Phase Behavior and Solid State Chemistry in Olivines

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May 20, 2009

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OVERVIEW

Timeline

- PI Joined BATT 2001
- Cathodes Task Started 2001
- Anodes Task Started 2006

Barriers Addressed

- Cycle life
- Abuse tolerance
- Energy density

Budget

• FY08	$500K
• FY09	$500K
• FY10	TBD

Partners

- Collaborations: Grey (Stony Brook) Kostecki, Doeff, Cabana (LBNL) Gabrisch (UNO), NCEM, ALS
- Interactions: Zaghib (HQ)
- Project lead: John Newman

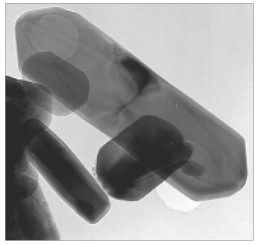
OBJECTIVES

- Synthesize and evaluate new electrode materials with improved energy density.
- Investigate the relationships of structure, morphology and performance of electrode materials, with emphasis on phosphates and intermetallics.
- Explore kinetic barriers and utilize the knowledge gained to design and develop electrodes with high energy density, good rate performance and enhanced stability.

MILESTONES

June 2008	Report rate and cycling performance of lithium alloy and/or cermet electrodes with capacity exceeding 400 mAh/g.
July 2008	Report results of phase transition, rate and stability studies of Li_xMnPO_4 cathode materials.
June 2009	Report rate and cycling performance of Li alloy and/or intermetallic electrodes with capacity exceeding 500 mAh/g.
July 2009	Report on mechanisms governing $LiMnPO_4$ performance and measures to improve utilization and rate.
September 2009	Report experimental results on new cathode materials.

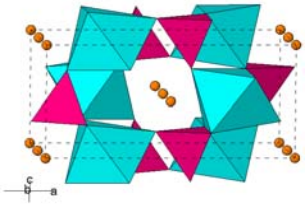
APPROACH



- Identify candidate electrode compositions by systematic analysis of phase diagrams and literature reports.
- Synthesize novel materials and/or unique structures for examination using XRD, electron microscopy, vibrational spectroscopies, and electroanalytical techniques.
- Characterize known and modified electrode materials (e.g. $LiMnPO_4$) and establish correlations between crystal structure, morphology and performance.

APPROACH – $LiMnPO_4$

	$LiFePO_4$		$LiMnPO_4$
Voltage	3.4 V		4.1 V
Capacity	170 mAh/g		171 mAh/g
Density	3.6 g/cm^3		3.4 g/cm^3
Energy Density	2.08 Wh/cm^3		2.38 Wh/cm^3
Volume Change	6.6 %		9.5 %
	High Rate (20 C)		Low Rate (C/10)

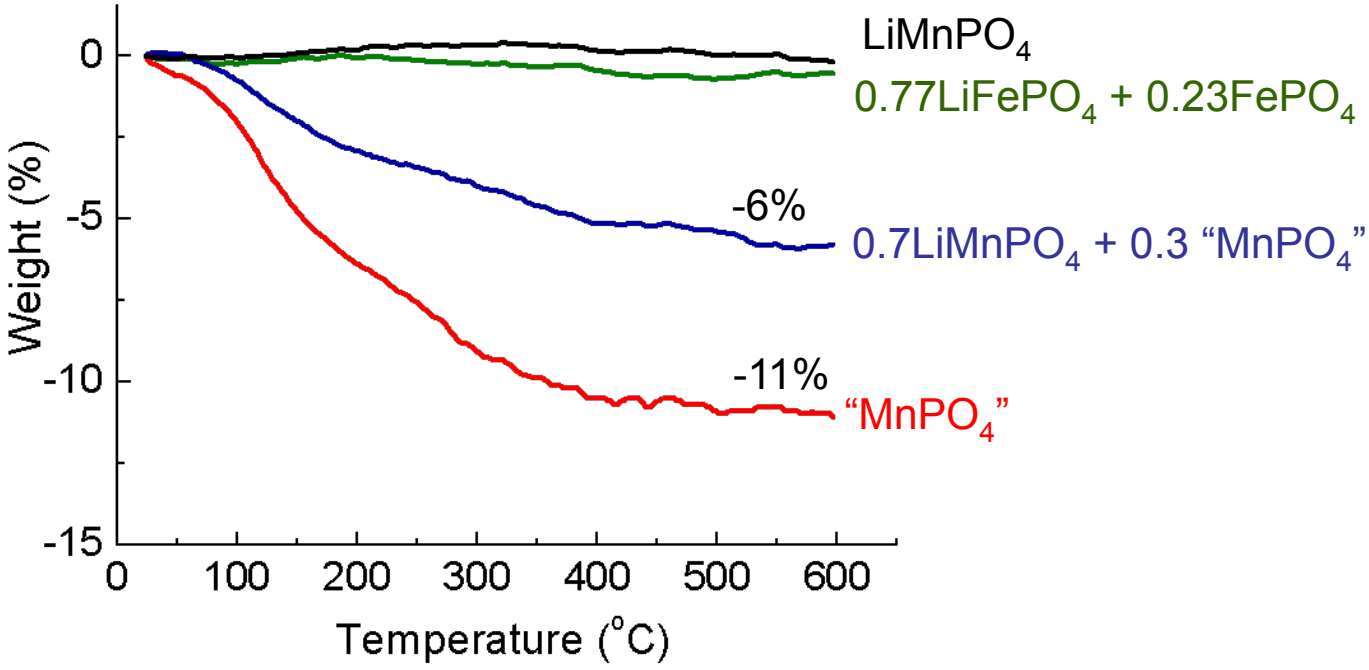


- What makes $LiMnPO_4$ perform poorly?
- Is the phase transition mechanism the same as in $LiFePO_4$?
- How do composition, microstructure and morphology affect performance?
- What can be done to improve its intrinsic properties?
- What can be done to improve electrode structure?
- Prepare samples with controlled morphologies.
- Investigate fundamental properties.

TECHNICAL ACCOMPLISHMENTS

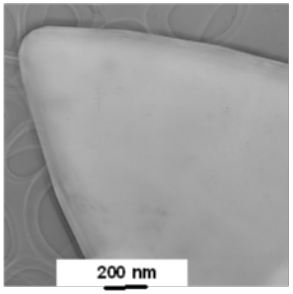
Instability of MPO_4 phases:

- $LiFePO_4$ and $LiMnPO_4$ melt without decomposition at 970 °C and 1020 °C, respectively.
- $FePO_4$ densifies at 580 °C to electrochemically inactive quartz-like $FePO_4$(Whittingham).
- $MnPO_4$ decomposes to $Mn_2P_2O_7$ + O2 beginning around 200 °C.

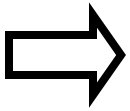


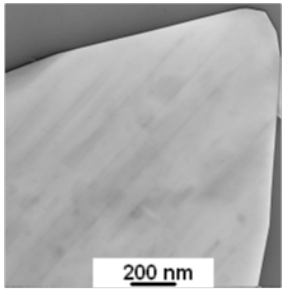
TECHNICAL ACCOMPLISHMENTS

Internal strain in $MnPO_4$ results in decrepitation when Li is removed.

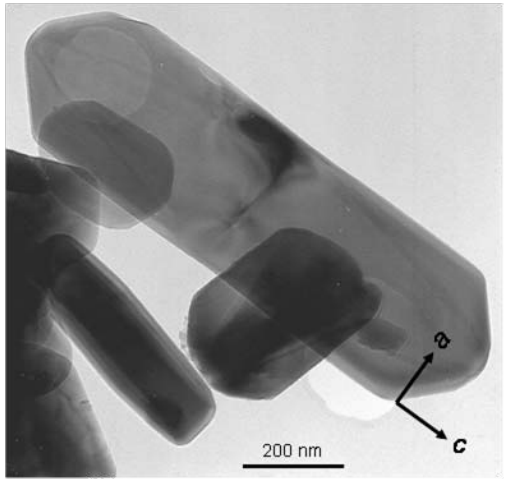


$LiFePO_4$

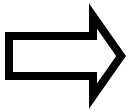


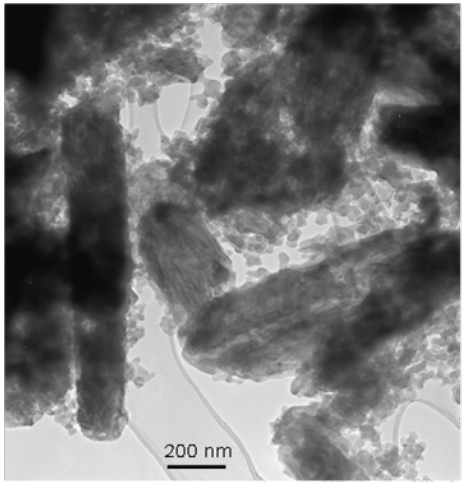


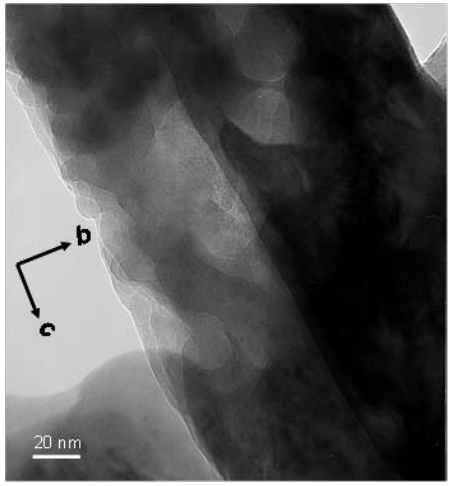
$FePO_4$



$LiMnPO_4$



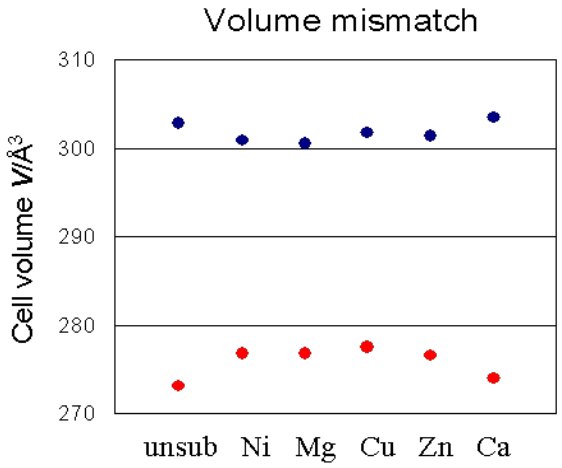


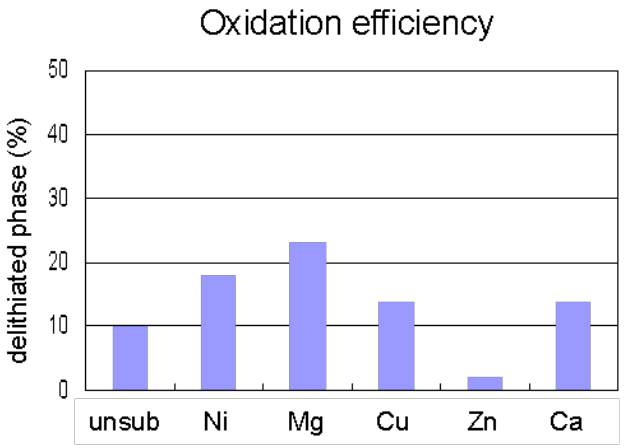


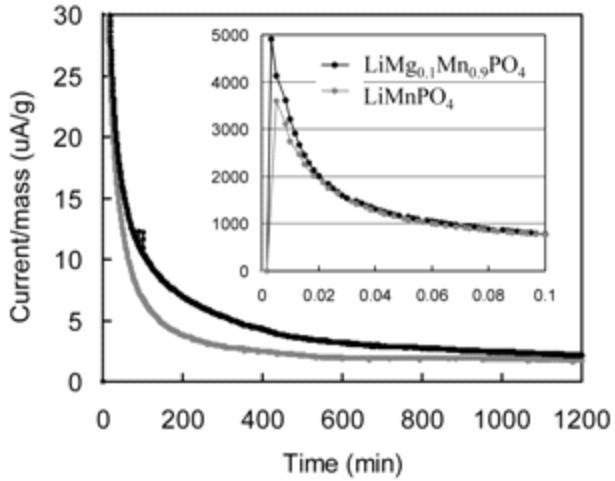
$MnPO_4$

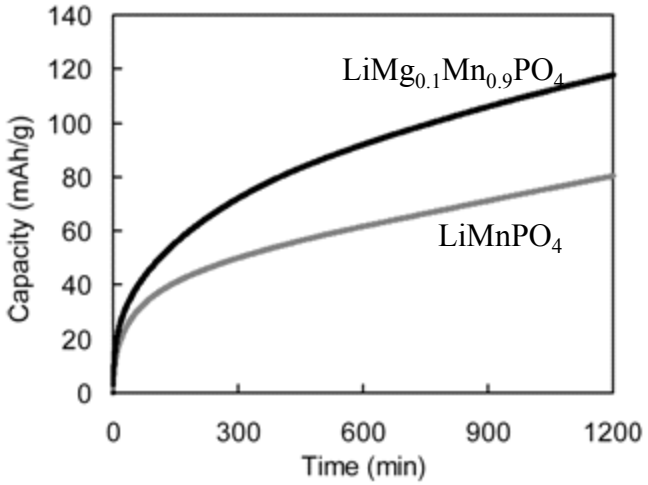
TECHNICAL ACCOMPLISHMENTS

Substituted olivines $LiMn(M')PO_4$



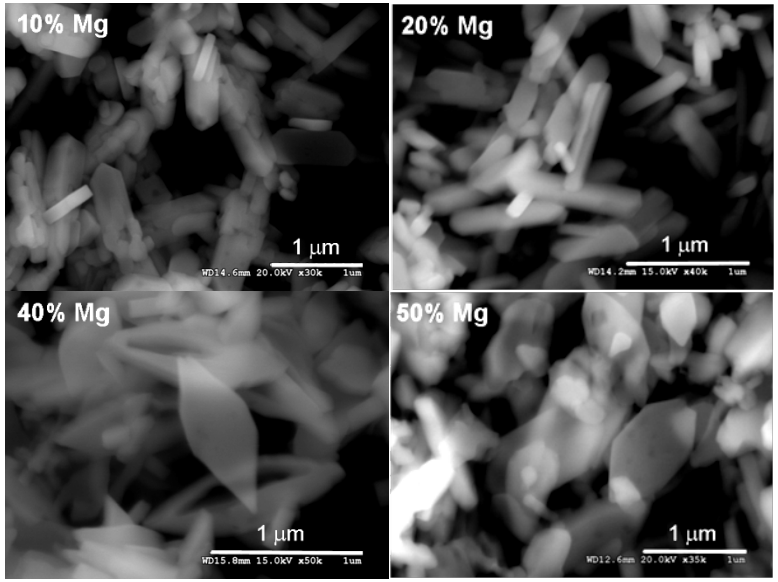


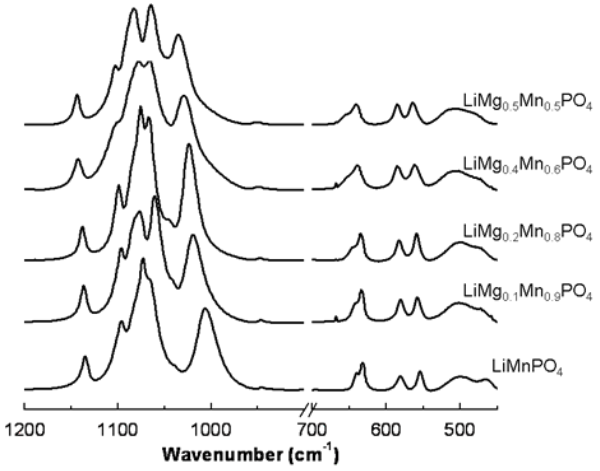




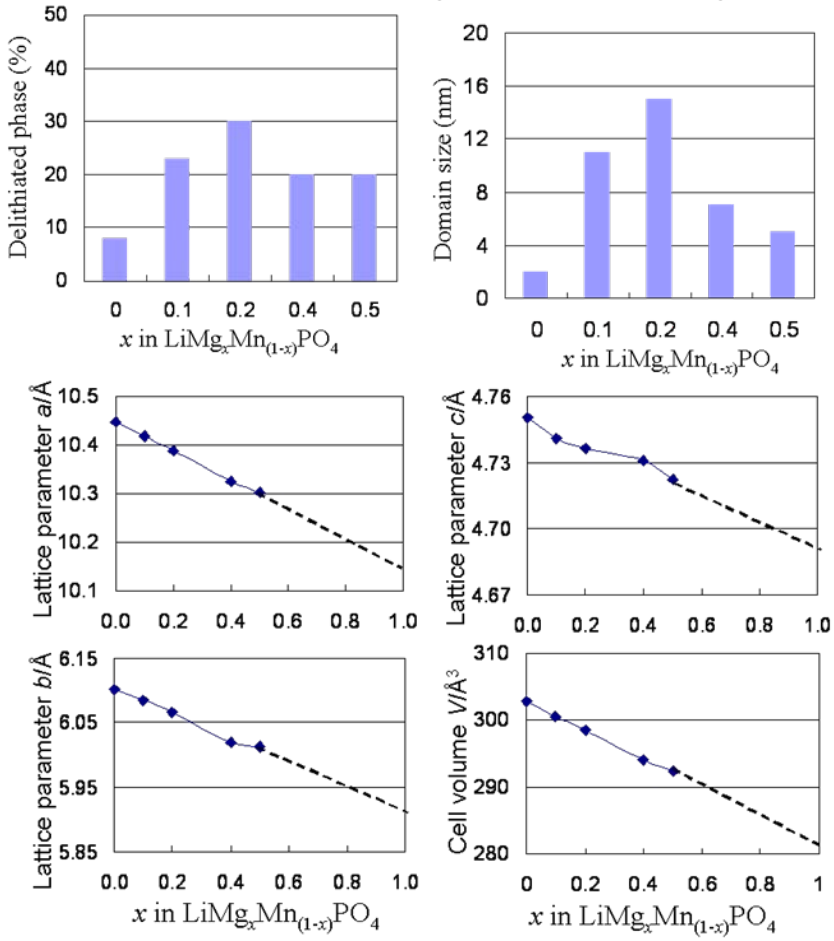
TECHNICAL ACCOMPLISHMENTS

Hydrothermal $LiMn(Mg)PO_4$ Crystals





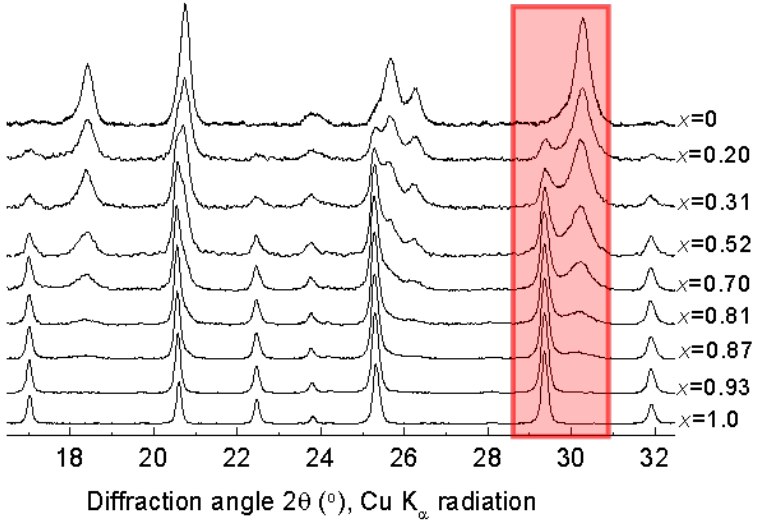
Delithiation efficiency and crystallinity of delithiated phase highest for 20 % Mg.

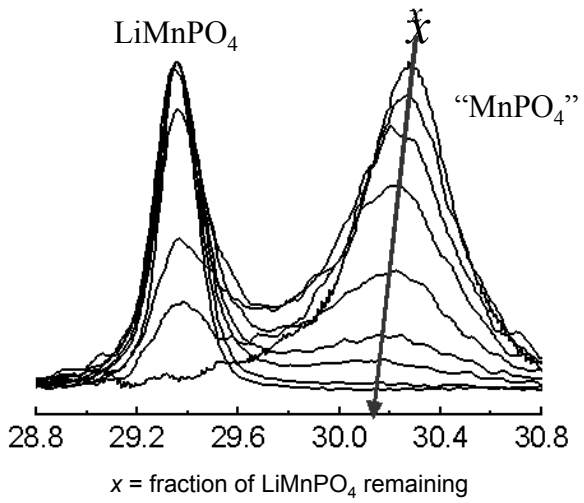


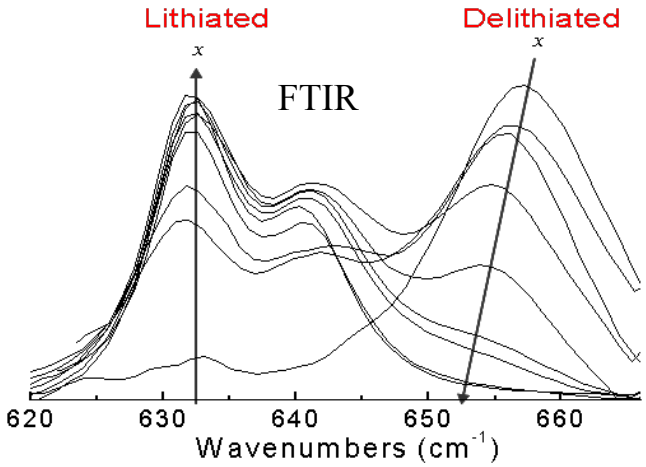
Lattice parameters agree with those reported by Whittingham.

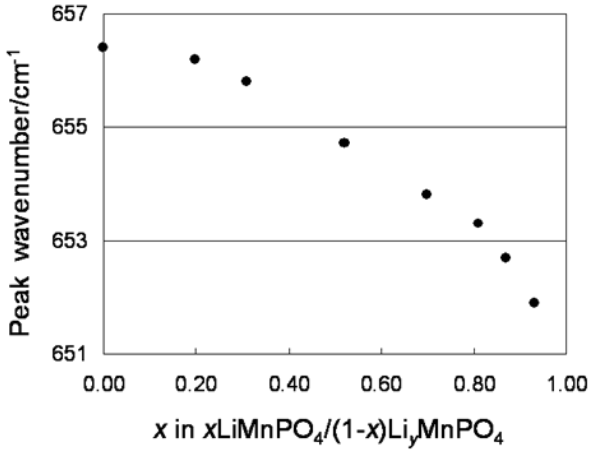
TECHNICAL ACCOMPLISHMENTS

Nonstoichiometric Phases in the $LiMnPO_4$ System









TECHNICAL ACCOMPLISHMENTS

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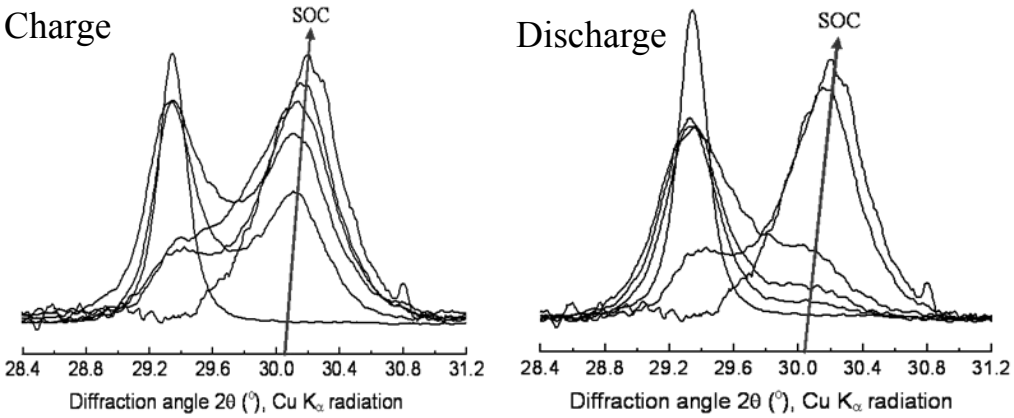
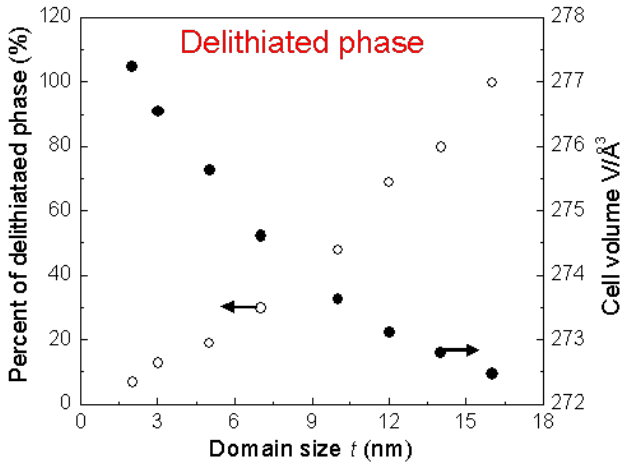
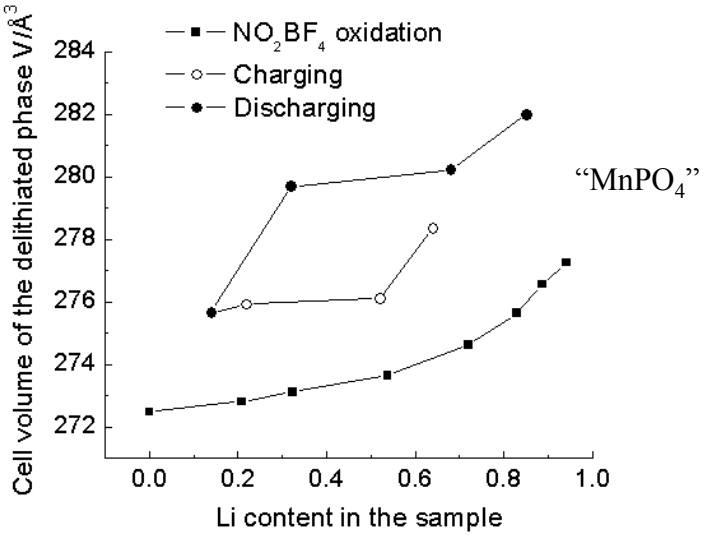
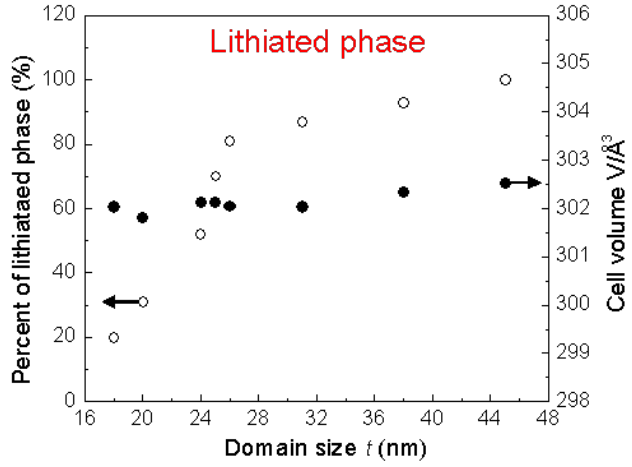




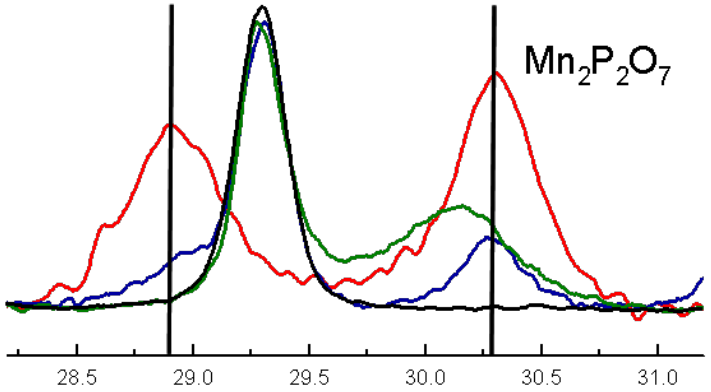


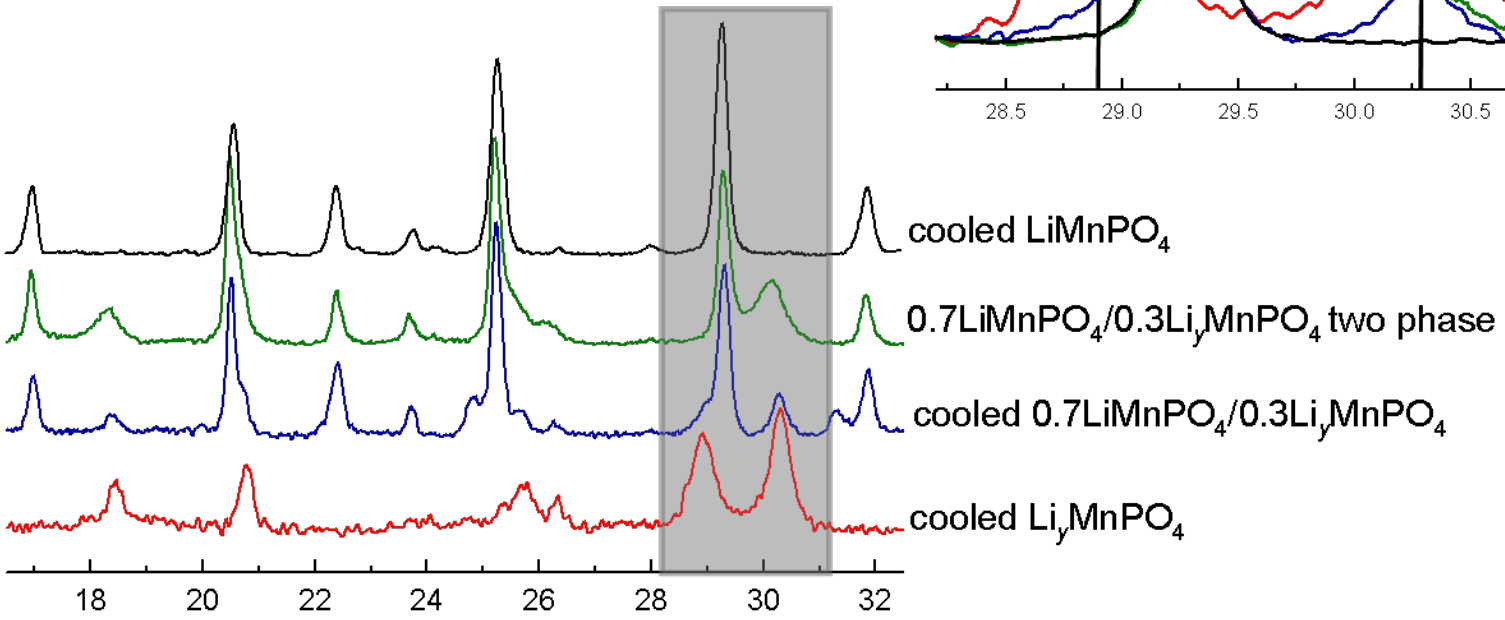


Non-stoichiometry was not observed in the lithiated phase ($LiMnPO_4$).

TECHNICAL ACCOMPLISHMENTS

- No evidence for Li_xMnPO_4 solid solution formation at elevated temperatures.
- Instead, $MnPO_4$ decomposes to $Mn_2P_2O_7$.





APPROACH - ANODES

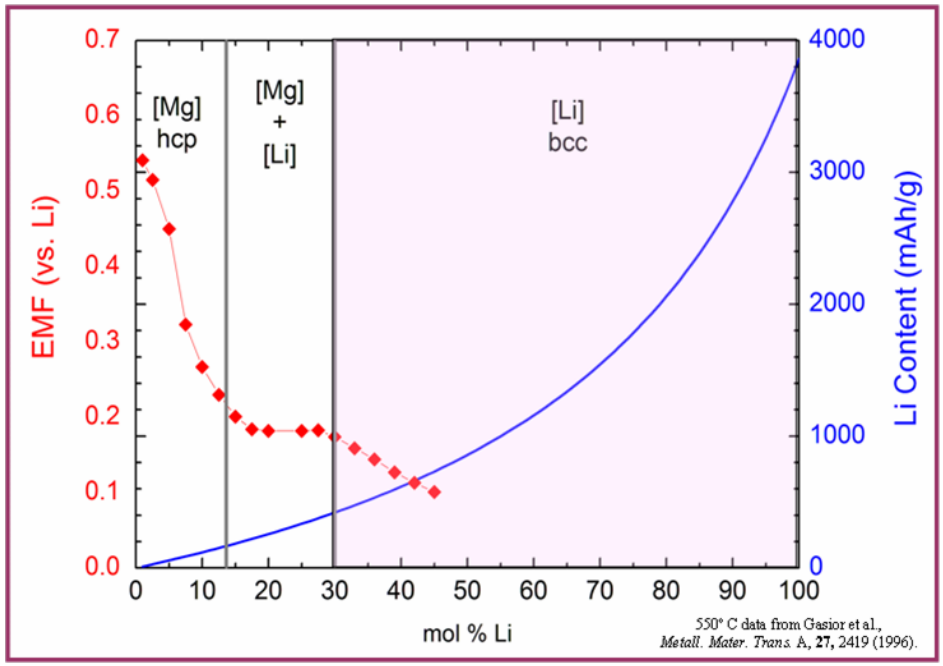
- Can lithium alloys or intermetallics safely replace carbon?
- What are their limitations (rate, loading, temperature)?
- Are there convenient synthetic routes?
- How can anode irreversible capacities be reduced?

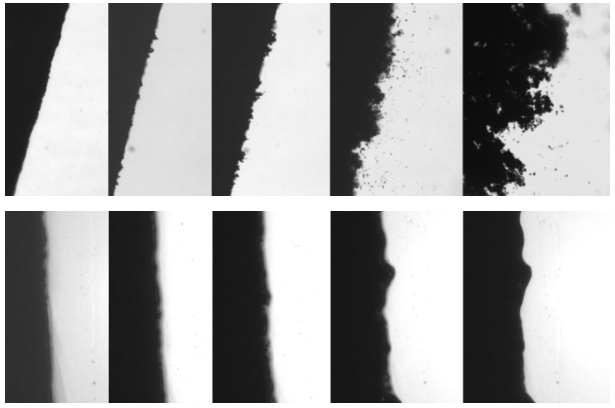
- Prepare and study lithium alloys such as Li-Mg.
- Use metathesis reactions to prepare finely divided lithium, lithium alloys and intermetallics.

TECHNICAL ACCOMPLISHMENTS

Li-Mg Alloys

- Two solid solution ranges
- bcc [Li] from 30 – 100 % Li
- Very large capacities
- Dendrite formation inhibited
- Higher melting points than Li





0 16 46 94 192 cycles

Pure Li

$Li_{0.7}Mg_{0.3}$

Foil

Challenges

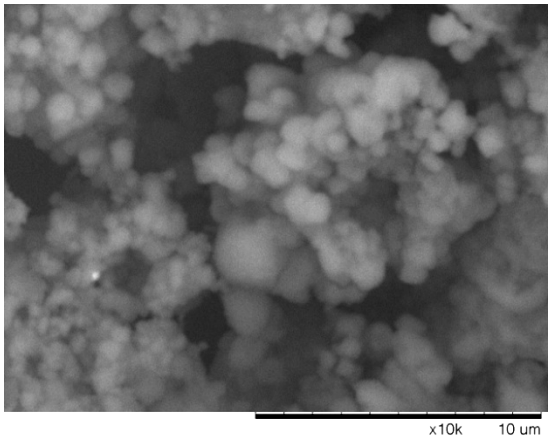
- Difficult to make in lab
- Potential too close to Li
- Conventional electrolytes not appropriate
- Low surface area

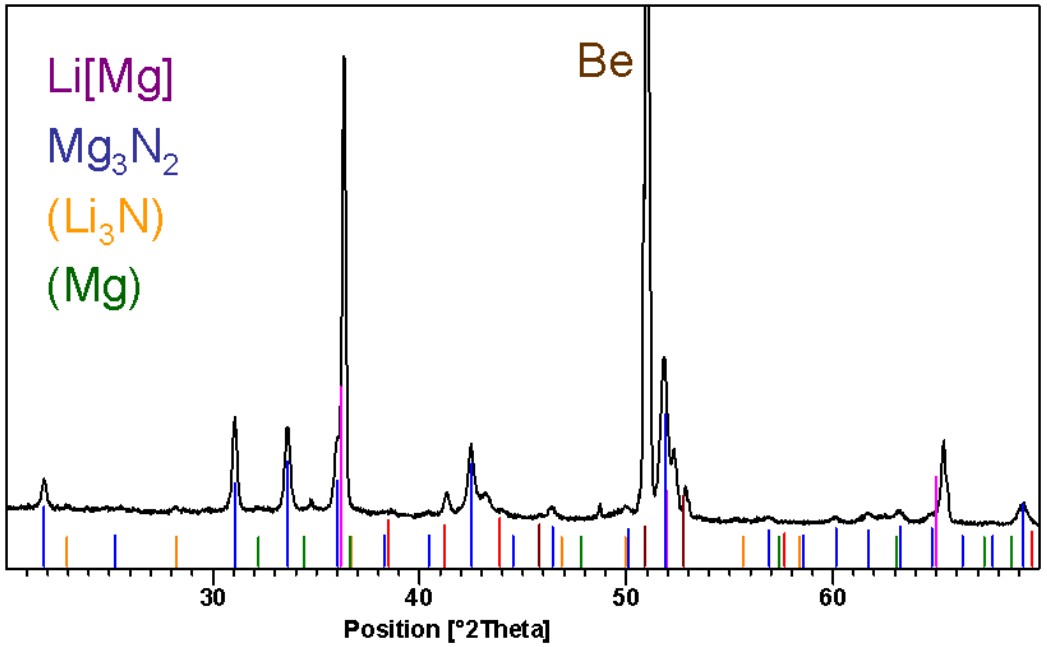
TECHNICAL ACCOMPLISHMENTS

Alloy Synthesis by Metathetic Reactions

$$2Li_3N + 3Mg \rightarrow 6Li + Mg_3N_2$$

$$2Li_3N + (3+x)Mg \rightarrow Li_6Mg_x + Mg_3N_2$$

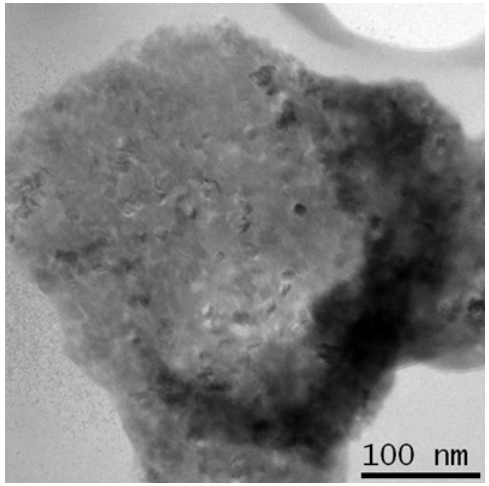


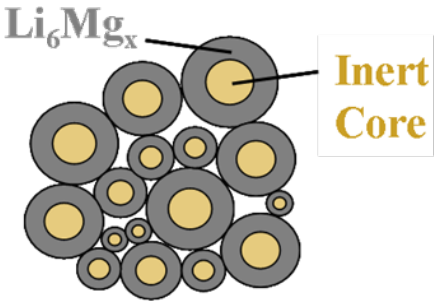


- Dry powders easily mixed, formed **before** or **after** reaction
- Large metal volume fraction, **no carbon**, **no binder**, ceramic component is inert
- Porosity controllable, **high surface area** possible.
- **Inert ceramic component** reduces magnitude and adverse effects of volume changes.

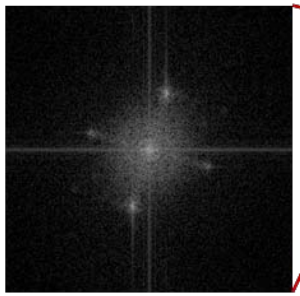
TECHNICAL ACCOMPLISHMENTS

Alloy Synthesis by Metathetic Reactions

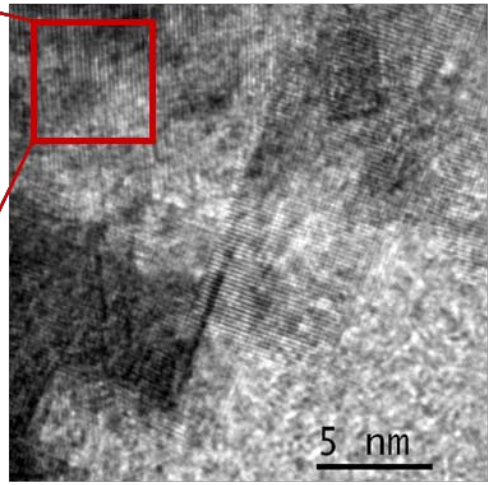


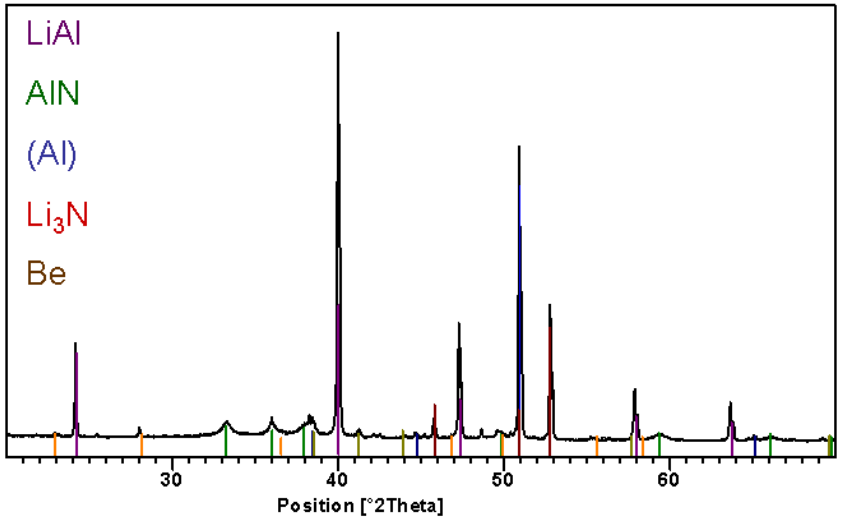


$Li_{0.7}Mg_{0.3}$:Mg_3N_2 cermet contains 51% Li[Mg] alloy by weight, 74% by volume



Mg_3N_2 inclusions in alloy matrix





$$Li_3N + Al \rightarrow 3Li + AlN$$

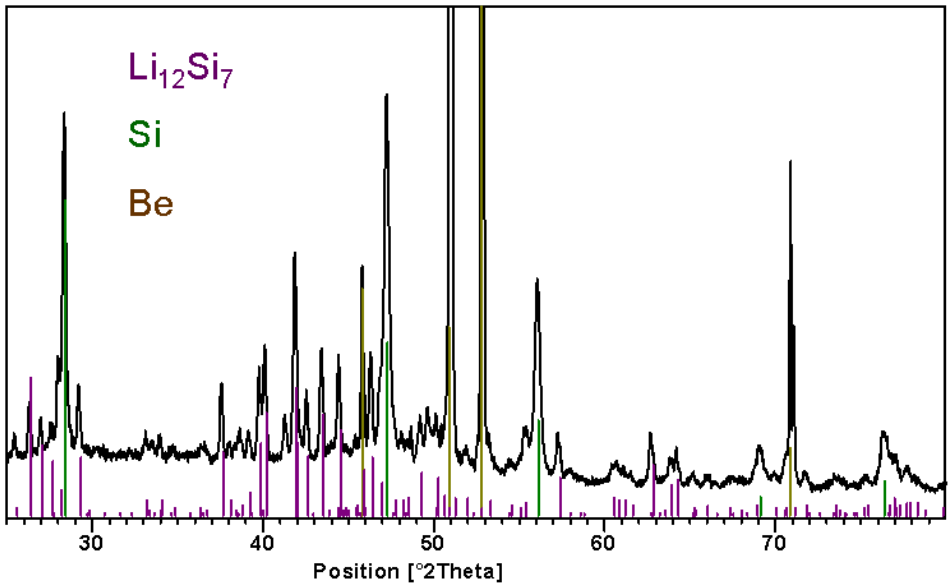
$$4Li_3N + 4Al \rightarrow 3LiAl + AlN$$

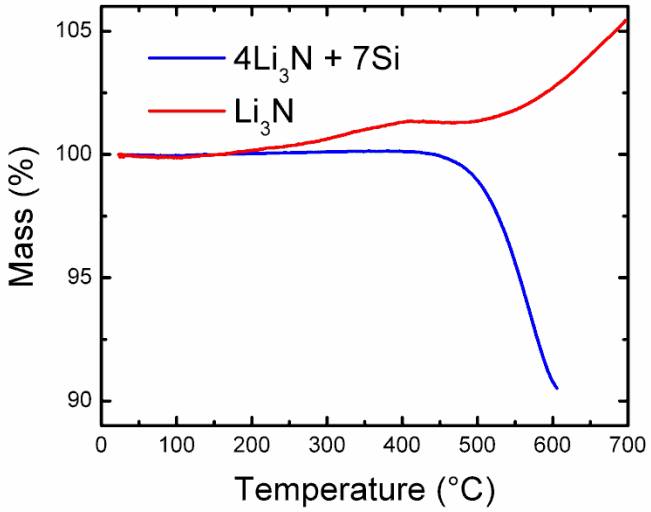
Finely-divided Li-Al powders without grinding.

TECHNICAL ACCOMPLISHMENTS

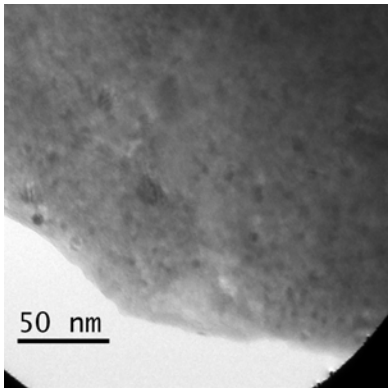
Li-Si Intermetallics from Li_3N

$$4Li_3N + 7Si \rightarrow Li_{12}Si_7 + 2N_2$$



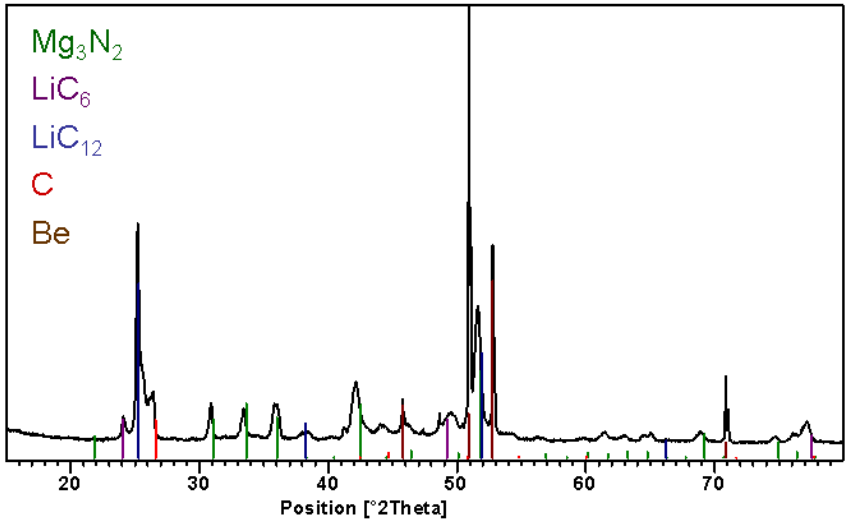


- $Li_{12}Si_7$ and other Li-Si compounds can be made without having to handle lithium or grind massive product ingots.
- Free flowing powders with high surface area.
- No solid byproducts.
- First cycle irreversible capacity reduced or eliminated.
- Also works with Sn.



TECHNICAL ACCOMPLISHMENTS

- Reactions of Li_3N with Mg or Al can make pure lithium in situ.
- This can be used to pre-lithiate other alloys or even carbonaceous anodes.
- No washing to remove organic reagents.
- Easier to handle than lithium powder.
- Inexpensive.
- 10 % of graphite capacity (typical irreversible 1st cycle loss) produces only 2 wt % residual AlN



$$2Li_3N + 3Mg + 36C \rightarrow 6LiC_6 + Mg_3N_2$$

$$2Li_3N + (3+x)Mg \rightarrow Li_6Mg_x + Mg_3N_2$$

$$(Li_3N + Al + 18C \rightarrow 3LiC_6 + AlN)$$

FUTURE WORK

- Complete fundamental studies of olivine cathodes.
- Synthesize and evaluate new cathode materials combining inherent safety with improved energy density. (New task in FY09 delayed by continuing resolution.)
- Continue to explore kinetic barriers to design and develop electrodes with high energy density, good rate performance and enhanced stability.
- Prepare and evaluate ternary solid solution alloys with higher potentials and greater stability toward electrolyte components.
- Explore pretreatment strategies to address irreversible capacity losses in carbon and non-carbon anodes.

SUMMARY

- The existence of non-stoichiometric phases in the $LiMnPO_4$ system is reported for the first time.
- A comprehensive study was carried out of particle decrepitation and the effects of divalent ion substitution on physical and electrochemical behavior of Mn olivines.
- The development and electrochemical significance of intermediate line phases in the Li_xFePO_4 system were studied. (Not reported here, publication in progress.)
- One-step syntheses of Li, Li-Mg, Li-Al, Li-Si and Li-Sn compounds from lithium nitride have been developed.
- The method may have applications in pretreatment of anodes to reduce irreversible capacity losses.