USABC PHEV Battery Development Project

Cyrus Ashtiani
ENERDEL
Project ID # ES004

OVERVIEW

Develop a battery system to match safety of the $Li_4Ti_5O_{12}$ anode with a stable high voltage 4.8V spinel cathode $LiMn_{1.5}Ni_{0.5}O_4$

TIMELINE

- Start: March 2008
- Finish: September 2009
- No cost extension to March 2010
- Last deliverable: March 4, 2010
- 100% completion

BARRIERS

- Development of a high voltage cathode
- Development of a high voltage electrolyte

PARTNERS

- Argonne National Laboratory

BUDGET

- Total project funding: $2.5 million 50-50% cost-share
- Funding received in FY08: 1.1 million
- Funding received in FY09: 1.4 million

OBJECTIVES

BASIC PREMISE	Explanation
	Use LTO Anode for Safety
	Use a high voltage cathode to make up for anode's higher operating voltage for better energy density

TASK 1: Cathode Material Development

- Obtain/Evaluate high voltage Mn Spinel from commercial vendors
- $LiMn_{1.5}Ni_{0.5}O_4$ synthesis and scale up under contract to ANL
- Material evaluation in large-format cells

TASK 2: Electrolyte Development

- Obtain and test HV electrolyte s from commercial sources
- Use HV electrolytes developed under contract by ANL

TASK 3: Cell Design/Development

- Scale up from coin cell to pouch cell
- Process optimization with new cathode to achieve homogeneous electrodes

TASK 4: Cell Testing

- Performance characterization tests
- Cycle life tests

MILESTONES: GATES & DELIVERABLES

Date	G/D	Accomplishment
7-15-08	G	Demonstrated safety of LTO based cell in a 5Ah design. Passed nail penetration test matrix at the worst-case abuse condition (100%SOC, 55°C)
12-24-09	D	Delivered 20-2.7Ah "CD size" LNMO/LTO "Gen1" cells to Idaho National Laboratory
3-3-10	D	Delivered 17-2.7Ah "CD size" LNMO/LTO "Gen1a" cells to Idaho National Laboratory incorporating enhanced ANL coated positive material
3-3-10	D	Delivered 3 CD sized LNMO/LTO cells to National Renewable Energy Laboratory for thermal characterization

APPROACH – MATERIAL DEVELOPMENT (+)

- Synthesize and scale up LNMO material production to allow fabrication of large format cells using pilot production equipment
- Surface coating to suppress reactions on the HV cathode

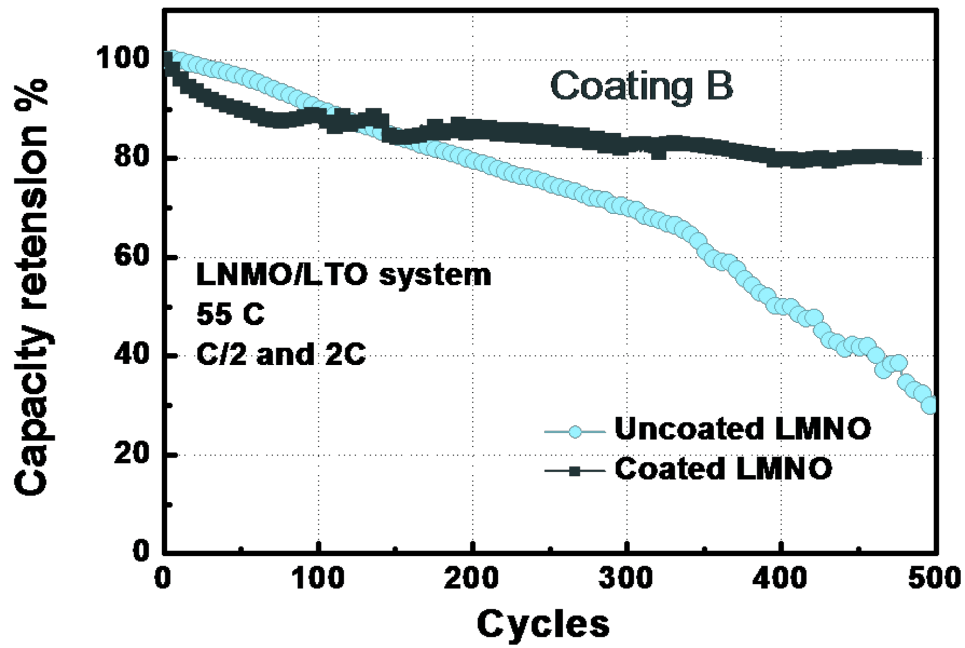
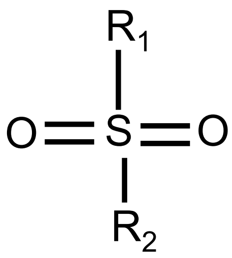
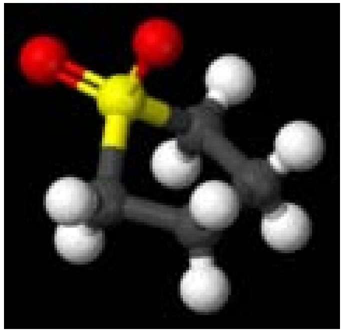


Fig. 1. Cycle life comparison of ANL-synthesized coated high voltage spinel with commercial sources of LNMO (w/o coating)

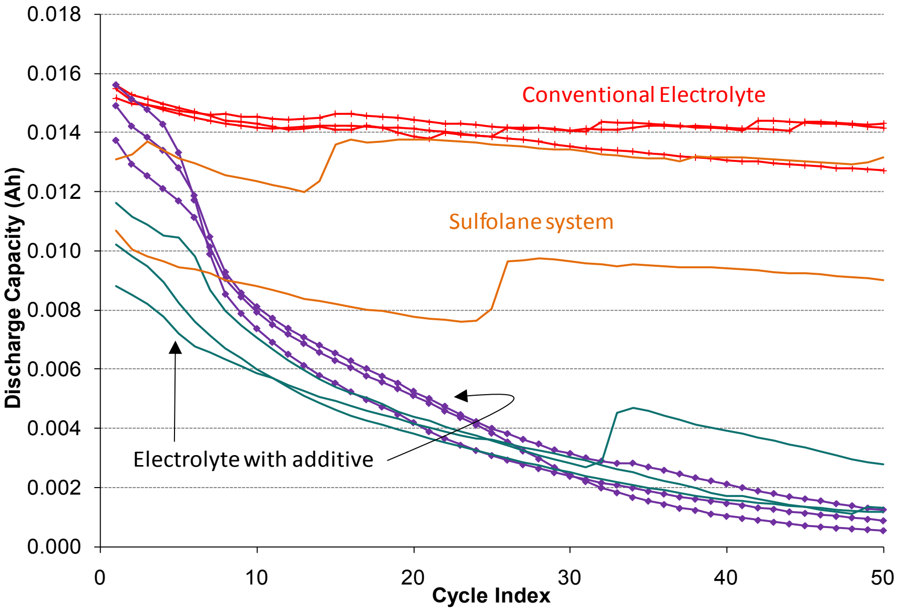
APPROACH – ELECTROLYTE DEVELOPMENT

- Use /develop electrolyte systems that show stability up to 5V
- ENERDEL initially screened several electrolyte systems using cyclic voltammetry data
  - Sulfolane-based solvents
  - Ionic liquids
  - Fluorinated solvent systems
  - SEI forming additives
- Cells were made with electrolytes that passed initial screening and subsequently tested on cycle life test for screening
- High purity conventional electrolyte has produced best results thus far





Tetramethylene sulfone (Sulfolane) $C_4H_8O_2S$



APPROACH – CELL DEVELOPMENT

- A negative-limited cell design was devised to reduce high potential on the positive electrode, thus reducing the likelihood of electrolyte oxidation

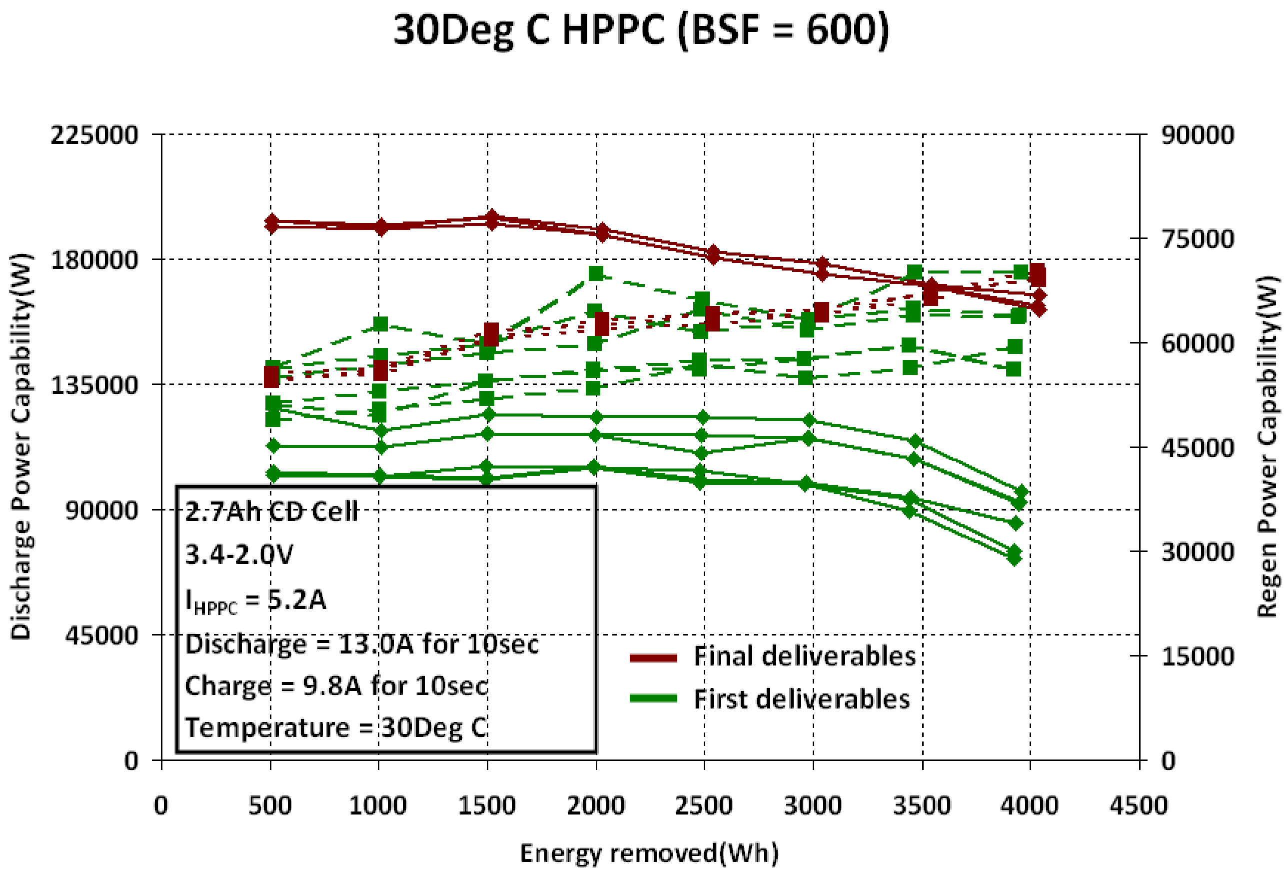
- Results indicate material processing to play a great role on performance of the LNMO cathode material.

- ENERDEL optimized processing and mixing of the slurry for the cathode to improve electrode performance.

- ENERDEL already has extensive experience with LTO which facilitated scaling for anode electrode development.

APPROACH – CELL TESTING

- Evaluate cell performance using HPPC test protocol for the 2.7Ah (CD size) cells scaled to full BSF, and demonstrate improvement



GAP ANALYSIS VS. USABC-PHEV GOALS

Attributes		High Power/Energy Ratio Battery			
	Unit	USABC	EnerDel Gen0 BOL	EnerDel Gen1 BOL	EnerDel GenX BOL
Reference Equivalent Electric Range	miles	10	10	10	10
Peak Pulse Discharge Power - 2sec / 10sec	kW	50 / 45	100, 10sec	180, 10sec @50% SOC	65 / 58.5 with 3.4 kWh
Peak Regen Power (10sec)	kW	30	65, 10sec	60, 10sec @50%SOC	39 with 3.4 kWh
Available Energy for CD mode, 10kW rate	kWh	3.4	4.4	4.4	4.42 with 50 / 45 kW
Available Energy for CS mode	kWh	0.5	0.5	0.55	0.65 with 50 / 45 kW
Mininum Round-Trip Energy Efficiency (USABC HEV Cycle)	%	90	-	>97%	>97
Cold cranking power at -30°C, 2sec - 3pulse	kW	7	-	19.8	7, min V: 1.5
CD Life / Discharge Throughput	Cycles/MWh	5,000 / 17	-	956/2.7	5,000 / 17
CS HEV Cycle Life, 50Wh Profile	Cycles	300,000	-	10,000+	300000 (TBD)
Calendar Life, 35°C	year	15	-	-	15 (TBD)
Maximum System Weight	kg	60	360	87, cells only	60
Maximum System Volume	Liter	40	240	50, cells only	40
Maximum Operating Voltage	V dc	400	360	360	360
Minimum Operating Voltage	V dc	>0.55 x Vmax	198	198	198
Maximum Self-discharge	Wh / day	50	-	-	<50
Thermal Performance @-30°C			-	-	10%
Thermal Performance @-10°C			-	-	30%
Thermal Performance @0°C			-	-	50%
Thermal Performance @50°C			-	-	>100%
System Recharge Rate at 30°C	kW	1.4 (120V/15A)	-	-	1.4 (120V/15A)
Unassisted Operating & Charging Temperature Range	°C	-30 to +52	-30 to +52	-30 to +52	-30 to +52
Survival Temperature Range	°C	-46 to +66	-46 to +66	-46 to +66	-46 to +66
Maximum System Production Price @ 100k units / yr	$	1700	2544	2544	2544
Battery Size Factor			80,000	600	100

TECHNICAL ACCOMPLISHMENTS

Positive Material Development

- Successful scale-up of LNMO cathode material to 10kg batches
- More than 80 Kg of material was used in the course of program
- Demonstrated enhanced cycling at higher temperatures using surface-coated ANL high voltage spinel

Electrolyte Development

- Screened promising HV electrolytes.
- High purity conventional electrolytes resulted in best cycle-life thus far

Cell Design & Development

- Scaled up from a coin cell to a 2.7Ah "CD size" cell
- Developed a negative-limited cell design to limit positive electrode potential for oxidation

Deliverables

- A total of 40-2.7Ah "CD size" cells were shipped to INL and NREL

FUTURE WORK – PROJECT COMPLETED

- ENERDEL will continue testing the PHEV cells in-house

- Continue efforts for evaluating and developing a stable LNMO cathode material with surface coating
  - Third party sources of cathode material will continue to be evaluated.

- Continue research and screening of high voltage stable electrolytes
  - Ionic liquids
  - Fluorinated solvent systems

- Continue cell design optimization to fully utilize LNMO potential for both higher voltage and higher charge capacity

COLLABORATIONS

Partner

- Argonne National Laboratory
  - Supplied $LiMn_{1.5}Ni_{0.5}O_4$ surface coated cathode material for use in all cell deliverables in the program
  - Synthesized and evaluated electrolytes for use in the high voltage lithium-ion system.
  - Validated negative capacity limited cell design

SUMMARY

- ENERDEL developed a lithium-ion cell employing a 5V spinel cathode with LTO anode and demonstrated chemistry's safety and performance for PHEV applications.

- Pairing the high voltage spinel LNMO with LTO improved the energy density of the cell while benefiting from LTO excellent safety characteristics

- Demonstrated scale-up of the synthesized positive material, as well as the cell from a coin-size to a "CD" size p0uch cell

- A variety of electrolyte systems were screened for HV stability and a high purity conventional electrolyte was selected to carry on cell design & development

- An anode –limited cell was designed to suppress oxidation on the HV cathode

- Side reactions on the positive electrode were further reduced by a surface coating on the LNMO