners

- SUNY Binghamton
- University of Washington

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Objectives

- Develop cost-effective, high energy cathode based on lithium metal phosphate materials suitable for PHEV and EV applications.
- Investigate the feasibility of high capacity cathode based on lithium metal phosphate with high lithium concentration.
- Develop renewable, organic cathode materials with high capacity, stable cycling and high rate performances.

Milestones (FY09)

- Synthesize and characterize $LiMnPO_4$ with high energy (>150 mAh/g) and rate capability. – *on going*
- Investigate the feasibility of Li_2CoPO_4F with two reversible Li^+ ions. – *finished*
- Synthesize and characterize poly(anthraquinonyl sulfide) (PAQS) with redox process based on the quinonyl group (>200 mAh/g). – *on going*

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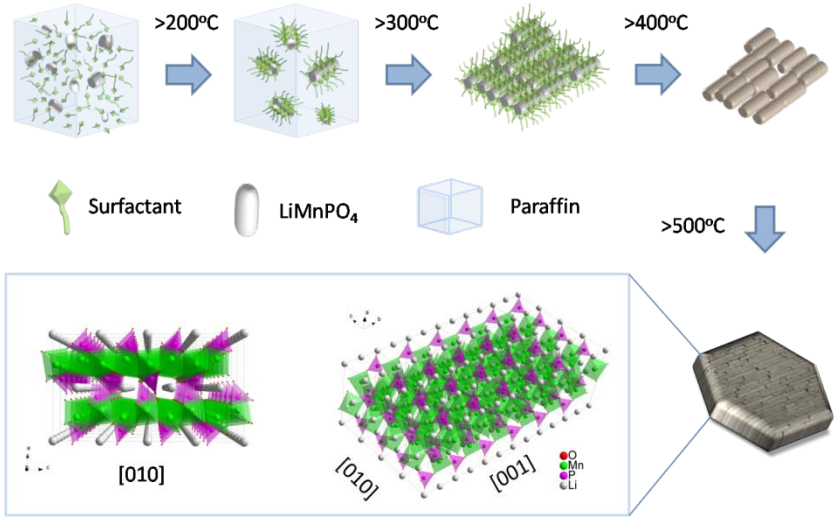
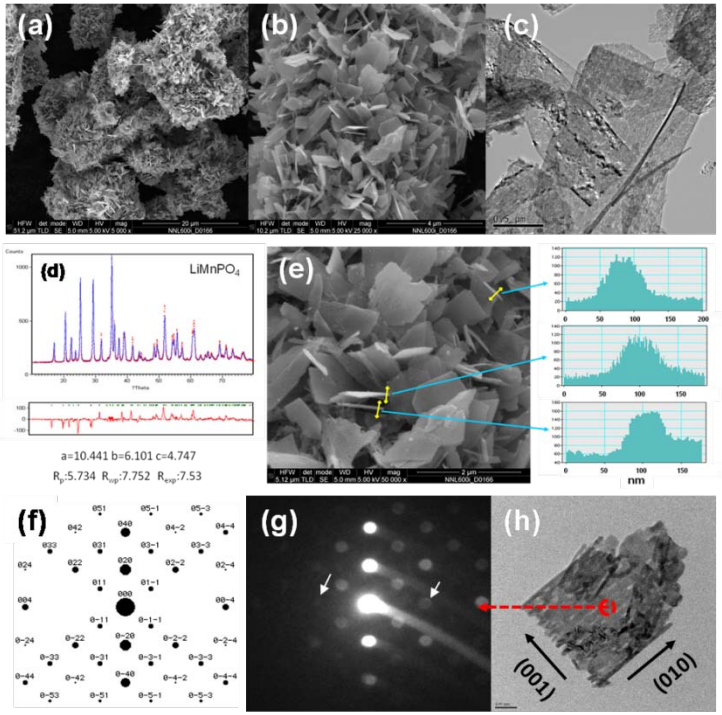
Approach

- Synthesis of $LiMnPO_4$ and Li_2CoPO_4F
  - Single step solid state reaction for $LiMnPO_4$in molten hydrocarbon.
  - Novel and cost-effective precipitation method for $LiMnPO_4$.
  - Optimize the lithium content to improve the long term cycling of $LiMnPO_4$.
  - Solid-state reaction for Li_2CoPO_4F.
- Characterization of cathode candidates for Li-ion batteries
  - XRD and TEM characterization
  - Electrochemical evaluation
  - Investigate on the thermal stability of $LiMnPO_4$.
- Synthesis of renewable organic cathode materials
  - Investigate the effect of electrolytes on the long term cyclability
  - Develop novel binder to further improve the cycling stability and rate performance.

Technical Accomplishments: $LiMnPO_4$ Synthesized in Molten Hydrocarbon Has Preferred Growth Orientation





❖ Oleic acid was used as a surfactant and paraffin acts as a non-polar solvent that facilitate thermodynamically preferred crystal growth without agglomeration.

- Pure phase of $LiMnPO_4$ was obtained after 550ºC calcination.
- As-prepared $LiMnPO_4$ nanoplates are well dispersed without stacking.
- $LiMnPO_4$ nanoplates consists of a porous structure formed by self-assembled nanorods aligned in a preferred orientation with high specific surface area of 37.3m^2/g.

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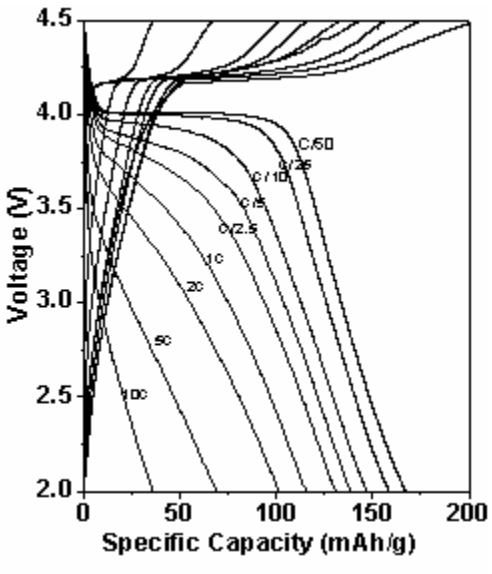
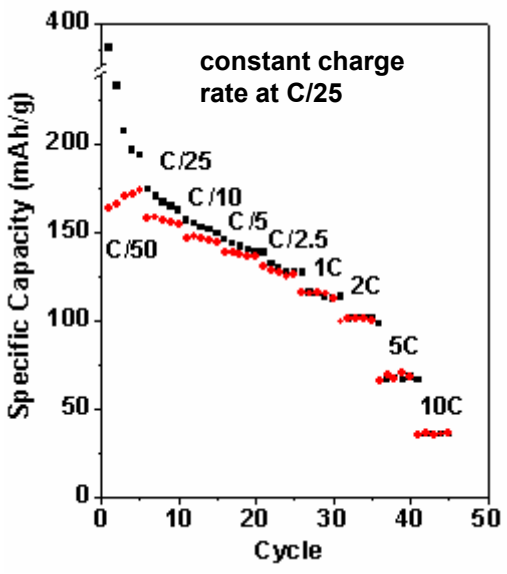
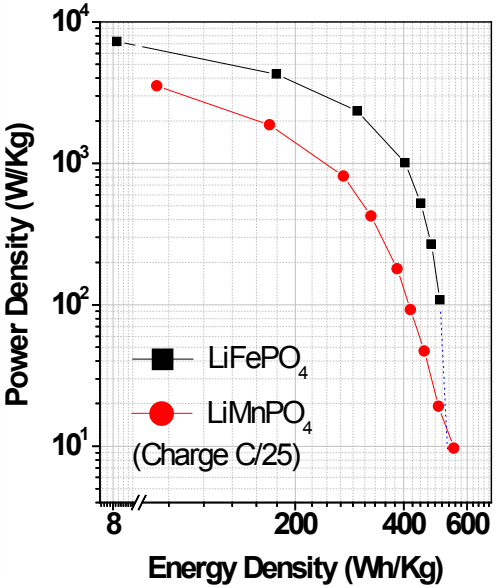
Technical Accomplishments: High Performance $LiMnPO_4$ Synthesized in Molten Hydrocarbon







- Specific capacity of 168mAh/g was achieved which is close to the theoretical capacity of $LiMnPO_4$.
- Flat voltage plateau at ~ 4.1 V indicates the phase transition between $LiMnPO_4$ and $MnPO_4$.
- At 1C and 2C rate (PHEV constant output) capacity retention is 120 mAh/g and 100 mAh/g, respectively.
- Ragone plot indicates that the discharge power density is close in $LiMnPO_4$ and $LiFePO_4$ when fully charged at C/25; At low power (< 30 W/kg), energy density of $LiMnPO_4$ becomes comparable or higher than $LiFePO_4$.

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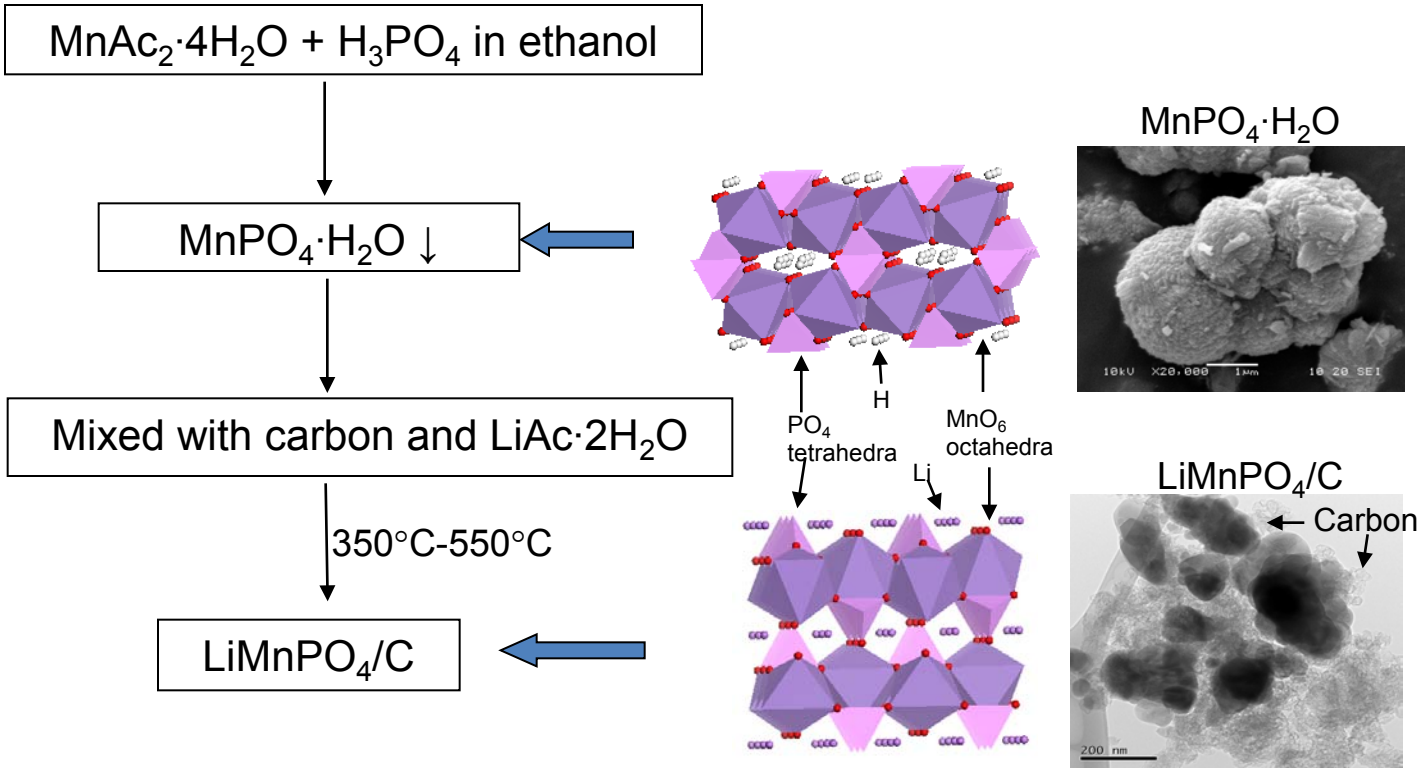
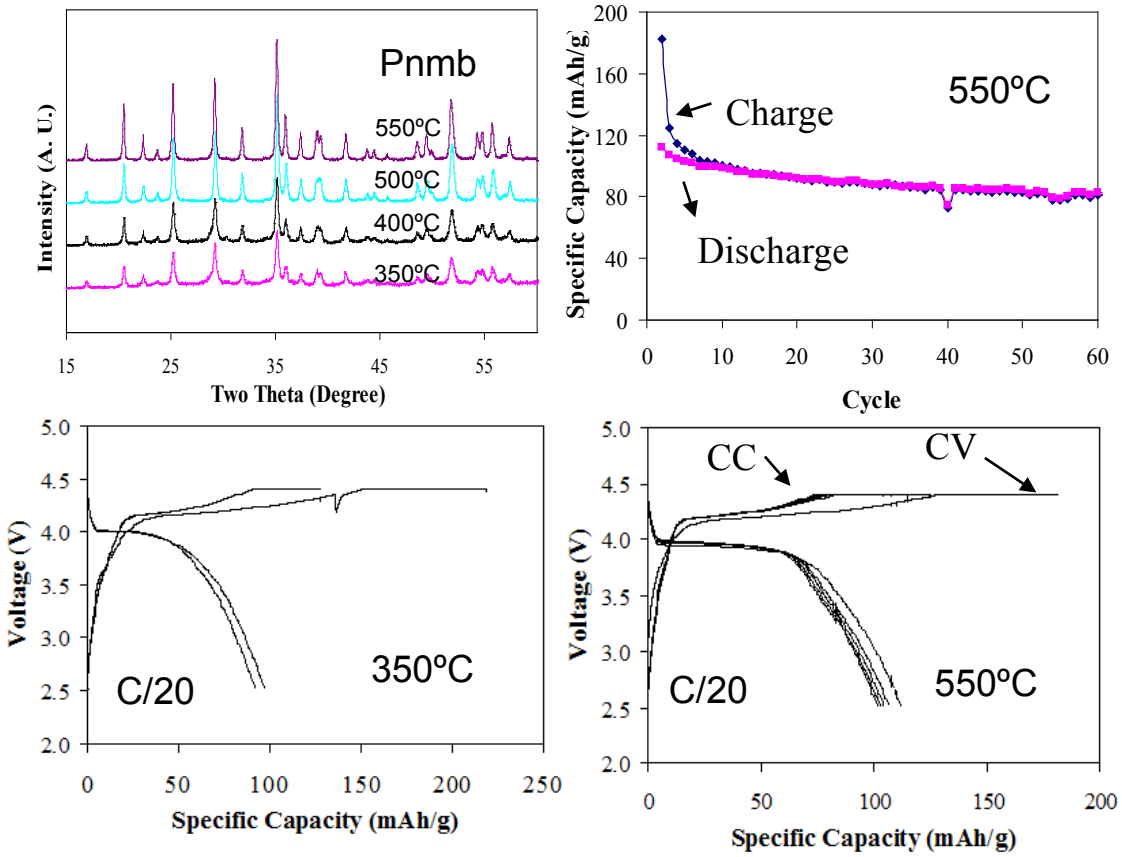
Technical Accomplishments: $LiMnPO_4$ Prepared by Low-cost Precipitation Method



- Cost-effective and environmentally benign.
- $MnPO_4 \cdot H_2O$ precipitated quickly in ethanol; Stable in air for long time storage.
- Uniform nano-sized $LiMnPO_4$ forms at a temperature as low as 350°C due to the structural similarity with $MnPO_4 \cdot H_2O$ precursor.

Technical Accomplishments:
Pure $LiMnPO_4$ Forms at 350°C by Precipitation Method



- Pure $LiMnPO_4$ is obtained at as low as 350°C.
- Complete crystalline $LiMnPO_4$ forms at 550°C.
- Coulombic efficiency increases from 61% to 85% after 1st cycle and then close to ~ 100%.

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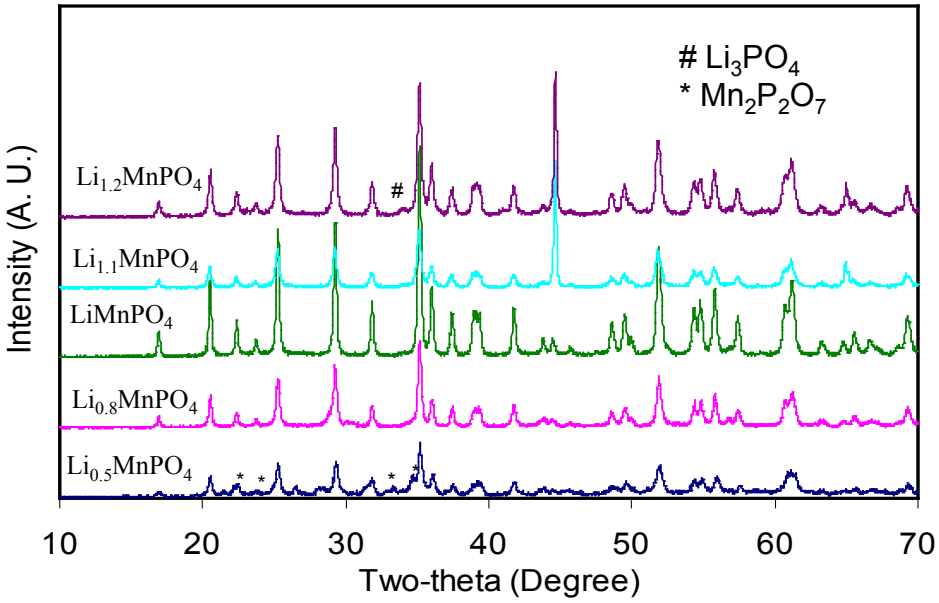
Technical Accomplishments:
First Report on Non-stoichiometric Li_xMnPO_4 (x=0.5~1.2)



	Li (mole)	Mn (mole)	Initial discharge capacity at C/50 (mAh/g)
$Li_{0.5}MnPO_4$	0.492	1	73
$Li_{0.8}MnPO_4$	0.774	1	113
$LiMnPO_4$	0.997	1	135
$Li_{1.1}MnPO_4$	1.078	1	146
$Li_{1.2}MnPO_4$	1.198	1	155

- Precipitation method provides an unique approach to study non-stoichiometry of $LiMnPO_4$ (the conventional methods forms Li_3PO_4 first when using non-stoichiometric ratio of starting materials).
- Single phase does exist between $Li_{0.8}MnPO_4$ and $LiMnPO_4$.
- Very strong peak forms at 44.6° when Li ≥ 1.0.
- Li/Mn ratio in each sample matches well with ICP results.
- At C/50 rate, the initial discharge rate increases with increasing lithium content.

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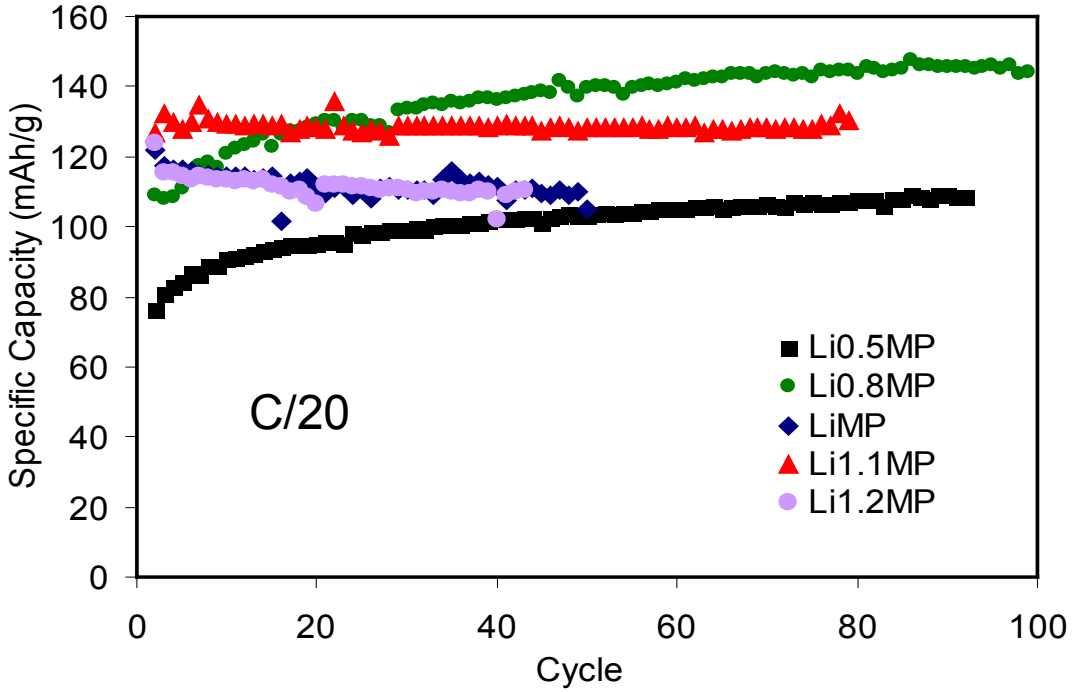
Technical Accomplishments:
Lithium Contents Affect the Electrochemical Performances of Non-stoichiometric Li_xMnPO_4 (x=0.5~1.2)



- The first discharge capacities are ~120 mAh/g for $LiMnPO_4$, $Li_{1.1}MnPO_4$ and $Li_{1.2}MnPO_4$.
- $Li_{1.1}MnPO_4$ exhibits the minimal capacity fading in 80 cycles.
- The increase of discharge capacity with cycling is observed for both $Li_{0.5}MnPO_4$ and $Li_{0.8}MnPO_4$.

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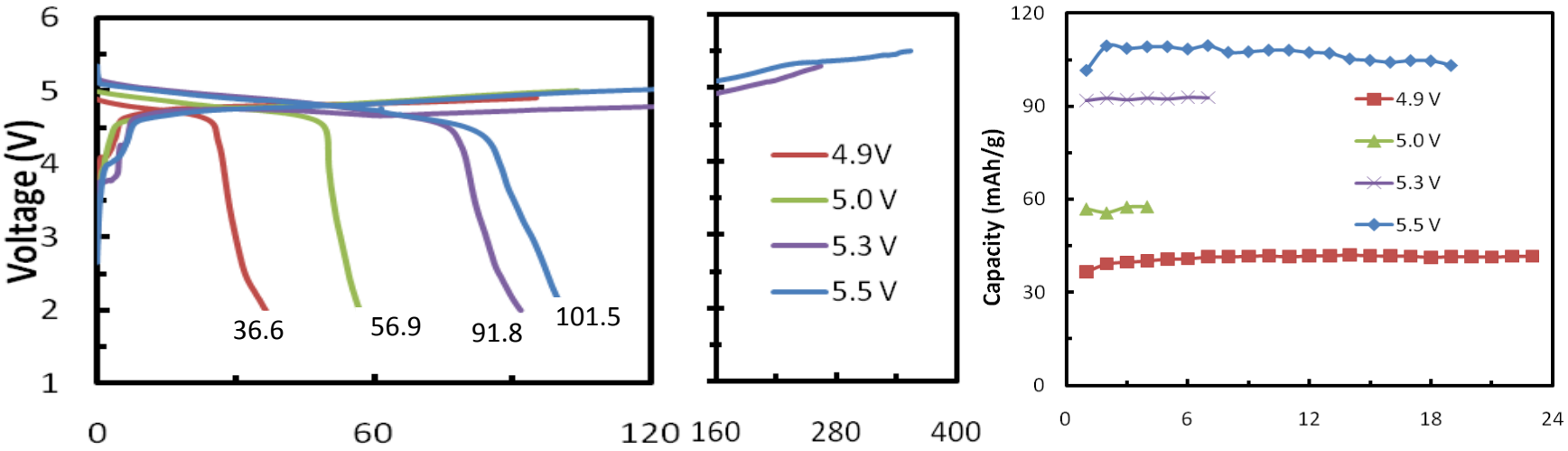
Technical Accomplishments:
1st Report on Electrochemical Cycling Behavior of Li_2CoPO_4F



- Li_2CoPO_4F was prepared by high temperature solid state reactions, in which the mixture of precursors was sintered at 600°C for 24h and then 700°C for another 24h under Ar-H_2 (97.4:2.6, v/v).
- Discharge capacity increases with increasing cut-off voltages.
- Up to one mol Li^+ ions are reversibly extracted/intercalated within 2.0-5.5 V. Second lithium cannot be removed electrochemically, probably due to the strong bonding between F^- and the second Li^+.
- Stable cycling is consistent with the structural evolution observed in XRD pattern.

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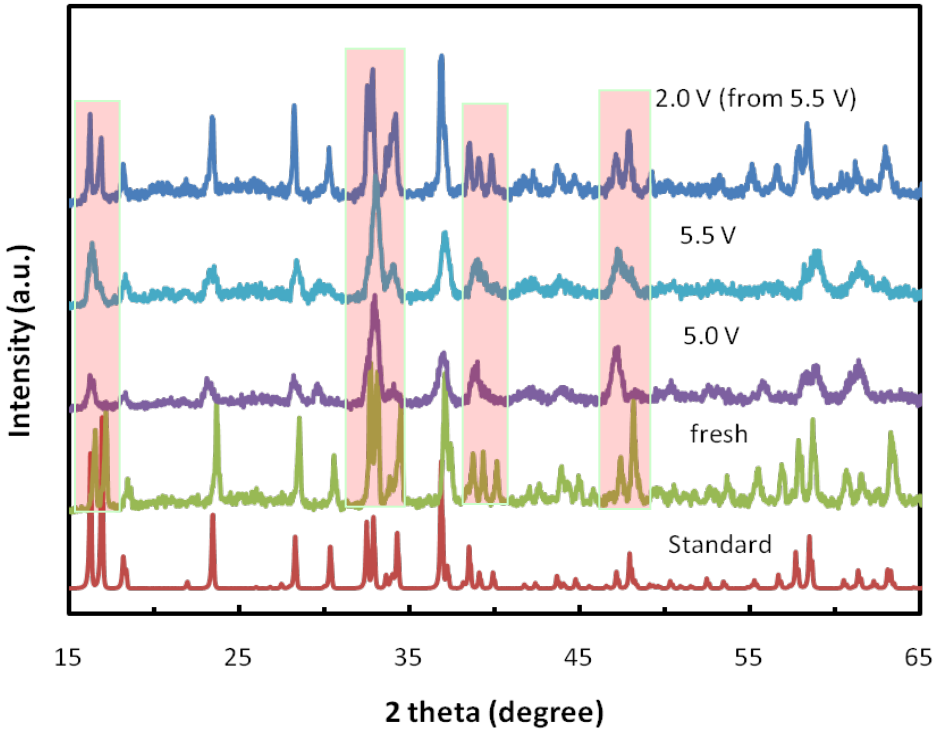
Technical Accomplishments: X-ray Shows Reversible Structural Evolution of Li_2CoPO_4F During Cycling



- Pure phase of Li_2CoPO_4F is synthesized and evaluated.
- Peak broadening occurs when charged to 5.0 V indicating the crystallite amorphization.
- From 5.0 V to 5.5 V minor structural changes are observed suggesting the existence of a stable partially de-lithiated phase at high voltage.
- Li_2CoPO_4F exhibits good structural reversibility when discharged back to 2.0 V.

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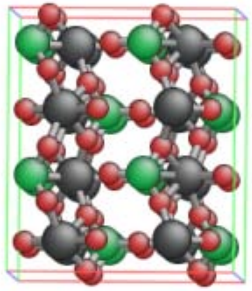
Technical Accomplishments: DFT Analysis on Thermal Stability of T^MPO_4

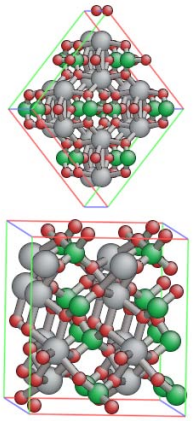


T^MPO_4

pnma

Possible decomposition reaction pathway:

$$2T^MPO_4 \leftarrow \rightarrow T^M_2P_2O_7 + 0.5\ O_2(g)$$

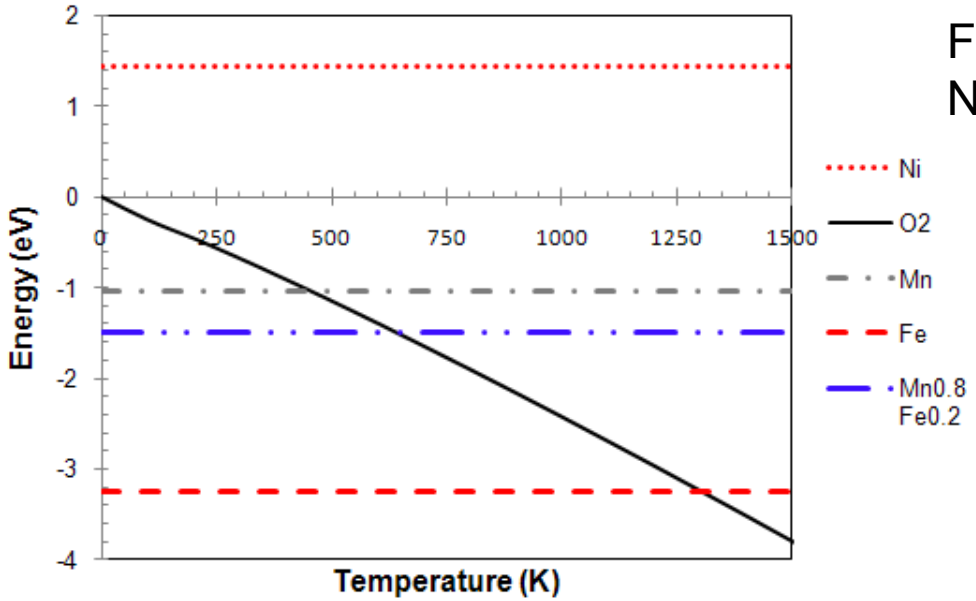


β phase

$T^M_2P_2O_7$

γ phase

Energy difference of $E(2T^MPO_4)-E(T^M_2P_2O_7 + 0.5\ O_{2(0\ K)})$



$Mn_2P_2O_7$: β phase, <0.02 eV/FU lower

Fe_2P2O_7: β phase, <0.01 eV/FU lower

$Ni_2P_2O_7$: γ phase, 0.2 eV/FU lower

- $NiPO_4$: Unstable even at room temperature
- $MnPO_4$: Stable up to 450K

  exp. Value:423~473 K

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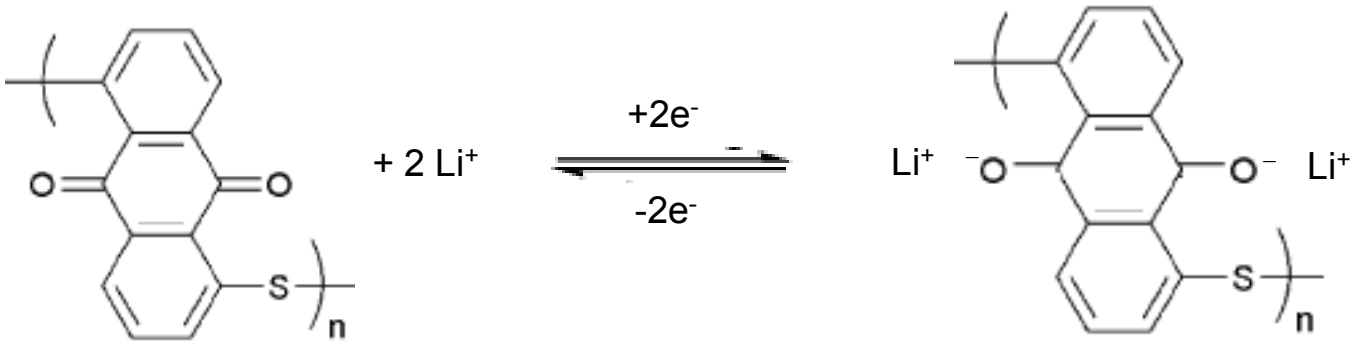
Technical Accomplishments:
Organic Cathodes with 2 Electrons Per Redox Center



Poly(anthraquinonyl sulfide) (PAQS)

- 2 moles of Li^+ reversibly react with PAQS leading to a high theoretical capacity of 225 mAh/g.
- Electrochemically active site is O instead of S on the ring thus S is insoluble in the electrolyte.
- Cost effective and renewable organic cathode is prepared through a simple polycondensation which has already been commercially used in the synthesis of poly(p-phenylene sulfide).

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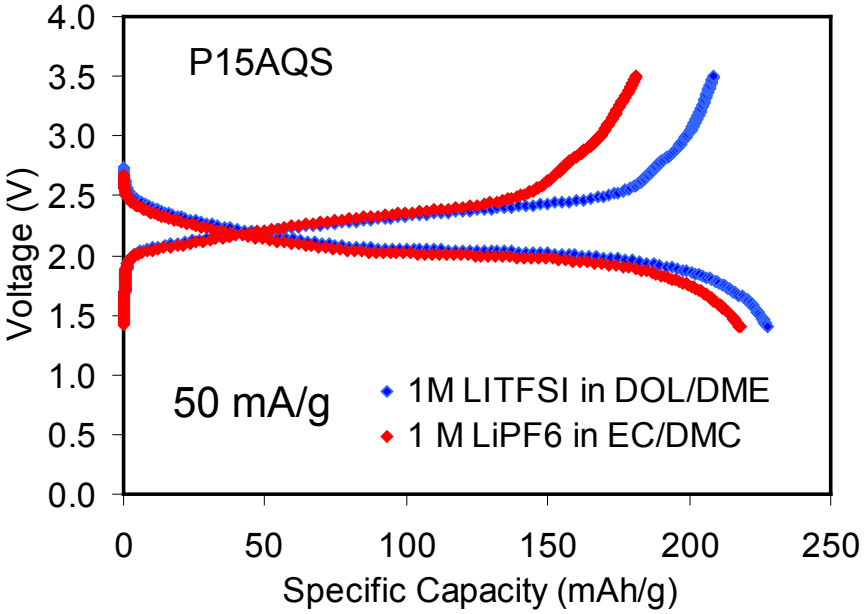
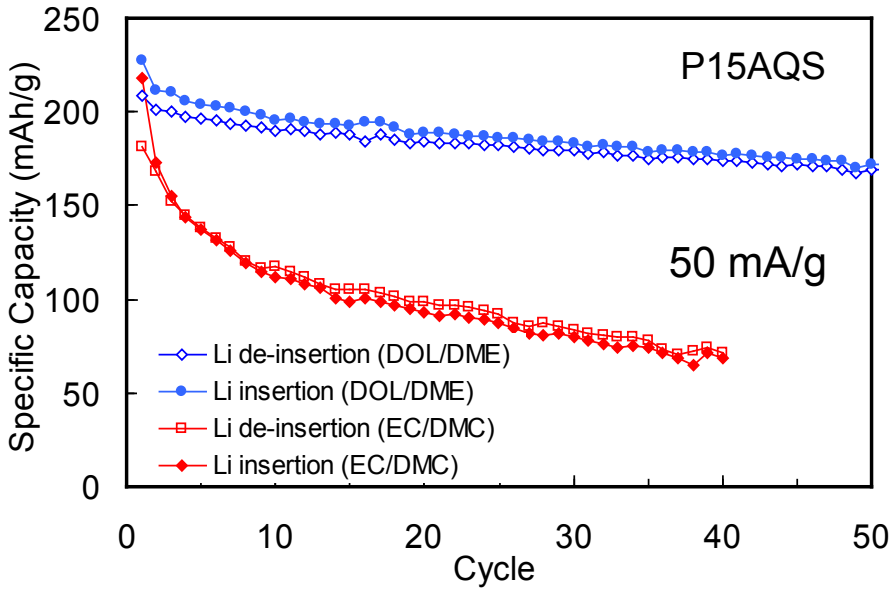
Technical Accomplishments: Electrolytes Strongly Affect the Performances of Organic Cathode





- High reversible capacity above 200 mAh/g.
- Operation voltage is tunable by the addition of functional groups.
- Increased initial capacity and reduced polarization in DOL/DME electrolyte.
- Much more stable cycling in DOL/DME electrolyte than in EC/DMC electrolyte.
- Capacity retention is ~ 80% after 100 cycles in DOL/DME electrolyte.

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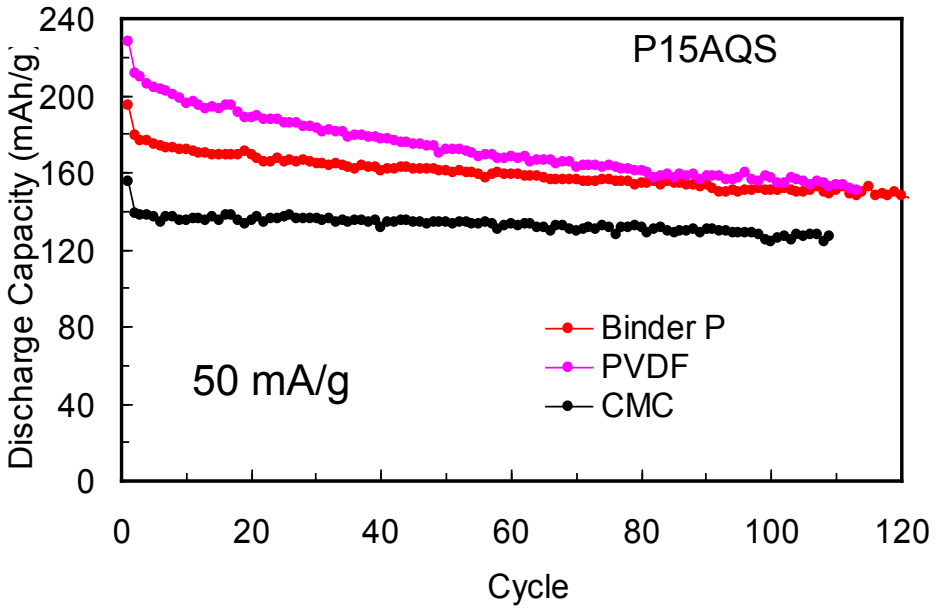
Technical Accomplishments:
Binders Affect The Performances Organic Cathode
(Electrolyte: 1M LITFSI In DOL/DME)



- Initial capacity of P15AQS: PVDF > Binder P> CMC (Binder P represents the new binder developed in PNNL).
- Binder P improves the cycling stability of P15AQS;
- Influences of different binder on the rate capability is under investigation.
- Optimization of carbon/binder P ratio is underway.

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Collaboration and Coordination with Other Institutions

Partners:

- SUNY Binghamton: Collaborations on the characterization of $LiMnPO_4$ prepared by precipitation method.
- University of Washington: Collaborations on the development of high rate cathode $Li_3V_2(PO_4)_3$.

Future Work - FY2010/FY2011

- Optimize $LiMnPO_4$ structure to increase its Coulombic efficiency in the first cycle and the rate capability.
- Continue to investigate the non-stoichiometric Li_xMnPO_4 and prepare gradient concentration phosphate materials -combination of experimental characterization and modeling calculation to understand the influence of lithium content on the performances of phosphates.
- Combination of $LiMnPO_4$ with high voltage cathode($LiNi_{0.5}Mn_{1.5}O_4$) to optimize the electrochemical performance of the whole composite electrode.
- Investigate the high rate performance of $Li_3V_2(PO_4)_3$.
- Increase the operation voltage of organic cathode by adjusting the functional groups on the ring (higher energy density); Improve the cycling stability and rate performance of the organic cathode by optimizing electrolytes and binders.

Summary

- ✓ **High performance $LiMnPO_4$ is successfully prepared through different cost-effective approaches.**
  - High reversible capacity achieves ~ 168 mAh/g at C/25 rate.
  - The electrochemical performances of non-stoichiometric Li_xMnPO_4 ($0.5 \leq x \leq 1.2$) are reported for the first time.
  - Novel findings in $Li_{0.8}MnPO_4$ provide a clue to further activate $LiMnPO_4$ and are now under investigation.
- ✓ **The electrochemical cycling behavior of Li_2CoPO_4F is reported for the first time. Up to 1 mole Li^+ ion is reversible.**
- ✓ **Organic cathodes based on anthraquinone polymer are prepared and characterized.**
  - Initial capacity is above 200 mAh/g.
  - Both binders and electrolytes affect the electrochemical performances of organic cathodes.
  - Stable cycling (>80% capacity retention after 100 cycles) and good capacity retention are observed by using Binder P and the electrolyte composed of 1M LITFSI in DOL/DME.

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- ✓ Team Members:
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