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Low Cost SiO_x-Graphite and High Voltage Spinel Cathode

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DOE-BATT Review Meeting

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This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start date: March 2009
- End date: December 2012
- 60% completed

Barriers

- Low energy
- Poor cycle/calendar life

Budget

- Total Project Funding: $1095K
- FY11 funding $365K
- FY10 funding $365K
- FY09 funding $365K

Partners

- V. Battaglia, V. Srinivasan and R. Kostecki (LBNL)
- J. Goodenough (U. Texas)
- M. Thackeray (ANL)
- C. Julien, A. Mauger (U. Paris 6)
- X.Q. Yang (BNL)

Objectives

- **Synthesize and evaluate $LiMn_{3/2}Ni_{1/2}O_4$ as high voltage cathode material.**

- **Replace graphite anode with an alternative material that meets the requirement for low cost and high energy.**

- **Develop *in-situ* and *ex-situ* SEM and TEM techniques to analyze the SEI layer properties.**

- **Cell assembly of 18560 with the BATT chemistry.**

Approach

- **HQ efforts in the BATT program to investigate and improve SEI layers on alternative anodes include several tasks:**
  - **Prepare laminate anode films and powders, and supply them to investigators in Topic 3a involved with SEI analysis using different techniques (*in-situ*, *ex-situ*).**
  - **Identify benefits of binder (SBR, Polyimide, EPDM) compared to PVDF in new anode and cathode materials.**

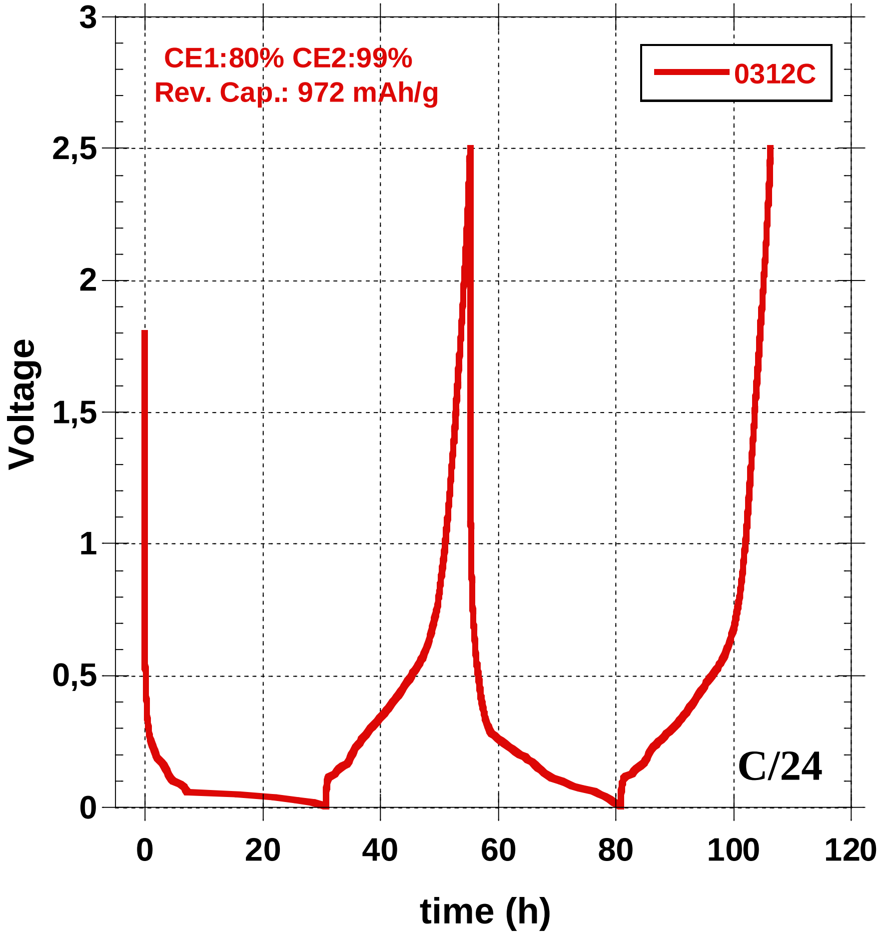
- **Investigate performance of high-voltage spinel cathode in laboratory cells.**
  - **Stabilize the $LiMn_{3/2}Ni_{1/2}O_4$ cathode by protecting its surface with more stable material to suppress the secondary reaction with the electrolyte.**
  - **Synthesize $LiMn_{3/2}Ni_{1/2}O_4$ at HQ and supply the optimized material to BATT investigators for evaluation.**

- **Utilize *in-situ* and *ex-situ* SEM and TEM to investigate the SEI layer on the anode and cathode.**

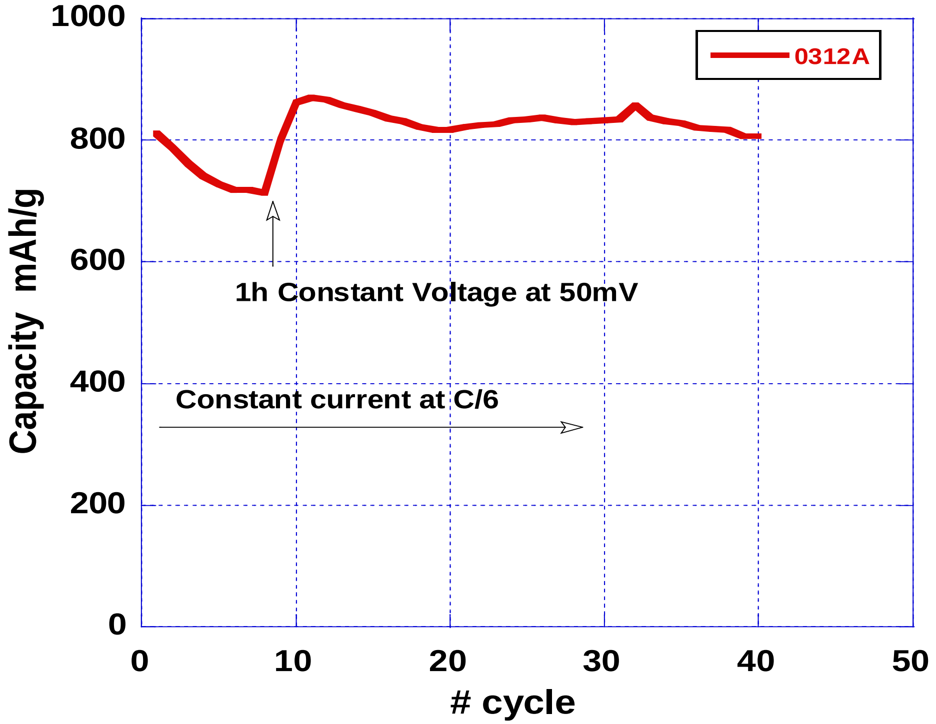
MILESTONES

- **Completed evaluation of the effect of the binder on the SiO_x anode performance.**
- **On going**
  - **Developed process to stabilize the surface of the $LiMn_{3/2}Ni_{1/2}O_4$ cathode.**
  - **Synthesized $LiMn_{3/2}Ni_{1/2}O_4$ cathode material and supply BATT investigators.**
  - **Developed *in-situ* and *ex –situ* SEM and TEM techniques to investigate the SEI layer on the anode and the interface on the $LiMn_{3/2}Ni_{1/2}O_4$ oxide spinel.**
  - **Evaluation of 18650 cells assembled at HQ**

(C-SiO_x+ Graphite (1:1)) Anode

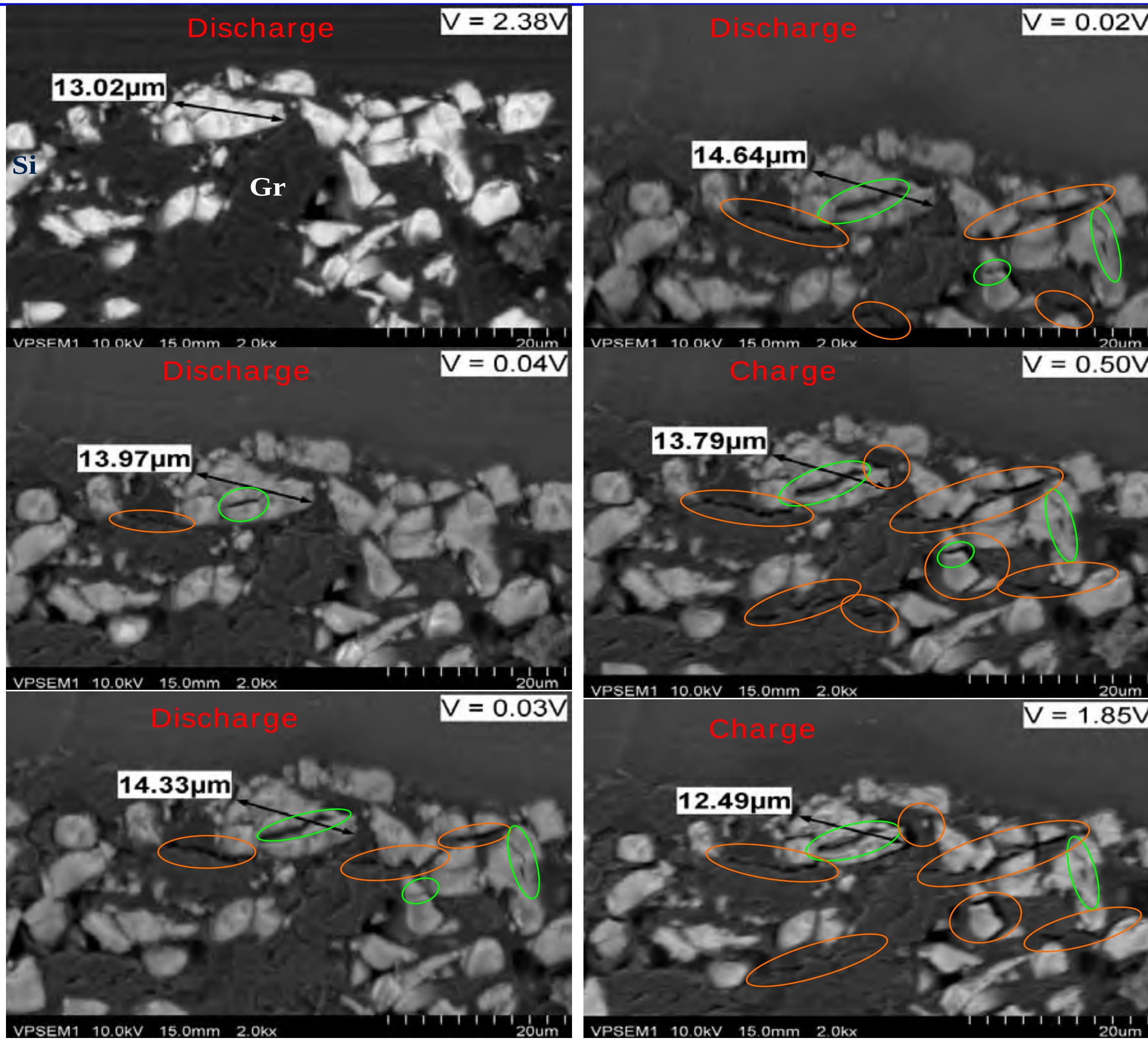


Binder: polyacrylonitrile butadiene
1M LiPF6-EC-DEC+ 2%VC



- By using polyacrylonitrile butadiene as binder, the 1CE was 80% and the reversible capacity was 972mAh/g.
- The constant voltage step at discharged state (50mV) improves the cycling performance.

(C-SiO_x+ Graphite (1:1)) Anode: *In-Situ*



Binder: Polyimide
Discharge/Charge: C/24
1M $LiPF_6$-EC-DEC+2%VC

Technical Accomplishments

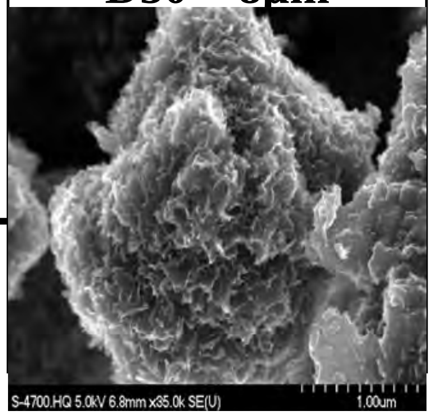
- The *in-situ* studies revealed that larger particles (~13μm) start to develop cracks at around 0.1V and the smaller particles (< 2μm) are more stable.
-Some fissures were observed and the particles are delaminated .

(C-SiO$_x$+ Graphite (1:1)) Anode: In-Situ

Movie

Si-Based Anode

C-SiO$_x$-graphite
D50 ~ 8µm



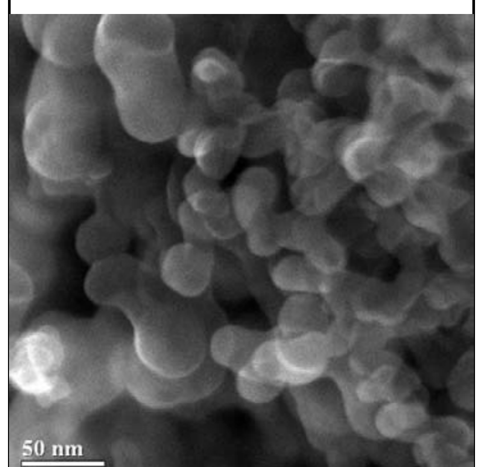
EC1: 80%
1058 mAh/g

In-situ SEM

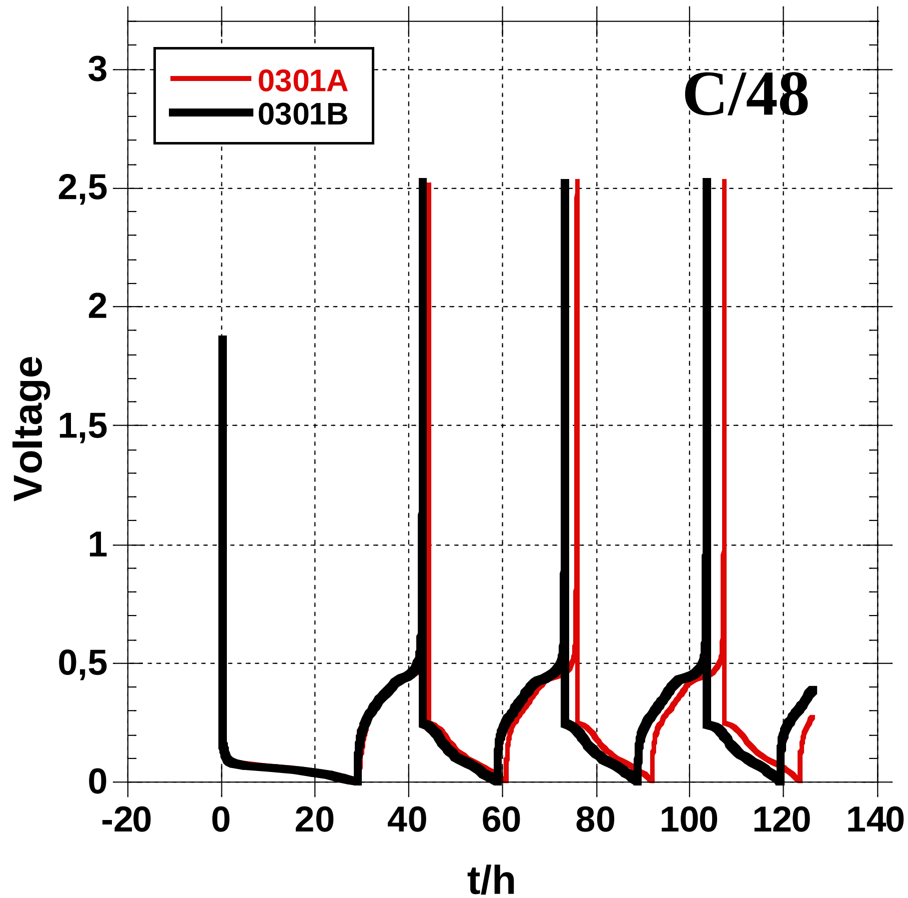
Bigger particle (~13µm) cracks during the first discharge

Smaller particle is needed

Si nano



Si-Nano Material for Anode



Li coin type cell
Binder: Polyimide
1M $LiPF_6$-EC-DEC+2%VC

Discharge/Charge: C/48
T=25°C

Cell:	**0300A**	**0300B**
EC1 (%):	50	49
EC3 (%):	96	96
Qrev (mAh/g):	1224	1153

- **The reversible capacity was only 1220mAh/g for the Si-nano material at low rate:**
  - ➢ **Carbon coating is needed**
  - ➢ ***In situ* SEM studies needed to analyze low-capacity behavior.**

Cathode Material Plan

High Voltage Cathode
$LiMn_{3/2}Ni_{1/2}O_4$

Charging $LiMn_{3/2}Ni_{1/2}O_4$ requires high voltage (4.9V), which could induce it's degradation in performance. Protecting the $LiMn_{3/2}Ni_{1/2}O_4$ surface can minimize this side reaction.

HQ Synthesis
$LiMn_{3/2}Ni_{1/2}O_4$

Optimized material be will sent to the BATT PIs

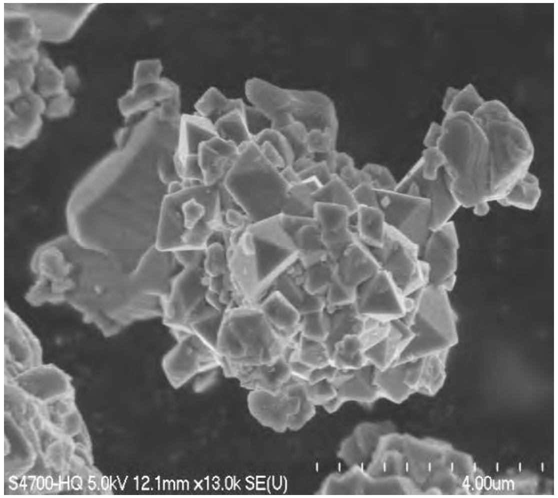
Surface protection of LMN cathode

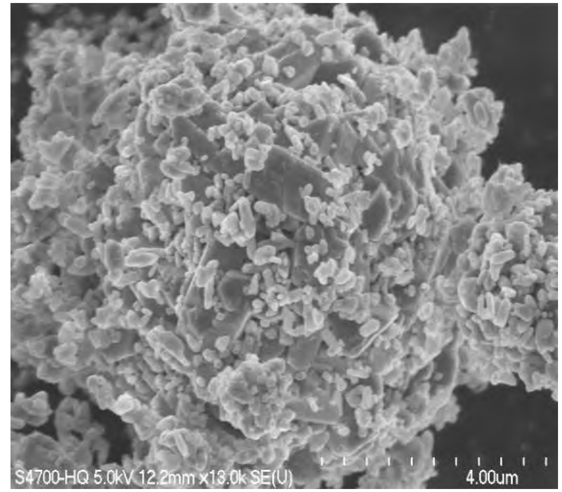
LFP coated LMN (dry process)

Oxide and ceramic LMN surface treatment (wet process)

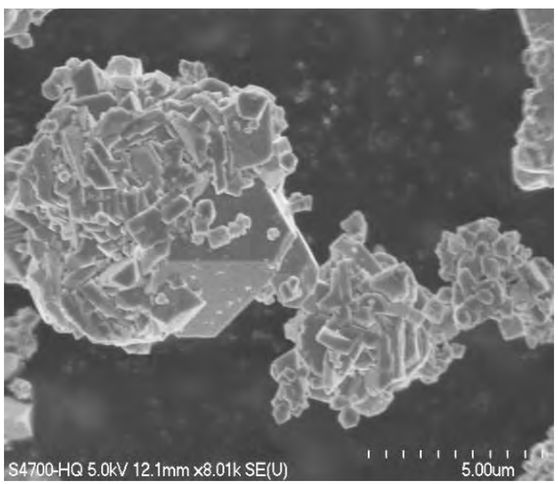
- **Ni-O**
- **Mn-O**
- **$LiCoPO_4$**
- **$AlPO_4$**

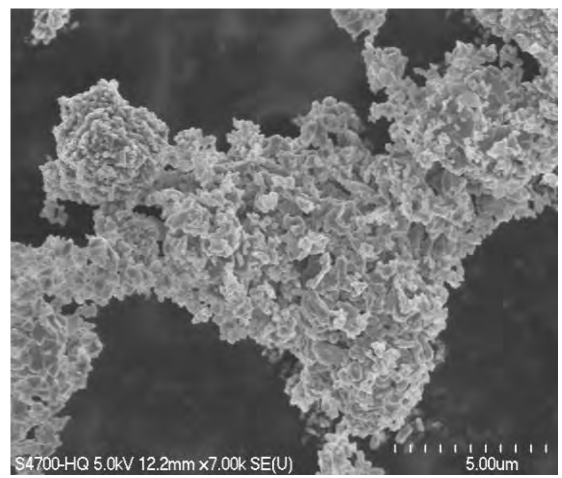
$LiFePO_4$ Coated $LiMn_{3/2}Ni_{1/2}O_4$: SEM





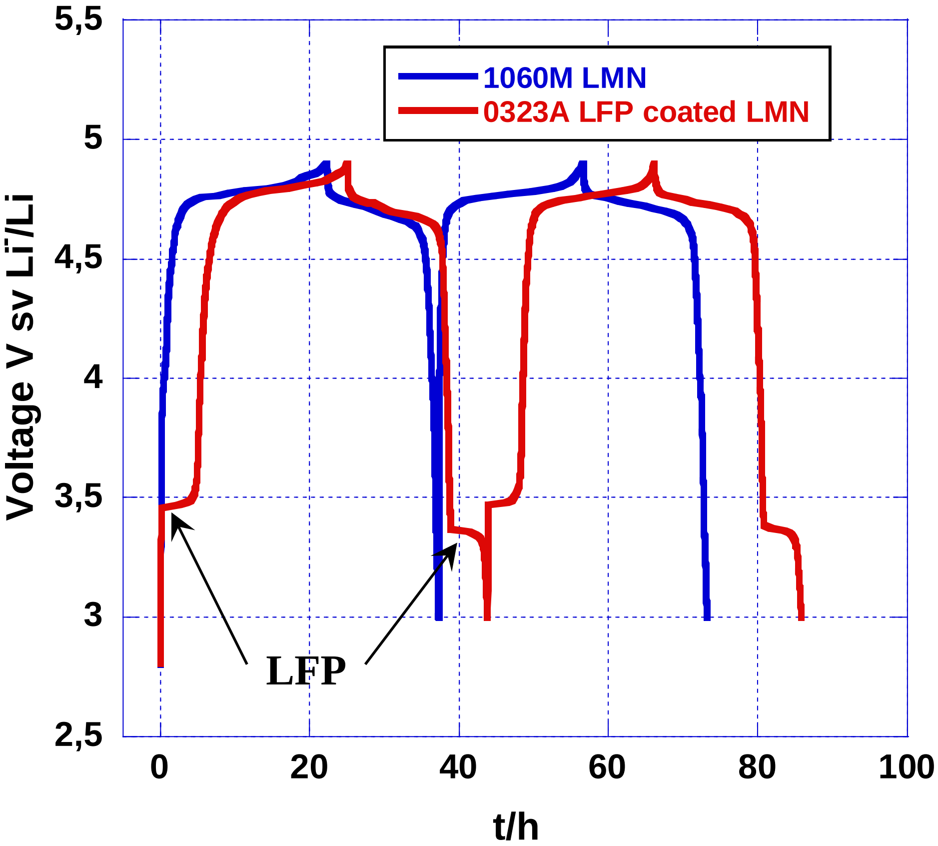
$LiMn_{3/2}Ni_{1/2}O_4$ — **Dry process** → $LFP(LiMn_{3/2}N_{i1/2}O_4$





-The $LiMn_{3/2}Ni_{1/2}O_4$ was successfully coated with $LiFePO_4$ using dry process.

LiFePO$_4$ Coated LiMn$_{3/2}$Ni$_{1/2}$O$_4$: Formation

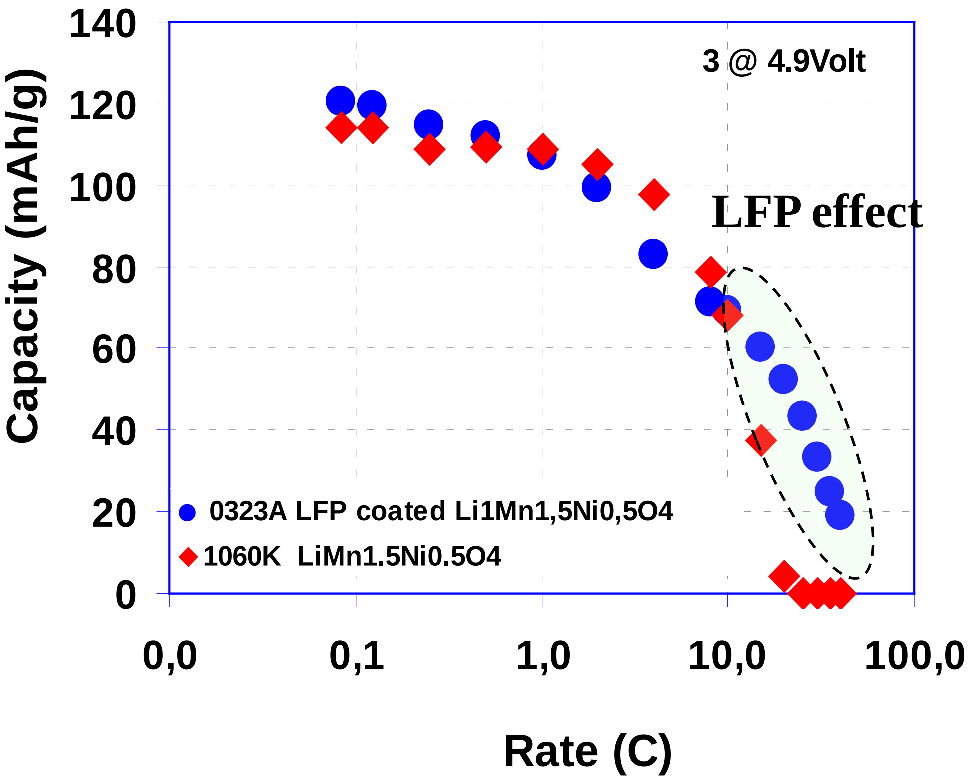


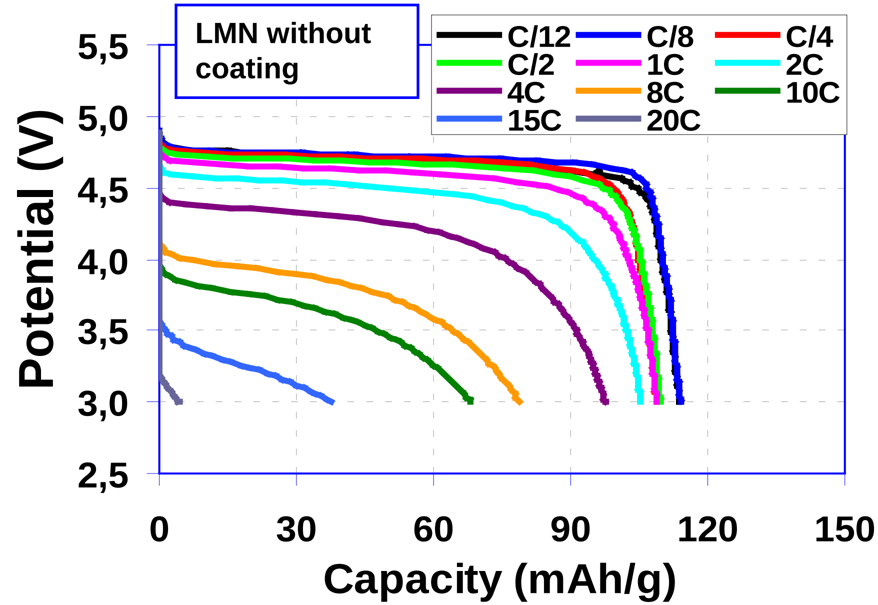
LiFP(LiMn1.5Ni0.5O4):20(80) Wt%
Discharge/Charge: C/24
1M LiPF6-EC-DEC+ 2%VC

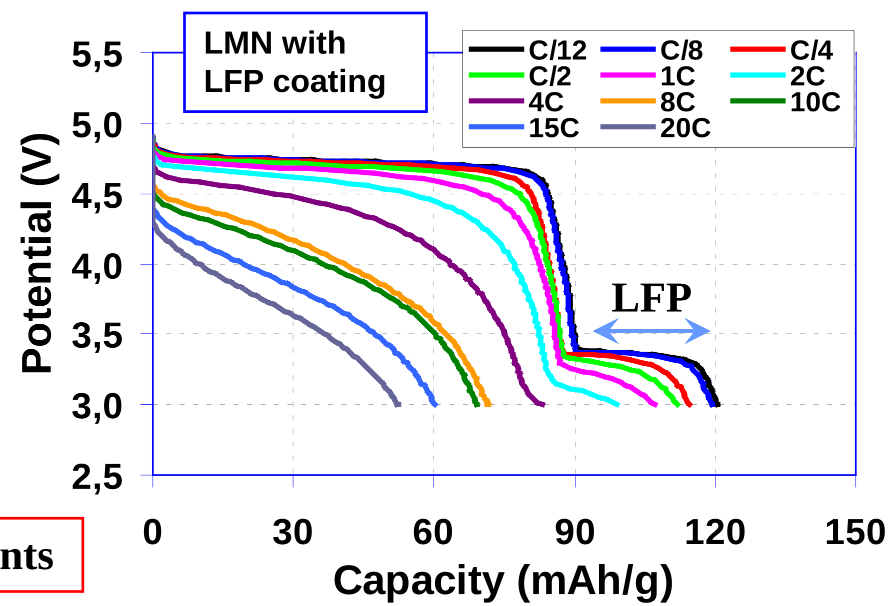
	EC1 (%)	EC2 (%)	Cap (mAh/g)
LFP coated (LiMn$_{1.5}$Ni$_{0.5}$O$_4$)	**76**	**88**	**123**
LiMn$_{1.5}$Ni$_{0.5}$O$_4$	**67**	**86**	**104**

-The LiMn$_{3/2}$Ni$_{1/2}$O$_4$ was successfully coated with LiFePO$_4$ using dry process.

$LiFePO_4$ Coated $LiMn_{3/2}Ni_{1/2}O_4$: Ragone Test







-The high power performance was improved With LFP-coated $LiMn_{3/2}Ni_{1/2}O_4$.

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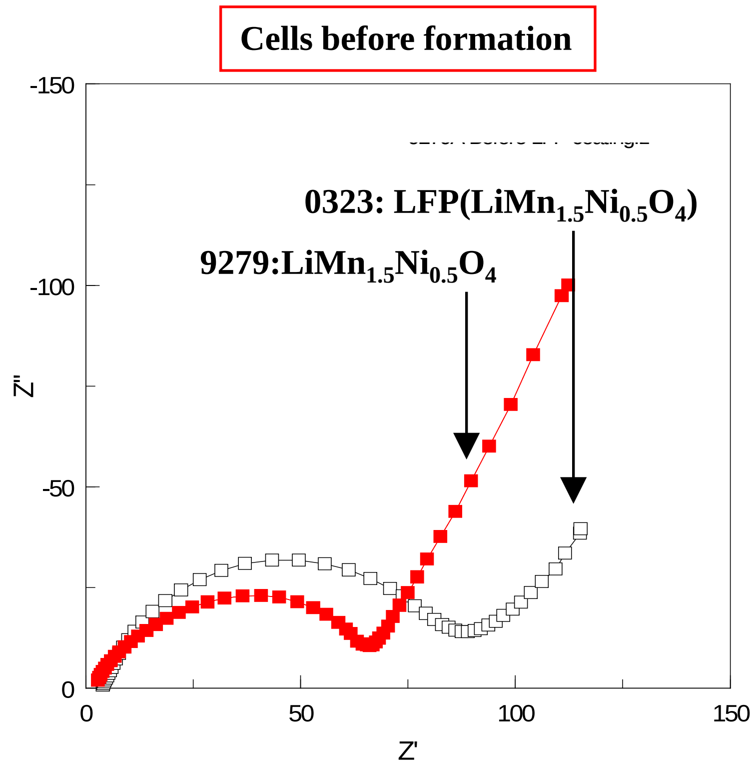
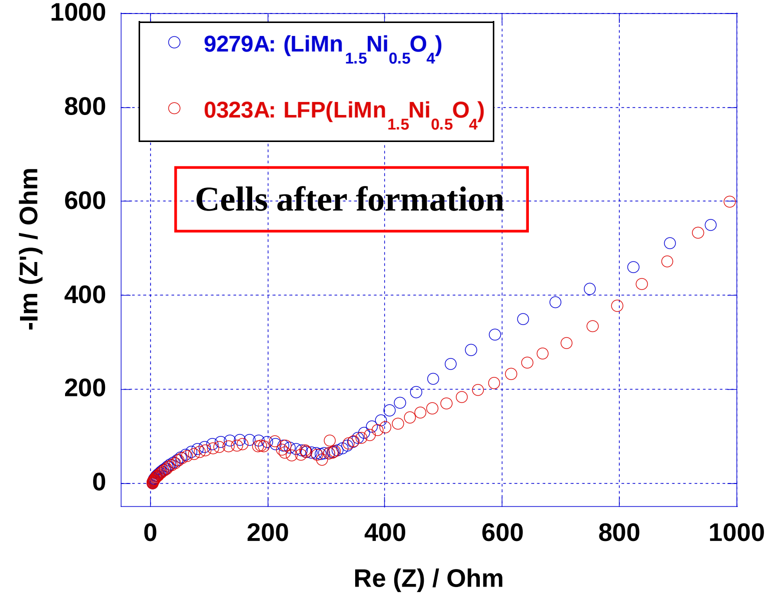
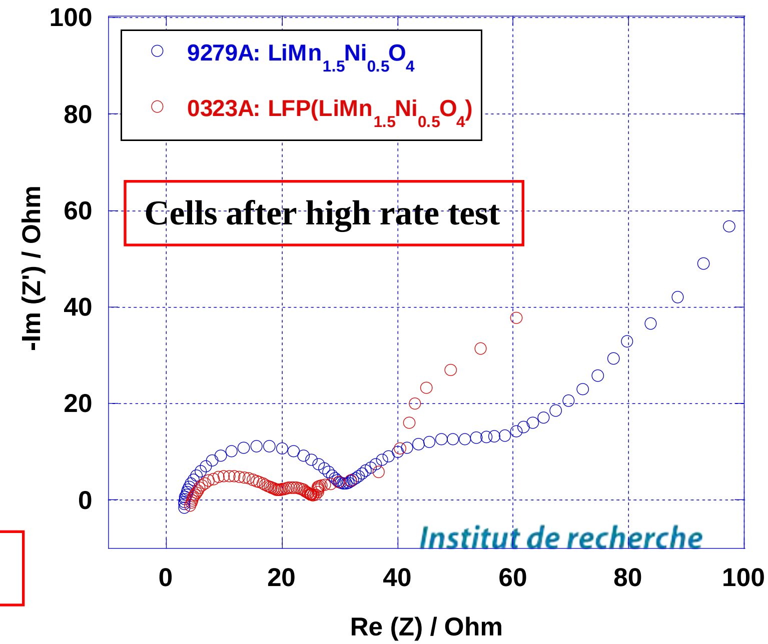
Technical Accomplishments

$LiFePO_4$ Coated $LiMn_{3/2}Ni_{1/2}O_4$: Interfaces







-A comparable interface was obtained after the formation cycles.
-The interface changed after high rate test to the LFP-coated $LiMn_{3/2}Ni_{1/2}O_4$.

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Technical Accomplishments

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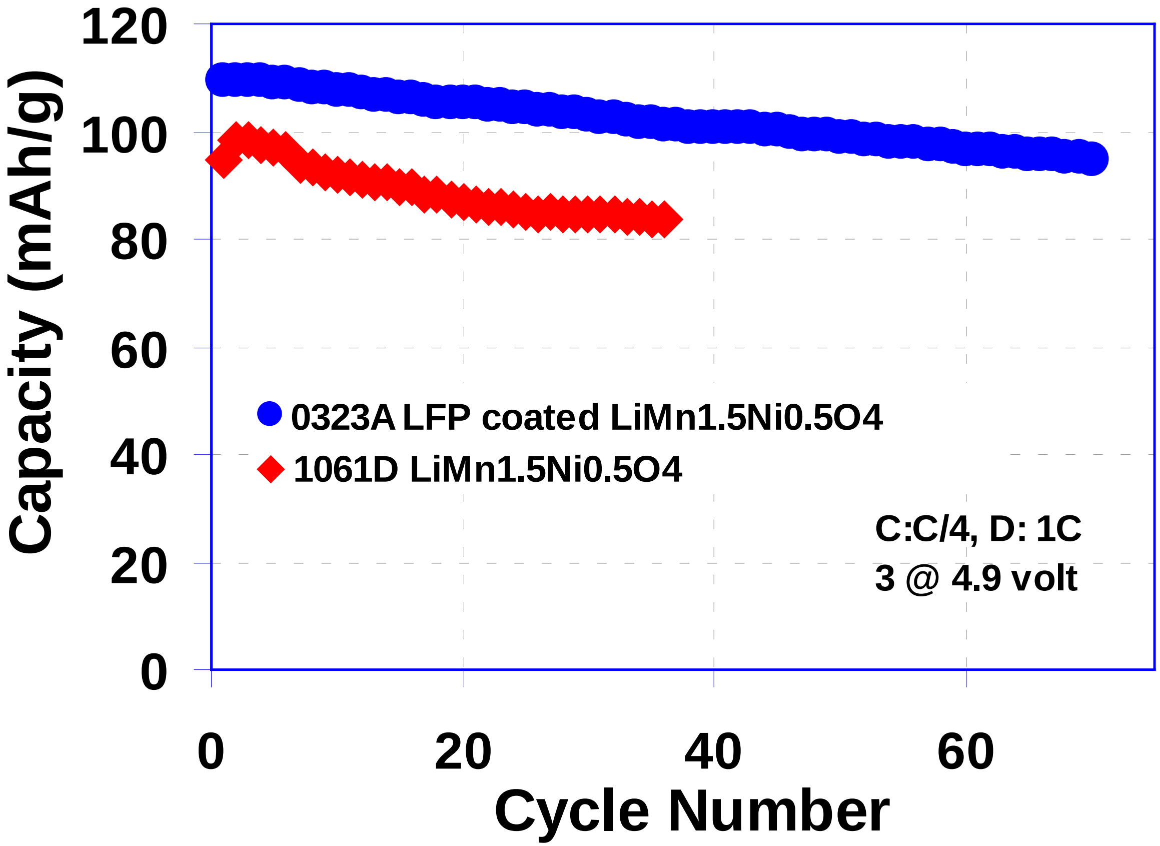
LiFePO$_4$ Coated LiMn$_{3/2}$Ni$_{1/2}$O$_4$: Cycling

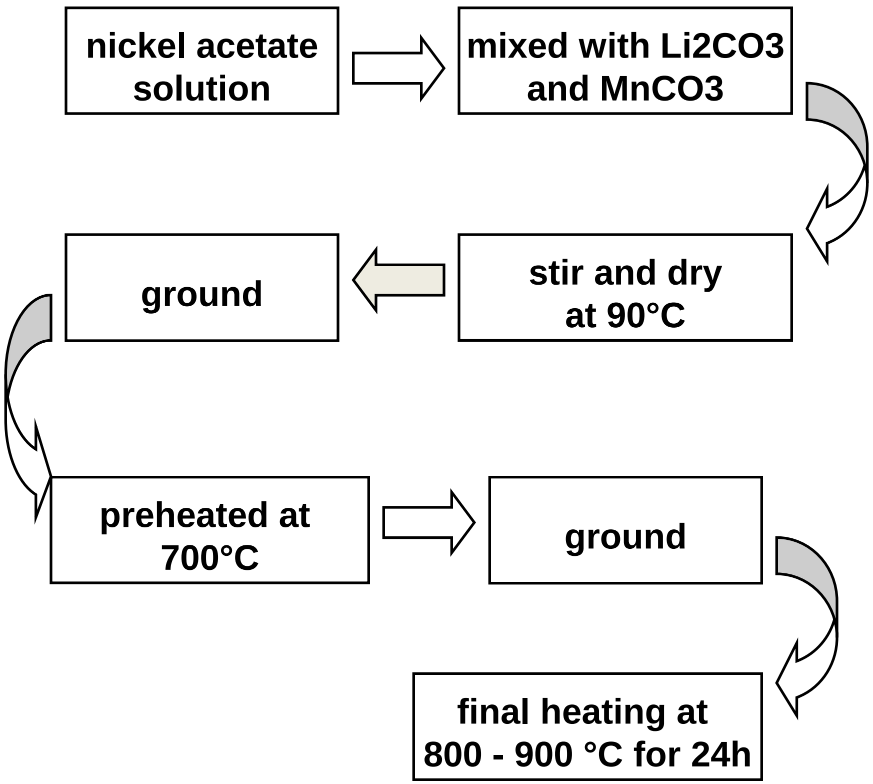


-The LFP-coated LiMn$_{3/2}$Ni$_{1/2}$O$_4$ cathode showed less capacity fade (3-4.9V) cycled at 1C compared to uncoated one.

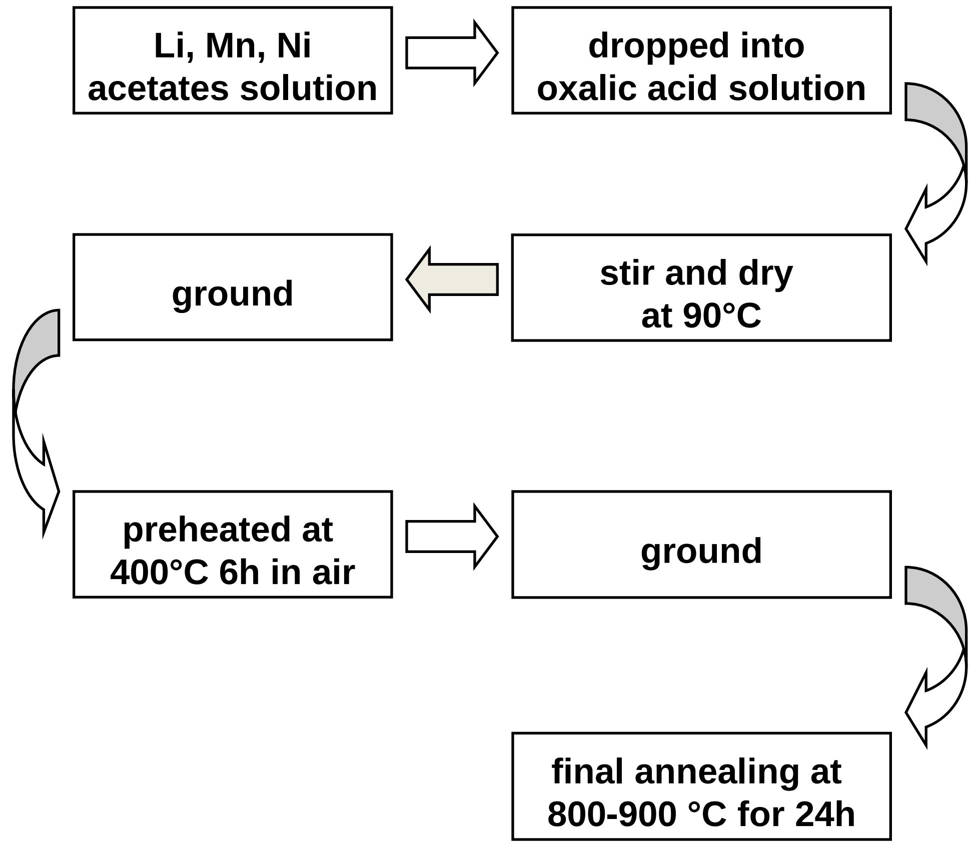
Technical Accomplishments

$LiMn_{3/2}Ni_{1/2}O_4$: HQ-Synthesis

Solid-State process (SS sample)

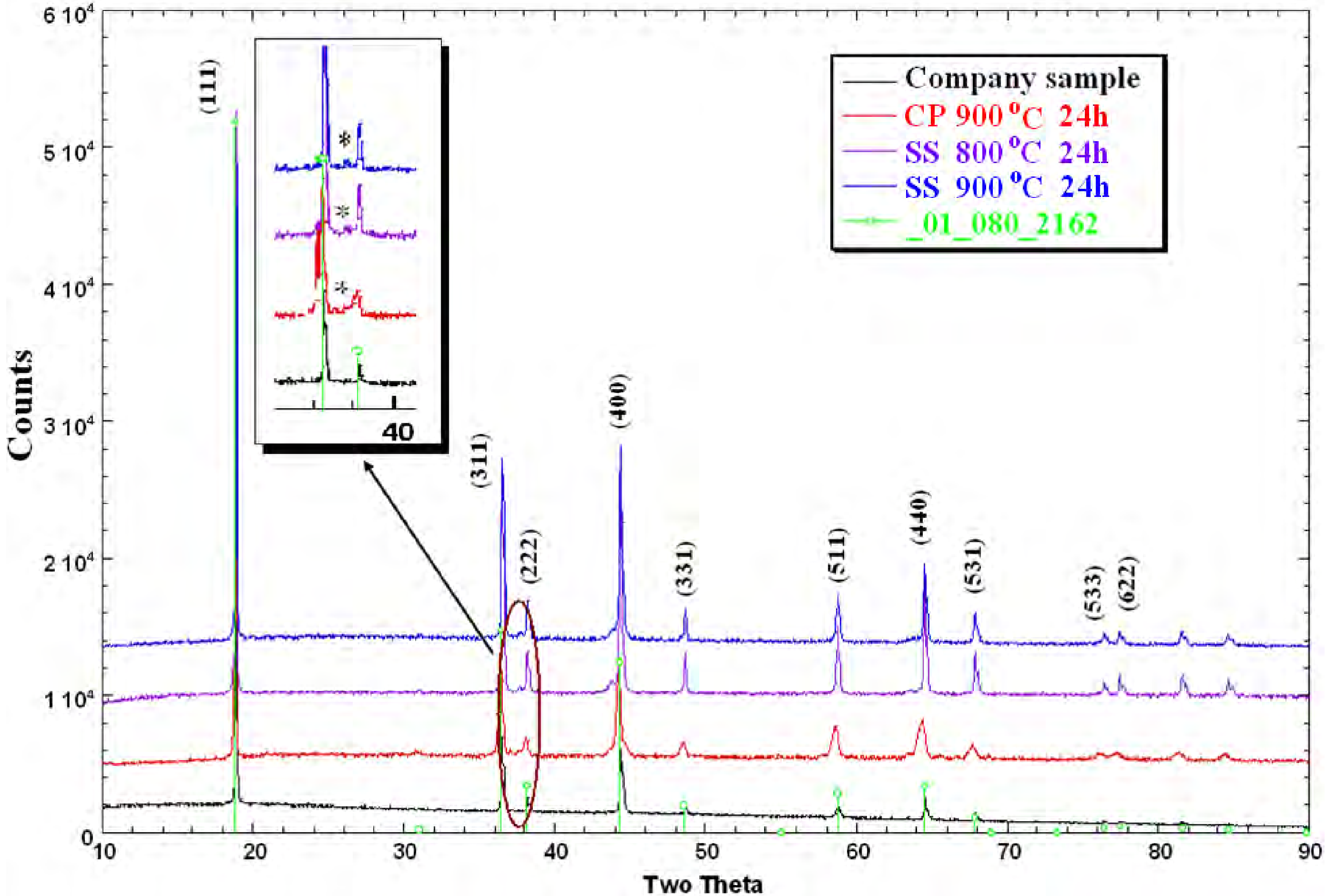


Co-Precipitation method (CP sample)



3 samples of $LiMn_{1.5}Ni_{0.5}O_4$ were sent to Vince Battaglia (LBNL) for evaluation.

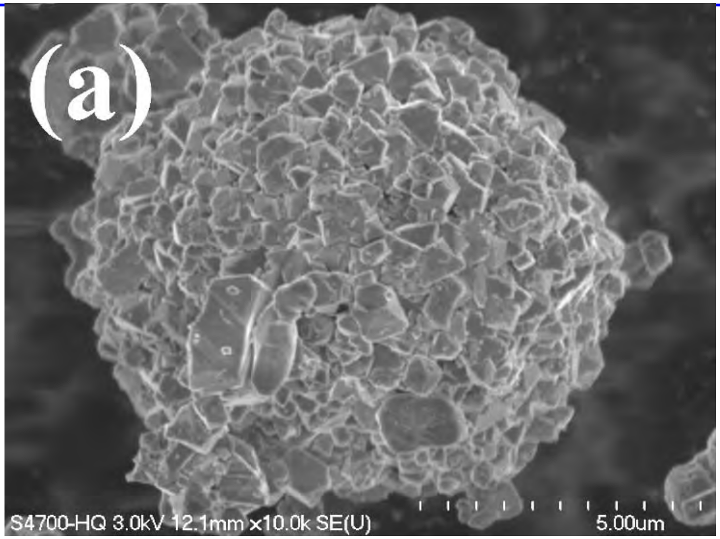
HQ Synthesis of $LiMn_{3/2}Ni_{1/2}O_4$: XRD



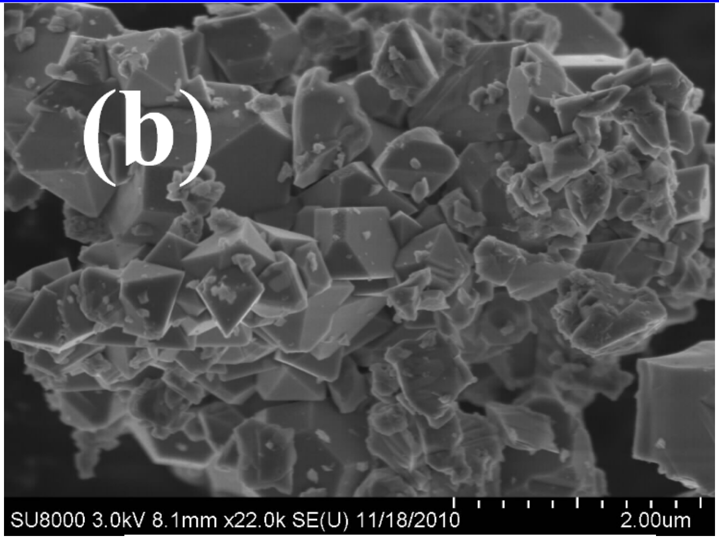
-Trace impurities (2θ = 38° and 45°) were found in HQ samples, probably due to loss of oxygen and/or lithium at high temperature.

- Samples crystallize better with disordered structure at higher temperatures.

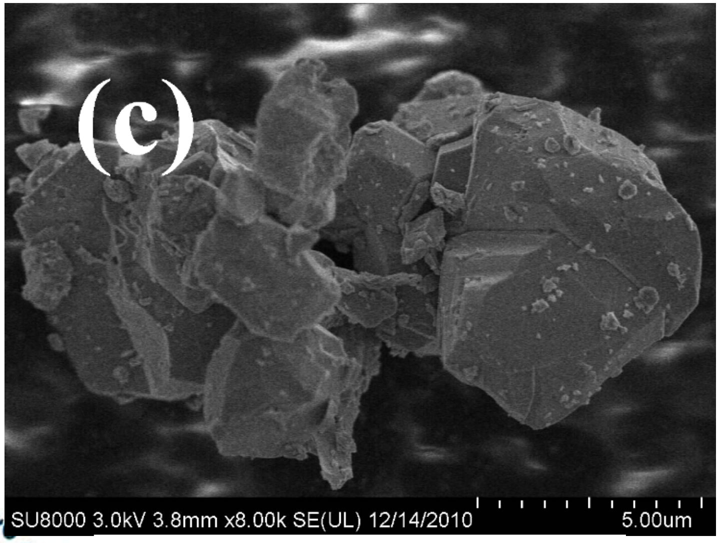
HQ Synthesis of $LiMn_{3/2}Ni_{1/2}O_4$: SEM



(a) Company sample



(b) Co-Precipitation (CP) sample



(c) Solid State (SS) sample

Particle size: SS > CP > company sample

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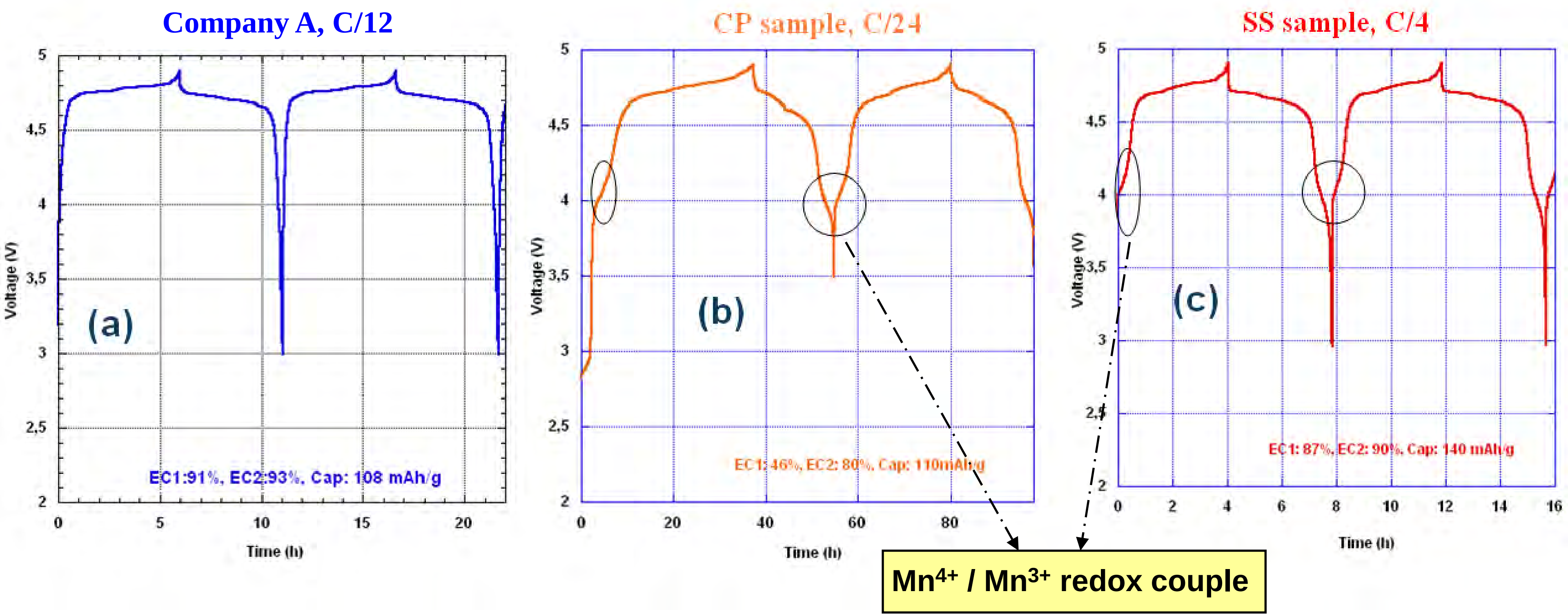
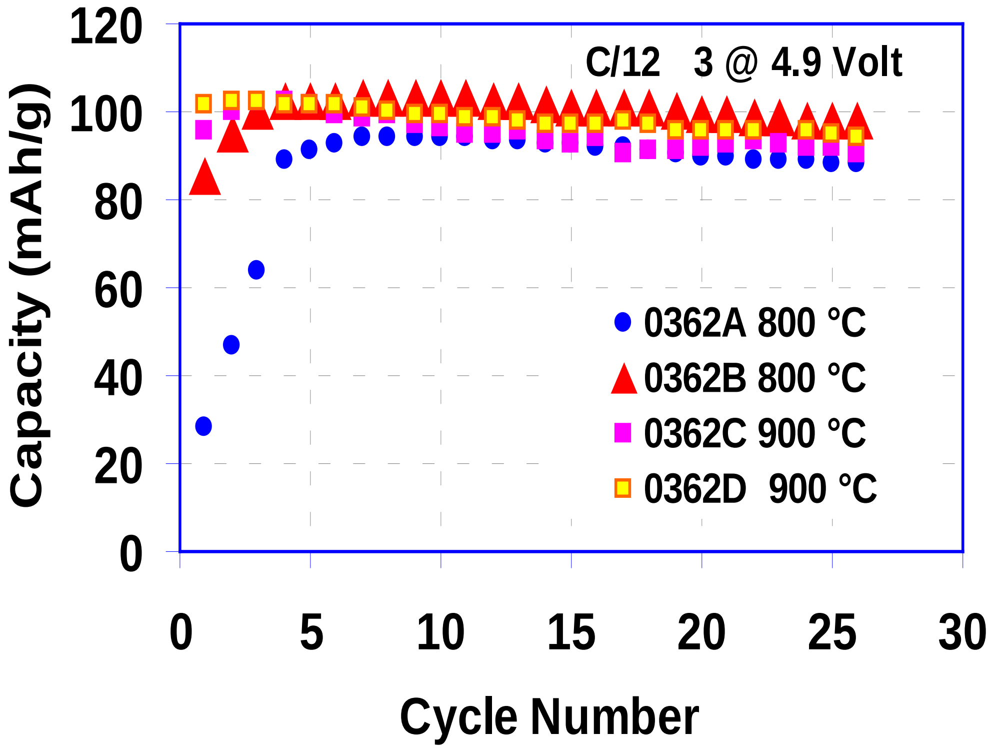
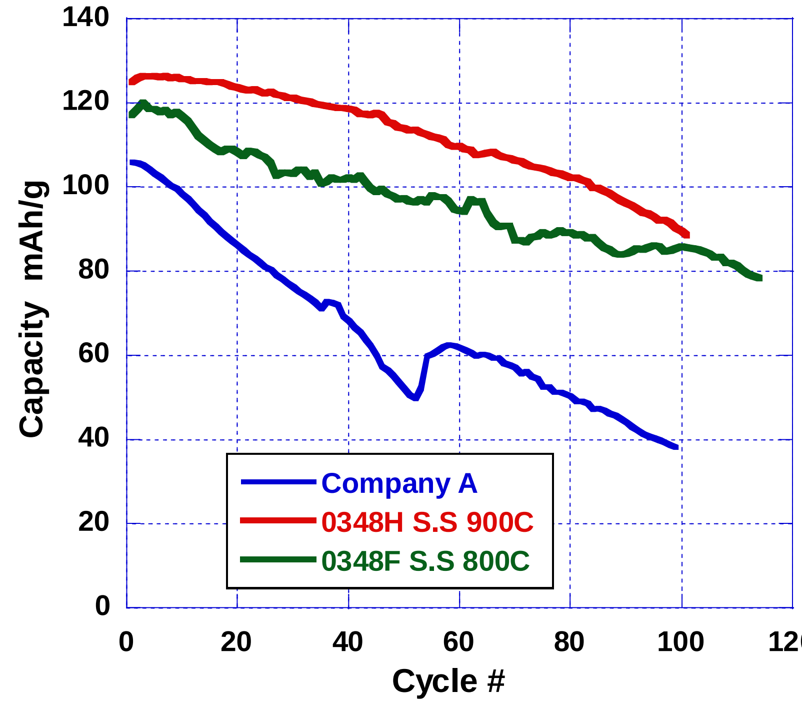
HQ Synthesis of $LiMn_{3/2}Ni_{1/2}O_4$: Formation



The oxygen deficiency under high annealing temperature resulted in the Li_{1-x}-Ni_x-O impurities (2θ = 38° and 45° in XRD) as well as small amount of reduced Mn^{3+} (Mn^{4+}/Mn^{3+}) redox couple shows voltage plateau at 4.1 V).

HQ Synthesis of $LiMn_{3/2}Ni_{1/2}O_4$: Cycling

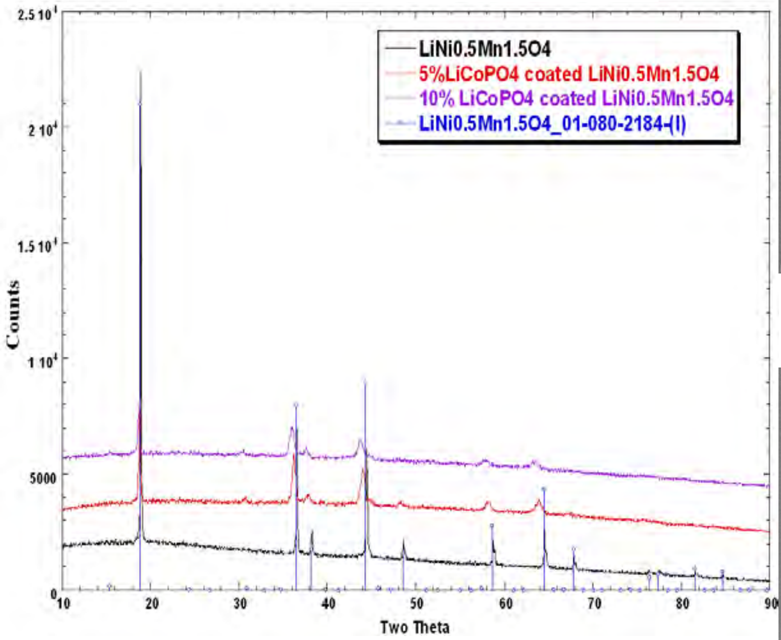




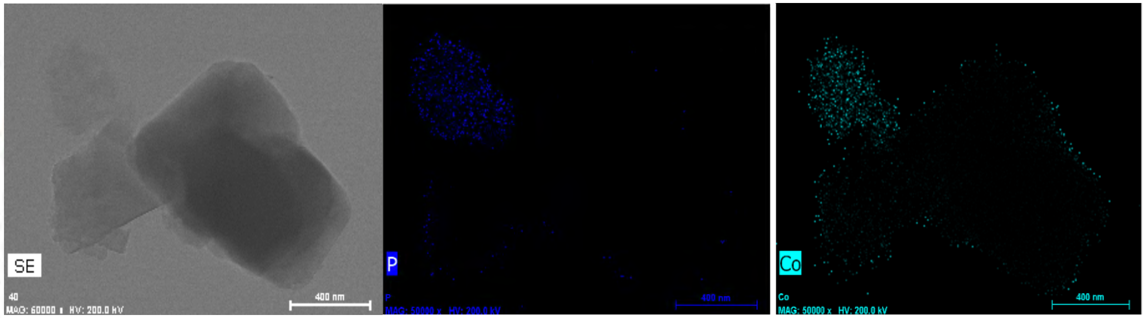
Materials synthesized at higher temperature show improved results

LiCoPO$_4$-Coated $LiMn_{3/2}Ni_{1/2}O_4$

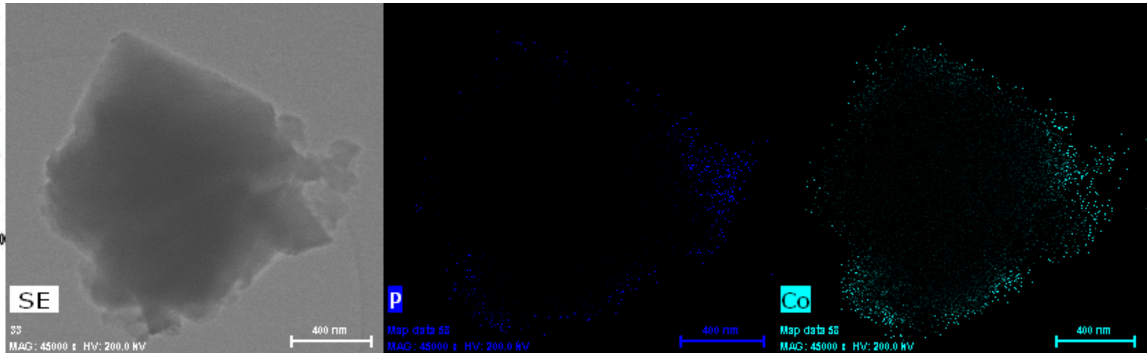
LiCoPO4 coated LNM in Ar



1 wt.% LiCoPO4 coated-LNM



5 wt.% LiCoPO4 coated-LNM



With traditional sol-gel method, no obvious impurities were detected in LiCoPO$_4$-coated LNM, but the diffraction peaks shift to lower angles, indicating the lattice parameters change after coating, probably some of the Mn^{4+} were reduced to Mn^{3+} in Ar.

Summary

Si Based Anode

- The C-SiO_x-graphite based anode with the polyacrylonitrile butadiene binder showed a reversible capacity of 972mAh/g and 1st coulombic efficiency of 80%, and quite stable cycling capacity at C/6.
- The effect of the binder on the (SiO_x: Gr (1:1)) anode performance is the following:

  Reversible Capacity: Polyimide > polyacrylonitrile butadiene > SBR > PVDF

  1st coulombic efficiency: SBR > polyimide = polyacrylonitrile butadiene > PVDF
- *In-situ* studies of the SiOx anode showed evidence that the larger particles (~ 13µm) start to crack at about 0.1V, but the smaller particles (< 2µm) are stable. Also some fissures were observed and the particles delaminate.
- Si-nano material based anode with the polyimide binder showed a reversible capacity of 1150mAh/g and 1st coulombic efficiency of 50%.

Spinel $LiMn_{3/2}Ni_{1/2}O_4$ Cathode Material

- Trace impurities observed in HQ-synthesized LMN samples; higher temperature leads to better crystallization with disordered structure. The highest reversible capacity obtained was 140mAh/g.
- C-$LiFePO_4$ nano-particles were coated on the LMN surface using a dry process, and promising results were obtained at 1C rate.
- $LiCoPO_4$ coating in argon does not change the bulk structure of LMN, but some Mn^{4+} may be reduced to Mn^{3+}.
- Developing in-situ SEM and TEM tools for the anode and cathode materials.
- Evaluation of 18650 cells fabricated at HQ was started.

Future Activities

- **Remainder of this year**

  - **Continue evaluation of mixed graphite-SiO_x and nano-Si as an alternative anode.**
  - **Continue improving the performance of the HQ-synthesized $LiMn_{3/2}Ni_{1/2}O_4$ cathode for high energy, and send the optimized samples to PIs in the BATT Program for evaluation.**
  - **Continue exploring surface stabilization of the high-voltage $LiMn_{3/2}Ni_{1/2}O_4$ cathode.**
  - **The successful *in-situ* SEM studies on the anode has encouraged us to continue studies on the Si and SiO_x with different binders, and to investigate the surface of $LiMn_{3/2}Ni_{1/2}O_4$ cathodes.**
  - **Evaluate high-voltage stable electrolytes with $LiMn_{3/2}Ni_{1/2}O_4$ cathode.**
  - **The 18650 cells fabricated at HQ show promising results that will be helpful to other BATT investigators who want to take advantage of the HQ coating, calendering equipment and cell assembly facilities.**
  - **Fabricate and test 18650 cells with oxide-$LiMn_{3/2}Ni_{1/2}O_4$ cathodes and SiO_x/graphite anodes, and provide cells to investigators in the BATT program for evaluation.**

- **All milestones completed**

Technical Back-up Slides

Installation for fabrication of 18650 cylindrical cells

18650 cells

Slitting and cutting machine

Necking machine

Winding machine

Installation inside the dry room

Dry room

Electrolyte filling machine

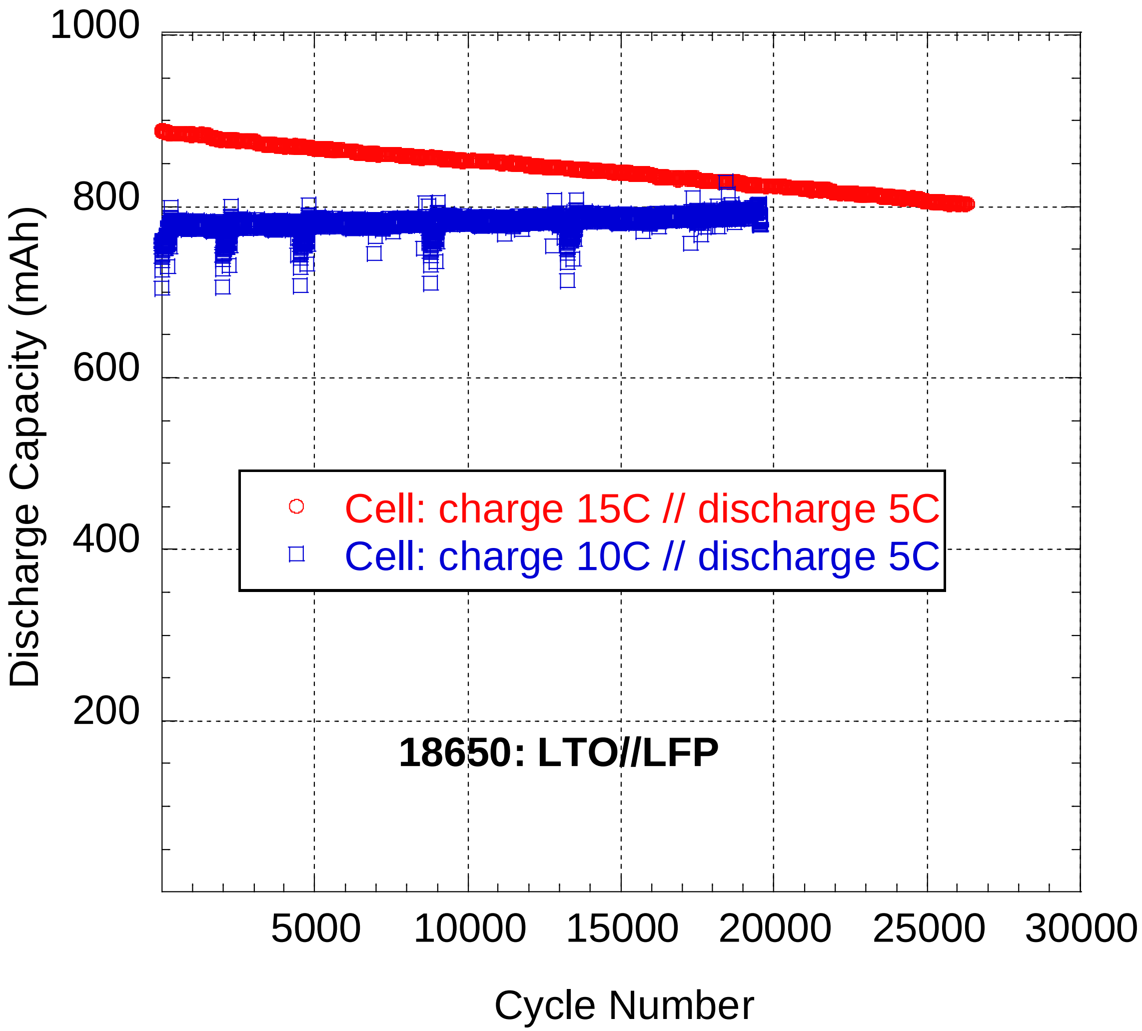
Heating type rollpress machine

Ultrasonic welding machine

Spot-welding machine

Crimping machine

18650 Cells LTO/LFP



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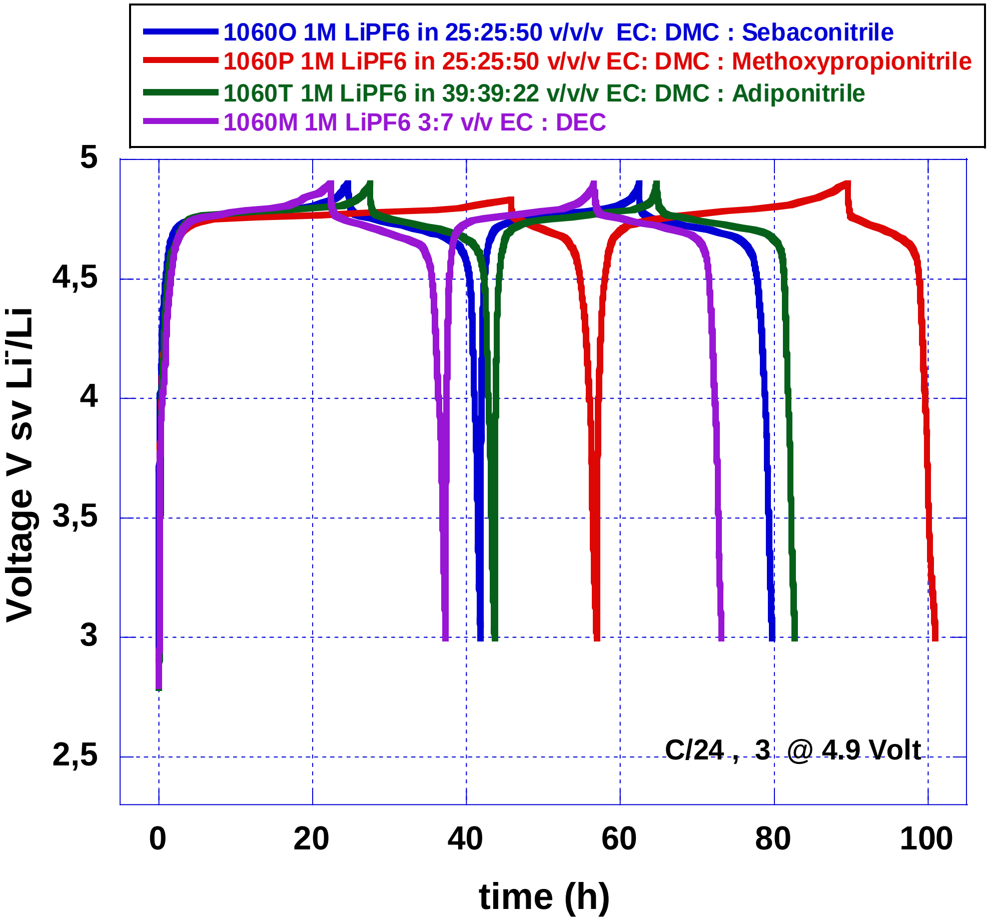
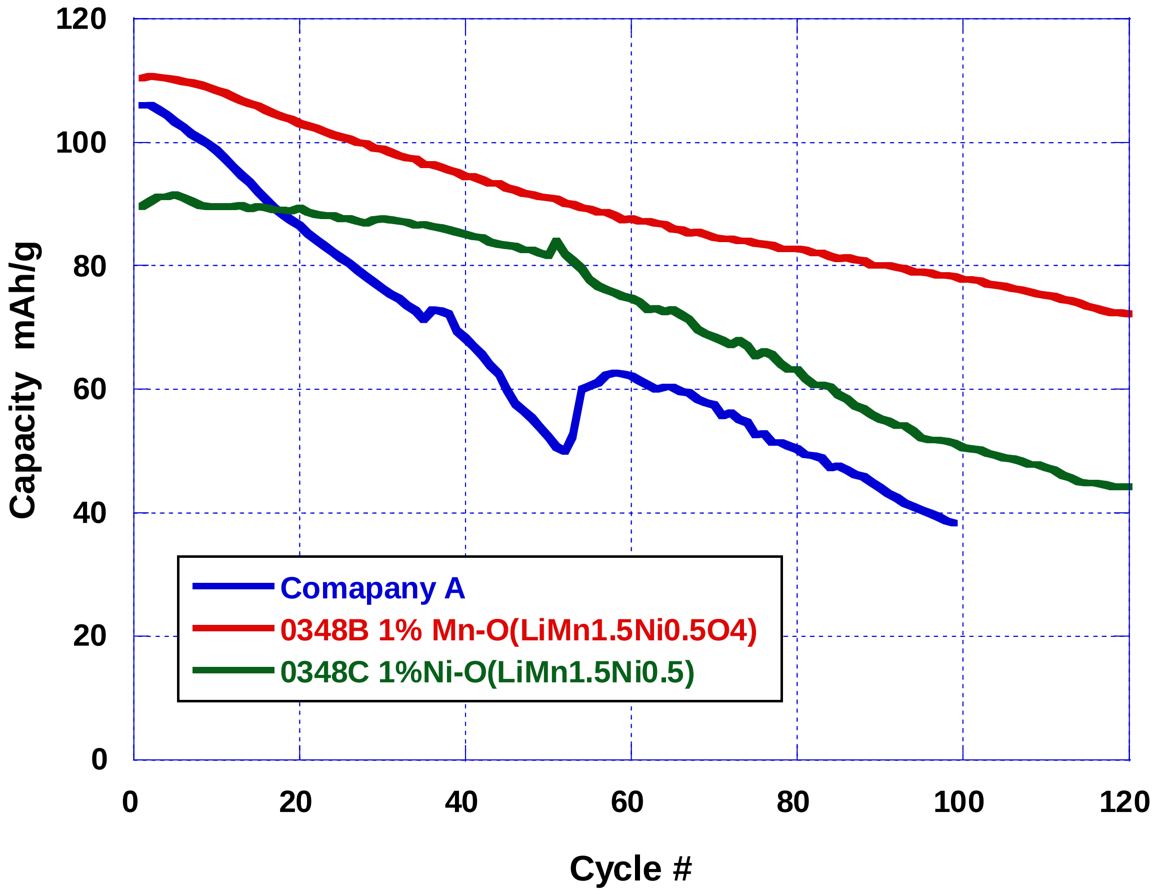
Electrolytes Stable at High voltage



Electrolyte Configuration	1st EC (%)	Rev. Cap. (mAh/g)
1M LiPF6 in 25:25:50 v/v/v EC: DMC : Sebaconitrile	70	111
1M LiPF6 in 25:25:50 v/v/v EC: DMC : Methoxypropionitrile	24	73
1M LiPF6 in 39:39:22 v/v/v EC: DMC : Adiponitrile	59	116
1M LiPF6 3:7 v/v EC : DEC	67	104

-The best charge-discharge performance was obtained during the formation cycles with an electrolyte containing Sebaconitrile as additive.

Oxide-coated $LiMn_{3/2}Ni_{1/2}O_4$:



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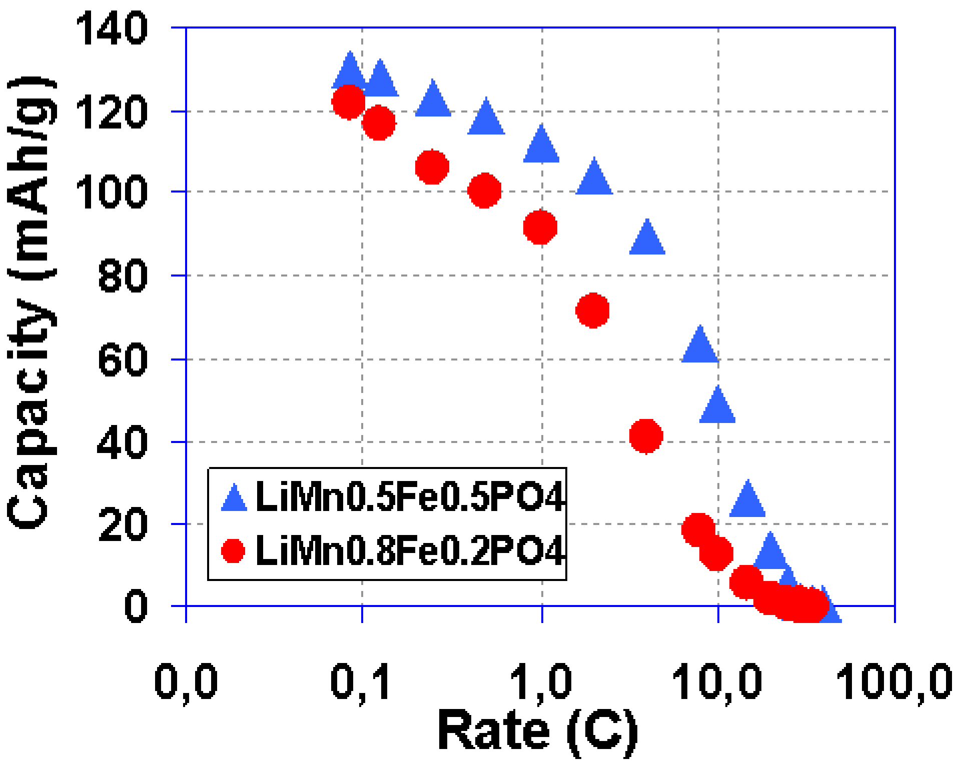
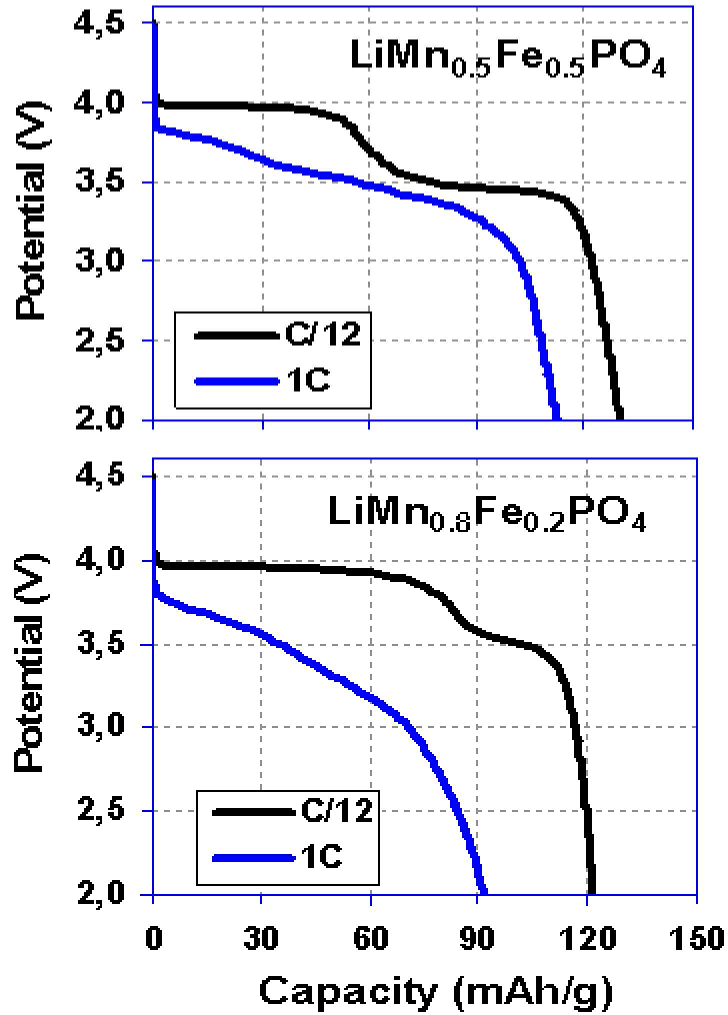
$LiMn_{(1-x)}Fe_xPO_4$ Cathode Material





-The substituted $LiMn_{1-x}Fe_xPO_4$ suffers at high rates, and the composition limit for power application should not exceed Mn content of 0.5.

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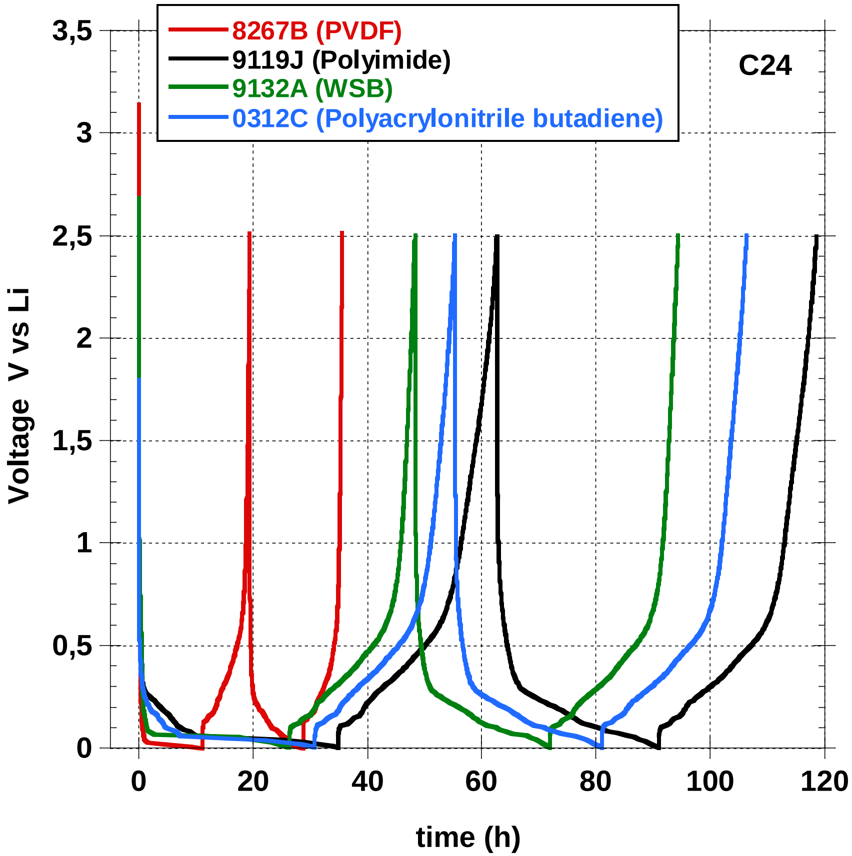
(SiO_x+ Graphite (1:1)) Anode: Binder Effect



Li coin type cell
1M $LiPF_6$-EC-DEC+2%VC

Discharge/Charge: C/24
T=25°C

	PVDF			WSB			Polyimide			polyacrylonitrile butadiene		
	Capacity (mAh/g)			Capacity (mAh/g)			Capacity (mAh/g)			Capacity (mAh/g)		
	Discharge	Charge	Eff. (%)	Discharge	Charge	Eff. (%)	Discharge	Charge	Eff. (%)	Discharge	Charge	Eff. (%)
Cycle 1	642	472	74	995	843	85	1332	1067	80	1177	941	80
Cycle 2	541	394	73	904	861	95	1085	1058	98	984	972	99

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