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%

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

## Barriers addressed
- High cost of cathode
- Low energy/low rate
- Safety

## Partners
- SUNY Binghamton
- University of Washington
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$_2$CoPO$_4$F 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
Approach

➢ Synthesis of LiMnPO₄ and Li₂CoPO₄F
  - Single step solid state reaction for LiMnPO₄ in molten hydrocarbon.
  - Novel and cost-effective precipitation method for LiMnPO₄.
  - Optimize the lithium content to improve the long term cycling of LiMnPO₄.
  - Solid-state reaction for Li₂CoPO₄F.

➢ Characterization of cathode candidates for Li-ion batteries
  - XRD and TEM characterization
  - Electrochemical evaluation
  - Investigate on the thermal stability of LiMnPO₄.

➢ 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:
LiMnPO₄ Synthesized in Molten Hydrocarbon Has Preferred Growth Orientation

- Pure phase of LiMnPO₄ was obtained after 550°C calcination.
- As-prepared LiMnPO₄ nanoplates are well dispersed without stacking.
- LiMnPO₄ nanoplates consists of a porous structure formed by self-assembled nanorods aligned in a preferred orientation with high specific surface area of 37.3m²/g.

*Oleic acid was used as a surfactant and paraffin acts as a non-polar solvent that facilitate thermodynamically preferred crystal growth without agglomeration.*
Technical Accomplishments: High Performance LiMnPO₄ Synthesized in Molten Hydrocarbon

- Specific capacity of 168mAh/g was achieved which is close to the theoretical capacity of LiMnPO₄.
- Flat voltage plateau at ~ 4.1 V indicates the phase transition between LiMnPO₄ and MnPO₄.
- 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 LiMnPO₄ and LiFePO₄ when fully charged at C/25; At low power (< 30 W/kg), energy density of LiMnPO₄ becomes comparable or higher than LiFePO₄.
Technical Accomplishments:
LiMnPO$_4$ Prepared by Low-cost Precipitation Method

\[
\begin{align*}
\text{MnAc}_2 \cdot 4\text{H$_2$O} + \text{H}_3\text{PO}_4 \text{ in ethanol} & \rightarrow \\
\text{MnPO}_4 \cdot \text{H$_2$O} \downarrow & \\
\text{Mixed with carbon and LiAc} \cdot 2\text{H$_2$O} & \\
\rightarrow 350^\circ \text{C}-550^\circ \text{C} & \rightarrow \text{LiMnPO}_4 \cdot \text{C}
\end{align*}
\]

- Cost-effective and environmentally benign.
- MnPO$_4 \cdot \text{H$_2$O}$ precipitated quickly in ethanol; Stable in air for long time storage.
- Uniform nano-sized LiMnPO$_4$ forms at a temperature as low as 350$^\circ$C due to the structural similarity with MnPO$_4 \cdot \text{H$_2$O}$ 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%.
Technical Accomplishments:
First Report on Non-stoichiometric Li$_x$MnPO$_4$ ($x=0.5$~$1.2$)

- Precipitation method provides an unique approach to study non-stoichiometry of LiMnPO$_4$ (the conventional methods forms Li$_3$PO$_4$ 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 $\geq 1.0$.

- Li/Mn ratio in each sample matches well with ICP results.

- At C/50 rate, the initial discharge rate increases with increasing lithium content.
Technical Accomplishments:
Lithium Contents Affect the Electrochemical Performances of Non-stoichiometric \( \text{Li}_x\text{MnPO}_4 \) \( (x=0.5\text{~}1.2) \)

- The first discharge capacities are \(~120\) mAh/g for \( \text{LiMnPO}_4 \), \( \text{Li}_{1.1}\text{MnPO}_4 \) and \( \text{Li}_{1.2}\text{MnPO}_4 \).
- \( \text{Li}_{1.1}\text{MnPO}_4 \) exhibits the minimal capacity fading in 80 cycles.
- The increase of discharge capacity with cycling is observed for both \( \text{Li}_{0.5}\text{MnPO}_4 \) and \( \text{Li}_{0.8}\text{MnPO}_4 \).
Technical Accomplishments:

1st Report on Electrochemical Cycling Behavior of Li$_2$CoPO$_4$F

- Li$_2$CoPO$_4$F 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.
Technical Accomplishments:
X-ray Shows Reversible Structural Evolution of Li$_2$CoPO$_4$F During Cycling

- Pure phase of Li$_2$CoPO$_4$F 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$_2$CoPO$_4$F exhibits good structural reversibility when discharged back to 2.0 V.
Technical Accomplishments: DFT Analysis on Thermal Stability of TMPO₄

Possible decomposition reaction pathway:

2TMPO₄ ⇌ TM₂P₂O₇ + 0.5 O₂(g)

Energy difference of $E(2TMPO₄) - E(TM₂P₂O₇ + 0.5 O₂(0 K))$

- Mn₂P₂O₇: β phase, <0.02 eV/FU lower
- Fe₂P₂O₇: β phase, <0.01 eV/FU lower
- Ni₂P₂O₇: γ phase, 0.2 eV/FU lower

- NiPO₄: Unstable even at room temperature
- MnPO₄: Stable up to 450K
  exp. Value: 423~473 K
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).
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.
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.
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$_3$V$_2$(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$_x$MnPO$_4$ 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$_3$V$_2$ (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 ≤ x ≤ 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: