

III

# Advanced Battery Development

USABC Battery Development Projects

Advanced Lithium Battery Cell Technology

Low-cost Processing Research

Advanced Materials and Processing (FY 2008 DOE FOA)

Small Business Innovative Research Projects (SBIR)





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## III. Advanced Battery Development

One of the primary objectives of the Energy Storage effort is the development of durable and affordable advanced batteries and ultracapacitors for use in advanced vehicles, from start/stop to full-power HEVs, PHEVs, and EVs. The battery technology development activity supports this objective through projects in several areas:

- Full-scale battery R&D under multiple battery development contracts—conducted through the United States Advanced Battery Consortium (USABC),
- Numerous advanced cell, materials and components contracts—administered through the National Energy and Technology Laboratory (NETL), and
- Small Business Innovative Research (SBIR)—to fund early-stage R&D for small businesses/entrepreneurs.

All battery development projects are conducted with a set of technical goals in mind and in order to overcome specific technical barriers which prevent the large-scale commercialization of advanced automotive batteries.

### Technical Goals

- By 2014, develop a PHEV battery that enables a 40 mile all-electric range and costs \$3,400.
- By 2022, reduce PEV battery cost to \$125/kWh.

### Technical Barriers

- **Cost** – The current cost of Li-based batteries is approximately a factor of four too high on a kWh basis for PEVs and approximately a factor of 50% too high on a kW basis for HEVs. The main cost drivers being addressed are the high costs of raw materials and materials processing, cell and module packaging, and manufacturing.
- **Performance** – The performance advancements required include the need for much higher energy densities to meet the volume and weight requirements, especially for the 40 mile PHEV system and longer range EVs, and to reduce the number of cells in the battery (thus reducing system cost).
- **Abuse Tolerance** – Many Li batteries are not intrinsically tolerant to abusive conditions such as a short circuit (including an internal short circuit), overcharge, over-discharge, crush, or exposure to fire and/or other high temperature environments. The use of Li chemistry in the larger (PEV) batteries increases the urgency to address these issues.
- **Life** – A 15-year life with 5,000 HEV cycles or 1,000 EV cycles is unproven.

### Technical Targets

- Focus on the small-scale manufacture of cells, batteries, and advanced materials for high-power applications (HEVs) and high-energy applications (e.g., PEVs).
- Attempt to meet the summary requirements for EVs, PHEVs, HEVs, and Lower-energy energy storage systems (LEESS) developed with industry – as shown in Table III - 1, Table III - 2, and Table III - 3.

### Accomplishments

- The R&D activity remains fully underway with multiple battery development contracts being conducted through the USABC.
- Numerous advanced cell, materials, and components contracts are ongoing – administered through the National Energy and Technology Laboratory (NETL).

**Table III - 1: Summary of USABC performance targets for EV batteries<sup>9</sup>****USABC Goals for Advanced Batteries for EVs - CY 2020 Commercialization**

<b>End of Life Characteristics at 30°C</b>	<b>Units</b>	<b>System Level</b>	<b>Cell Level</b>
Peak Discharge Power Density, 30 s Pulse	W/L	1000	1500
Peak Specific Discharge Power, 30 s Pulse	W/kg	470	700
Peak Specific Regen Power, 10 s Pulse	W/kg	200	300
Useable Energy Density @ C/3 Discharge Rate	Wh/L	500	750
Useable Specific Energy @ C/3 Discharge Rate	Wh/kg	235	350
Useable Energy @ C/3 Discharge Rate	kWh	45	N/A
Calendar Life	Years	15	15
DST Cycle Life	Cycles	1000	1000
Selling Price @ 100K units	\$/kWh	125	100
Operating Environment	°C	-30 to +52	-30 to +52
Normal Recharge Time	Hours	< 7 Hours, J1772	< 7 Hours, J1772
High Rate Charge	Minutes	80% ΔSOC in 15 min	80% ΔSOC in 15 min
Maximum Operating Voltage	V	420	N/A
Minimum Operating Voltage	V	220	N/A
Peak Current, 30 s	A	400	400
Unassisted Operating at Low Temperature	%	> 70% Useable Energy @ C/3 Discharge rate at -20 °C	> 70% Useable Energy @ C/3 Discharge rate at -20 °C
Survival Temperature Range, 24 Hr	°C	-40 to + 66	-40 to + 66
Maximum Self-discharge	%/month	< 1	< 1

<sup>9</sup> For more details and for additional goals, see [http://www.uscar.org/guest/article\\_view.php?articles\\_id=87](http://www.uscar.org/guest/article_view.php?articles_id=87).

**Table III - 2: Summary of USABC performance targets for PHEV batteries**

<b>Characteristics at End of Life (EOL)</b>		<b>High Power/ Energy Ratio Battery</b>	<b>Moderate Energy/Power Ratio Battery</b>	<b>High Energy/ Power Ratio Battery</b>
Reference Equivalent Electric Range	miles	10	20	40
Peak Pulse Discharge Power (2 sec/10 sec)	kW	50/45	45/37	46/38
Peak Regen Pulse Power (10 sec)	kW	30	25	25
Available Energy for CD (Charge Depleting) Mode, 10 kW Rate	kWh	3.4	5.8	11.6
Available Energy in CS (Charge Sustaining) Mode	kWh	0.5	0.3	0.3
Cold cranking power at -30°C, 2 sec – 3 pulses	kW	7	7	7
CD Life / Discharge Throughput	Cycles/MWh	5,000/17	5,000/29	5,000/58
CS HEV Cycle Life, 50 Wh Profile	Cycles	300,000	300,000	300,000
Calendar Life, 35°C	year	15	15	15
Maximum System Weight	kg	60	70	120
Maximum System Volume	Liter	40	46	80
Maximum Operating Voltage	Vdc	400	400	400
Minimum Operating Voltage	Vdc	>0.55*V <sub>max</sub>	>0.55*V <sub>max</sub>	>0.55*V <sub>max</sub>
Maximum self-discharge	Wh/day	50	50	50
System Recharge Rate at 30°C	kW	1.4 (120V/15A)	1.4 (120V/15A)	1.4 (120V/15A)
Unassisted Operating & Charging Temperature	°C	-30 to +52	-30 to +52	-30 to +52
Survival Temperature Range	°C	-46 to +66	-46 to +66	-46 to +66
Maximum current (10 sec pulse)	Amp	300	300	300
Maximum System Production Price @ 100k units/year	\$	\$1,700	\$2,200	\$3,400

**Table III - 3: Summary of USABC performance targets for power assist hybrid electric vehicles**

<b>Characteristics</b>	<b>Lower Energy Energy Storage System (LEESS)</b>	<b>Power Assist (Minimum)</b>	<b>Power Assist (Maximum)</b>
Pulse discharge power (kW)	20 (10 sec)	25 (10 sec)	40 (10 sec)
	55 (2 sec)		
Peak Regenerating Pulse Power (kW)	30 (10 sec; 83 Wh)	20 (10 sec; 55 Wh pulse)	35 (10 sec; 97 Wh pulse)
	40 (2 sec; 22 Wh)		
Total Available Energy (kWh)	0.056 (Discharge)	0.3	0.5
	0.083(Regenerative)		
	0.026 (Both)		
	0.165 (Total vehicle window)		
Cycle Life (cycles)	300k	300k; 25-Wh cycle (7.5 MWh)	300k; 50-Wh cycle (15 MWh)
Cold-cranking Power at -30°C (kW)	5 (after 30 day stand at 30°C)	5 (three 2-sec pulses, 10-sec rests between)	7(three 2-sec pulses, 10-sec rests between)
Calendar Life (years)	15	15	15
Maximum System Weight (kg)	20	40	60
Maximum System Volume (liters)	16	32	45
Production Price @ 100k units/year (\$)	\$400 (Selling price per system)	\$500	\$800
Unassisted Operating temperature Range (°C)	-30 to +52	-30 to +52	-30 to +52
Survival Temperature Range (°C)	-46 to +66	-46 to +66	-46 to +66

## III.A USABC Battery Development Projects

### III.A.1 EV Battery Development (Envia Systems)

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Start Date: December 2010  
Projected End Date: July 2013

#### Objectives

- Develop and evaluate high capacity manganese rich (HCMR™) cathode materials and screen various electrolyte formulations that meet the material target specifications.
- Design, build and test large capacity pouch cells integrating Envia's HCMR™ cathode and optimized electrolyte formulations that meet the USABC minimum goals for long term commercialization.

#### Technical Barriers

One challenge is to develop a cathode material with very specific electrochemical performance and incorporate it into a cell expected to meet numerous USABC cell targets. Many of the cell target specifications as with the material specifications will require optimization and balance in order to meet the various targets. In the cell, a balance between energy and power will exist and in the material, a compromise between specific capacity and cycle and calendar life will exist. This project consists of developing the best materials and integrating them in an optimal cell design to meet the USABC targets.

Another challenge is that the HCMR™ cathode is a relatively new material. Unlike other more established cathode chemistries where there is an abundance of data and performance trends, HCMR™ cathode data in many occasions (specially for large cell data) is being reported for the first time.

Envia's HCMRTM/graphite cells potentially operate at higher voltages than commercially available cells. In order to meet the USABC targets, this will require an electrolyte that operates at high voltages, low and high

temperatures and supports long cycle and calendar life. Some specific barriers that have been addressed throughout this project are:

- High irreversible capacity loss (IRCL)
- Oxygen loss during cycling ( $\text{Li}_2\text{MnO}_3 \rightarrow \text{MnO}_2 + 2 \text{Li}^+ + 1/2\text{O}_2$ ), which leads to gassing in the pouch cell
- High DC-Resistance
- Fade in average voltage upon cycling
- High Manganese dissolution leading to poor cycle life and calendar life

#### Technical Targets

- Develop a high specific capacity cathode (>200mAh/g at C/3) able to meet the energy, power, cycle life, calendar life and cost targets.
- Develop and utilize a high voltage, stable electrolyte formulation that can operate in the temperature range of -40°C to 55°C and be able to support high energy and power, a cycle life of 1,000 cycles and a calendar life of 10 years.
- Design, develop, build and test ≥20Ah cells, which meet the USABC minimum goals for long term commercialization of EVs.

#### Accomplishments

- Envia down-selected an HCMR™ cathode after extensive material development with respect to composition, dopants and surface coatings. The material development consisted of optimizing the chemical and physical properties of the cathode to improve the specific discharge capacity, rate capability, cycle life, transition metal (TM) dissolution, and DC-resistance of the material.
- The down selected cathode materials were scaled up to kilogram levels and integrated in large capacity cells to support a total of nine project cell builds.
- A new baseline electrolyte was selected based on improved low temperature performance while maintaining similar room temperature cycling stability, power and energy characteristics compared to Envia's high voltage baseline electrolyte.

- Envia has met a majority of the stringent requirements for electric vehicle (EV) batteries. Envia demonstrated meeting the gravimetric and volumetric power and energy targets from 20Ah capacity pouch cells.



## Introduction

Envia Systems proposed to develop large capacity (20Ah-40Ah) pouch cells based on a novel high-voltage lithium rich cathode chemistry containing a layered-layered structure. The layer-layer composition is made up of interconnected  $\text{Li}_2\text{MnO}_3$  and  $\text{LiMO}_2$  domains. Upon initial charging to high potentials (>4.5V vs  $\text{Li}^0$ ), the material gets activated resulting in lithium extraction from the  $\text{Li}_2\text{MnO}_3$  component along with the loss of oxygen. This lithium removal gives rise to a first cycle irreversible capacity loss.

The new cathode chemistry can also be written in the form of  $\text{Li}_{1+x}\text{Ni}_\alpha\text{Co}_\beta\text{Mn}_\gamma\text{O}_2$  where the major TM component is Manganese, which reduces the amount of the costlier Nickel and Cobalt components. Having a high amount of manganese in the structure translates to high capacity, increased safety, and low cost.

## Approach

Our approach is very cathode centric, as we believe that the cathode is the biggest driver of overall performance and cost. New lithium-rich cathode compositions have been created with the layered-layered structure  $x\text{Li}_2\text{MnO}_3(1-x)\text{LiMO}_2$  where M= Ni, Co, Mn. In general, when the cathode chemical composition, surface nanocoating and morphology are changed, the cathode specific capacity, IRCL, average voltage, cycle life, and tap density of the material change. We will also explore dopants that are able to reversibly intercalate greater amounts of lithium, while controlling the oxidation state of the transition metal components ( $\text{Ni}^{+2}$ ,  $\text{Co}^{+3}$  and  $\text{Mn}^{+4}$ ) and retaining the crystal structure of the cathode.

Another way to engineer and control the cathode specific capacity, IRCL and average voltage is by having a nanocoating covering the surface of the cathode. The nanocoating has been shown to stabilize the cathode structure by preventing unwanted side reactions with the electrolyte and reducing the amount of cathode TM dissolution. As part of the project, various nanocoating compositions, as well as coating thicknesses will be explored and optimized. The thickness and uniformity of the nanocoating are dependent on the particle morphology (particle size, surface area and porosity) and reaction conditions.

Initial testing is performed using coin cells or 1Ah pouch cells and will be scaled up to larger pouch cells. Electrochemical and battery testing are being performed, along with material characterization using various analytical techniques.

## Results

In this first USABC project, Envia has met a majority of the stringent requirements for EV batteries. Envia demonstrated meeting the gravimetric and volumetric power and energy targets from 20Ah capacity pouch cells. Low temperature energy retention was shown to meet the specifications from room temperature to -30°C. DST cycle life testing is still ongoing with the latest data showing greater than 800 DST cycles (9 RPTs) while both energy and discharge power continue to stay above the 80% beginning of life (BOL) target (see Figure III - 1).

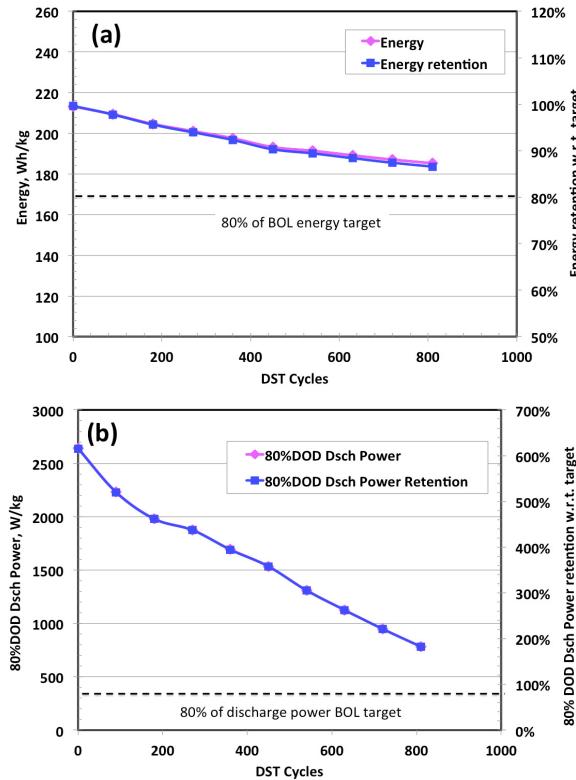


Figure III - 1: DST cycle life test results in terms of energy (a) and discharge power (b) for 20Ah capacity pouch cells

Calendar life testing is also ongoing with promising results being shown after seven months of testing. The models to properly predict the calendar life continue to be developed as more data continues to be collected. During the course of the project, the cell-to-pack conversion factors and pack-related costs were calculated by working with a system integration

company. The pack related costs for a 40kWh pack were determined to be \$2,626 and volumetric and gravimetric energy and power cell-to-pack multiplication factors found to be 58% and 70%, respectively. Cell cost analysis was also performed determining the cell related selling price to be \$258/kWh.

Envia has been successful in meeting most of the USABC goals for EV batteries. With respect to calendar life, it is debatable as to whether our cells will meet the 10 year mark. Ideally we would be able to test the cells for 10 full years to determine this qualification, but that is not practical. Preliminary calendar life results at 30°C from our latest cells, suggest promising calendar life results. Envia continues testing and more data will be available to validate the calendar life models and life predictions.

### Conclusions and Future Directions

In its first USABC project, Envia has been able to meet all of the energy and power goals without maximizing the energy of the cathode by operating between 2.2V and 4.35V. As a continuation of the work, Envia continues to be committed to meeting the aggressive USABC cell targets to enable widespread adoption of EVs. Recently, new more aggressive USABC targets for EVs were made public together with a request for proposal information (RFPI). In order to have a better chance to meet the targets, Envia will propose to integrate high capacity lithium-rich cathodes with high capacity silicon-based anodes. Only in this combination can the new aggressive cost and energy targets be met. During this proposal, Envia will also partner with leading silicon chemical companies, as well as with leading electrolyte, separator and pre-lithiation companies. Having the right partners during the development will increase the probability of meeting the technical targets and ensuring that the developed technology can be mass-produced and commercialized.

## III.A.2 EV Battery Technology Assessment Program (Farasis Energy, Inc.)

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Subcontractor: Farasis Energy, Inc.

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Start Date: July 2012

End Date: August 2013

### Objectives

- Manufacture pouch cells based on BASF produced HENCM high capacity cathode material and Farasis cell technology.
- Conduct performance, life and safety testing of cells in parallel with DOE National Laboratories.

### Technical Barriers

New high capacity and high voltage cathode materials offer great promise in meeting the battery performance and cost goals required for the commercial acceptance of electric vehicles (EVs). However, Li-ion cells using these new materials can experience a range of challenges that can limit the full realization of their potential and must be addressed at both the material and cell level. These challenges include minimizing impedance and achieving acceptable cycle life at elevated voltages and temperatures, maximizing cathode material long term stability and ensuring the safety of large energy dense cells.

### Technical Targets

- Manufacture large, 30Ah Li-ion pouch cells suitable for EV applications based on BASF produced HENCM cathode material.
- Demonstrate the potential to meet DOE EV performance and safety goals through evaluation at Farasis and DOE National Laboratories.

### Accomplishments

- Demonstration of over 1,000 cycles in prototype small pouch cells cycling at a C/3 rate at 25 °C.
- Manufacture and delivery of 50, 30 Ah Li-ion pouch cells to DOE for evaluation at Idaho National Laboratory (INL), Sandia National Laboratory (SNL) and the National Renewable Energy Laboratory (NREL).



### Introduction

Farasis Energy, Inc proposed to produce and supply prototype high energy density Li-ion cells to USABC based on their current commercial 25Ah Li-ion pouch cell for detailed testing and evaluation. The cells were developed using the new transition metal layered-layered type cathode material originally developed at Argonne National Laboratory. BASF, a fully licensed supplier for this class of material is one of the few companies capable of producing these developmental materials on a large scale with commercial quality and consistency. Farasis has developed material processing and cell design methods to address some of the inherent issues associated with the performance and utilization of these cathode materials that have been major barriers to their commercialization, despite the major increase in gravimetric energy density they offer over current commercial cathode material alternatives. Beginning with cathode material supplied by BASF, Farasis proposed to process, build and supply Li-ion cells to USABC in a similar form factor to our current 25 Ah cells but with an almost 20-30% greater energy density.

### Approach

Farasis Energy, Inc currently produces a range of Li-ion cell and battery products including a 25 Ah, NCM cathode based pouch cell (Figure III - 2). The form factor and performance make it ideal for use in a range of automotive EV systems (Figure III - 3). We proposed to use this commercial form factor as the basis for the deliverable prototype cells.



Figure III - 2: Commercial 25 Ah Li-ion pouch cell

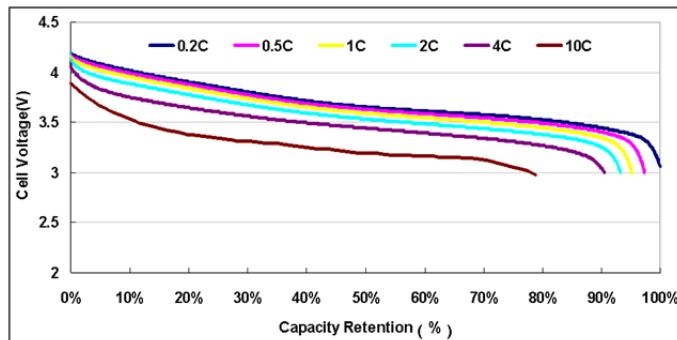


Figure III - 3: Rate capability of 25 Ah Li-ion pouch cell

To ensure the greatest performance and to enable us to optimize the cell design and material utilization, Farasis started with BASF's HENCM "Layered-layered" cathode material produced from their pilot manufacturing plant to make the cells. Additional processing of the materials prior to building the cells was conducted at Farasis. Initial batches of small prototype pouch cells were planned to deliver to DOE for initial evaluation.

## Results

Farasis manufactured both small pouch cells and large pouch cells as deliverables for this program. Cathode material from BASF was processed at Farasis Hayward and then used at its manufacturing facility to make pouch cells on its pre-production line. Figure III - 4 shows cycling data from prototype small pouch cells cycled at C/3 discharge rate.

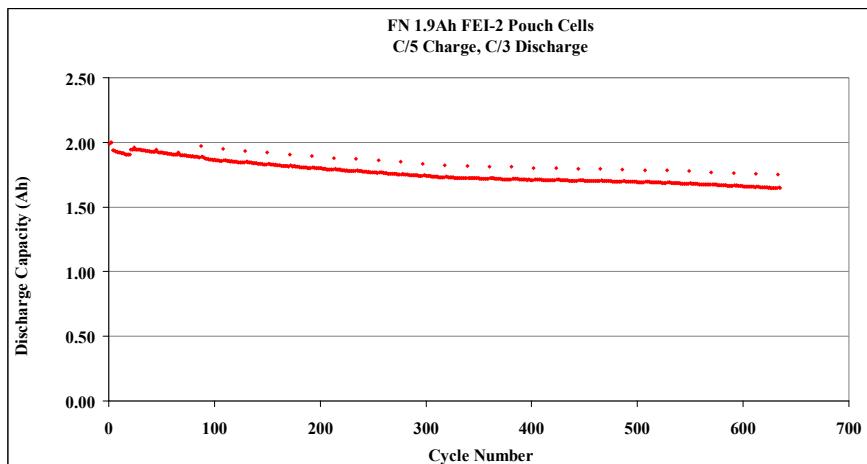
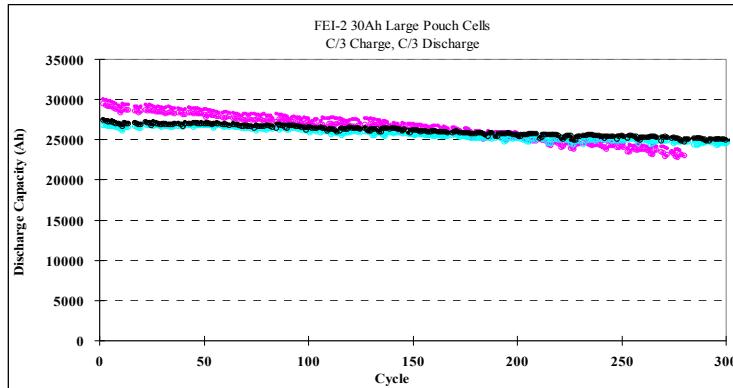


Figure III - 4: 2.0 Ah Li-ion pouch cell cycling data: C/5 charge, C/3 discharge

Figure III - 5 shows cycling data for several early prototypes of the 30 Ah cell design tested at Farasis

before the final production build. These cells were cycled with a C/3 charge and discharge rate.



**Figure III - 5: 30 Ah Li-ion pouch cell cycling data: C/3 charge, C/3 discharge**

Farasis shipped a large quantity of processed cathode material to its factory in March 2013 for the final deliverable cell build. Approximately 80 30 Ah cells were built at the factory using a design based on the 25 Ah production pouch cell form factor. Seventy cells were shipped to Farasis in Hayward, CA and 46 of these cells were shipped to Idaho National Laboratory for performance testing, Sandia National Laboratory for safety testing, and the National Renewable Energy Laboratory for thermal evaluation. The cells will be tested at these facilities and at Farasis over the next 6 months.

and DOE aimed at meeting the USABC PHEV battery performance targets. These cells will be evaluated both at Farasis and at the National Laboratories over the coming months. Farasis will continue its development of this high capacity Li-ion cathode chemistry to further improve the performance of this system. This technology has the potential to meet the long term USABC goals for PHEV and EV battery systems.

### Conclusions and Future Directions

Farasis has successfully delivered large high energy density Li-ion pouch cells for evaluation by USABC

### III.A.3 EV Battery Technology Assessment (SK Innovation)

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Subcontractor: SK Innovation

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Start Date: November 2012

Projected End Date: January 2014

#### Objectives

- Develop and validate a pure NCM battery system
  - High energy density
  - Long life performance
  - High abuse tolerance

#### Technical Barriers

One of the concerns about pure NCM system is safety. Therefore, improved ceramic coated separator and a new electrolyte system are required.

SK applied ceramic coated separator with superior strength and heat stability based on SK's own technology and also adjusted the electrolyte system.

#### Technical Targets

The USABC minimum electric vehicle (EV) battery technical targets for the system are listed in Table III - 4.

#### Accomplishments

- Validation of power density with over 600W/L and specific discharge and charge powers of over 460W/kg and 480W/kg
- Development of 40Ah cell with 230Wh/L and specific energy 150Wh/kg
- Successful life performance with over 2,000 cycles (expected)

Table III - 4: Summary of USABC targets for the system being developed

Parameter(Units) of fully burdened system	USABC minimum goals
<b>Power density (W/L)</b>	460
<b>Specific power</b>	300
<b>Dis. 80%DOD/30s (W/kg)</b>	
<b>Specific power</b>	150
<b>Regen, 20%DOD/10s (W/kg)</b>	
<b>Energy density</b>	230
<b>C/3 Discharge rate (Wh/L)</b>	
<b>Specific energy</b>	150
<b>C/3 Discharge rate (Wh/kg)</b>	
<b>Specific power/Specific energy ratio</b>	2 : 1
<b>Total pack size (kWh)</b>	40
<b>Life (Years)</b>	10
<b>Cycle life - 80% DOD (Cycles)</b>	1,000
<b>Power &amp; Capacity degradation (% of rated spec)</b>	20
<b>Operating environment (°C)</b>	-40 to +50 20% performance loss (10% desired)
<b>Normal recharge time</b>	6 hours (4 hours desired)
<b>High rate charge</b>	20-70% SOC < 30minutes @150 W/kg (<20min @ 270W/kg Desired)
<b>Continuous discharge in 1hour – No failure (% of rated energy capacity)</b>	75



#### Introduction

As the requirements for the EV market are getting more demanding in energy density and life including driving distance, SKI has developed and introduced high energy 40Ah (LMO-free) cells for this USABC EV technology assessment program. SKI set a goal of higher energy density and improved calendar life maintaining good cycle life and stability, and also developed 40Ah cell with Mn-spinel free and named it LMO-free E400. The LMO-free cell can avoid Mn-dissolution which brings crucial deterioration at high temperatures, so this program's cell is expected to have an improved calendar life.

SKI also applied a thermally superior ceramic coated separator and developed electrolyte formulation with adjusted electrolyte additives for LMO-free system. From performance validation tests, LMO-free

E400 could maintain other electrical performance as in previous systems.

### Approach

SKI applied pure NCM as cathode material to get high energy density and to avoid crucial deterioration at high temperature. However, high Ni-content NCM has a detrimental effect on the abuse tolerance and cycle life. In order to obtain structural stability, SKI has researched surface-coated NMC with stable materials. The surface-treated particles have shell-core morphology, that is, SC-NMC.

In addition, we enhanced the separator properties to minimize shrinkage of the separator at high temperatures, and developed the new electrolyte system which is an optimized formulation for the new cathode.

Cycle life and calendar life are expected to improve significantly after eliminating the Mn-spinel.

### Results

**Core Test.** SKI tested 18 cells in total (6 cells for cycle life and 12 cells for calendar life) and measured that the average capacity is over 40 Ah at current condition of C/3, C/2 and C/1 (Figure III - 6).

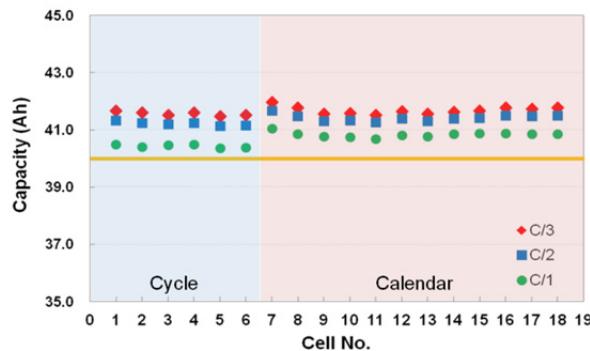


Figure III - 6: Constant current discharge test for LMO-free E400

100% DST Discharge capacity at the DST power of 400W/kg is 40.8Ah on average.

Peak power capability was calculated as shown below and showed a result of over 670W/kg.

$$\text{Peak power} = I_{\max} \cdot (V_{\text{IRFree}} + R \cdot I_{\max})$$

48h stand test showed very stable capacity retention with 0.95% capacity loss.

**Life Performance.** After successfully completing the core tests, six batteries have been in testing for cycle life. Cycle life tests will be conducted until End of Life (EOL).

Approximately, 4 cycles are accumulated per day and RPTs are being conducted every 100 cycles (~1/month). Figure III - 7 shows C/3 capacity retention and results show 91.3% of retention at 800 cycles. Similar tendency is seen in DST capacity retention (92.7%) and peak power retention (94.7%).

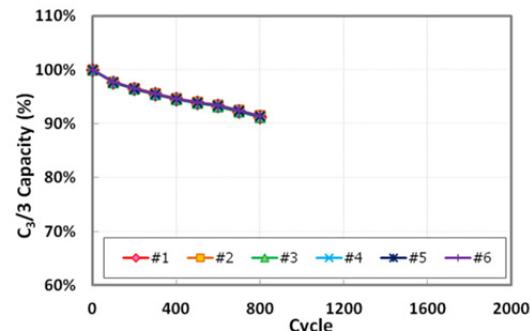


Figure III - 7: C/3 capacity retention of LMO-free E400 in cycle life

Calendar life tests are ongoing at four different temperatures of 25, 35, 45, and 55°C. Each battery is charged to SOC 100% at the C/3 rate and allowed to rest in an open circuit condition at the desired temperature for 4 weeks. At the end of 4 weeks, the batteries undergo RPTs at 30°C. Figure III - 8 shows C/3 capacity retention at four temperatures after 24 weeks and the results show 94.4%, 91.5%, 87.4%, and 81.0%, respectively.

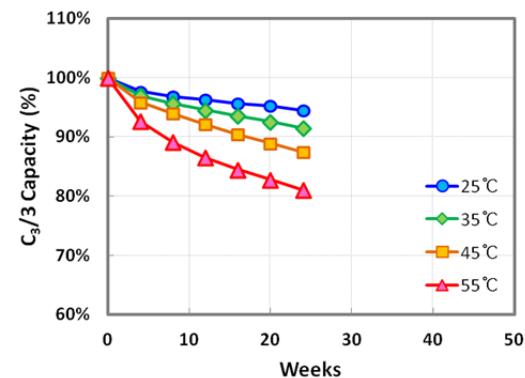


Figure III - 8: C/3 capacity retention of LMO-free E400 in calendar life

There is no significant degradation to 45°C and similar tendency is shown in DST capacity retention (96.1%, 92.4%, 89.0% and 82.2% at 25°C, 35°C, 45°C and 55°C; after 24 weeks).

However, comparatively high degradation is observed at 55°C and this appears clearly in peak power retention (98.4%, 95.8%, 92.9% and 76.8% at 25°C, 35°C, 45°C and 55°C, respectively; after 24 weeks). We can presume that unstable SEI forms on anode surface

from electrolyte decomposition between 45°C and 55°C, and it brings comparatively high capacity irreversibility.

Abuse tests were carried out and LMO-free E400 showed stable behavior after abuse tests as shown in Table III - 5. SKI followed SAND 2005-3123 abuse tests manual which was distributed by SNL, and some specific test conditions (e.g., resistance for short circuit;

1mΩ and 10mΩ) were given by SNL for this program. Abuse tests were performed and the tested cells met most of the established goals, with the exception of the thermal ramp test. In the case of thermal ramp test, the objective of the test is monitoring thermal onset through temperature increase. The LMO-free cell turned out to be stable up to 180°C.

**Table III - 5: Summary of abuse test results for LMO-free E400**

Items		Conditions	LMO free 400
Thermal Stability	Thermal Stability	SAND 2005-3123; Increasing temp. up to 200°C (hold 30min every 20°C from 110°C to 200°C, with 5°C/min ) @ SOC90%	L4 (mainly leakage, no smoke)
	Thermal ramp	SAND 2005-3123; Increasing temp. up to thermal runaway with 5°C/min @ SOC90%	Stable up to 180°C
Nail Penetration	Face	SAND 2005-3123; Pin dia=3mm, Speed 80mm/s @ SOC100%	L3
	Edge		L3
Short Circuit	Resistance 1mΩ	SAND 2005-3123; @ SOC100%	L3
	Resistance 10mΩ		L3
Overdischarge		SAND 2005-3123; 1C, 1.5h @SOC100%	L2

### Conclusions and Future Directions

SKI has evaluated LMO-free E400 and cycle life and calendar life will be continuously conducted until RPT10. Currently, based on capacity retention of 80%, cycle life is expected to exceed 2,000 cycles and calendar life of over 70 weeks at 45°C and 100% SOC – SKI will estimate battery life with RPT10 data at the end of the program. SKI would like to continuously develop and modify cell design including electrolyte optimization and adjustment of cathode formulation in order to improve safety further.

## III.A.4 Advanced High-Performance Batteries for Plug-In Hybrid Electric Vehicle Applications (JCI)

**Renata Arsenault, USABC Project Manager**

Subcontractor: Johnson Controls Inc.

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Start Date: April 1, 2012

End Date: March 31, 2014

### Objectives

- Build on the prismatic cell platform developed in the previous program and achieve a step-change in energy density from 275 Wh/L to a 375 Wh/L stretch goal.
- Achieve cost target of \$250/kWh for the prismatic cell.
- Target EUCAR 4 abuse tolerance rating or better.
- Deliver two generations of prismatic cells.

### Technical Barriers

- Higher specific capacity cathode materials of interest have reduced thermal stability (reduced life).
- Novel electrode material processing techniques may have a negative impact on performance and life.
- Lowering the power to energy ratio must not result in an unacceptable reduction in low temperature power.
- Higher upper voltages adversely affect life and require countermeasures to stabilize the chemistry.
- Abuse tolerance improvements require material and process innovation to overcome impact on life and cost.

### Technical Targets

- Available Energy (Charge Depleting mode): 5.8 kWh for 20-mile system at End of Life (EOL).
- Energy Density: 375 Wh/L (stretch goal).

- Packaged Energy Cost: \$250/kWh for cell.
- EUCAR 4 abuse tolerance rating or better.

### Accomplishments

- Evaluated multiple cathode materials from six suppliers. Two materials remain as candidates after exhaustive down selection trials.
- Mid-program cells demonstrated a 25% capacity increase.
- Projected final cell design translates to 40% cost reduction at the system level.
- Dry compounding trials achieved desired reduction of solvent and binder. High resistance growth and cost have eliminated this process technique going forward.
- Paste mix processing was evaluated using an in-line compound mixer as a potential enabler of solvent reduction goals. Promising results were obtained, attaining the high electrode densities needed for the cell energy density targets. Testing through December 2013 will assess potential for anode and cathode high solids processing.
- Evaluated 4.2V and 4.3V upper voltage limits in parallel with electrolyte development (base solvents and additives) for enhanced stability. Demonstrated results at 4.2V have allowed  $V_{max}$  increase from 4.1V.
- Mechanical improvement activity resulted in mandrel elimination as well as current collector and coating area optimization, plus alternate fill hole closure method down-selection. Results inform final build choices.
- Abuse tolerance improvements focused on Thermal Protective Barrier (TPB), ceramic coating on anode, ceramic separators, electrolytes and cathodes with functional overcharge additives, all leading to improved over-charge protection and enhanced understanding.



### Introduction

In 2011, JCI completed a three-year program which developed a first generation NMC-graphite, rigid prismatic cell technology headed for commercialization

in late 2013. This \$4.1 million, 2 year follow-on program builds on the first generation platform. The theme of this program is to achieve a major energy density improvement of the cell.

Between the conclusion of the previous program and the kick-off of this program, the

upward march in energy density continued, through continuous improvements made in process, materials and mechanical design. This improvement is seen in Figure III - 9.

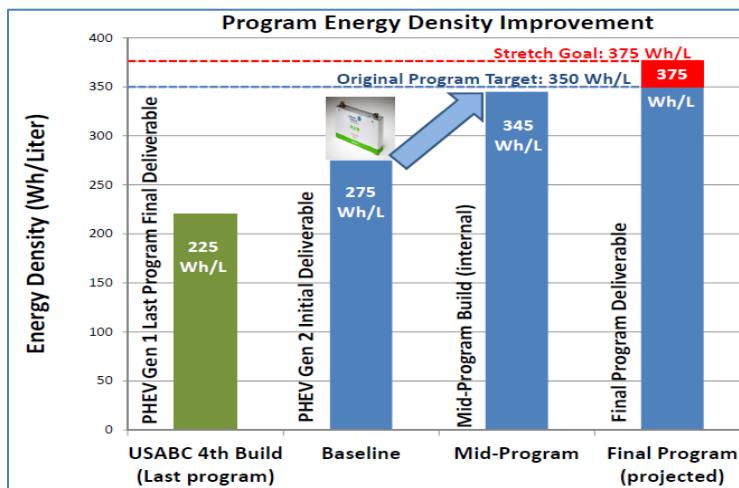


Figure III - 9: Energy density roadmap

## Approach

The objective of the program is to increase the energy density of the cell technology and drive down the cost to capacity ratio, either directly (with increased mAh/g, reduced BSF and cost) or indirectly (with improved critical enablers: life and abuse tolerance). The focus is on active materials that fall midway on the ‘state-of-the-art’ to ‘high-risk’ continuum, striving to exploit their full, unrealized potential through concerted material, process, and mechanical design innovation. Specifically, the family of  $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$  (where  $x>1/3$ ) is targeted for the positive electrode coupled with a graphitic negative material. Module and system development have been excluded from the program to focus resources on closing the gap in cell technology. If achieved, derivative system-level benefits of cost, volume and mass reduction will be realized and gap chart targets will be met.

Increased energy density is being pursued on four discrete levels: 1) active material specific capacity increase, 2) electrode composition (increased active material to inactive constituents ratio), 3) electrode densification, and 4) maximizing space occupied by the electrode coil in the cell envelope and increasing coated electrode width.

The following five improvement areas form the framework of the program, and all converge toward the central program goal of reducing the \$/kWh metric.

**Higher Energy Density Materials.** JCI is focusing on high-nickel NMC cathode materials. Compared to the baseline NMC111, high-nickel materials exhibit reduced structural and thermal stability, manifested by accelerated aging and lower abuse tolerance. To address this, stabilized active materials (doped, coated, and / or surface treated) from six global suppliers were evaluated.

Lithium-rich layered-layered cathode materials are also being evaluated to identify the main barriers that need to be overcome prior to commercialization.

**Electrode Processing Optimization.** Novel slurry processing techniques are being studied with two objectives: 1) reducing the quantity of N-Methyl Pyrrolidinone (NMP) solvent used in the positive electrode manufacturing process by 18-22% (result: cost reduction) and 2) improving the electrode handling through calendaring and winding to support electrode densification (result: increase in cell energy density).

Drivers for the amount of solvent, conductive agent and binder used in the current process are intimately linked to the type of mixing applied. JCI's process uses the classic industry approach for solids dispersion. Alternative methods of first compounding or pre-mixing active material with the conductive agent are being explored as paths to solvent reduction and associated increase in active to inactive material ratios and energy density.

**Electrode Design Optimization.** Electrode optimization focuses on reducing the power to energy

ratio (P:E) to the practical boundary where acceptable performance and life characteristics are maintained. This is being achieved by the aforementioned campaigns to increase specific capacity of the active material, increase energy density of the coated electrodes, and increase the loading level itself.

#### **Increased Upper V Limit and Increased SOC Window.**

Increasing the upper voltage limit beyond its current value of 4.1 V offers increased energy density and reduced \$/kWh, but may adversely impact life and abuse tolerance. To surmount these issues, stabilized active materials and electrode and interface stabilization will be evaluated.

Stabilization of the negative electrode/electrolyte interface would in turn allow expansion of the SOC window beyond 70% thus offering an opportunity to reduce the Battery Size Factor (BSF) and hence cost. Test efforts seek the lowest operating voltage limit where the inevitable trade-offs in life remain acceptable in magnitude. Expansion efforts would focus on moving from 25 to 95% SOC to a stretch goal of 15 to 95% SOC.

#### **Mechanical Design and Advanced Manufacturing.**

Significant effort is directed at advancing the cell design and manufacturing processes, striving to minimize the void volume in the cell and achieve a step-change reduction in component and assembly costs. Some of the concepts being investigated

are: thin wall cans with special features, mandrel elimination, current collector design optimization, reduced foil margin (wider electrode coated width), electrolyte fill hole closure using torsional ultrasonic welding, and low pressure vent development.

**WBS 5.0 Abuse Tolerance.** Abuse tolerance improvement is a *critical enabler* to all other work aimed at increasing energy content of the cell, and is being pursued on multiple parallel fronts:

- *High temperature separator.* JCI is working closely with separator developer Entek to optimize their ceramic filled separator technology and solve several manufacturing related issues.
- *JCI's Thermal Protective Barrier (TPB) technology.* JCI applied TPB on the anode in the last program and are now optimizing TPB coating, including thickness, coverage, and uniformity.
- *Overcharge protection additives.* These are being tested both in the electrolyte and in the electrode itself.

## **Results**

For discussion purposes, the key design versions from the previous program are defined in Table III - 6.

**Table III - 6: Version parameters and base & mid-program performance**

Cell Type	Size	1C_Rate Capacity (Ah)	Energy Density (Wh/L)	Discharge Power (10s, 50%SOC) (W)	Discharge R (10s, 50%SOC) (mOhm)	P/E Ratio
<b>USABC 4<sup>th</sup> Build (Last Program)</b>	141x124x22.6	23.7	245	1510	1.99	17
<b>Baseline New Program</b>	148x91x26.5	27.0	275	1540	1.92	16
<b>Mid-Program</b>	148x91x26.5	33.3	345	1880	1.60	16
<b>Final</b>	148x91x26.5	36	375	TBD	TBD	TBD

The new electrolyte additive developed in the last program and anode active material implemented in the baseline cell have remarkably low cell resistance growth during storage at elevated temperatures. This can be seen in Figure III - 10, which shows cell resistance increasing only 13% and 34% after one year calendar life at 45°C and 60°C respectively.

The prismatic cell representing mid-program results has an increased energy density of 26%. It shows good discharge and regeneration power capability, with similar power/energy ratio as baseline. With increased upper voltage at 4.2V, the resistance growth in calendar life at 60°C is higher than baseline at 4.1V after 100 days. However, their capacity fade remains the same as the baseline at 4.1V, as seen in Figure III - 11.

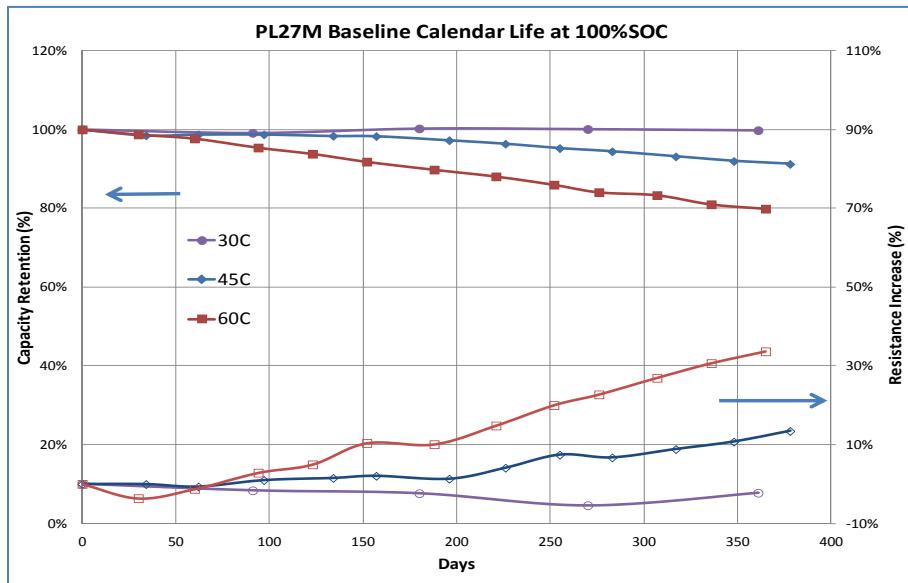


Figure III - 10: Baseline prismatic cell calendar life

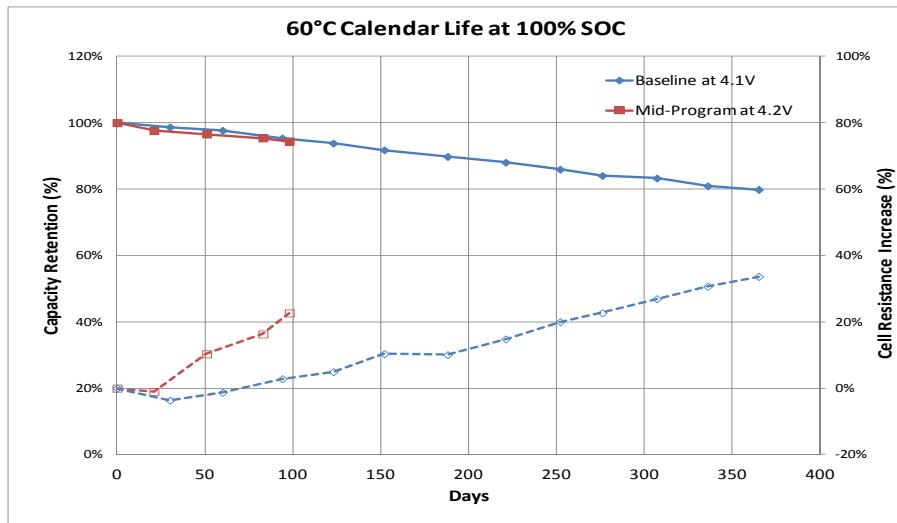


Figure III - 11: Mid-program cell calendar life at 60°C

Results by development area at month 18 (of 24) are presented below:

**Higher Energy Density Materials.** Six suppliers of candidate nickel-rich NMC have been engaged and the materials (designated Cat\_1 through Cat\_6) are at various stages of testing. Different NMC stoichiometries have been evaluated to identify high energy materials with good power and life. The tests have shown that the high nickel NMC has low thermal stability. Despite high initial capacity, high nickel NMC suffers high capacity degradation and poor life at high temperatures. Several suppliers provided high nickel NMC with surface treatment, but this significantly increased cell resistance.

Development activities have improved its capacity fade over initial versions, but end of life (EOL) capacity is lower than baseline (111) at EOL.

Three NMC materials have been down-selected as candidates for the final design, the baseline material (Cat\_1), Cat\_2 NMC (442) and Cat\_4 (improved 111).

Lithium-rich layered-layered oxide cathode material was evaluated paired with a high voltage electrolyte in 1-3 Ah pouch cells. It has very poor capacity fade, and a large voltage fade during cycle life. Further work with it is not planned.

**Electrode Processing Optimization.** The two approaches studied for solvent reduction through improved electrode processing methods are shown in Figure III - 12. Dry compound mixing yielded material which met solvent reduction targets, but cell testing has

shown high resistance and poor calendar life behavior. This is attributed to the excessive shear undergone by the material during compounding. This process is no longer being considered for high solids mixing.

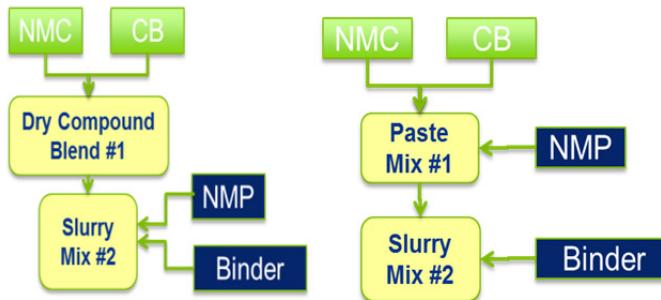


Figure III - 12: High solids mixing approaches using dry compounding (left) and paste mix (right) methods

A second method being tested to achieve the high solids targets is paste mixing. With this method, materials are combined with a portion of the solvent in an in-line compound mixer to achieve the work needed for the initial combination of materials to contribute to reduced solvent demand. The internal workings of this pre-blending equipment are shown in Figure III - 13. Following initial trials, equipment was rented and installed in the JCI Pilot line for further testing of electrode processing and resulting cell evaluation. Initial electrodes produced, shown in Figure III - 13, appear promising for achieving good uniformity with calendaring to the high density targets for improved energy density. Electrode quality after calendaring is a significant accomplishment not realized with previous trials. A solvent reduction of 13% was achieved, still below the 18% target. However, optimization work continues.



Figure III - 13: Paste mixing equipment and electrodes

An alternate (higher risk/higher reward) process incorporating aqueous binder (allowing total solvent elimination) was pursued for the positive. This offers a significant cost reduction opportunity by avoiding the need to capture the evaporated NMP solvent from the electrode process. The application of water-based binder

for the cathode has shown minimal adverse impact in cell testing. Primary efforts have focused on quantifying the potential corrosion effects of the water-based cathode slurries as this corrosion can have detrimental effects on life and cell resistance. Evaluations indicate no impact on stability of the water-based slurry with 30 minutes of contact with aluminum foil, well beyond the normal processing time before electrode drying. Scaled up mixing and electrode processing is scheduled for February 2014.

**Electrode Design Optimization.** Different approaches were tested to optimize electrode design. Higher electrode loading was proven not to be efficient. Electrode densification delivered more capacity, and better power and life. A new conductive carbon has improved electrode processing and cell performance. The anode optimization has been applied in the mid-program cells.

**Increased Voltage Limit.** Accelerated testing began with prismatic cells at upper voltages of 4.1, 4.2 and 4.3V. The 4.2 V group showed acceptable power and energy fade. The first generation (baseline) 4.3 V tests were stopped due to poor results. Chemistry stabilization improvements have demonstrated life at 4.2V that meets EOL targets. 4.2V has been selected as the standard upper voltage limit.

A few electrolyte additives tested at 4.3V imparted some stability improvement. Overall, however, capacity saw a crossover with cells at 4.2V.

To maximize cell energy utilization, the usable SOC window was widened from 95%-25% to 95%-15% SOC. The cycle life of baseline cells has shown excellent performance, even with the expanded SOC window (see Figure III - 14).

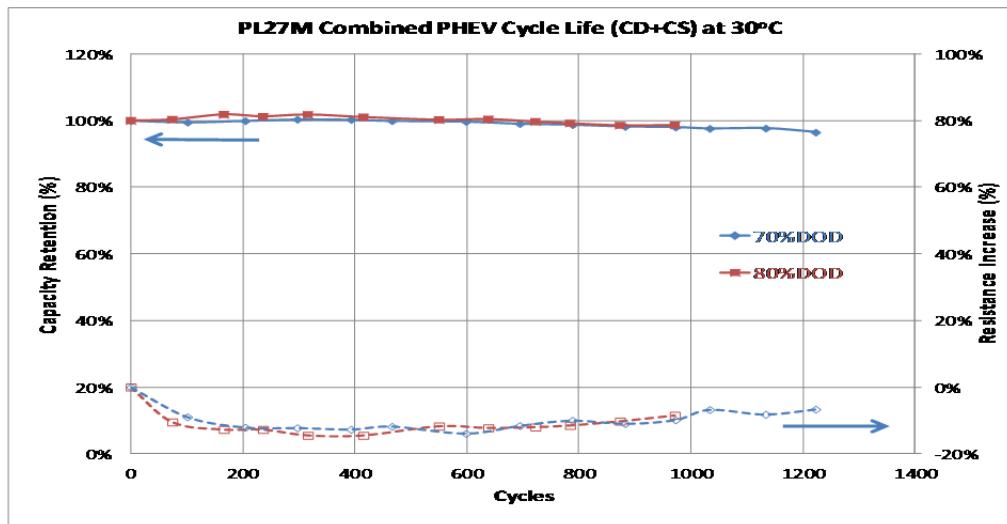


Figure III - 14: PHEV cycle life: 95%-25% vs 95%-15%SOC

#### Mechanical Design and Advanced

**Manufacturing.** Numerous concepts were studied that have the potential to dramatically drive down component cost and assembly complexity, increasing cell energy density and performance.

- Torsional ultrasonic welding was selected as the lead alternative fill hole closure method after extensive evaluation of competing methods. The novel sealing process was

successfully developed in a production-like environment (Figure III - 15). The approach shows great potential to reduce cell void volume and replace baseline rivet insertion.

- The design of a thin wall can with inwardly embossed features was completed. It has the potential to reduce the complexity of tolerance management and clamping forces needed in future module designs.

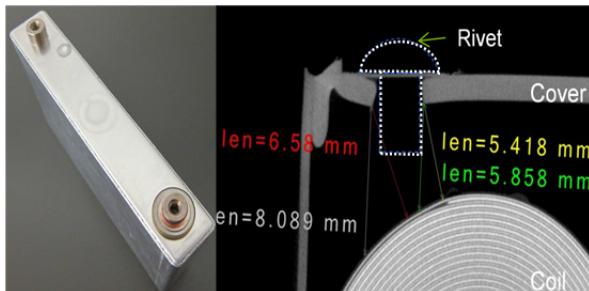
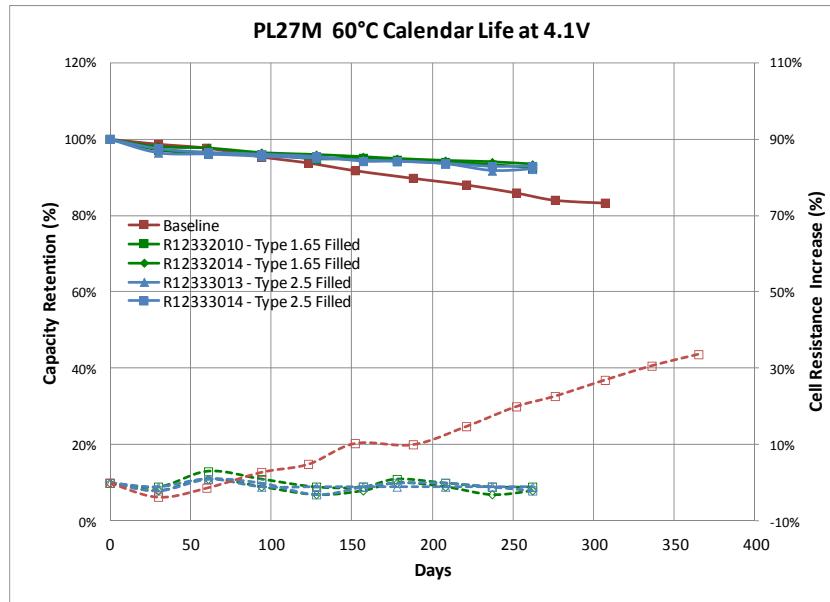


Figure III - 15: Cell sealed by torsional ultrasonic welding

- Mandrel-less cells produced in the mid-term build are on test with promising results and are planned for incorporation into the final build.
- Current collector width was optimized using results of component level high current pulse tests. This, along with foil margin reduction and electrode layout redesign, increased cell capacity by 4.5%.
- A low pressure vent is being developed to investigate whether earlier activation and associated release of thermal energy and fuel

might avoid or mitigate thermal runaway. Abuse testing with prototypes is planned.

**Abuse Tolerance:** Joint trials were conducted with Entek to address manufacturing and performance issues of the ceramic filled separator. These separators provided remarkable improvement in cell resistance, power capability, and life. At 25°C, cell power improved by 30%, and 20% at -25°C. In calendar life at 60°C, no resistance increase was measured after 262 days at 4.1V.



**Figure III - 16: Ceramic separators calendar life at 60°C**

Excellent performance was also found when cells with ceramic filled separators were tested at 4.2V at 70°C. After one year storage, cell resistance only increased 34%.

Ceramic filled separators lack the shutdown function which is considered to be an essential safety attribute for high energy cells. Efforts with Entek to adjust the ceramic/ polyolefin ratio to achieve full or partial shutdown and retain the life-enhancing properties were not successful.

Thermal Protective Barrier (TPB) technology was optimized on thickness, coverage and uniformity, resulting in tangible improvements in abuse tolerance results.

Two cathode additives were found to delay the onset of thermal runaway during overcharge with no adverse

impact on life detected thus far. A formulation of electrolyte additives for overcharge control showed very promising results with more work required.

### Next Steps

Convergence of design choices based on this work has started. From this, final cells will be produced and delivered in CY Q1 2014.

### FY 2013 Publications/Presentations

1. Presentation to the 2013 DOE Annual Peer Merit Review Meeting (May 13, 2013).

## III.A.5 Development of a High-Performance PHEV Battery Pack (LG Chem)

### Paul Groshek, USABC Project Manager

Contractor: LG Chem Power, Inc.

### Mohamed Alamgir, Program Manager

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### Subcontractor:

LG Chem, Seoul, South Korea

Start Date: January 1, 2008

Projected End Date: March 31, 2010

### Objectives

- This is a 24 month program focused on developing a Li-ion pack technology that meets the energy, power and life requirements of the 40-Mile PHEV program of the USABC. A key part of the work is aimed at developing a cell that will significantly reduce cost to meet the USABC pack cost target by utilizing high specific energy cathode materials.
- An important objective of the program is also to develop an automotive-grade, self-contained battery pack using a refrigerant-based cooling system. The goal is to increase the efficiency of the thermal management system to increase life, lower cell count and more importantly, lower pack cost. The system is expected to be much more efficient and robust than its liquid-cooled counterpart commonly used in PHEV packs.

### Technical Barriers

The project is addressing the following technical barriers.

- (1) Validation of the high capacity of new generation of Mn-rich cathode materials.
- (2) Demonstration of cycle-life of > 5,000 cycles
- (3) Demonstration of calendar-life of 15 years
- (4) Make considerable progress towards achieving the USABC pack cost target of \$3,400.

### Technical Targets

- Establish the high specific energy of new generation of Mn-rich cathode materials.
- Demonstrate both cycle- and calendar-life under USABC test conditions.
- Develop a cooling system that is electrically and mechanically robust and efficient.
- Develop a pack design that is modular, easy to manufacture and close to the USABC cost target.

### Accomplishments

- Extensive studies of the material and electrode properties such as morphology, surface area and porosities were carried out to identify electrode formulations optimal from performance as well as from life points of view.
- Process variables such as formation conditions which affect the amounts of gas generated as well as life have been examined and optimized.
- Since this high capacity cathode material necessitates the use of high-voltage electrolyte additives to prolong life at high voltage have been studied.
- Cyclability of the cathode has been found to be strongly dependent on the charge voltage as well as the SOC window of operation. Key among the root causes for cell degradation is the dissolution of Mn from the cathode particles and subsequent passivation of the anode.
- Stabilization of the cathode particle surface leads to significantly improved life characteristics.
- Material we have developed in-house demonstrates state-of-the-art cathode capacity as well as life. Current estimates show that this material when fully developed will lead to a cell cost target of below \$200/kWh.
- The thermal system and pack volumetric efficiency have been significantly improved by optimizing compressor and evaporator designs, as well as by improving the contact between the thermal fins and the cold plate.
- Modules and packs have been designed, built and delivered to the National Labs for testing.



## Introduction

Development of a cost-effective, high performance battery is a prerequisite for the successful introduction of PHEVs and EVs. The advent of new high specific energy cathode materials has opened up significant opportunities to achieve this objective. Low-cost, high capacity cathode materials using a large operational SOC window will result in the use of less of active materials, thus lowering the pack cost. In addition, development of a thermal management system that is more robust and simpler to implement than conventional, liquid cooled system is also important for advanced, next generation battery pack technologies.

## Approach

To achieve the proposed objectives for a 40-Mile PHEV program, we have been studying cell chemistries based on next-generation Mn-rich layered-layered compounds, our patented Safety Reinforcing Separator (SRS) and a laminated packaging cell design. The goal is to understand, develop and optimize this cathode chemistry, corresponding anode and electrolyte compositions in order to meet the USABC targets for performance, life and cost. Evaluation of critical factors such as cathode and anode compositions, effect of binders and electrolyte compositions as well as the identification of conditions optimum for cycle- and calendar-life are the important tasks of the program.

Another important aspect of the work is to develop a pack that has superior thermal management using indirect cooling entailing a refrigerant-cold plate system. This work is aimed at developing a thermal system that will be thermally and mechanically robust with optimized volumetric and gravimetric efficiencies as well as cost.

## Results

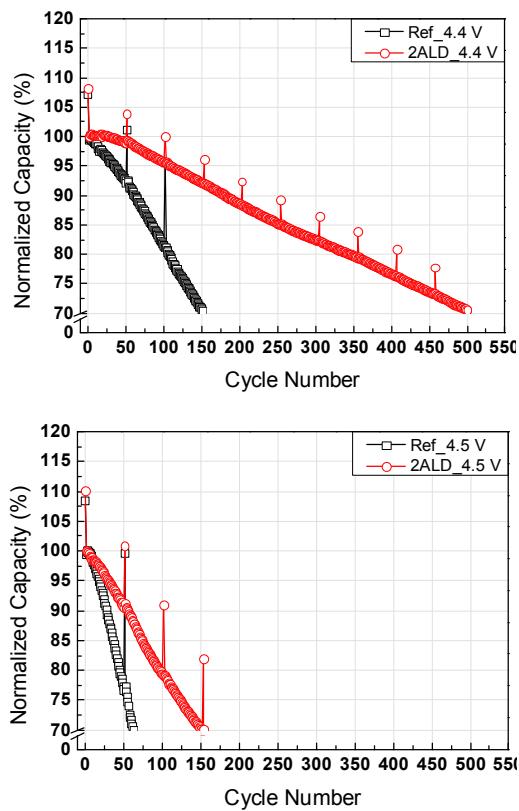
**Characterization of the Mn-rich cathode.** The layered-layered compound  $x\text{Li}_2\text{MnO}_3(1-x)\text{LiMO}_2$  with reported capacities  $> 250 \text{ mAh/g}$ . has one of the highest specific energies of any high voltage cathode material currently being studied. To obtain such high capacity, however, the material needs to be charged to voltages around 4.6V. Additionally, it is characterized by high surface area and low conductivity at low SOCs. There is also the phenomenon of voltage sagging throughout life that lowers cell energy and is also undesirable from battery control point of view. To improve upon these drawbacks, we carried out systematic studies to optimize electrode formulations, evaluated cell

performance as a function of charge voltages, modified cathode particle surfaces using a variety of approaches, studied a range of electrolytes and optimized cell process parameters such as formation conditions, etc. These studies led to the following key observations.

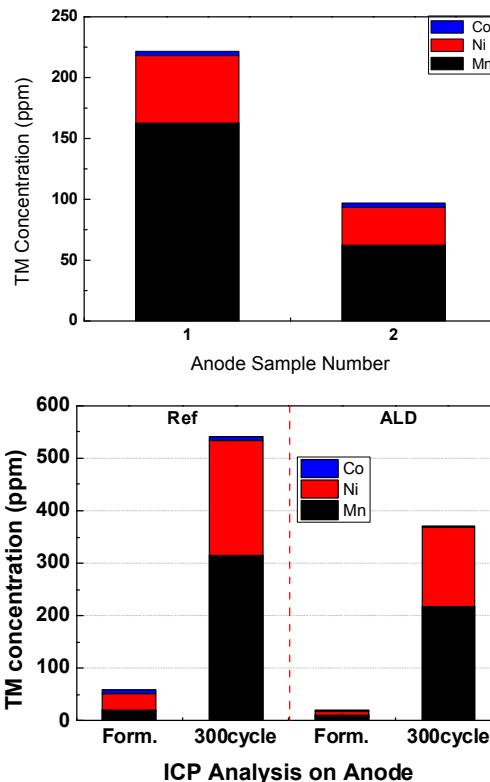
Durability of the cell is critically dependent on the charge voltage. Operation above ~4.35V leads to significant reduction in cycle-life. Cathode surface modification and electrolyte composition appear to mitigate these drawbacks to some extent (Figure III - 17, Figure III - 18).

- a. Considerable amount of gas generation takes place during activation and high voltage operation. This causes significant cell swelling and premature cell failure. Surface treatments of the cathode particle show good improvement.
- b. Voltage sagging appears to stem from the continuous structural evolution of the cathode material. Surface coatings do not appear to be effective in alleviating this phenomenon.
- c. Dissolution of Mn from the cathode and its migration to and subsequent passivation of the anode remains the key mechanism that appears to control the life of this Mn-rich high capacity cathode. Modification of the particle surface using coatings appears to significantly improve the life of the cell.

**Pack Development.** As mentioned above, we have developed a compact and self-contained battery pack system utilizing a refrigerant-to-coldplate cooling concept, (Figure III - 19). The essential components for this cooling system are solid fins, a cold plate, compressor and evaporator. Studies were carried out to optimize these components with respect to cooling and volumetric efficiency, manufacturability and cost. For example, we studied compressors of different ratings (e.g., 12V, dual 12V or a single 24V) to determine their efficacy in thermally managing the cells during cycling. Two iterations of module and pack builds have been carried out in course of the program.



**Figure III - 17:** Effect of charge voltage and surface coatings on cycle-life. Top: Data showing the beneficial effect of ALD surface coating on the cycle-life at 45°C. The cell was charged at 0.5C and discharged at 1C. Bottom: When the charge voltage was raised to 4.5V, instead of 4.4V as in Top figure, there is a substantial decline in cycle-life



**Figure III - 18:** Top) Effect of formation voltage on the amount of transition metal deposited on carbon anode. Sample 1 was formed at 4.6V. Sample 2 was formed at 4.4V. Note the significantly large quantity of Mn deposited at 4.6V. Bottom) Effect of surface coating on Mn dissolution. ALD coating reduces Mn dissolution both during formation as well as cycling

The packs were subjected to automotive drive-cycles to assess their capability in thermally managing the cells during cycling. Figure III - 20 shows the data for a pack using a dual 12V compressor system and cycled at an ambient temperature of 40°C and US06 drive pattern. The data show that the cooling system was effective in maintaining the cell temperatures at around 32°C. It took ~30 mins to reach the steady-state. The bottom picture compares the efficiencies of packs using different compressors. The dual 12V system showed the best efficiency in cooling the packs. The steady-state, however, for all three packs were reached within ~30 mins. The cold-plate temperatures for the three systems are also plotted. A key observation from all our pack data is that the thermal system was efficient in cooling the cells and maintaining the modules within a narrow range of temperature.



**Figure III - 19:** Top: Schematic of the PHEV-40 mile pack we have developed. The thermal chamber containing elements such as the compressor, the cold-plate and the evaporator is on the right while the electrical chamber is on the left; Bottom: picture of the finished pack as delivered to the National Labs

### Conclusions and Future Directions

While the Mn-rich cathode has the potential of delivering very high specific energy, several key drawbacks need to be mitigated to make it a long-life, low-cost cathode. Various approaches we have studied show that there are considerable opportunities to improve the cathode material properties. Extensive test data involving analytical studies have clearly established the usefulness of our approaches toward improving the performance and life of the cells. However, none of the methods we have investigated thus far was able to fully alleviate the key challenges of Mn dissolution, gassing and voltage sagging, which leads to poor life.

Multiple design iterations have led to the development of a pack using an indirect cooling method comprising a refrigerant-to-cold plate system. These packs have been built and delivered to the USABC for testing by the National Labs.

### FY 2013 Publications/Presentations

1. Presentation at the 2013 DOE Annual Peer Review Meeting, Washington, DC, May 2013.

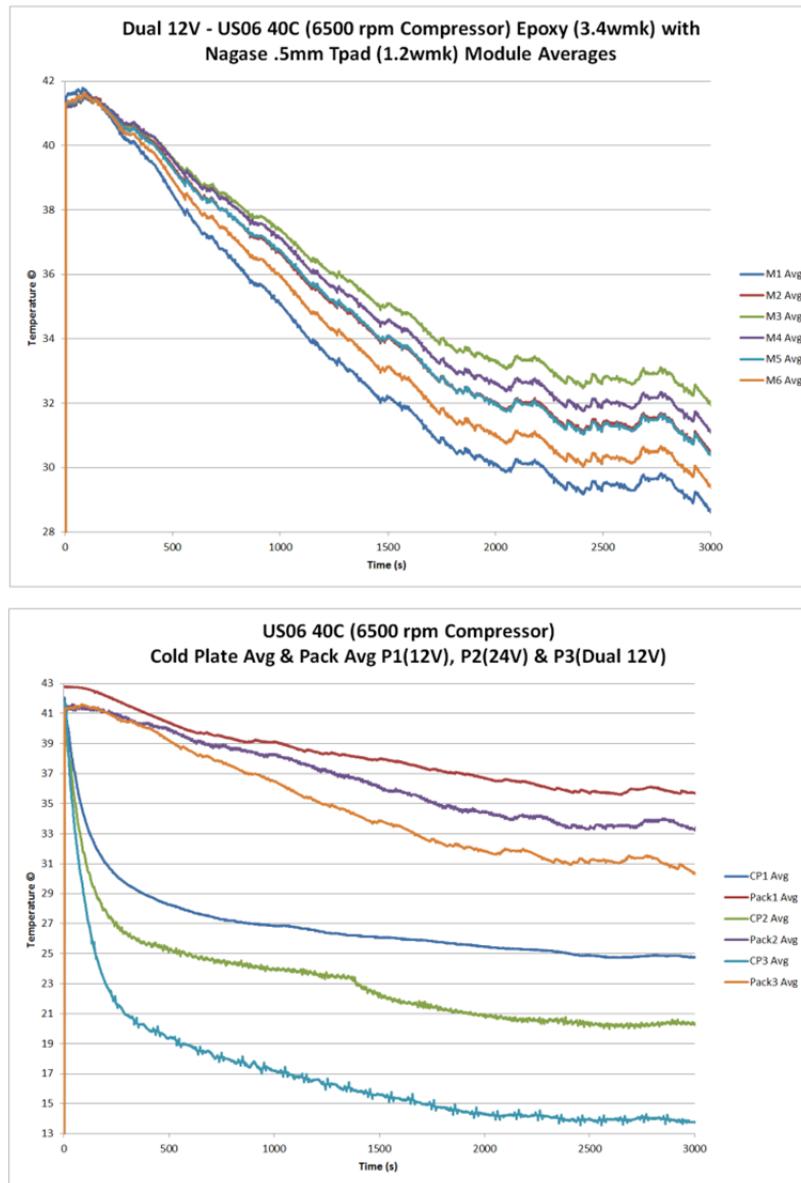


Figure III - 20: Examples of the thermal performance of the pack using the cooling system we have developed. Top figure shows the average temperature of the modules during US06 cycling at 40°C. The data show that the modules are within 4°C of each other, indicating uniform and efficient cooling. Bottom figure compares three different packs using different compressor ratings (single 12V, dual 12V and a 24V. The associated cold-plate temperatures are also shown in the graph. The cold plate temperature is the bottom curve

## III.A.6 Energy Storage System for High Power HEV Applications (Maxwell)

### Scott Jorgensen, USABC Program Manager

Subcontractor: Maxwell Technologies, Inc.

### Allen Stoneberg, Program Manager

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#### Collaborators:

University of Rhode Island

Start Date: January 2011

Projected End Date: March 2014

### Objectives

- Design, build, and test hybrid ultracapacitor cells and packs capable of meeting USABC goals for LEESS HEV applications.
- Extend device upper voltage range above 4.0 V with good life and low temperature performance.
- Develop and demonstrate a new design architecture for cell and system which is cost effective, small and light.

### Technical Barriers

- Low temperature performance (operation at -30°C).
- Energy density (increased stable operating voltage window).
- Cell and system cost decreases.

### Technical Targets

- Develop a hybrid capacitor cell and associated module to meet LEESS HEV power and energy goals.
- Develop and utilize a stable electrolyte system that has a voltage window of 4.0 V or higher and can operate in the temperature range of -30 to 55 °C.
- Identify optimal electrode materials for higher energy, lower impedance, and stability at increased potential over lifetime, and lower cost relative to existing commercial capacitive technologies.

- Identify a separator that represents a significant cost reduction while maintaining or exceeding existing performance and safety metrics.

### Accomplishments

- Completed the development and fabrication of third generation 3.8 Wh hybrid ultracapacitor cells. Representative cells have been sent to Idaho National Laboratory for testing.
- Produced over 1,000 third generation cells in support of module build utilizing Maxwell's low cost dry electrode fabrication process.
- Finalized the design of the Maxwell LEESS Module incorporating key features to optimize cost, weight and volume.
- Completed production of LEESS modules and packs in support of internal and testing at national labs per the FreedomCAR Battery Test Manual.
- Demonstrated over 390,000 HEV cycles with first generation cells. These cells are still exceeding performance requirements.
- 15% reduction of EOP Projected Cost matching SOW requirement.



### Introduction

Maxwell Technologies is developing a new energy storage system based on a novel hybrid ultracapacitor to meet LEESS HEV requirements while maintaining long life, excellent safety, and low cost. While conventional ultracapacitors generally lack the energy density required for automotive traction applications, Maxwell's hybrid technology almost triples the energy density of state of the art conventional ultracapacitors. New approaches to packaging and manufacturing are focused on significantly reducing the system cost. Key improvements to be demonstrated over existing capacitive technologies are increased energy density and low temperature performance at a size, weight, and cost that is practical for consumer vehicle use.

### Approach

Leveraging its capabilities in low cost ultracapacitor manufacturing, Maxwell has developed a new large format hybrid ultracapacitor cell capable of cycling to at least 4.0 V. The compact and economical design of this

large cell is being leveraged to produce the lowest cost and smallest/lightest system possible while meeting LEESS power and energy requirements. Cell performance has been improved by:

- Identifying and selecting the highest performing anode and cathode carbons leveraging over a decade of previous carbon screening work.
- Identifying and selecting a stable electrolyte in conjunction with the University of Rhode Island.
- Identifying and characterizing separator materials with good performance but significant cost reduction.
- Use of a completely dry electrode fabrication process (solvent-free, reduced processing) to decrease cell manufacturing cost and increase cell lifetime.
- Quantifying performance/weight/size reduction of new cell architecture via cell-level electrochemical and physical testing.

Cells and systems will be tested for performance and life at Idaho National Laboratory, for abuse tolerance at Sandia National Laboratories, and for thermal performance at the National Renewable Energy Laboratory.

## Results

**Electrode Development.** The electrode material and processing method for third generation cells was finalized at the end of 2012. Focus in 2013 was on the scale-up of electrode for larger quantity cell production. Ongoing optimization of the Maxwell electrode dry process for improved electrode physical and performance characteristics have yielded opportunities for overall improved cell performance.

**Electrolyte Development.** The current Maxwell control electrolyte was selected for the third generation cell and has proven to be stable in a temperature window of -20 to 55°C. Ongoing electrolyte screening has identified a stable candidate that meets the -30°C operational requirement that will undergo further evaluation beyond the program.

**Cell Development.** 3.8 Wh third generation cells have been designed, produced and shipped to Idaho National Laboratory for testing per the USABC Battery Test Manual. Internal HPPC BOL data indicates that the cell chemistry meets LEESS EOL performance targets (Figure III - 21).

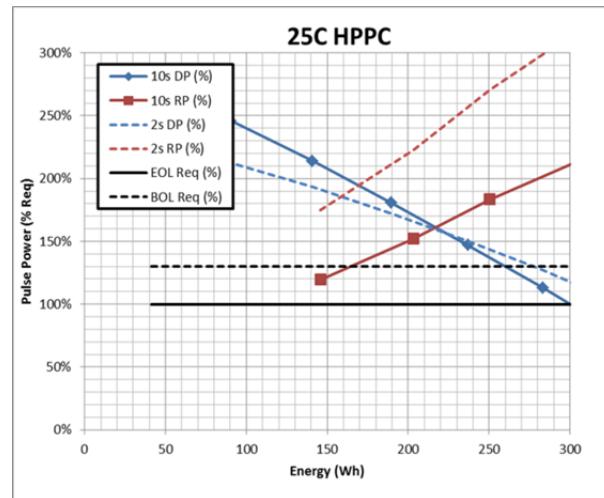


Figure III - 21: 3.8 Wh third generation HPPC BOL pulse power capability

**LEESS Module Development.** The LEESS Module (Figure III - 22) has been designed and tested and high-level prototypes have been completed. Full modules and sub-modules have been shipped to Idaho National Laboratory (performance), National Renewable Energy Laboratory (thermal) and Sandia National Laboratories (safety) for evaluation.



Figure III - 22:- Maxwell LEESS module

**Cost Modeling.** System cost is a critical program element and all decisions from cell component selection to system design have been driven by the cost model in order to deliver the lowest cost, highest value system possible. Projected end of program cost is \$920 – matching the program target of \$920.

## Conclusions and Future Directions

In 2013, the third generation cell chemistry and configuration was finalized and scalable production processes validated. Maxwell testing has confirmed that cell safety, stability and performance meet program requirements with the exception of low temperature operation related to electrolyte selection. Over 1,000

cells have been produced and screened. The full scale LEESS Module deliverables have been designed, assembled and shipped for USABC evaluation.

Gap analysis as of Q3 2013 (Table III - 7) indicates that, with the exception of low temperature performance and size/weight, the system is on track to meet power and energy performance targets.

Current attention will be focused on the internal and USABC testing of the Maxwell LEESS Module and cells. Although the cell architecture has been frozen since mid-year for module production and USABC testing, Maxwell has made key electrolyte and electrode performance improvements that will enable the -30°C

operational requirement and increase power density by the end of the program but beyond available time for USABC testing. These cell material improvements in turn will enable both size and weight reductions at the system level.

### FY 2013 Publications/Presentations

1. 2013 DOE Annual Peer Review Meeting Presentation.

**Table III - 7: 2013 Q3 gap analysis**

USABC LEESS PAHEV		USABC REQUIREMENTS at EOL		PROMISED – EOL (PER SOW)		PROJECTED Deliverable End of Program - EOL	
End of Life Characteristics	Unit	PA (Lower Energy)		PA (Lower Energy)		PA (Lower Energy)	
2s / 10s Discharge Pulse Power	kW	55	20	55	20	55	20
2s / 10s Regen Pulse Power	kW	40	30	40	30	40	30
Maximum current	A	300		300		250	
Energy over which both requirements are met	Wh	26		26			
Energy Efficiency	%	95		95		96.1	
Cycle-life	Cycles	300,000 (HEV)		300,000 (HEV)		300,000 (HEV)	
Cold-Cranking Power at -30°C	kW	5		5		3	
Calendar Life	Years	15		15		15	
Maximum System Weight	kg	20		22		35	
Maximum System Volume	Liter	16		25		33	
Maximum Operating Voltage	V <sub>dc</sub>	<=400		<=400		320	
Minimum Operating Voltage	V <sub>dc</sub>	>=0.55 V <sub>max</sub>		>=0.55 V <sub>max</sub>		0.56	
Unassisted Operating Temperature Range	°C	-30° - 52°		-30° - 52°		-20° - 52°	
30° - 52°	%	100		100		67	
0°	%	50		50		37	
-10°	%	30		30		21	
-20°	%	15		15		9	
-30°	%	10		10		6	
Survival Temperature Range	°C	-46 to +66		-46 to +66		-46 to +66	
Selling Price/System @ 100k/yr)	\$	\$400		\$920		\$920	
Hardware Level		System		System		System	
Capacity	Wh					310	
Battery Size Factor (BSF)						80	

## III.A.7 12 Volt Start/Stop Battery Development (Saft)

### Harshad Tataria, USABC Program Manager

Subcontractor: Saft

### Michael Duffield, Program Manager

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#### Subcontractors:

Wildcat Discovery Technologies

Virginia Commonwealth University

Start Date: April 2013

Projected End Date: March 2014

- Identify polymer materials that can hermetically seal the stack from external moisture and prevent electrolyte egress.
- Optimization of LTO and electrolytes for -30°C performance, while maintaining calendar life and cycle life up to 75°C

### Accomplishments

- Saft has successfully supplied NMC based Li-ion cells for high power, high temperature automotive application.
- Saft is producing the NMC line of products in two formats, cylindrical and prismatic.
- Saft LTO technology has excellent power capability with a 15s pulse-discharge impedance of around 1.6 mΩ in small cells.



### Objectives

- To develop an advanced, high-performance battery for 12V Start-Stop (12VSS) vehicle applications based on Saft's advanced NMC-LTO lithium-ion battery technology.

### Technical Barriers

The cost of automotive battery is the single most critical challenging requirement and a generally acknowledged critical path to widespread deployment of the Li-ion battery in the automotive industry. About 20% of the cost of a robust cell design in volume-production today is in the cell hardware. Cell hardware is anything other than electrodes including the foils, separator, and electrolyte. Another 50% cost burden is added as cells are integrated into a turnkey battery pack. Thus, the hardware in a Li-ion battery pack is responsible for a combined 80% of the cost add-on before indirect costs (G&A, O/H, and Profit), and is the single most significant part of the total unit cost.

A dramatically different approach to the way Li-ion cells are fabricated and assembled into a battery is needed for a significant reduction in the hardware cost.

### Technical Targets

- Develop a novel cell assembly process which reduces the overall battery cost.
- Reduce elevated temperature impedance growth in order to meet cycle life requirements.

### Introduction

Saft's NMC-LTO technology will meet or exceed the USABC requirements for this application. Saft can meet all of the performance requirements for power, cycle life, cold cranking power, etc. using the LTO technology already demonstrated. Integration of Saft's high temperature stable NMC technology will allow for additional improvements to cell calendar life. Accordingly, this development program will scale up the Saft LTO technology from small cells to a 10-20Ah PHEV-2 VDA size prismatic cell as a demonstration of the ability to meet cost and size requirements.

### Approach

A key innovation in the effort, primarily focused on cost reduction, is combining the cell and module packaging in a single injection-molded thermoplastic polymer (IMTP) monoblock. Further proposed cost reductions include optimization of the electrolyte and NMC cathode to meet the cold-cranking requirements. LTO is a chemistry particularly well suited to this optimization, as the lack of solid-electrolyte interphase (SEI) allows for the use of very low cost, low temperature electrolytes.

In order to reduce the electrode material costs, the LTO manufacturing process is being addressed by large volume manufacturers of TiO<sub>2</sub> for the paint industry. This could result in extremely low cost LTO, giving a significant cost advantage over graphite-based Li-ion.

With the cost reduction advantages offered by LTO chemistry and the monoblock module design, the proposed NMC-LTO monoblock battery system will meet the USABC cost target.

## Results

**Polymer Material Study.** Saft is currently working with Virginia Commonwealth University (VCU) Department of Chemical and Life Science Engineering to conduct polymer material studies. A paper study of potential polymer candidates for the battery case has been completed. Based on Saft's polymer requirements, VCU has identified a number of polymer candidates.

VCU will now begin lab studies of the polymer candidates. Lab studies will include moisture absorption, chemical degradation, mechanical properties, and thermal degradation.

**Electrolyte Development.** Initially cells have been built using our low temperature electrolytes which were

previously developed for our graphite anode Li-ion cells. The study of novel electrolytes is limited with LTO based Li-ion cells. Saft is investigating numerous typical and atypical solvents. In addition, we are studying different salts and molarities. The testing of the electrolytes (using SAFT-provided electrodes) is subcontracted to Wildcat Discovery Technologies (WDT). These tests of coin cells will screen for low temperature performance, and gas generation at 70°C.

We are focusing our work to a select set of electrolyte formulations for optimal low temperature performance while maintaining stable high temperature impedance growth. After we have narrowed the electrolyte studies using Wildcat Discovery Technology's rapid prototyping and testing, we will examine these select electrolytes for gas generation. An example of the components to be studied is given in Table III - 8. The investigation will focus on component formulations 1 to 8.

**Table III - 8: Electrolyte formulation test matrix**

Formulation No.	Solvent - Dissolve Salts			Solvent - Mobility	Solvent - Low Temp		Salts	
	A	B	C	D	E	F	LiBF <sub>4</sub>	LiPF <sub>6</sub>
Baseline 1 (1 M salt)	X			X		X		X
Baseline 2 (1.3M salt)	X			X		X		X
9	X	X		X			X	
10		X		X			X	
1		X	X	X	X		X	
2	X	X			X		X	
3	X	X	X			X	X	
4	X	X				X	X	
5	X				X		X	
6	X			X	X		X	
7		X				X	X	
8		X		X		X	X	

**Cell Development.** There are three cell deliverables within the program. The first occurred after three months in the program and consisted of 5 LP10 Ah cells for early review and testing by USABC. The second is a set of 15 LTO-NMC prismatic cells. These will be delivered to USABC after approximately nine months in the program for independent testing & evaluation (reference cell). The final capacity of these cells will vary due to a fixed hardware size. It is currently estimated that the cells will have a capacity of 10-15Ah. The third and final deliverable is a set of 20 optimized LTO-NMC cells in PHEV-2 VDA size housings at the

end of the program. These prismatic cells will also be built in a stacked electrode configuration and have a capacity of 10-15Ah.

The first deliverable of five LP10 Ah sized cells has been built and shipped to Idaho National Laboratory for testing according to the USABC 12V Start-Stop manual.

Internal Saft testing reveal the deliverable cells meet cold cranking spec at 75% SOC at the end of the 4.0 second pulse and ~65% at the end of the 0.5 second pulse (Figure III - 23). However, the cells are not aged, thus the data reflects beginning of life performance.

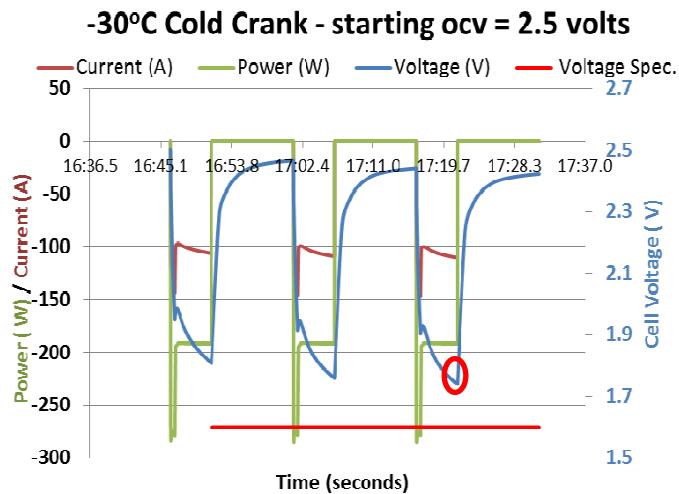


Figure III - 23: Cold crank results of 1<sup>st</sup> deliverable cells

Cycling at 30°C on one cell from the deliverable cell lot is given below (Figure III - 24). The impedance

growth is presently 3-4% impedance growth at 800 cycles and stabilizing.

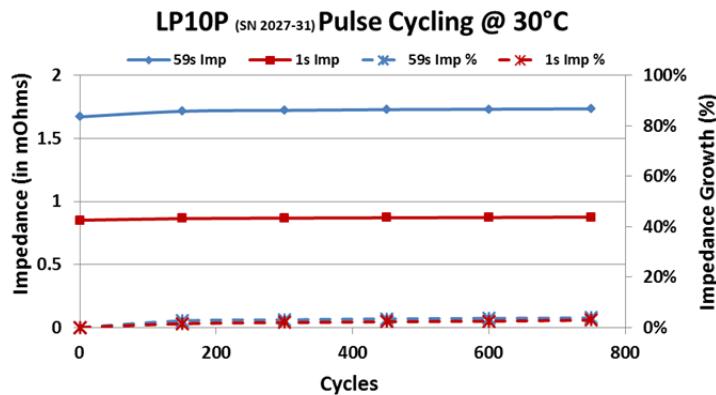


Figure III - 24: Impedance growth results

### Conclusions and Future Directions

Saft is currently seven months into the one year development program. Saft internal testing of 1<sup>st</sup> deliverable cells has shown that the cells could meet or exceed most USABC Start-Stop performance targets.

The areas of concern for the LTO-NMC cell development continue to be cold crank power at lower states of charge, high temperature impedance growth, and the current high cost of the LTO material. During the remaining months of this program, Saft will continue to evaluate and test ways to reduce or eliminate these concerns. A Design of Experiment is underway to identify the key contributors to high temperature impedance growth and the electrolyte studies currently being conducted at Wildcat Discovery Technologies

will lead to an optimized low temperature electrolyte for use in the final deliverable cells.

Saft is interested in continuing its development of the LTO/NMC cell for wide scale use in 12V start-stop automotive applications.

### FY 2013 Publications/Presentations

None.

## III.A.8 Development of an Advanced, Lithium Ion, 12V Start-Stop Battery (Leyden Energy, Inc)

### Chulheung Bae USABC Program Manager

Subcontractor: Leyden Energy, Inc.

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Start Date: February 2013

Projected End Date: March 2014

- Develop pack design and balancing circuitry for 12V "A" prototype pack at Flextronics.
- Deliver up to 50 20Ah cells and three 12V packs to USABC at the end of the program

### Accomplishments

- Met USABC -30°C cold-cracking targets at 100% and 50% SOC in 2.2Ah prototypes and 20Ah cells.
- Projecting >450k USABC shallow cycles at 30°C with the latest 2.2Ah prototype cells.
- Developed and evaluated 15+ surface treatments to improve high temperature calendar and cycle life of LTO-LMO cells.
- Delivered requested total of 28 prototypes cells for evaluation to ANL and NREL.
- Designed and built first 20Ah cells at Dow Kokam
- Designed a balancing circuitry and assembled first 40Ah 12V prototype packs at Flextronics.



### Introduction

Leyden Energy is developing an affordable, advanced lithium-ion 12 V Start-Stop battery to meet performance, life and cost targets of the USABC's RFP for "Development Of Advanced High-Performance Batteries For 12V Start-Stop Vehicle Applications". Leyden is engaging with a high volume cell manufacturer (Dow Kokam) and a capable pack manufacturer (Flextronics) to leverage their respective expertise and resources to address technical challenges and advance low cost, domestic manufacturing. The key elements of our program include:

- Use of an LTO/LMO couple with Leyden's Li-imide<sup>TM</sup> electrolyte to enable a system that meets target capacity, cold cranking power, cycle life, calendar life and price targets.
- Advancement of Leyden's technical foundation and leveraging of Dow Kokam's investment in large volume, domestic lithium-ion manufacturing.
- Utilization of an innovative cell and battery design to result in a lower weight and lower volume system, approximately 7.2 kg and 6 liters.

### Technical Targets

- Develop an LTO-LMO cell that meets USABC 12V Start-Stop performance targets. Most important targets are -30°C cold-cranking and 30°C 450k cycle life.
- Scale up the coating capability at Leyden and produce anodes and cathodes for the deliverables. Design and assemble 20Ah cells at Dow Kokam facility for USABC deliverables.

- A rapid program timeline with development running 14 months until 3/31/14, including “A” sample prototype delivery in 14 months to designated National Labs enabling production “C” samples in 30 months.

## Approach

Two major technical challenges of the program are the cold-cranking power at -30°C and high temperature cycle and calendar life.

For the cold-cranking power, Leyden Energy’s approach is to optimize electrode thicknesses and press densities and formulate a low temperature electrolyte solvent base that allows for superior low temperature operation. The LTO system is unique compared to graphite anode batteries as it does not require high melting point ethylene carbonate (EC) as a solvent. EC is the biggest impediment to good low temperature performance. Electrolyte solvent base development approach is focused on a combination of propylene carbonate and butyrolactone with linear carbonates, low melting point esters and nitriles.

Long cycle life and calendar life targets are addressed by employing Li-imide™ electrolyte with the additive packages designed to improve cycle life of LTO-LMO cells and, most importantly, surface treatments of LTO material. The reduction of electrolyte on the catalytically active surface of LTO is understood to be the main reason of high temperature power fade and gassing.

Cell design, pack design, manufacturability and cost targets are addressed by close cooperation with our manufacturing partners. Leyden is leveraging Dow Kokam’s expertise in automated high volume cell manufacturing and Flextronics knowledge and experience in circuitry and pack development and manufacturing.

## Results

**Cold cranking and power capability.** Leyden Energy has made significant progress since the beginning of this program in improving low temperature performance of the LTO-LMO cells as shown on Figure III - 25. We are meeting stringent USABC cold-cranking requirements in 2.2Ah cell prototypes at 100% and 50% SOC and are close to the target and maximum DOD as presented on Figure III - 26.

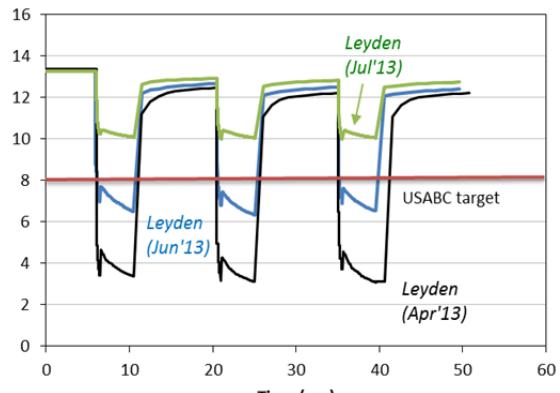


Figure III - 25: Improvements in 100% SOC -30°C cold-cranking performance over the course of the program; recalculated to pack level

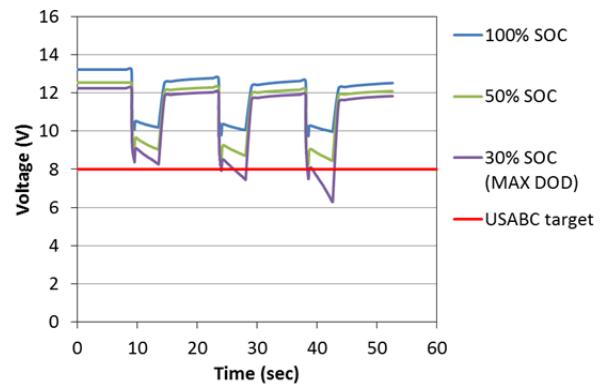


Figure III - 26: Cold-cranking performance of 2.2Ah LTO-LMO prototype cells at various SOC; recalculated to pack level

Improvements in cold-cranking performance were accompanied by an overall increase in rate capability that resulted in the ability of the cells to handle continuous 40C discharge (Figure III - 27) and superior power for auto-start function, *i.e.*, ability of the system to deliver 1 sec 6kW pulses over a wide range of temperatures and SOC (Figure III - 28).

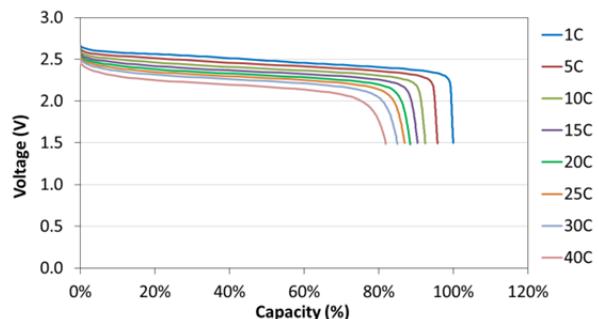


Figure III - 27: Rate performance of 2.2Ah prototype cells

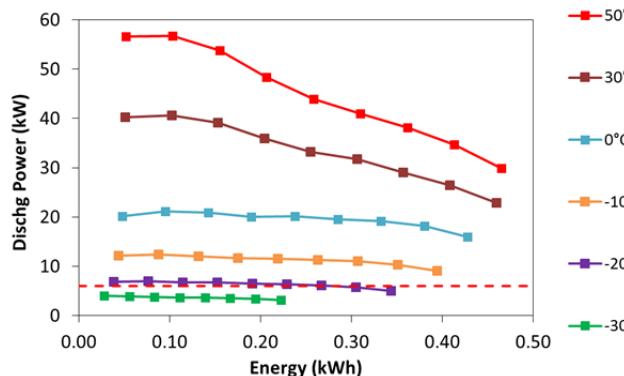


Figure III - 28: Thermal performance test on 2.2Ah prototype cells

Superior charge acceptance, even at low temperatures, is distinguishing feature of the LTO chemistry. It remains high and significantly above 2.2kW target to enable regenerative braking across a wide range of SOC as USABC L-HPPC pulse data demonstrates in Figure III - 29.

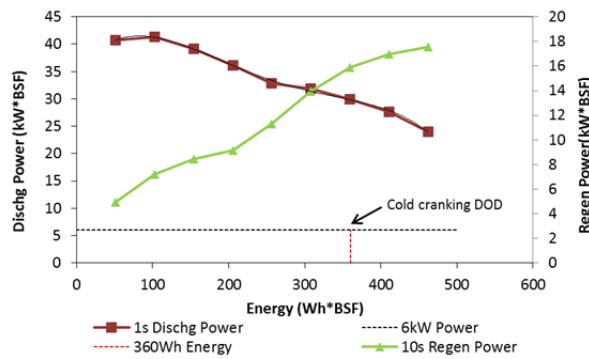


Figure III - 29: USABC L-HPPC test on 2.2Ah prototype cells

**Cycle life.** Cycle life at 30°C and higher temperatures remains the focus of Leyden development. Over the past few months, Leyden has finalized the choice of LMO and LTO materials in terms of high temperature cycle life; developed and optimized electrode formulations, completed process development for prototype cell assembly and initiated work on formation thermal treatments that improve high temperature performance. This allowed us to meet the USABC cycle life requirements: as shown on Figure III - 30; we project to reach >450k shallow cycles at 30°C.

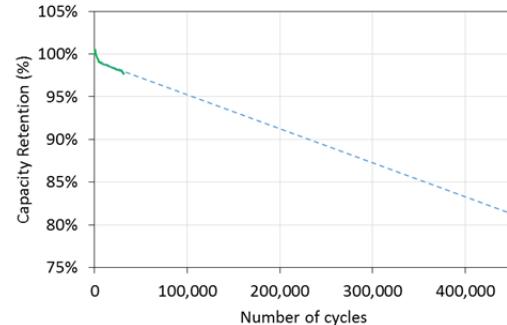


Figure III - 30: USABC shallow cycling at 30°C on 2.2Ah cells

Leyden has also demonstrated stable shallow cycling at 50°C (shown in Figure III - 31) for the cells delivered to ANL and NREL.

Further improvements in cycle life at high temperature are expected to emerge from our development work on an electrolyte additive package and surface treatments. To date, Leyden has evaluated >15 surface treatment techniques. The test results comparison of the most promising surface treatments are shown on Figure III - 32.

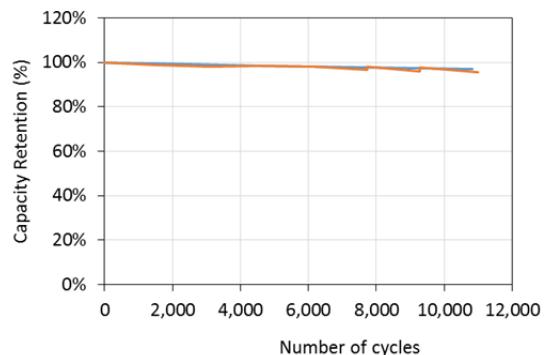


Figure III - 31: USABC shallow cycling at 50°C on 2.2Ah cells

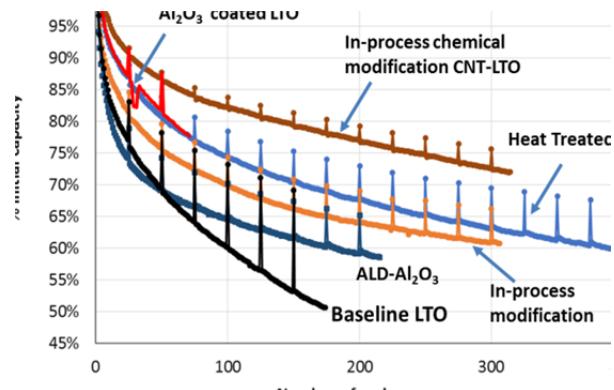


Figure III - 32: Comparison of most promising surface treatments in 0.8Ah prototype cells in 60°C unconstrained cycling; 1C/1C 1.5-2.7V

**Cell development.** Over the course of this program Leyden transitioned from 0.8Ah prototypes to 2.2Ah prototypes. The new cell design incorporates thicker (300 $\mu$ m) and wider (20mm) aluminum tabs resulting in low 1.5m $\Omega$  impedance and the ability to support up to continuous 50C discharges and 100C pulses. Process development included qualification of a new automated stacker, new top and side sealer as well as improved ultrasonic welder horn design.

During the month of October, we assembled the first 20Ah cell prototypes (see Figure III - 33). Electrodes were coated at Leyden and shipped to Dow Kokam where they were punched, dried, stacked and packaged. Ready-to-fill cells were shipped to Leyden for filling and formation.



Figure III - 33: 2.2Ah and 20Ah cell prototype

We confirmed capability of the cells to support cold-cranking requirements and initiated limited cycle life testing. After aging and binning, a number of cells were shipped to Flextronics to assemble the first 12V 40Ah packs.

**Pack and electronics.** Balancing circuitry (see Figure III - 34) for the prototype packs was developed independently by both Leyden and Flextronics. The circuitry decreases the charging current to a cell if its voltage exceeds a set threshold. The parasitic currents of the circuitry were confirmed to be in double digits of microamps.

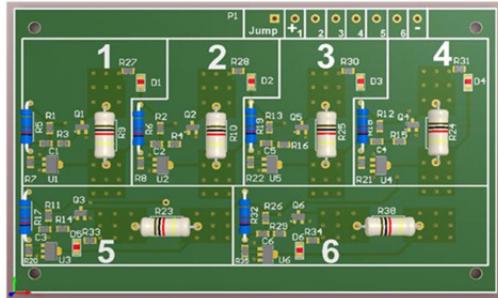


Figure III - 34: Leyden pack balancing circuitry

Pack concept drawings were completed and prototypes were assembled during the month of November.

The pack consists of 2p cell modules with thermal barrier/expansion pads between the cells constrained by aluminum plates with a molded retention frame positioned around the cell. Modules are connected to each other with two sets of aluminum bus bars; cell tabs protrude through the bottom bus bars and are clamped with a top bus bar. The module and pack drawing are shown in Figure III - 35 and Figure III - 36 below.

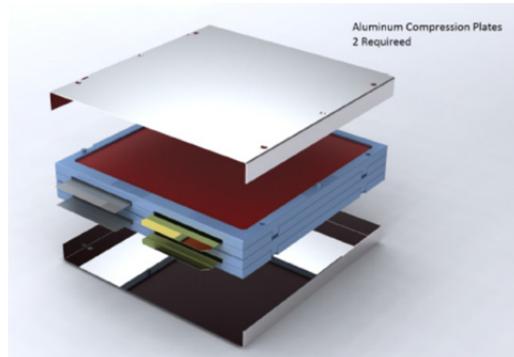


Figure III - 35: Cell module assembly drawing



**Figure III - 36: 12V 40Ah LTO-LMO pack drawing**

**Cost targets.** Leyden Energy has prepared a cost model for the cells and packs based on the template provided by USABC. Based on the data stemming from Leyden's manufacturing experience in Asia, Dow Kokam's expertise in domestic manufacturing and Flextronics pack assembly experience, we have formulated three cost scenarios and presented our findings to USABC. We remain optimistic in achieving the cost targets making LTO-LMO system a competitive solution for 12V Start-Stop systems.

#### FY 2013 Publications/Presentations

1. Florida Battery Seminar, March 2013, Ft. Lauderdale, FL: Start-Stop Lithium-ion Battery Enabled by Li Imide™ Electrolyte System
2. The Battery Show, September 2013, Novi, MI: Battery Trends for Micro-Hybrid Applications (Expanding Start / Stop and Increasing Electrification)

#### Conclusions and Future Directions

Leyden Energy is proud to present significant progress towards meeting the goals of USABC for a 12V Start-Stop battery. Over the duration of this program, Leyden Energy has significantly improved the power and cold-cranking of the LTO-LMO system and demonstrated the ability to meet USABC long cycle life and calendar life requirements. Samples to validate these results were delivered to ANL and NREL per the contract schedule.

Leyden Energy would like to continue its development of the LMO-LTO cells and packs to further improve the performance of this system. Specifically, over the next several months, Leyden will focus on surface coatings and electrolyte development to improve the high temperature cycle life and survival test results. We will continue the internal testing of the prototype cells from the first deliverables build.

Leyden is committed to proceed with the second, optimized 20Ah cell build at Dow Kokam to fulfill cell and pack deliverables to USABC at the end of the program.

## III.A.9 Multifunctional, Inorganic-Filled Separator Development for Large Format Li-ion Batteries (ENTEK)

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Subcontractor: ENTEK Membranes LLC

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Start Date: August 22, 2011

Projected End Date: December 31, 2013

### Objectives

- Deliver a quantity of 18650 cells with silica filled separator and control cells with unfilled polyolefin separators to USABC.
- Continue data collection and analysis for cells still one test.

### Technical Barriers

The project addresses conflicting separator requirements, technical barriers and material cost issues.

(A) Thermal stability and minimum puncture requirements trend in opposite directions with filler contents: high thermal stability requires high inorganic phase contents (> 50 wt %), while high puncture strength requires high polymeric phase contents.

(B) Production of defect free precursor films for biaxial stretching with good thickness uniformity in machine and cross machine direction as well as low polymer crystallinity.

### Technical Targets

- Thickness: less than 25  $\mu\text{m}$
- Permeability: MacMullin Number less than 11
- Wettability: Rapid wet out in electrolytes
- Pore Size: less than 1  $\mu\text{m}$
- Puncture Strength: greater than 300 gf / 25.4  $\mu\text{m}$
- Thermal Stability at 200°C: less than 5% shrinkage
- Tensile Strength: Less than 2% offset at 1000 psi

- No adverse effects on cell performance due to presence of fillers in the separator

### Accomplishments

- All technical targets have been met except puncture, 285 gf @ 25.4  $\mu\text{m}$  versus target of 300 gf @ 25.4  $\mu\text{m}$ .
- Cell test results for 18650 cells with silica-filled separator are reproducible and when compared to controls built with unfilled polyolefin separator:
  - Cycle life is 80% longer.
  - Self-discharge is lower.
  - Low temperature performance is better.



### Introduction

For small commercial lithium-ion cells under abuse conditions, such as external short circuit or overcharging, the separator is required to shutdown at temperatures well below where thermal runaway can occur. Shutdown results from collapse of the pores in the separator due to softening or melting of the polymer, thus slowing down or stopping ion flow between the electrodes. Nearly all Li-ion battery separators contain polyethylene as part of a single or multi-layer construction so that shutdown begins at ~130°C, the melting point of polyethylene. After shutting down, residual stress and reduced mechanical properties above the polymer melting point can lead to shrinkage, tearing, or pinhole formation in the separator.

For larger cells such as those used in hybrid, plug-in hybrid and electric vehicles (HEV, PHEV, EV), shutdown may or may not be required depending on the specific application and system design. In HEV applications, failure modes in which separator shutdown might play a role are handled at a system level. For this reason high temperature melt integrity may be more important than shutdown.

In Phase II of this project, ENTEK produced silica-filled, UHMWPE gel process separators with low impedance and excellent high temperature, mechanical and dimensional stability at pilot and production scale. Extrusion, biaxial orientation, extraction and annealing have been performed step wise to date. The goal of Phase III of this project is to optimize processing and separator performance and to supply samples to battery

makers who will test silica filled separators in large format batteries in order to determine the commercial viability of this technology.

## Approach

ENTEK will:

- Deliver a quantity of 18650 cells with silica filled separator and control cells with unfilled polyolefin separator to USABC for testing by DOE labs.
- Extrude and biaxially orient additional films filled with the preferred spray dried and jet milled silica to improve dispersion. An ample quantity of separator will be prepared to serve as inventory for samples needs.

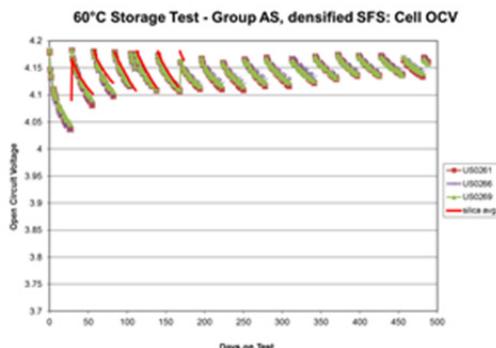
## Results

**Deliverables.** In October 2013, a set of 18650 cells were shipped to INL and Sandia for abuse testing, as shown in Table III - 9.

**Table III - 9: A summary of 18650 cells shipped for abuse testing**

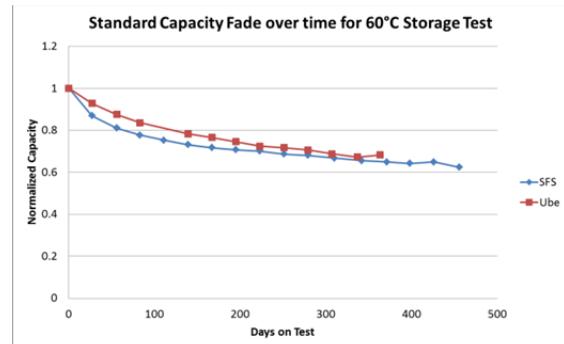
	Control cells	SFS cells
INL	23	20
Sandia	12	10
Total	35	30

**Cell Testing.** 60°C Calendar Life Test. Figure III - 37 shows OCV vs. days on storage for 18650 cells made with densified silica filled separator. The control cells are off test after 28 weeks at 60°C. Three cells with densified SFS are still on test at 60°C after 69 weeks.



**Figure III - 37: 18650 cells with silica-filled separators**

Figure III - 38 below compares standard capacity (30°C) fade for 18650 cells made with silica filled separator and a tri-layer polyolefin separator both stored at 60°C.



**Figure III - 38: Standard capacity fade 60°C storage test**

## Conclusions and Future Directions

Based on a limited amount of testing, abuse tolerance of cells made with silica filled separators is as good as cells made with an unfilled polyolefin separator; while cycle life, self-discharge and low temperature performance of silica filled cells is significantly better than unfilled controls

The improvement in cell performance for cells with silica- filled separators was unexpected and has potential advantages for new cell designs and applications.

## III.B Advanced Lithium Battery Cell Technology

### III.B.1 Silicon-Nanowire Based Lithium Ion Batteries for Vehicles with Higher Energy Density (Amprius)

#### Bruce Mixer, NREL Program Manager

Grant Recipient: Amprius

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#### Subcontractors:

Nissan, BASF, Yardney Technical Products

Start Date: October 2011

Projected End Date: January 2015

#### Objectives

- Extend the cycle life and increase the capacity of Amprius' silicon nanowire anodes.
- Identify electrolyte formulations that improve the performance of Amprius' silicon nanowire.
- Design, build and test large format cells integrating Amprius' silicon nanowire anodes with BASF's NCM cathodes.
- Deliver large format cells that meet DOE goals for energy density, power density, cycle life and calendar life.

#### Technical Barriers

- Development of silicon anodes capable of the long cycle life required for electric vehicles (EVs).
- Development of silicon anodes capable of the high loading as necessary for high energy density.
- Matching of silicon anodes with NCM cathodes capable of long cycle life and high energy density.
- Optimization of electrolyte formulations for long cycle life, high energy, and high conductivity over a wide temperature range.
- Production of silicon anodes and full cells in large vehicle form factors.

#### Technical Targets

Amprius will match its next generation silicon nanowire anode with BASF's high-energy NCM cathode to demonstrate large format cells capable of:

- Energy density of at least 500 Wh/l.
- Power density of at least 500 W/l.
- Cycle life of 300-1,000 cycles at 80% depth of discharge.
- Calendar life of at least 5-10 years.
- A durable design for affordable mass production.

#### Accomplishments

- Set anode, electrolyte and cathode performance targets.
- Confirmed the compatibility of Amprius' silicon nanowire anodes with NCM cathodes.
- Improved anode design to enable longer silicon cycle life.
- Increased the cycle life of full cells matching silicon nanowire anodes with NCA and NCM cathodes.
- Identified additives that extend silicon cycle life.
- Improved the stability of the solid electrolyte interphase (SEI) that forms on the surface of the silicon electrode.
- Purchased and installed equipment to increase silicon nanowire anode production capabilities and enable the production of silicon nanowire anodes in larger form factors.
- Qualified the NCM cathode to be integrated into the baseline cells.
- Designed, built and delivered 18 baseline cells matching graphite anodes with NCM cathodes.



#### Introduction

Today's lithium-ion batteries have very limited room to improve energy density or specific energy. Their active materials are used at energy capacities close to their theoretical limits and their packaging has been

largely optimized. New active materials are needed to boost performance and extend EV driving range.

Amprius has proven silicon's potential as a new anode material. Silicon offers nearly 10 times the theoretical energy of graphite, the traditional anode for lithium-ion batteries. However, when charged with lithium ions, silicon swells to up to four times its volume, causing capacity fade and mechanical failure. Because of swelling, conventional approaches to silicon anodes have not produced cells with the cycle life required for EV applications.

Amprius' anode replaces graphite with silicon nanowires. Amprius' unique nanowire structure addresses swelling by enabling silicon to expand and contract internally (see Figure III - 39). Amprius does not rely on particle-to-particle contact and is able to maintain high electrical conductivity.

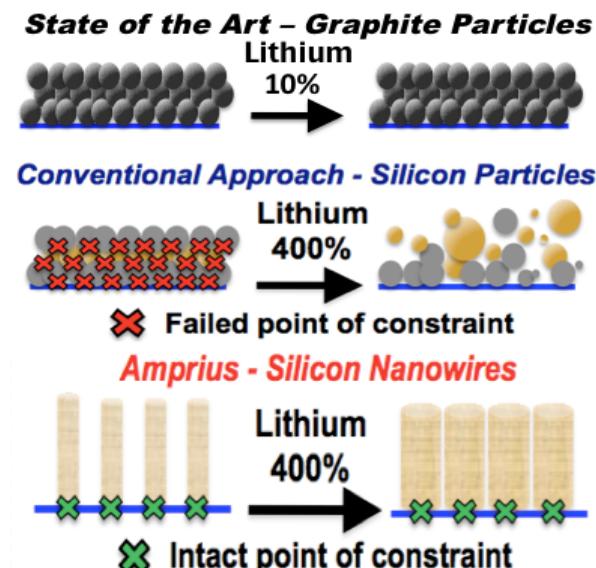


Figure III - 39: Silicon swelling causes capacity fade and mechanical failure. Amprius' nanowires address swelling by allowing silicon to swell successfully

### Approach

Amprius is coordinating the three-year project and leading the anode development effort. BASF is supplying cathode materials and supporting development and integration. Yardney Technical Products is contributing to cell design and integration, including cathode development with BASF, cell physical design, separator selection, and ensuring the compatibility of cell additives. Nissan North America is providing guidance regarding customer requirements.

During Phase I, Amprius conducted experiments to increase the cycle life of its first generation anode material. Amprius' work included both material and

electrochemical efforts. Yardney procured and qualified baseline cathodes. To minimize manufacturing risk later in the project, baseline cells matching graphite anodes with BASF's NCM 1:1:1 cathodes were designed, built and delivered.

During Phase II, Amprius will increase the capacity of its silicon nanowire anode material through internal structure modification. Amprius will also pair its silicon anode with BASF's NCM 5:2:3 and high-energy NCM cathodes. Before pairing, Yardney will quantify BASF's cathode against commercial competition, then optimize cathode composition. Amprius will then deliver interim cells matching Amprius' silicon anodes with NCM 1:1:1 cathodes.

During Phase III, Amprius will focus on optimizing cells matching Amprius' silicon nanowire anode and BASF's high-energy NCM cathode. Amprius will also confirm secondary performance criteria including safety. Yardney will help integrate Amprius' anode and BASF's cathode into large 20 Ah cells and conduct safety testing. Amprius will then deliver final cells matching Amprius' silicon anodes with high-energy NCM cathodes.

### Results

**Anode Development.** Amprius improved the performance of its next generation silicon nanowire anode. Amprius adjusted the porosity, crystallinity, length, height and diameter of its nanowires, reviewing SEM images of electrodes built from different recipes and studying the volume expansion at different lithiation stages. By tuning these process parameters, Amprius increased the cycle life of its silicon anode in full silicon/NCA and silicon/NCM cells. Figure III - 40 details the cycle life of laboratory cells matching silicon anodes with NCA cathodes.

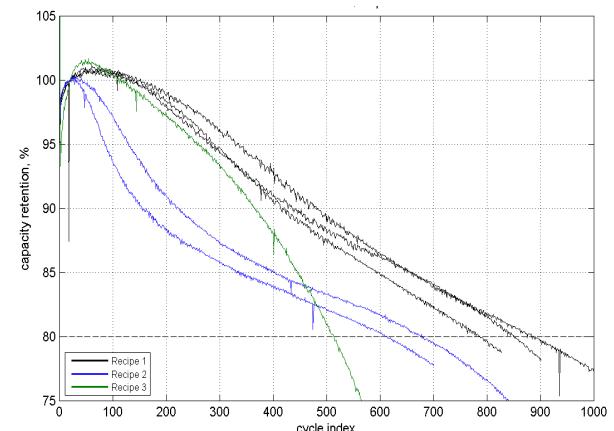


Figure III - 40: Amprius improved the cycle life of laboratory cells matching silicon anodes and NCA cathodes

**Electrolyte Development.** By studying the specific conditions on silicon's surface that result in the formation of the SEI, Amprius was able to develop a better understanding of SEI formation and manage the configuration of silicon and the composition of the electrolyte to enable a more stable SEI.

Amprius also tested various electrolyte formulations and identified additives that extend cycle life and enable silicon cells to maintain high conductivity over a wider temperature range. Figure III - 41 reviewed the boost various additives provided to the median cycle life of early-stage laboratory cells built from silicon nanowire anodes.

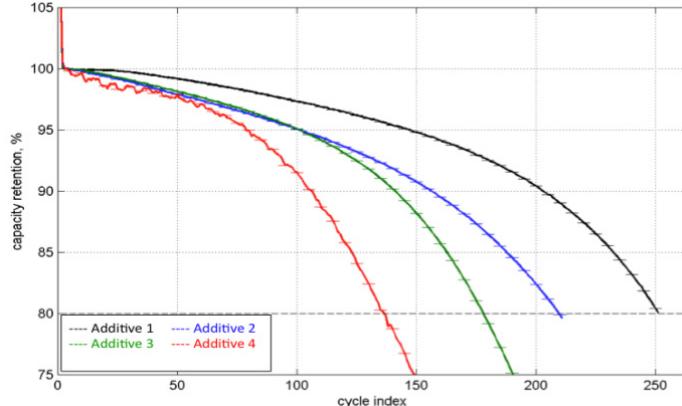


Figure III - 41: Amprius identified additives that extended the cycle life of early-stage, silicon-based lab cells

**Cell Design and Baseline Cell Delivery.** Eighteen (18) baseline cells were designed, built and delivered to Idaho National Laboratory. These large vehicle form factor cells matched graphite anodes with NCM cathodes. Their production during Phase 1 will minimize manufacturing risk later in the project. Figure III - 42 shows the cells in fixtures during cell acceptance testing.

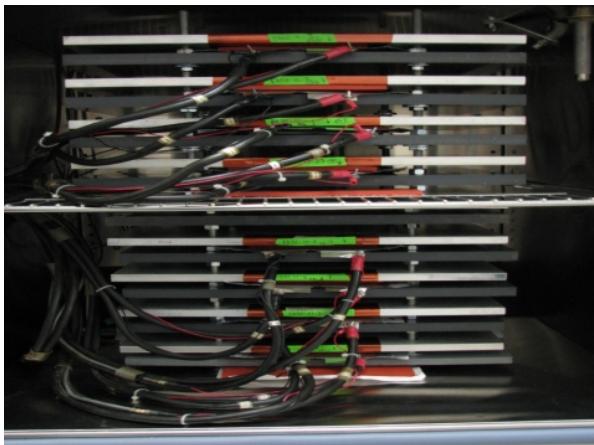


Figure III - 42: Amprius delivered to the DOE 18 baseline cells matching graphite anodes and NCM cathodes

## Conclusions and Future Directions

During the project's first phase, Amprius improved the cycle life of its silicon nanowire anode and advanced silicon electrochemistry. Yardney designed and built baseline cells.

During the project's second phase, by further tuning nanowire structure, Amprius will continue to extend the cycle life of its silicon nanowire anode and increase the capacity of its anode. Amprius will also deliver 18 vehicle form factor cells matching Amprius' silicon nanowire anodes with BASF's NCM 1:1:1 cathodes. These interim cells will have a specific energy of at least 250 Wh/kg.

Next year, in preparation for Phase III deliverables, Amprius will also pair its silicon anode with BASF's NCM 5:2:3 and high-energy NCM cathodes. Yardney will also qualify BASF's high-energy cathode.

## III.B.2 Development of Large Format Lithium-Ion Cells with Higher Energy Density (Dow Kokam)

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Dow Kokam, LLC, Contractor

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Subcontractors:  
Wildcat Discovery Technologies, Inc.  
Oak Ridge National Laboratory

Start Date: October, 2011  
Projected End Date: March 2015

### Objectives

The objective of this project is to research, develop, and demonstrate Li-ion battery cells that are capable of achieving an energy density of at least 500 Wh/l while maintaining comparable performance standards in terms of cycle life, calendar life, and durable cell construction and design capable of being affordably mass produced.

### Technical Barriers

The energy density needed to both effectively and efficiently power electric vehicles (EV) is not available with current lithium ion cell technology. Today's solution falls significantly short of meeting the general consumer's cost and life expectations. In order for the EV industry to be successful, battery cell with twice the energy density must be developed.

### Technical Targets

- Develop and optimize new materials and design of lithium ion cells which will double the energy density of commercially available cells from 260 – 340 Wh/L to 500 – 750 Wh/L.
- Implement these improvements to mass production system exceeding 500 W/L, superior overall performance and cost compared to currently available PHEV and EV

cells, and safety comparable to today's commercial Li-ion cells.

- Improve EV battery affordability by reducing cell cost to \$0.20 – 0.25/Wh.

### Major Accomplishments

- Samples of 2 Ah baseline cells with NMC and graphite as the active materials were delivered to Argonne National Laboratory for evaluation.
- Both of the high capacity anode (HCA) materials tested by Dow Kokam have demonstrated >2,500 mAh/g. However, satisfactory performance can be obtained only when the utilization is controlled below 1,250 mAh/g. Dow Kokam is testing full cells with HCA and high voltage cathode (HVC) materials.
- In addition to the cobalt phosphate-based HVC materials, Dow Kokam added NMC-class HVC materials to the list of evaluations. Leveraging the experiences learned from another program, funded by the Department of Defense (DoD), Dow Kokam has demonstrated energy densities of >500 Wh/L with the HVC/graphite chemistry.
- One high capacity cathode (HCC) material has demonstrated >260 mAh/g. However, it has been difficult to produce this material in a cost effective way. Dow Kokam decided to stop the synthesis of this material; however, we will evaluate other established HCC materials from commercial suppliers.



### Introduction

Dow Kokam proposed to develop a large format battery cell design that could double the energy density of current lithium-ion cells.

According to our calculations, this can be done by either increasing the operating voltage of the cell or increasing the capacity of the active materials. Therefore, a parallel approach has been taken. A high voltage phosphate-based cathode material and a lithium-rich based high capacity cathode (HCC) material, both developed by Wildcat Discovery Technologies (WDT), will be evaluated using silicon-based high capacity

materials or conventional graphite as the anode. 2 Ah format sample cells will be used as a common platform during the evaluation of the materials. 40 Ah production size cells will be produced and delivered to demonstrate that the materials can be scaled up to a production scale manufacturing environment.

## Approach

The following approach will be taken to achieve the goals:

- Design and fabricate baseline cells in 2 Ah format. The cell design is a direct reduction of the 40 Ah production cell produced by DK.
- Develop a cell performance model to represent the behavior of the cell. This model will be used to predict the performance of cells when the novel materials described above are used.
- Evaluate those novel materials in half-cell format to understand their performance. The data will be used to design full cells with these materials as the electrodes.
- Design and construct a small-volume slot die coating system that can produce electrodes with very little material and have the same quality as production scale electrodes.
- Design and fabricate samples cells, of the 2 Ah format, using HVC and HCC materials as the cathode and HCA or conventional graphite as the anode.
- Design and fabricate a full size, 40 Ah cell that can be produced in DK's cell manufacturing facility.
- Collaborate with WDT to develop the cathode materials and with Oak Ridge National Laboratory (ORNL) to characterize these materials.

## Results

**Baseline cell.** Cells were designed, built, and tested. Test results show that these 2 Ah cells behave very similar to the 40 Ah, large format, cells Dow Kokam manufactures. Eighteen cells have been delivered to Argonne National Laboratory for testing.

**High Capacity Anode Material.** Two silicon-based anodes were selected. The maximum specific capacities of these materials were both above 2,500 mAh/g. However, if utilized above 1,250 mAh/g the materials showed fast decay. It was found that matching the electrode designs between the HCA and the cathode is extremely important to the performance of the cell. Sample cells made with HVC and HCA were fabricated and tested at Dow Kokam. To date, cells with

570 mAh/L energy densities has been demonstrated, Figure III - 43. Optimization of cell design is in progress.

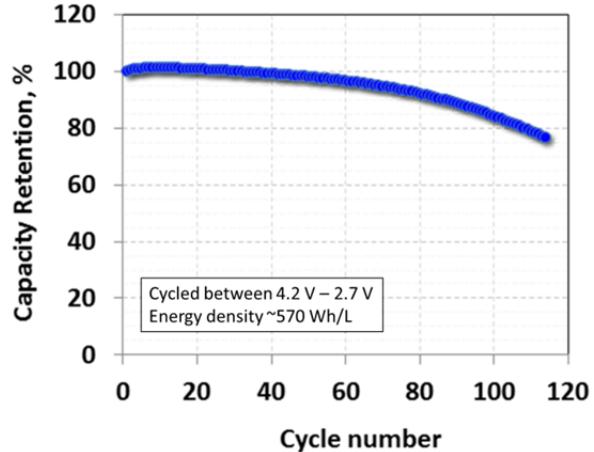


Figure III - 43: Cycle performance of an HVC/Si-based anode cell

**High Voltage Cathode Material.** In addition to the CM1 material developed by WDT, Dow Kokam has also been testing NMC-class materials operating at higher voltages under a research program funded by the Department of Defense. Applying the knowledge gathered, Dow Kokam has demonstrated 500 Wh/L energy density using HVC with graphite in a 2 Ah cell format. The energy density of these cells using HVC and HCA is expected to be >600 Wh/L. When charged to 4.4 V, the energy density of an HVC/graphite cell at various discharge rates is shown in Figure III - 44.

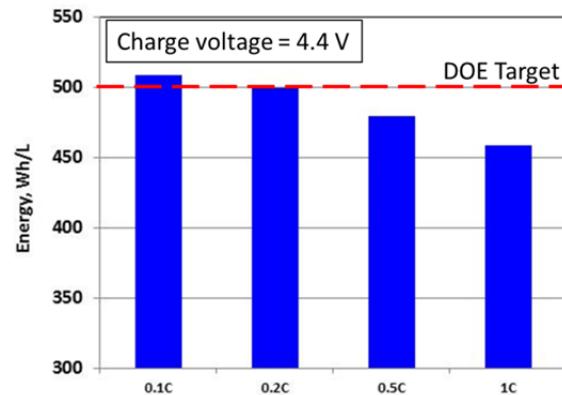
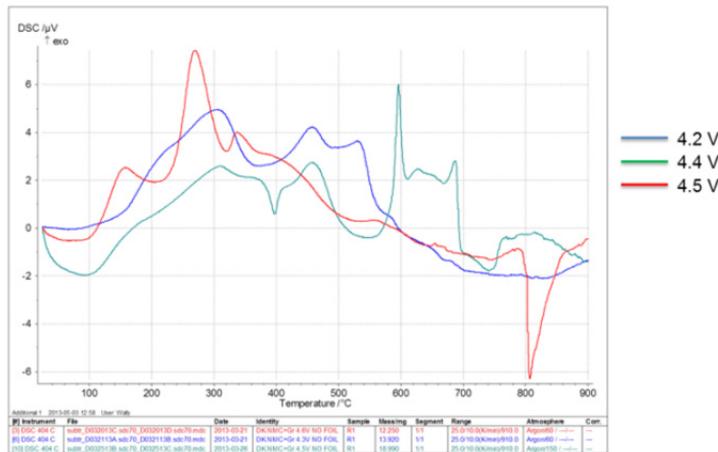


Figure III - 44: Energy density of an HVC/graphite sample cell

The stability of this material as a function of the charge voltage was investigated by differential scanning calorimetry (DSC) at ORNL. It was concluded that the behavior of this NMC material, when charged to 4.4 V is similar to when it is charged to 4.2 V below ~600°C, as shown in Figure III - 45.



**Figure III - 45: Thermal behavior of a high voltage NMC material when charged to various voltages**

**High Capacity Cathode Material.** A lithium-rich oxide material has been selected by WDT as the HCC material. The capacity of the material synthesized using lab-scale equipment has achieved >260 mAh/g of capacity. However, the usable capacity decreased when synthesized using an affordable technique, Table III - 10.

**Table III - 10: Characteristics of HCC by various synthesis methods.**

Target	Solution		Solid State
	Best	Control	Best
Capacity (mAh/g)	260	266	233
Usable Capacity (mAh/g)	260	266	153
Energy (Wh/kg)	1000	972	825
Rate (% 1h)	80	77	74
			81

Given the limited resources available for this effort, Dow Kokam decided to stop the development of affordable synthesis techniques. Instead, we will acquire other HCC materials from commercial suppliers.

### Conclusions and Future Directions

- Baseline cell test results show that the design and fabrication are suitable to produce cells with the same performance as commercial, large format, cells manufactured by Dow Kokam. Cells have been delivered to Argonne National Laboratory for testing.

- Dow Kokam evaluated the cell performance of HCA materials and demonstrated >2,500 mAh/g of specific capacity. However, the performance is sensitive to the electrode design and matching between the HCA and the cathode. Dow Kokam will optimize the electrode design to improve cell performance.
- Dow Kokam has satisfied the goal of >500 Wh/L in energy density using HVC and graphite anode. It will continue to improve the energy density of cells using HVC and silicon-based HCA.
- Due to the difficulties to synthesize the HCC affordably within limited resources, Dow Kokam will stop the work at WDT and source HCC material from commercial suppliers.
- DK believes, from the results obtained so far, it is moving in the right direction and will continue with the development of cells with HVC and HCC.

### FY 2013 Publications/Presentations

- 2013 DOE Annual Peer Review Meeting Presentation
- 2013 Technical Review Meeting

## III.B.3 Innovative Cell Materials and Designs for 300 Mile Range EVs (Nanosys)

**John Tabacchi, NETL Program Manager**

Award Recipient - Nanosys, Inc.

**Yimin Zhu, Nanosys, Inc. – PD/PI**

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Phone: 650-331-2232; Fax: 408-240-6900

E-mail: [yzhu@nanosysinc.com](mailto:yzhu@nanosysinc.com)

Subcontractor:

A123 Systems

200 West Street

Waltham, MA

Start Date: October 2011

Projected End Date: September 2014

### Objectives

- We propose to develop a 700~1,000 mAh/g Si anode (SiNANOde™) with a target cycle-life of >800, and an eventual goal of achieving an energy density of 1,600 mAh/g at the end of the program. An ideal target will be a cell with 350 Wh/kg and 800 Wh/L, which is capable of driving 300 miles on a single charge and achieving a cell level cost target of <\$150/kWh.

### Technical Barriers

In order for EVs to achieve mass adoption and make a significant dent in U.S and global CO<sub>2</sub> production, the key problems of driving range per charge and cost per kWh must be addressed.

Barriers addressed:

- Performance: Low Wh/kg & Wh/L
- Life: Poor deep discharge cycle life.
- Cost: High \$/kWh.

### Technical Targets

- Anode Targets: 700-1,000 mAh/g and > 800 cycle; 1,600 mAh/g as needed at end of the project.
- Cathode Targets: 255 mAh/g and >800 cycles; other well-performed cathode and >800 cycles at end of the project.

- Cell Targets: 350 Wh/kg, 800 Wh/L, <\$150/kWh at end of the project.

### Accomplishments

- We have achieved the full cell cycling performance of >1,000 cycles using baseline SiNANOde and have been continuously improving it.
- We have demonstrated SiNANOde specific capacity as high as 1,678mAh/g with >92% first cycle coulombic efficiency.
- A 700 ~1,000 mAh/g SiNANOde has exhibited a cycle life of >700 cycles.
- We have produced SiNANOde on different graphite substrate using low cost precursors and improved material production uniformity.
- Pouch cells have showed an energy density of 250Wh/kg using 550mAh/g baseline SiNANOde and LCO baseline cathode. The pouch cells have showed acceptable cell thickness increase of < 14% over 300 cycles. SiNANOde cell's self discharge and subsequent recharge is comparable to commercial graphite cells.
- The hysteresis effect is less pronounced for 8%SiNANOde full cell in comparison with 8%Si powder-graphite full cell.
- We have demonstrated the feasibility of using the SiNANOde and the improved cathode materials to make full cell with 300~400Wh/kg.
- We are optimizing SiNANOde electrode and other well-performed cathode to achieve higher electrode loading (3~5mAh/cm<sup>2</sup> one side).
- We have developed a new electrolyte C1.1 that enables higher coulombic efficiency and hence improved cycling performance.



### Introduction

Consumers have been frightened by high gasoline price at the pump reaching \$4 or even \$5/gallon. In the future, the biggest opportunities will be in fuel efficiency technologies for cars and light trucks. More and more people believe that batteries based on Li-ion technologies are the optimal solution for transportation.

The cell that we proposed with a novel SiNANOde™ and composite cathode will significantly advance the current state-of-the-art in Li-ion technologies.

## Approach

**Innovative Approach.** The objectives outlined above, will be accomplished by combining a high energy cathode technology with, SiNANOde™, a Si graphite composite. Cathode materials currently being used in PHEVs and EVs have a maximum capacity of ~150 mAh/g or less. We will use the well-performed cathode or the composite cathode containing a layered component with high specific capacity. The major technology innovations will be undertaken to accomplish the objectives of this effort are:

1. Improve SiNANOde™ capacity from 650 mAh/g to 700~1,000 mAh/g in Phase I and to 1,600 mAh/g later. Graphite particle size and morphology will be further optimized to achieve this goal.
2. Achieve increased cycle-life from 220 to >800. To achieve this, innovative surface modification of the Si nanowire anode is required for improved stability and SEI formation. The electrolyte and binder chemistry will be optimized.
3. Achieve cell specific energy of 350 Wh/kg and energy density of 800 Wh/L by combining the above high energy anode and cathode materials. The baseline performance of the full cell at the onset of the effort is 210 Wh/kg and 400 Wh/L
4. Achieve cost reduction resulting in <\$150/kWh (cell level). This will be achieved by moving from synthetic graphite (\$35/kg) to natural graphite which is projected to be \$5-\$10/kg. Cost reduction will also be supported through increased efficiency in manufacturing processes and scale-up of both anode and cathode.

## Results

### Cycle Life Enhancement for 700~1000 mAh/g Anode.

We have been continuously working on producing pilot-scale manufacturing quantities of SiNANOde. The specific capacity of ~650mAh/g has been achieved and SiNANOde half cells can be cycled more than 1,200 times with a capacity retention of > 85%. Using an LCO cathode, the SiNANOde was integrated in the full cells and exhibited ~350 cycles at ~76% capacity retention (see Figure III - 46), which still showed much higher anode-specific capacity over graphite anode. After 200 cycles SiNANOde full cell showed a capacity fade rate comparable to graphite full cell.

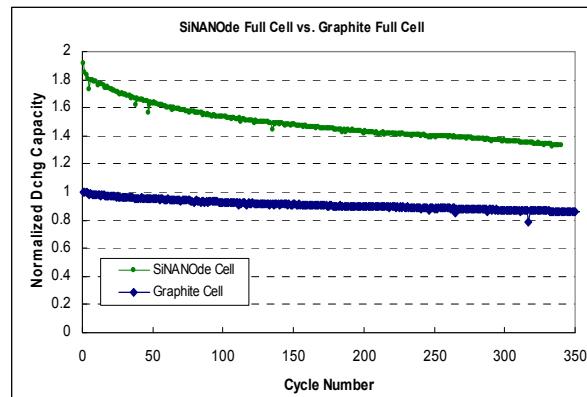


Figure III - 46: Baseline SiNANOde/LCO full cell

It is well known that OCV and SOC have a relationship based on the Nernst equation. As a peculiar problem for HEV battery, there is the voltage hysteresis phenomenon, in which measured OCV after charge (discharge) is higher (lower) than the estimated OCV by Nernst equation. This voltage hysteresis has been modeled by adding simple voltage modification term to the Nernst equation, by using a SOC-dependent voltage source including hysteresis. These method needs history information whether battery has been charged or discharged. And SOC and OCV no longer has a one-to-one relationship. Minimizing the voltage hysteresis is certainly critical. With the full cell SiNANOde/LCO this cell voltage hysteresis has been evaluated. Our SiNANOde cell voltage hysteresis effect is much less pronounced (<0.1V). The hysteresis effect is less pronounced for 8%SiNANOde/LCO full cell in comparison with 8%Si powder-graphite/LCO full cell (see Figure III - 47).

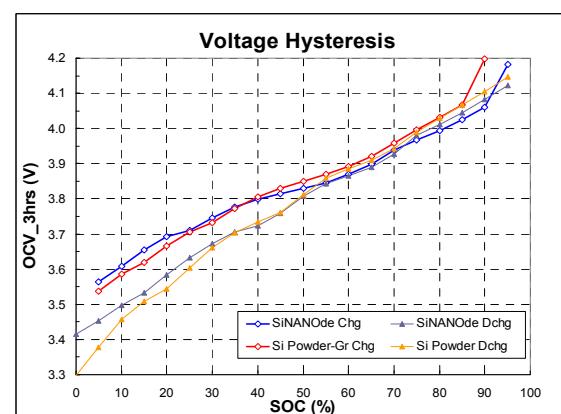
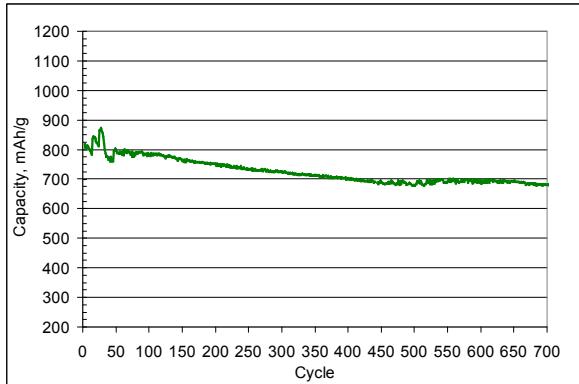


Figure III - 47: Voltage hysteresis of SiNANOde and Si powder-graphite full cells

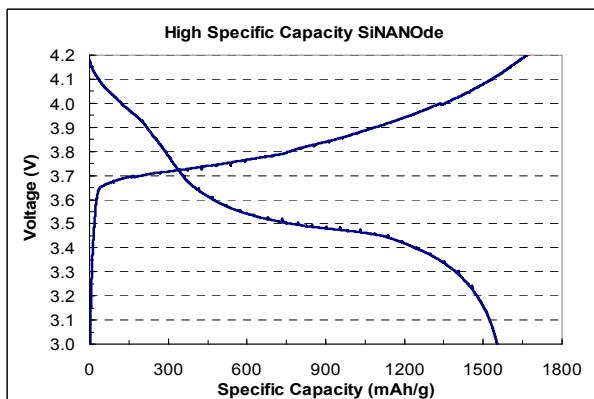
We have made improvement in the specific capacity of SiNANOde of up to 850mAh/g of reversible capacity. We further improved the conductivity of SiNANOde to optimize the SiNANOde material, which has showed longer cycling life of ~700 cycles at 81%

capacity retention at 0.3C cycling in half cells (see Figure III - 48). It should be noted that at beginning the cell has been used for various C-rate testings.



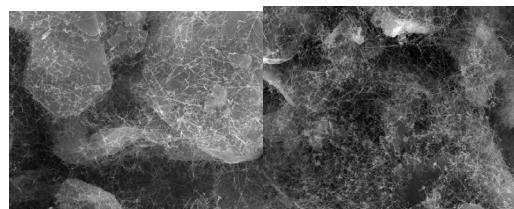
**Figure III - 48: SiNANOde half cell with 700~1000mAh/g**

**Enhanced Si Capacity 1,600 mAh/g Anode.** We are improving the high specific capacity of SiNANOde and obtained ca. 1,678mAh/g. The first coulombic efficiency is still more than 92%, shown in Figure III - 49. Various binders have been used to achieve better cycling performance (ongoing). Even though the specific capacity has been increased up to >1,600mAh/g the Si nanowires can also be uniformly distributed on the graphite powders, shown in Figure III - 50. This proves that the SiNANOde production approach allows Si-content to be tuned in a wide range to meet various application requirements.



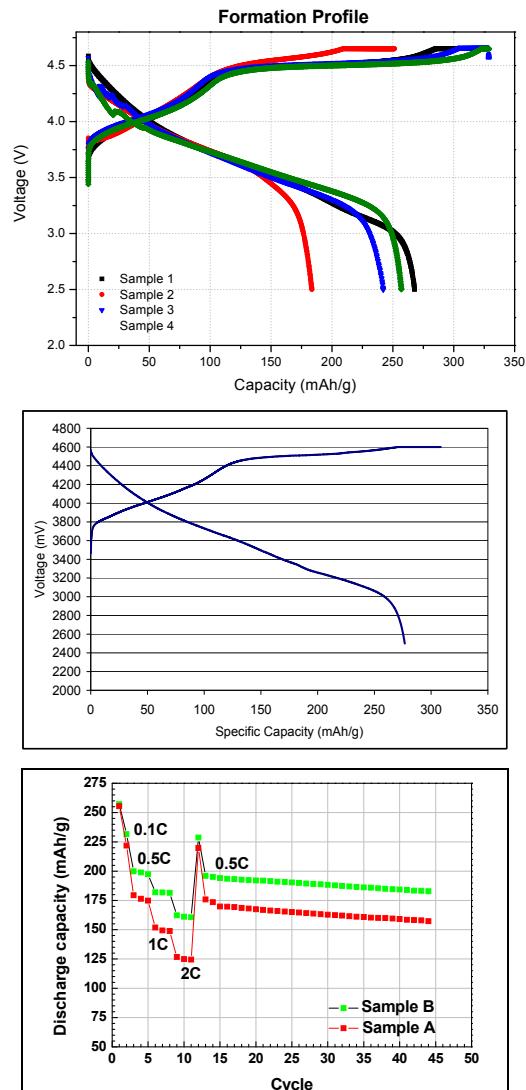
**Figure III - 49: >1600mAh/g SiNANOde's voltage profile**

**Optimization of Cathode Composition.** We have tested Mn-rich cathode materials in coin half cells to confirm their electrochemical performance, so that the optimal cathode will be combined with Si anode, SiNANOde.



**Figure III - 50: Uniform Si nanowire distribution on graphite powders for 700mAh/g (Left) and >1600mAh/g (Right)**

To improve the cathode materials, its surface has been modified in various ways to enhance capacity, see Figure III - 51 (Top). The ICE of the cathode electrode can be improved by optimizing its electrode composition in Figure III - 51 (Middle). Those improvements result in enhancement of its C-rate performance (Figure III - 51, Bottom).



**Figure III - 51: Voltage profiles and rate capabilities of cathode candidates**

It is critical to identify an appropriate high voltage electrolyte to enhance the cathode cyclability. The electrolyte composition has significant impact on the cycling performance of the cathodes. Cell #2 uses an electrolyte tailored to have high voltage stability, which shows much better cycling performance over the cell#1 that uses the regular electrolyte (Figure III - 52).

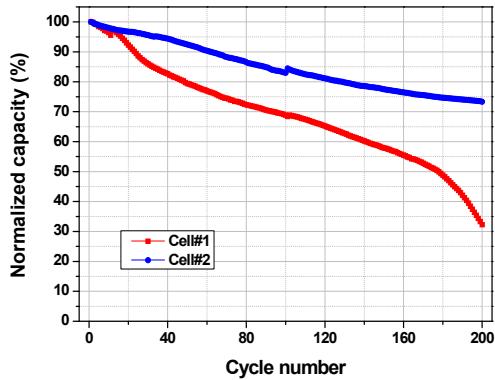


Figure III - 52: Cathode cyclability vs. different electrolyte

**Feasibility Test of High Energy Cells with Mn-rich Cathode and SiNANOde.** In order to demonstrate very high energy density in the cells using Mn-rich cathode and ~1,300 mAh/g SiNANOde, various cells were designed to achieve 250, 300, 350, and 400 Wh/kg. One key finding from this work is that the rate capability needs to be improved.

The cycle life test of each cell is carried out at 0.3C rate under 80% DOD. In the case of 400 Wh/kg-target cell, its initial capacity distinguishedly decreases, compared with other cells. The 400Wh/kg cell showed ~55% capacity retention at 150<sup>th</sup> cycle (Figure III - 53).

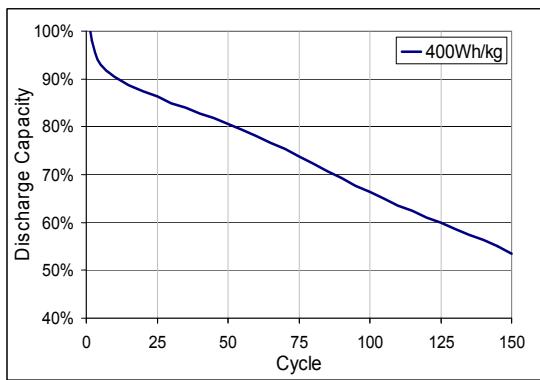


Figure III - 53: Cycle life at 0.3C rate (80% DOD)

The specific capacity of SiNANOde has been increased up to 1,300~1,400mAh/g by controlling Si nanowire content, shown in Figure III - 54. At beginning, the cell formation has been done at 0.05C. The high capacity SiNANOde material shows better cycle life at 0.5C (>88% retention so far). After 100 cycles, the cycle life will be typically more stable (see

Figure III - 54). This implies that the high capacity cathode also has negative impact on the cycle life of the high energy full cell (Figure III - 53), which suggests that in order to evaluate SiNANOde cyclability we should select other well-performing cathode (e.g., NCA or LCO or NCM).

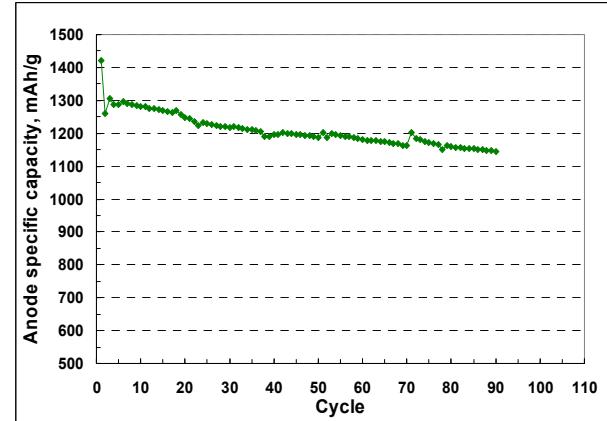


Figure III - 54: ~1300 mAh/g SiNANOde cyclability

**Cell Design Study for High Energy Cells with Mn-rich Cathode and SiNANOde.** It is found that the electrode loading is a dominant factor in demonstrating the high energy cell with Mn-rich cathode and SiNANOde. The electrodes with the desired high loadings are difficult to be coated on larger coater and result in the substantial increase in resistance. We have tried to prepare the electrode with higher loading through formulation work so that the pouch cells can be made in plant.

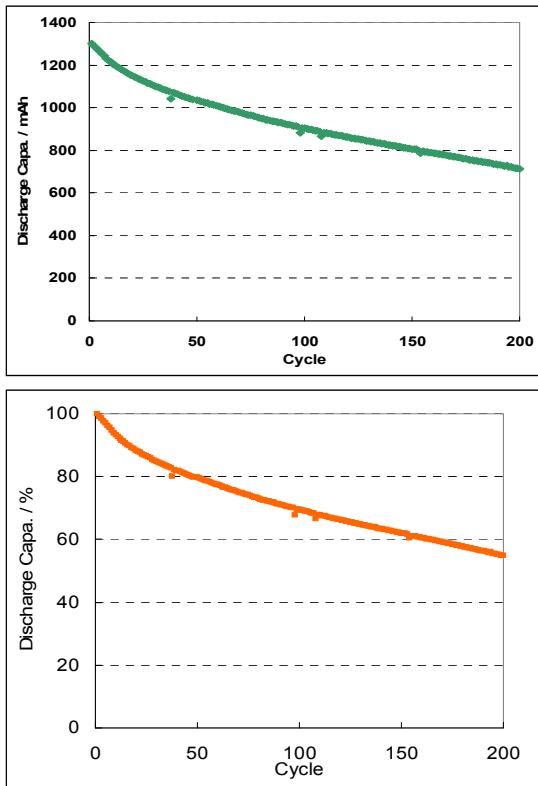
In addition, cell design study has been carried out using three different grades of Si anode with specific capacity of 600, 800 and 1200 mAh/g, respectively. Only processable electrodes with high loading are used for the cell design study. The cell operation voltage is up to 4.4 V or 4.5 V (Table III - 11).

Table III - 11: In plant – processable high loading electrode study for high energy cell design

Loading	600 mAh/g	800 mAh/g	1200 mAh/g
Processable (in plant), 4.4 V	225 Wh/kg	240 Wh/kg	255 Wh/kg
Not processable (in plant), 4.4 V (~1300 mg/25 cm <sup>2</sup> )	255 Wh/kg	275 Wh/kg	300 Wh/kg

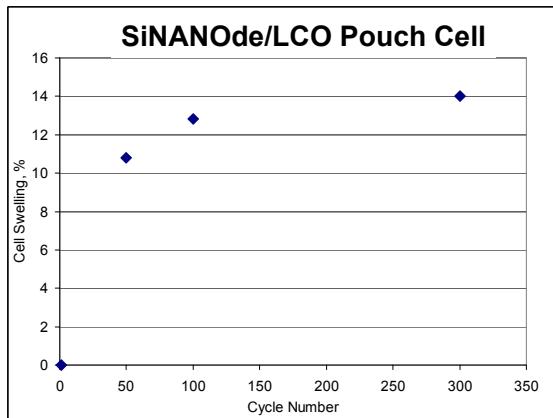
#### Cycle Life of 1.3 Ah Cell with 500~600 mAh/g Anode.

The 1.3 Ah pouch cells are built using the baseline 550 mAh/g SiNANOde and LCO cathode (Figure III - 55). An energy density of 250 Wh/kg can be achieved in the cells. As the electrode has been heavily calendered the capacity retention is about 55% at 200<sup>th</sup> cycle.



**Figure III - 55: Cycle life of 250 Wh/kg pouch cell using 550 mAh/g SiNANOde at 0.5C rate (DOD 100)**

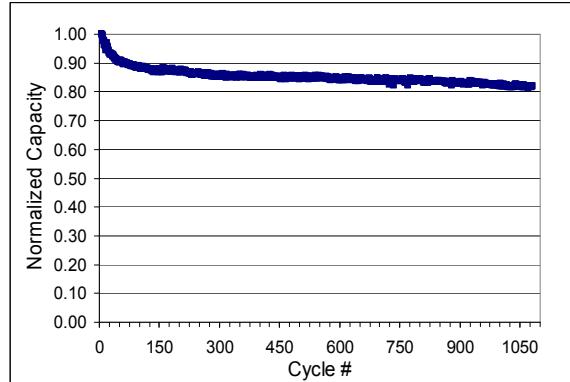
The pouch cells have showed acceptable cell thickness change of < 14% cell swelling over 300 cycles (Figure III - 56).



**Figure III - 56: Thickness change of High Energy Density Pouch Cells: SiNANOde/LCO**

Combining with the well-performed NCA cathode the SiNANOde full cell shows 80% retention after 1,000 cycles at +0.3C/-0.5C cycling. Relatively faster capacity fading was observed in the first 100 cycles (see Figure III - 57). Then the cell approached a more stable zone and last >1,000 cycles at a 80% retention. It

demonstrates that the SiNANOde can be very stable over cycles and also can be further improved by forming more stable SEI in the first 100 cycles.



**Figure III - 57: SiNANOde full cell cyclability**

SiNANOde cells' self-discharge properties have been investigated at 20°C for one month or at 60°C for one week. SiNANOde cell's self discharge and subsequent recharge is comparable to commercial graphite cells (Table III - 12).

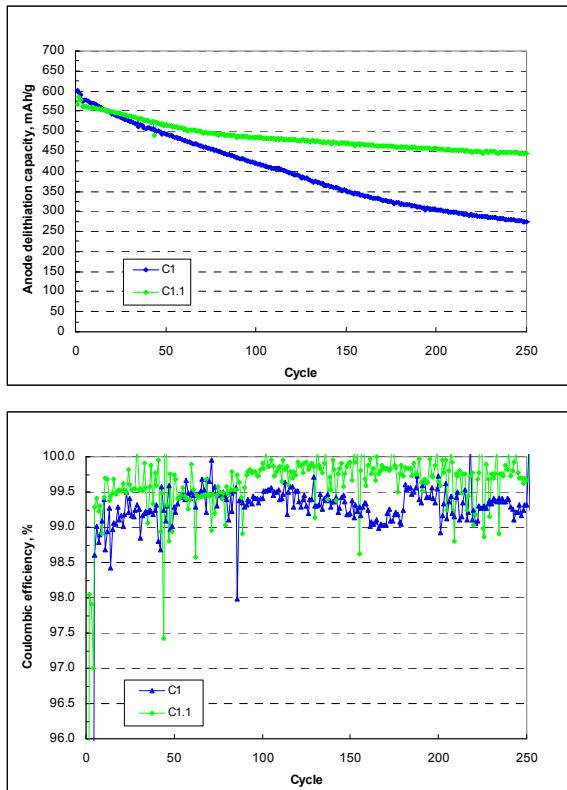
**Table III - 12: SiNANOde Cell Self discharge**

Condition	8% SiNANOde/LCO Normalized to Graphite/LCO Control
Retention % @20°C at end of 1 month	99.6%
Realized capacity upon recharge after discharging at 20°C for 1 month	98.7%
Retention % @60°C at end of 1 week	98.7%
Realized capacity upon recharge after discharging at 60°C for 1 week	99.3%

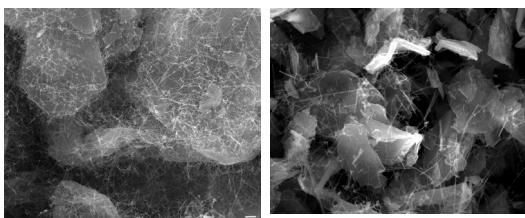
We have developed a new electrolyte C1.1 that enables higher coulombic efficiency and hence cycling performance compard to a cell with the baseline electrolyte C1 over 250 cycles (Figure III - 58).

SiNANOde development on different graphite substrates has been extensively explored, which results in a wide range of tunable Si nanowire density on the graphite substrate (Figure III - 59). Smaller graphite powders have higher surface area that can host more Si nanowires. It allows us to grow Si nanowires with >50%Si in the SiNANOde composite.

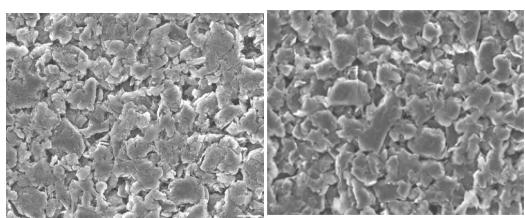
The 500~700mAh/g -SiNANOde pouch cells have already showed >620Wh/L in conventional 4.2 ~3.0V range. The SiNANOde electrode density can be as high as 1.5g/cm<sup>3</sup> (Figure III - 60) without breaking Si nanowires.



**Figure III - 58:** New electrolyte enables better cycling performance



**Figure III - 59:** Si Nanowire grown on larger graphite powders (Left) and smaller graphite powders (Right) for 700mAh/g



**Figure III - 60:** Calendered SiNANOde Anode (Left) and Graphite Anode (Right) with 1.5g/cm<sup>3</sup>

### Conclusions and Future Directions

We have made dramatic progress in Si composite anode (SiNANOde<sup>TM</sup>), Mn-rich cathode and cell performance improvement. The specific capacity of SiNANOde can be controlled in a range of 500 to

1,800mAh/g by tuning amounts of engineered silicon nanowires, as needed. Initial coulombic efficiency has been improved to more than 92% for all the SiNANOde products. Almost 100% utilization of Si capacity has been realized in the cells. By optimizing Si nanowire coverage and distribution on the desired graphite surface as well as by optimizing electrolyte and binder chemistry, cycle life has been greatly improved. We have demonstrated a cycle life of more than 700 cycles at a capacity retention of 81% for the SiNANOde with 700~1,000 mAh/g in half cell. We have also demonstrated good cycling performance of >1,000 cycles in the full cells combined with well-performed NCA cathodes.

Further cathode development has achieved a reversible capacity of >255 mAh/g and has improved its C-rate performance from 0.2C to >0.5C even at high loading. Therefore, we are able to make full cells with high specific energies of 300~400Wh/kg using the SiNANOde of 1,200mAh/g and the improved cathode materials of 255mAh/g.

We are determining the optimal Si percentage, electrode density and thickness so that we are able to achieve high energy density in the cells with good C-rate performance and cycling performance.

Pouch cell have attained an energy density of 250Wh/kg using 550mAh/g SiNANOde and LCO cathode. The pouch cells have showed acceptable cell thickness increase of < 14% over 300 cycles. SiNANOde cell's self discharge and subsequent recharge is comparable to commercial graphite cells.

The hysteresis effect is less pronounced for 8%SiNANOde full cell in comparison with 8%Si powder-graphite full cell.

We have developed a new electrolyte C1.1 that enables higher coulombic efficiency and hence cycling performance.

In addition, SiNANOde development on different graphite substrate has been extensively explored, which results in a wide range of tunable Si nanowire density on the graphite substrate.

The above results prove that the proposed technical approach is viable.

### FY 2013 Publications/Presentations

1. “Innovative Cell Materials and Design for 300 Mile Range EVs,” ES130\_Zhu\_2013\_p, U.S. DOE Vehicle Technologies AMR, 2013

## III.B.4 High Energy Novel Cathode/Alloy Automotive Cell (3M)

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Award Recipient - 3M Company

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Start Date: October 2011

Projected End Date: January 2015

### Objectives

- Develop a >2 Ah cylindrical wound or stacked pouch cell with high energy density at low cost for automotive application.
- Integrate advanced chemistries including an advanced high-voltage cathode, high capacity alloy anode and advanced electrolyte materials as well as enabling technologies related to electrode preparation and cell build such as binder, conductive agent, and processing aids.

### Technical Barriers

This project addresses the following technical barriers associated with the combination of high energy cathode and advanced alloy anode material:

- Low Cycle Life.
- Low Rate Capability.
- High irreversible capacity leading to low overall cell energy density.
- Large volume expansion of alloy anode.

### Technical Targets

- Establish a baseline cell with similar energy density to USABC EV targets with commercial LiMn<sub>1/3</sub>Ni<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> (NMC 111) cathode and graphite anode.
- Provide an advanced cell with at least 40% (1.4 x baseWh/L) increase in energy density compared to the baseline cell.
- Demonstrate as good or superior thermal stability, long-term cycling, and rate capability, of the advanced cell compared to baseline test cell.
- Demonstrate by calculation at least 25% lower cost per unit energy at the cell level for

comparative integrated advanced materials cell to a baseline materials cell.

### Accomplishments

- Downselected high energy core shell cathode and Si alloy anode materials for 18650 performance optimization.
- Demonstrated material scale up to multi kg levels.
- Optimized pilot process parameters to improve process robustness.
- Demonstrated advanced materials stability large scale dispersion preparation, electrode coating and 18650 assembly with advanced materials.
- Demonstrated >40% energy increase, with intermediate design (C/S||Si) in 18650 cells over baseline (NMC || Graphite).
- Improved cycle life using electrolyte formulations including novel high voltage (>4.5V) additives.
- Sampled 18650 format cells to ANL for testing; 18 cells with baseline materials and 6 cells with intermediate materials.



### Introduction

In order to design a lithium-ion cell with a stepfunction increase in energy, it is necessary to start from scratch with new well designed and matched active materials. First, the cathode needs to have a Cathode Energy Factor (CEF) beyond the traditional LCO and NMC materials. This invariably requires charging to higher cell voltage. Second, the cathode irreversible capacity has to "match" the irreversible capacity of the composite alloy anode. In fact, for cell balance and control of the lower cut off cell voltage, it is convenient if the irreversible capacity of the composite cathode is slightly larger than that of the anode. For the Active alloy it is critical to have the proper morphology (amorphous active phase), the proper particle size (microns), and the proper activity leading to a volume expansion of 110 to 120% upon lithiation. Next, the composite electrode has to be formulated with graphite for highest density and best inter particle contact, while still providing the required volumetric energy when fully lithiated. Finally, the electrolyte and separator must be stable against the two active composite

electrodes, across the complete cell voltage range, to eliminate any parasitic reactions.

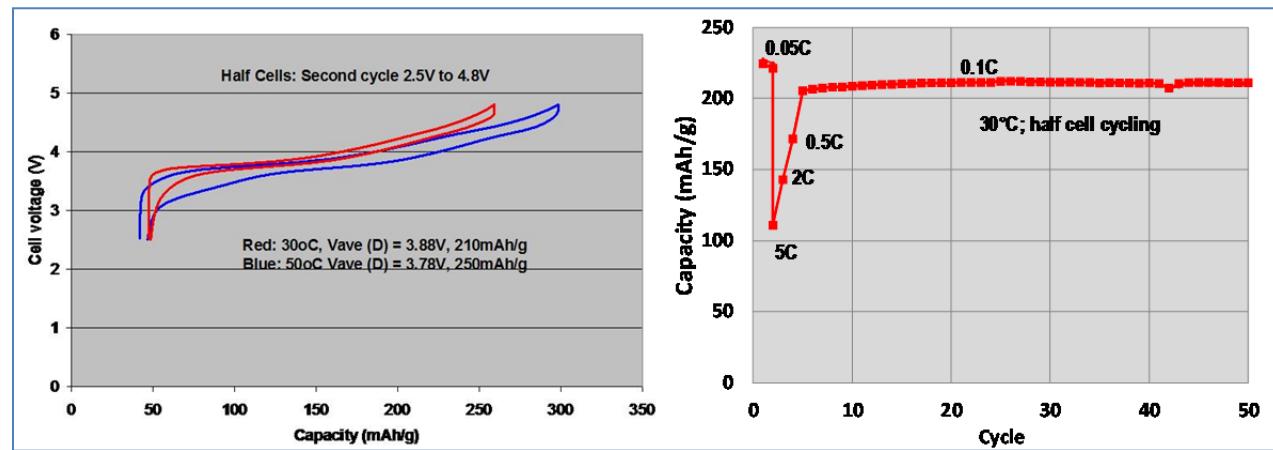
## Approach

The 3M team has been leveraging its expertise in R&D of lithium-ion batteries to develop a high energy cell using synergistically matched anode and cathode electrodes. To achieve the goal, a three phase approach has been taken. The phases are:

- Phase 1 - Verify baseline materials performance, and select advanced cell material candidates for further evaluation and optimization.
- Phase II - Integrate individual optimized materials into full cells and optimization of EV test cell.

**Table III - 13: Cathode Energy Factor comparison of different cathodes when matched to graphite or a Si composite**

	Oxide	Capacity X	Density X	Voltage X	Irrev Factor	=	Cathode Energy Factor
Electronics	LCO	0.179	3.75	3.99	0.95		2.54 (graphite)
	LCO	0.179	3.75	3.99	0.88		2.36 (alloy)
	NCA	0.196	3.5	3.78	0.97		2.51 (graphite)
Automotive	NMC	0.160	3.3	3.90	0.98		2.01 (graphite)
	NMC	0.160	3.3	3.90	0.95		1.96 (alloy)
Core-Shell	126M	0.230	3.4	3.84	0.95		2.85 (alloy)
	126T	0.220	3.4	3.88	1.00		2.90 (alloy)



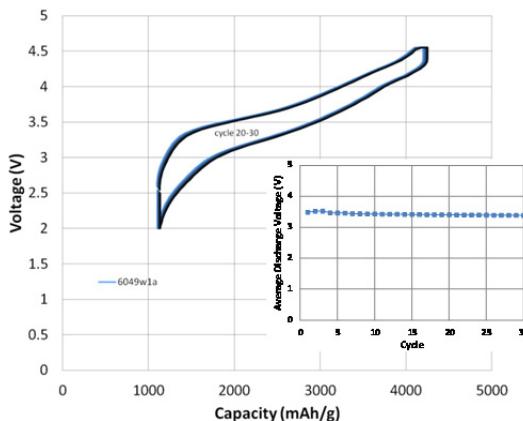
**Figure III - 61: Material Validation in coin cells vs. Li**

The material shows a stable voltage profile and less average discharge voltage fade during cycle life testing than the oxygen loss cathode materials. Figure III - 62 shows the data.

- Phase III – Perform final optimization of integrated advanced materials in EV test cells, complete cell evaluation, fabrication of final cells and submission of final cells to National Labs.

## Results

**Cathode Material Development.** The team has successfully developed a core shell (C/S) based high energy cathode material. Table III - 13 compares the two developed cathode material with baseline NMC material. 126T shows >35% CEF increase over the baseline. The capacity of the core shell cathode along with its flat cycling performance is shown in Figure III - 61.

Figure III - 62: Stable voltage curve than pure O<sub>2</sub> loss cathode

**Anode Material Development.** The team successfully developed a new Si anode composition,

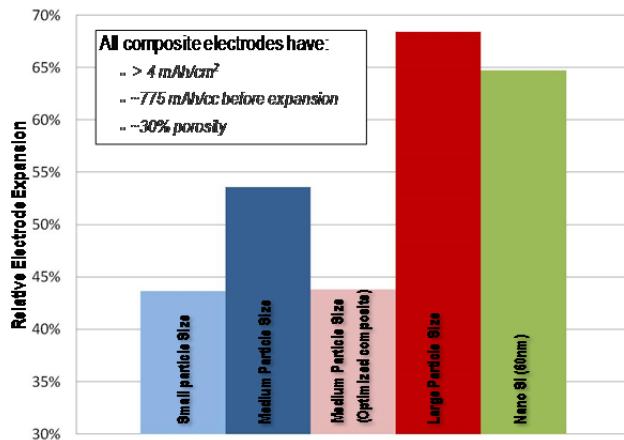


Figure III - 63: Si composite electrode expansion vs. particle size

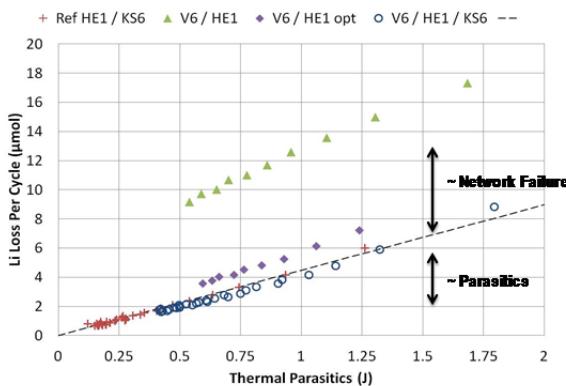


Figure III - 64: Calorimetry to characterize electrical network failure mechanisms

**Electrolyte Development.** A new electrolyte with significant improvement in cycle life of NMC||Si cell design was discovered (see Figure III - 65).

studied parameters for process optimization and scaled up material production. L20772 was down selected and is being tested for performance optimization. Key parameters to improve the performance of Si anode composite were also studied. One of key findings was the effect of particle size on the electrode expansion, as shown in Figure III - 63. Small particle (micron level) size and optimum electrode composite formulation are key for lower electrode expansion, at same mAh/cc. Nano Si electrode composite shows significantly high expansion compared to small particle size.

High precision measurements using *in situ* isothermal calorimetry were also performed on Si composite electrodes. Figure III - 64 shows the significance of flake graphite to overcome electrical network failure.

**Cell Development.** The advantage of the core shell cathode and Si anode is shown in Figure III - 66. The matched irreversible capacity helps to prevent the anode from going to a high potential during the bottom of full cell discharge.

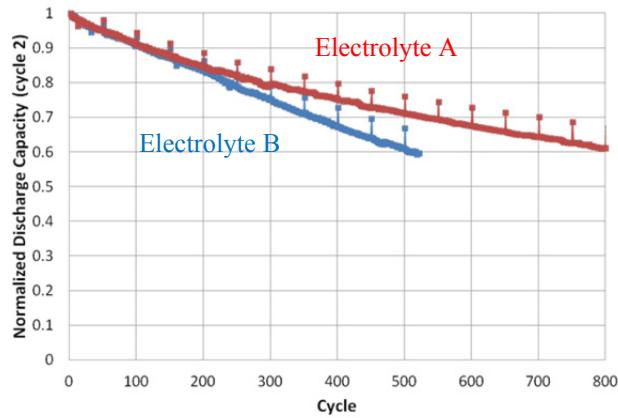


Figure III - 65: 18650 cell data comparing electrolyte A to B

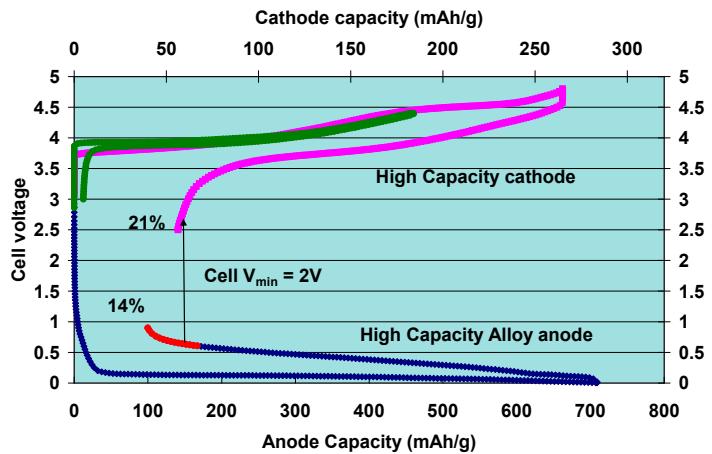
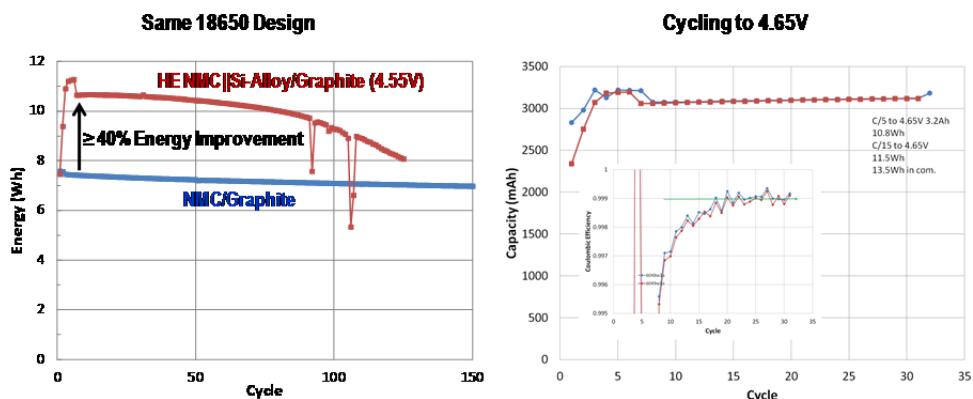
Figure III - 66: Matching 1<sup>st</sup> cycle efficiencies maximizes benefit of both materials

Figure III - 67: Energy increase and cycle life of C/S||Si design

Activities such as large scale dispersion, roll to roll electrode coating and drying were done to validate the energy improvement and characterize cycle life. 18650

format cells (C/S||Si) showed >40% energy increase over the NMC||Graphite cells (Figure III - 67).

However the cells start to fade after 100 cycles.  
Optimization of cycle life is in progress.

### Conclusions and Future Directions

The anode and cathode materials were down selected for future cycle life optimization. The team successfully demonstrated capability to scale up and make multi kg levels of these materials. Multiple roll to roll electrode coating and 18650 format cells were assembled. Over 40% improvement in energy was shown over the baseline design. The baseline data package was completed and 18650 cells with baseline and intermediate materials were shipped to ANL for energy validation.

Going forward, the team will focus on next level of scale up and optimize the performance of C/S||Si design in 18650 cell format.

### FY 2013 Publications/Presentations

1. 2013 DOE Annual Peer Review Meeting Presentation
2. 2013 Progress review at 3M

## III.B.5 Solid Polymer Batteries for Electric Drive Vehicles (SEEO)

### Bruce Mixer, NETL Project Manager

Grant Recipient: Seeo, Inc.

### Hany Eitouni

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Start Date: October 2011

Projected End Date: September 2014

### Objectives

- Develop, build, and test high-voltage solid polymer electrolyte cells with an energy density  $\geq 500$  Wh/l that meet USABC performance, lifetime and safety standards.
- Develop a robust commercialization plan that evaluates key risks associated with high-volume manufacturing and estimates cell production costs.

### Technical Barriers

This project addresses the following technical barriers:

- Cycling of Li metal anodes.
- Electrolyte stability at  $>4$ V cathode potentials.
- Mechanical performance of high-voltage cathode materials within solid polymer architecture.
- Interfacial performance of layered polymer electrolyte system.

### Technical Targets

- Evaluation of high-voltage cathode materials within polymer electrolyte system, including electrochemical stability and mechanical properties.
- Development of polymer materials stable to potentials of high voltage cathode materials.
- Scalable, repeatable synthetic method for polymers
- Robust, prismatic pouch cell design.
- Test and evaluation to USABC performance and abuse tolerance requirements.

### Accomplishments

In 2013, the project focused on:

- Development of polymeric materials to achieve target voltage stability, conductivity and mechanical properties, including evaluation of conductive salts for high-voltage stability in solid-state cells.
- Investigation of coating techniques to stabilize high-voltage cathode materials.
- Development and analysis of treated Li foil anodes using commercially-scalable production processes.



### Introduction

Achieving DOE performance targets for high energy cells requires new materials and approaches to electrochemical energy storage devices. Seeo proposes to meet these targets using high-capacity Li anodes and high-voltage cathode materials contained within a solid polymer electrolyte system which, in turn, enhances the lifetime, efficiency and safety of vehicle batteries.

### Approach

The project will be executed in three consecutive phases:

Phase I: Baseline Evaluation and Material Synthesis – Deliver 2Ah baseline cells to establish stability and performance of solid polymer electrolyte cells and perform initial synthesis and characterization of high-voltage materials

Phase II: Material Formulation and Scale-Up – Iterate on design of high-voltage materials, cycle laboratory-scale cells to isolate polymer-cathode couples and deliver interim design cells for technical review

Phase III: Cell Fabrication and Testing – Monitor stability and performance of large-area cells, execute internal performance and abuse tests and deliver final design cells for independent verification

### Results

High-voltage stable polymer materials and conductive salts demonstrated the requisite

electrochemical stability; improving conductivity and demonstrating long-term stability over cycle testing will be a focus of Phase III.

Treated Li foil samples provided by Seeo's project partner Hydro-Québec demonstrated a similar order of low impedance as that of the best performing commercial supplier tested. Replicating/improving this using thinner foils on the same production process is an ongoing activity; foils will be used as the anode for the project's final deliverable cells.

### Conclusions and Future Directions

In Phase I, Seeo's baseline cells established the stability of Seeo's solid polymer electrolyte system with high capacity Li anodes at a performance suitable for electric drive applications. In Phase II, Seeo focused on improving this baseline performance through incorporation of high-energy active materials and compatible solid electrolyte systems comprised of novel polymeric materials and conductive salts. In addition, Seeo investigated alternate techniques to stabilize high-voltage materials within a solid-state cell architecture. In Phase III, Seeo will isolate the most promising approach and deliver high-energy cells for testing to USABC protocol.

It is challenging to achieve high energy densities alongside safety and long-term reliability using conventional, Li-ion cells that utilize liquid electrolytes. Seeo's novel approach incorporates the inherent safety, speed of manufacturing and robust supply chain associated with solid polymer materials, thus offering a distinct opportunity to breakthrough traditional cost barriers associated with electric drive vehicle batteries.

### FY 2013 Publications/Presentation

None.

## III.B.6 Development of High-Energy Lithium Sulfur Cells (PSU)

### Christopher Johnson, DOE Program Manager

Subcontractor: Pennsylvania State University

### Donghai Wang, Program Manager

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#### Subcontractors:

EC Power, Subcontractor: Johnson Controls,  
Argonne National Lab

Start Date: September 30, 2011

Projected End Date: January 15, 2015

### Objectives

- Develop a novel nanocomposite sulfur cathode for lithium-sulfur batteries with high energy density, efficiency, and cycle life.
- Develop a novel Li-rich composite anode for Li-S batteries to improve cell cycle life.
- Develop novel electrolyte and electrolyte additives for Li-S batteries to improve cell efficiency, stability, and safety.
- Design, fabricate, test, and optimize the design of Li-S batteries using the above new technologies to maximize energy, power, abuse tolerance, and other favorable traits.
- Perform thermal testing of the developed Li-S cells and materials.

### Technical Barriers

- Polysulfide dissolution and shuttling, combined with degradation of the lithium metal anode and formation of an unstable SEI layer, can severely limit cell lifespan.
- High sulfur loading in the cathode is required for achieving a high energy density; however, high loading often leads to parts of the electrode becoming inaccessible to electrolyte, thereby decreasing energy density and cycle life.
- Cathodes must have high active material loading – however, the low density of sulfur and common composite materials (porous carbon, etc) make thin, crack-free, high-loading electrodes difficult to achieve.

- Electrolyte modifications that decrease polysulfide solubility or improve SEI layer stability often come at the cost of increased impedance and other issues.

### Technical Targets

- Scale up active material production to the 1 kg level.
- Design pouch cells with energy density > 400 Wh/l, 80% capacity retention after 200 cycles at C/2.
- Nail penetration testing at USABC EUCAR Level 3.

### Accomplishments

- Scaled up production of PSU-3 cathode material to the 0.5 kg level.
- Optimized coating techniques for high-loading, double-sided electrodes.
- Characterized and tested several new electrolytes for high-loading sulfur cathodes, along with additives for those electrolytes, enabling lower stable cycling, high capacity, high efficiency, and decreased self-discharge.
- Thoroughly characterized and optimized different Li powder based anodes.
- Optimized and tested design parameters for Li-S pouch cells.
- Fabricated and tested pouch cells with PSU-3 cathodes, Li foil and Li powder based anodes, different electrolytes, demonstrating above-design-capacity performance with LiP anodes, and identified possible failure mechanisms.



### Introduction

DOE goals require the development of a high-energy, high-power, high-efficiency, long-lasting, low-cost, and safe battery. This project aims to meet these goals by using the extremely promising lithium-sulfur battery chemistry. The S cathode has a theoretical capacity of 1,672 mAh/g with a nominal voltage of 2V. In addition, sulfur does not experience any significant size change during lithium insertion/extraction, making it very stable in principle.

The price of lithium-sulfur's great promise is the major challenges with which it is replete. Lithium

polysulfides – intermediate charge/discharge states of the cathode – are highly soluble in traditional electrolytes and can move throughout the battery, experiencing redox reactions and thus causing poor efficiency and loss of active material. Additionally, the lithium metal commonly used as the anode is vulnerable to mossy lithium and dendrite growth and cannot generally form a stable SEI layer, causing further capacity loss and safety concerns. These, combined with optimization and thermal safety considerations, necessitate a significant body of work to bring the Li-S to the commercialization stage.

## Approach

To design a superior lithium-sulfur battery, we will focus on several aspects of cathode, anode, electrolyte, and whole-cell study and design. On the cathode side, we aim to increase the sulfur loading, optimize the carbon framework's geometry and ability to adsorb lithium polysulfides, and enhance its practical usability and each-of-production. On the anode side, our work focuses on designing and optimizing lithium powder- and silicon-based composite anodes and determining the mechanisms behind their function. Electrolyte-wise, we are working to design new systems that improve SEI stability, decrease active material loss, increase active material utilization, and ensure battery safety. Additionally, we also seek to optimize battery fabrication parameters, ensure compatibility between all battery elements, and characterize the thermal safety and abuse tolerance of our Li-S system.

## Results

**Cathode.** PSU-3 cathode material production has been scaled up to the 0.5 kg level, thanks to the development of a specially-designed large-capacity reactor system, with 100 g of materials shown in Figure III - 68 for scale. This has created a constant flow of material for use in full cell testing and pouch cell development. Material properties have been standardized and performance is consistent from batch to batch. Scale-up of PSU-4 and PSU-6 high-rate, high-loading cathode materials is still being investigated for the final phase of the project. PSU-3 cathode fabrication has also been optimized so as to allow for making high-loading, double-sided electrodes, thereby increasing cell level energy density by decreasing the mass of the current collector in the cell.

In addition, rate and cycling performance of the PSU-3 and PSU-4 cathode materials have been investigated. PSU-3 cathodes with an active material loading of  $5 \text{ mg S/cm}^2$  can maintain a capacity of over 500 mAh/g even at 1C rate, and cycling performance

was also tested and found to be excellent within 50 cycles. PSU-4 cathodes showed a stable capacity of over 700 mAh/g at a C/3 rate.

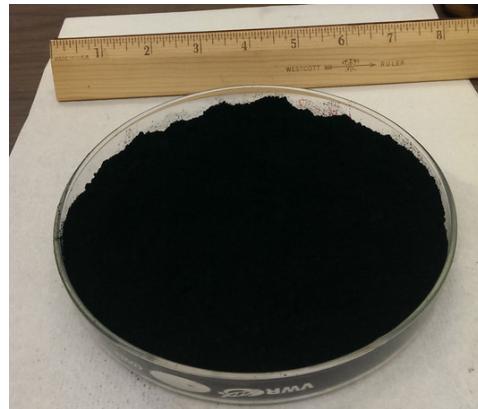


Figure III - 68: 100 g of PSU-3 sulfur cathode material, synthesized via a new large-scale reactor approach

**Anode.** Lithium powder/graphite (LiG) anodes have been tested in both full and half cells with various electrolytes. It was found that these anodes provided excellent half-cell stability (little capacity loss for 200 cycles at 0.5C rate) and a true capacity of over 1,000 mAh/g of electrode. However, full cell tests showed only modest performance (up to 400 mAh/g S, depending on choice of electrolyte).

Another novel lithium-powder-based anode material, dubbed LiP, was also tested and showed much stronger full-cell performance. Coin cell full-cell tests showed capacities of around 600 mAh/g S after 100 cycles. The N/P ratio and pressing of these anodes were also studied. It was found that pressed electrodes had superior performance to unpressed electrodes, possibly because excess porosity in the unpressed electrodes enabling easier polysulfide diffusion and a stronger shuttle effect. In addition, scanning electron microscopy (SEM) imaging of LiP anodes after cycling shows that they maintain their overall structure better than lithium foil anodes, which is good for long term cell stability.

**Electrolyte.** Several electrolyte systems have been tested this past year. Both PSU-E-1 and ANL-E-3 electrolytes showed promising performance, allowing for high-capacity stable cycling of sulfur cathodes. However, cells with PSU-E-1 electrolyte and high-loading cathodes were found to be quite sensitive to minor temperature fluctuations, while ANL-E-3 electrolyte was found to not perform well with high sulfur contents.

To overcome these limitations, new electrolytes were developed. The new PSU-E-5 electrolyte was aimed specifically at high-sulfur-loading cathodes. This electrolyte was found to allow for stable cycling of cathodes with  $\sim 5 \text{ mg S/cm}^2$  with a capacity of around

1000 mAh/g, as shown in Figure III - 69a. Its low viscosity also leads to low cell polarization.

ANL-E-4 fluorinated ether based electrolyte was shown to give high initial capacity and a decreased polysulfide shuttle effect. Several additives for this electrolyte were tested. Addition of 0.2M LiBr was found to help stabilize the capacity of cells with PSU-3 sulfur cathodes, Li foil anodes, and the new fluorinated electrolyte at around 800 mAh/g for 50 cycles, but did not improve the efficiency above ~95%; this is shown in Figure III - 69b. With an eye toward better utilizing Li<sub>2</sub>S formed at the end of the discharge process, anion

receptors – organic molecules which can form a strong coordination bond between the S<sub>2</sub><sup>-</sup> anion and the electron deficient atom such as B and Al – were also tested as electrolyte additives. Triethyl borate was found to increase coulombic efficiency, albeit with relatively low capacity retention. Finally, LiNO<sub>3</sub> was also tested in combination with the fluorinated electrolyte and was found to significantly improve efficiency, but not capacity retention, as it is not believed to prevent polysulfide dissolution.

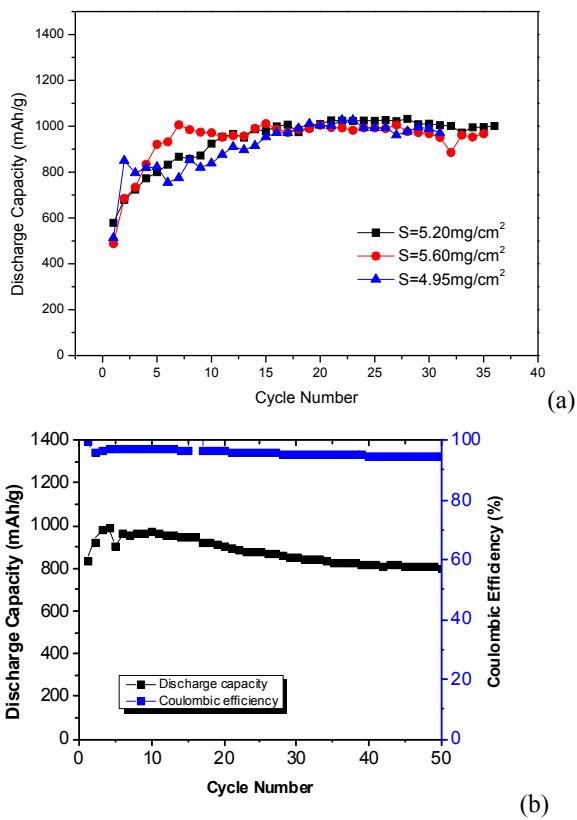


Figure III - 69: Cycling of cells with PSU-3 cathodes and a) PSU-E-5 electrolyte or b) ANL-E-4 fluorinated ether electrolyte with 0.2M LiBr

Several tests were also conducted to better understand the mechanism by which LiNO<sub>3</sub> improves battery performance. By testing cells with varying electrolytes having LiNO<sub>3</sub> concentrations, it was determined that LiNO<sub>3</sub> is used up during cycling and thus cannot provide long-term efficiency improvement, and furthermore, that it cannot prevent long-term loss of capacity. It was also found, by moving Li anodes from cells cycled in LiNO<sub>3</sub>-containing electrolyte to cells with LiNO<sub>3</sub>-free electrolyte, that LiNO<sub>3</sub> does not appear to form a very stable protective layer on the anode.

**Pouch Cell.** Initially, pouch cell designs were planned and optimized, particularly with regard to the

N/P ratio of cells. It was found that in order to achieve a cell-level capacity of 200 Wh/kg, the specific capacity must be 800 mAh/g S with an N/P ratio of 5.2, or over 900 mAh/g S with an N/P ratio of 2.0. This and other design factors were taken into account during pouch cell design.

Numerous pouch cells were fabricated and tested. Cells with Li foil anodes, PSU-3 cathodes, and baseline electrolyte with 0.4M LiNO<sub>3</sub> proved to have poor capacity, stability, and efficiency. Cells with 0.34 Ah designed capacities showed only a 0.2 Ah after 50 cycles, with an efficiency of only 40% by that point. Cells with 1.5 Ah designed capacity had at most a 1.19

Ah discharge capacity after 5 cycles, dropping to 0.95 Ah after 16 cycles, corresponding to an energy density of just 110 Wh/kg. In contrast, cells with LiP anodes and the same cathode and electrolyte showed more promising performance. The 0.34 Ah designed capacity pouch cell maintained a capacity of 0.32 Ah after 36 cycles, although efficiency was relatively low. 1.5 Ah design capacity pouch cells showed a discharge capacity of ~1.7 Ah – higher than the designed capacity – after 5 cycles, although the capacity decreased to ~1.2–1.3 Ah after 12 cycles. This fading and relatively low efficiency may be due to consumption of LiNO<sub>3</sub> in the cells. Performance of example cells with Li foil and LiP anodes is shown in Figure III - 70.

## Conclusions and Future Directions

Moving into the next year of this project, continued work will focus most heavily on pouch cell development and optimization. Further work on improving reliability and compatibility of the newest electrolytes and scaling up high-performance material production will continue, as will their testing in pouch cells. In addition, we will proceed to work on 4 Ah pouch cells and continue to optimize design parameters such as N/P ratio and electrode pressing. Concurrently, material development will continue in an effort to further improve cell performance. Safety evaluations, such as nail penetration and oven tests, will also be conducted.

## FY 2013 Publications/Presentations

### Journal Publications

1. Xu, T., Song, J. X., Gordin, M. L., Sohn, H. S., Yu, Z. X., Chen, S. R., Wang, D. H. Mesoporous Carbon-Carbon Nanotube-Sulfur Composite Microspheres for High-Areal-Capacity Lithium-Sulfur Battery Cathodes, *ACS Applied Materials & Interface*, **2013**, DOI: 10.1021/am4035784.
2. Song, J. X., Xu, T., Gordin, M. L., Zhu, P. Y., Lv, D. P., Jiang, Y-B, Chen, Y. S., Duan Y. H., Wang, D. H. Nitrogen-Doped Mesoporous Carbon Promoted Chemical Adsorption of Sulfur and Fabrication of High-Areal-Capacity Sulfur Cathode with Exceptional Cycling Stability for Lithium-Sulfur Batteries, *Advanced Functional Materials*, **2013**, DOI: 10.1002/adfm.20130263.
3. Chen, S. R., Dai F., Gordin, M. L., Wang, D. H. Exceptional electrochemical performance of rechargeable Li-S batteries with polysulfide-containing electrolyte, *RSC Advances* **2013**, 3, 3540.

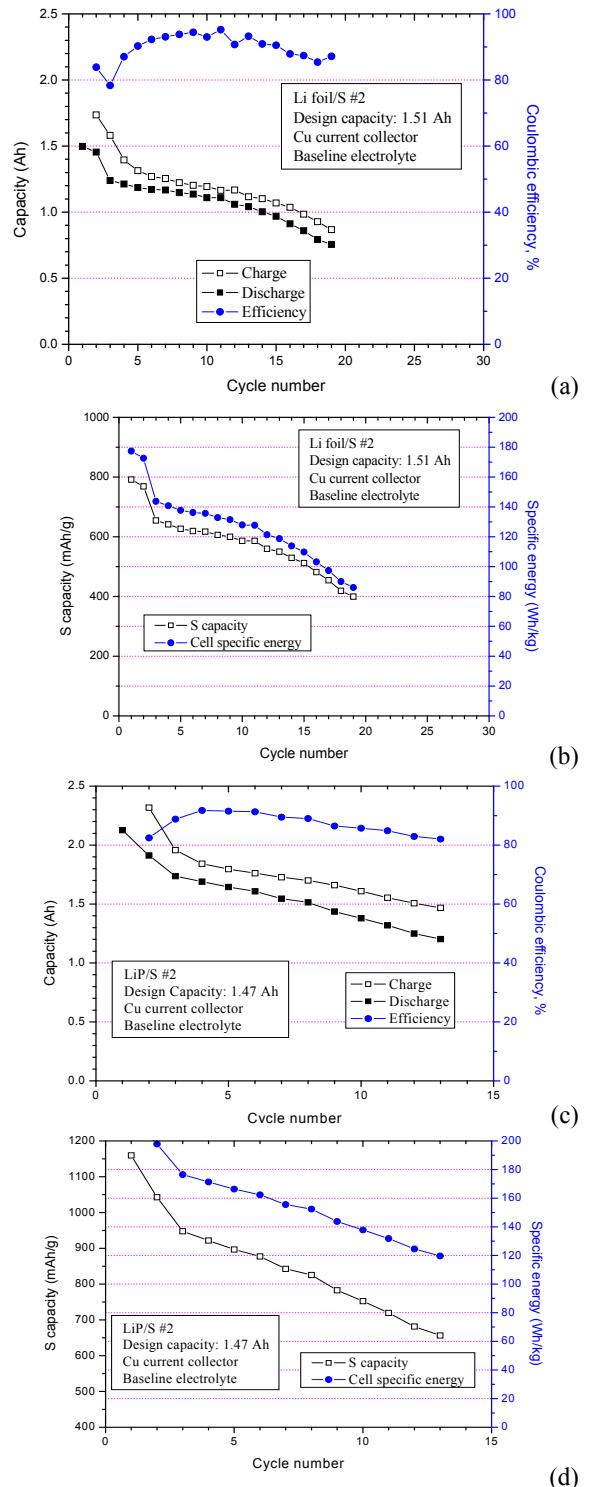


Figure III - 70: Cycling performance, efficiency, sulfur-specific capacity, and energy density of 1.5 Ah design capacity pouch cells with a) Li foil and b) LiP anodes, using PSU-3 cathodes and 1M LiTFSI and 0.4M LiNO<sub>3</sub> in DOL/DME (1:1, v/v) electrolyte

**Presentation**

1. 2013 DOE Annual Peer Review Meeting Presentation.
2. Wang, D. H. Development of Lithium-Sulfur Batteries, In Beyond Li-ion Symposium VI, Boulder, Colorado, June 2013.
3. Chen, S. Performance Booster: A Different Role of Polysulfide in Rechargeable Lithium-Sulfur Batteries, In the 224<sup>th</sup> ECS Meeting, San Francisco, CA, October 2013.

## III.B.7 Stand Alone Battery Thermal Management System (DENSO)

**Christopher Johnson, NREL Program Manager**

Subcontractor: DENSO International America, Inc.

**Brad Brodie, Project Manager**

DENSO International America, Inc.

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Start Date: October 2011

Projected End Date: September 2014

### Objective

Reduce the vehicle battery pack size by 20% (or increase driving range by 30%) through an optimized battery thermal management system.

### Technical Barriers

**Cost** – This project's first priority is to develop a thermal system that would allow battery pack size reduction of 20%. This is possible because current battery packs are oversized to guarantee they have acceptable performance for the advertised life of the battery pack. One major reason for the oversize of the battery pack is from cell degradation due to exposure to high temperatures. This project will attempt to address the exposure to high temperatures, and thus enable size reduction of the battery pack.

**Performance** – It is also known in the industry that cell performance is reduced at low temperatures. This project will also attempt to improve battery pack performance by efficiently warming the batteries in cold ambient temperatures.

### Technical Targets

- Develop a simulation program that will duplicate the battery thermal behavior in the vehicle.
- Develop a detailed thermal system design based on the information from the simulation program.
- Produce a prototype thermal system and bench test to prove the system is able to achieve the goals of the project.

### Accomplishments

- Established set test conditions to which the battery pack will be evaluated.
- Basic cell characteristics have been identified and used for the simulation model.
- Developed a battery pack simulation model using AMESim software which can duplicate the conditions from vehicle testing.
- Developed initial thermal system models in AMESim software.
- Evaluated scenarios based on input from Chrysler. Includes a mix of ambient temperatures and driving profiles.
- Battery model from Phase I was combined with thermal system, BMS, and battery life calculations into one simulation model.



### Introduction

The objective of this project is to design a thermal system that will enable a PHEV/EV battery pack size reduction by 20%. The project is broken into three phases. Phase I will involve understanding the thermal requirements for the battery pack. A simulation program will be established to duplicate the battery thermal behavior in the vehicle. Phase II is the design of the thermal system, using the battery pack model created in Phase I, that can both cool and heat the battery pack to allow the size reduction and performance improvement. In Phase III, prototype thermal system is made based on the design in Phase II. Phase III also includes bench testing to prove the system is able to achieve the goals of the project.

### Approach

The intent of the program is to demonstrate that a thermal system could enable the reduction of the battery pack size through optimal thermal management. The key points are considering performance at cold temperatures and battery life when exposed to high temperatures.

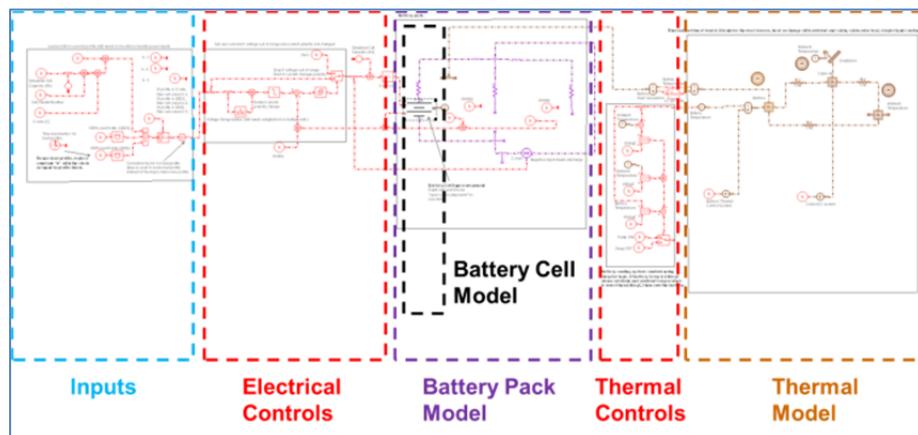
A battery pack model will be created in AMESim to simulate the battery pack. This will be done using equivalent circuit models (empirical), a physics-based model would be too complicated for the purpose of this

study. The type of Equivalent Circuit model is DC Resistance-Capacitor (RC).

After the battery model is created in Phase I, Phase II will involve incorporating the battery model with a thermal system model. This may not be easy because this needs to include a battery management system and influence of temperature from the vehicle cabin and the ambient to the battery pack. The conditions used for the evaluation are provided by Chrysler based on its experience with specifying the battery packs for electric vehicles. Each concept for the thermal system will be run, using the simulation program, through each driving and ambient temperature scenario. After that, the battery life will be determined using the NREL battery life model. Then, a comparison can be made between various thermal system concepts and the effect on battery life. If battery life is increased, the battery pack size can be reduced and still achieve the target life span for the battery packs.

## Results

Evaluation conditions were established among all members of the project, with strong input from Chrysler.



**Figure III - 71: Battery model using AMESim**

Using the battery model in Figure III - 71, one roadblock that was encountered was the time to run the simulation. There are about 25 scenarios that will be run on each thermal system technology to find the best option. However, simulation time was almost 80 hrs for just one scenario. After optimizing the simulation model for speed, and using a faster PC, the simulation time was reduced to 10 hrs. Further work will be done to further optimize the model and increase the speed.

## Conclusions and Future Directions

Because of the roadblock encountered with simulation speed, the project is delayed approximately

1.5 months. However, there is a recovery plan to get the project on schedule by the middle of 2014.

Because of the delay, there are currently no results to show how well the new system will reduce the battery pack compared to the base system. These works will occur in November and December of 2013. The final results of the simulations and thermal system performance should be ready to publish at the 2014 Annual Merit Review.

## III.C Low-Cost Processing Research

### III.C.1 Low-Cost Manufacturing Project (JCI)

#### Christopher Johnson, NREL Program Manager

Subcontractor: Johnson Controls, Inc.

#### YK Son, Principal Investigator

Johnson Controls, Inc.

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#### Subrecipients:

Maxwell Technologies, ENTEK Membranes

Start Date: October 2011

Projected End Date: January 2015

#### Objectives

- Research, develop and demonstrate the advanced Li-ion cell manufacturing processes and techniques such as non-N-methyl-2-pyrrolidone (NMP) electrode, direct coating separator, and fast formation to reduce the existing Li-ion manufacturing costs by 50%.
- Maintain or exceed existing battery performance and requirements.

#### Technical Barriers

- Dry processed electrode fabrication: A key challenge related to the preparation of solvent-free processed anode and cathode is achieving proper electrode thickness while producing desired active loading, porosity, pore size, and electrode structure. To overcome this challenge, new binders, powder mixing techniques, and new formulation are being developed to optimize active layer properties.
- Direct separator coating: There are multiple challenges for direct separator coating technology, such as producing a uniform microporous polymer film on the electrode surface and maintaining the rigidity of the microporous separator coating. Therefore, it requires investigating various polymers, solvents, inorganic materials including process conditions. Self discharge and calendar life

studies will be used to evaluate performance against these risks.

#### Technical Targets

- Develop dry processed cathode and anode electrodes to meet the existing wet coated electrode performance.
- Develop direct coated separator to meet the existing poly-olefin separator performance.
- Develop the fast formation process to meet the existing baseline formation process performance while improving cell uniformity and maintaining detectability.
- Develop a 15Ah Li-ion cell that integrates all three advanced technologies to meet a baseline NMC/Graphite cell performance, durability and safety.

#### Accomplishments

- Developed and proved out 15Ah NMC/Graphite baseline cell design with 155Wh/kg and 300Wh/l energy density.
- Developed lab scale pilot lines for dry electrode production and separator lamination for 3Ah integrated cell delivery.
- Developed 3Ah integrated cell design and process to incorporate dry processed electrodes and separator lamination technologies.
- Developed the activation process for fast formation.
- Developed interim cost model.



#### Introduction

Johnson Controls proposes to develop a portfolio of advanced manufacturing technologies to reduce the manufacturing cost of large format Li-ion cells by 50%. Three key technologies to be developed are: Non-NMP electrode, direct separator coating, and fast cell formation. The integration of these three advanced manufacturing technologies will achieve the targeted cost savings through the elimination of material, lower capital equipment expenses, and reduced energy and manufacturing costs.

## Approach

During the second phase of the program, we have developed and evaluated all targeted technologies – Non-NMP electrodes, direct coating separators – in coin cells and 3Ah pouch cells. The technologies that are under investigation for the 3 Ah pouch cell delivery are:

- Dry processed cathode, direct coated separator on dry processed anode.
- Aqueous cathode, direct coated separator on standard anode.

## Results

**Cell Development.** Johnson Controls has developed two designs for this project to serve as the baseline to support developing and evaluating new advanced technologies as shown in Table III - 14 and Figure III - 72.

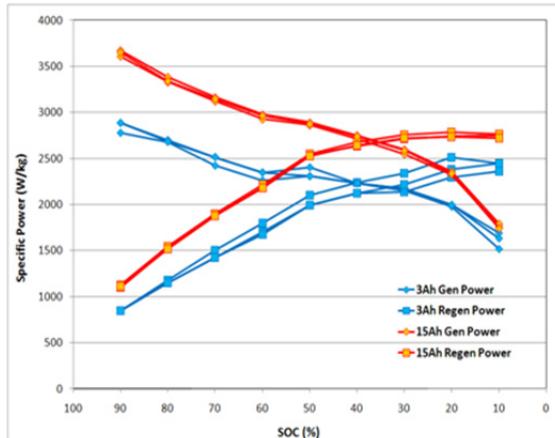
**Table III - 14: 3Ah / 15Ah baseline cell design**

Items		3Ah	15Ah	Reference
Chemistry	Cathode	NMC	NMC	* AG: Artificial Graphite ** PE: Poly Ethylene
	Anode	*AG	*AG	
	Separator	**PE	**PE	
Capacity (Ah)		3.18	15.3	@30°C  * Tested at 25°C
Energy Density	Specific (Wh/kg)	145	155	
	Volumetric (Wh/l)	251	300	
HPPC Power	Gen (W/kg)	2,307	*2,864	
	Regen (W/kg)	2,101	*2,541	
Cell Weight (g)		78	360	

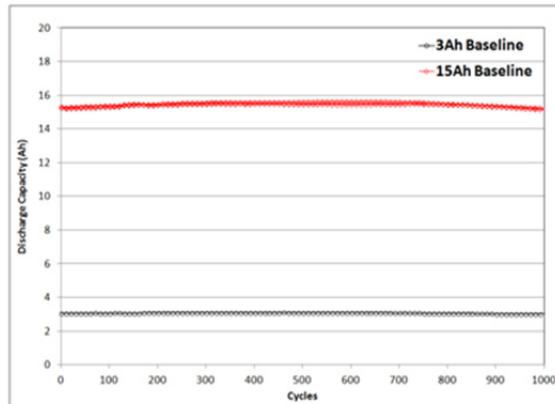


**Figure III - 72: 3Ah / 15Ah baseline cell**

The design of the baseline cells is intended for PHEV applications between high energy and high power performance. The test results are in line with the parameters of the design: The HPPC in Figure III - 73 shows a rate performance of 2,300W/kg for 3Ah cell, and 2,800W/kg for 15Ah cell, and it shows good capacity retention after 1,000 full cycles as shown in Figure III - 74.



**Figure III - 73: Baseline cell HPPC test: red: 15Ah baseline cell, blue: 3Ah baseline cell**

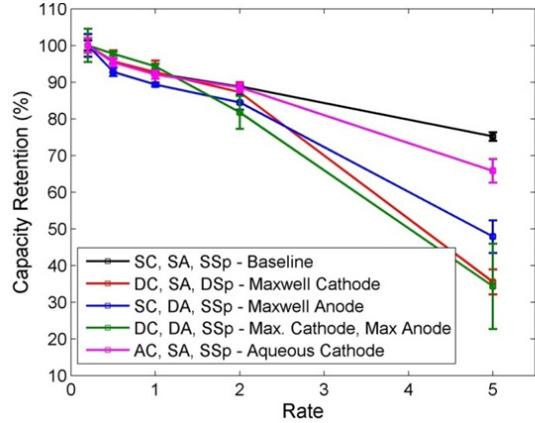


**Figure III - 74: Baseline cell full cycle life test: red: 15Ah baseline cell, blue: 3Ah baseline cell**

Overall, the baseline 3Ah and 15Ah cells have shown good and consistent results for most test items, and these will be used as the baseline data to compare the characteristics of the advanced technologies integrated cells.

**Dry Coated Electrodes.** Leveraging from previous experience in dry processed electrode production, critical mixing processes and binder candidates have been identified for the production of Li-ion battery anodes and cathodes. Overall, dry processed electrodes have improved significantly in both cycle life and power performance in 2013. However, their high current rate

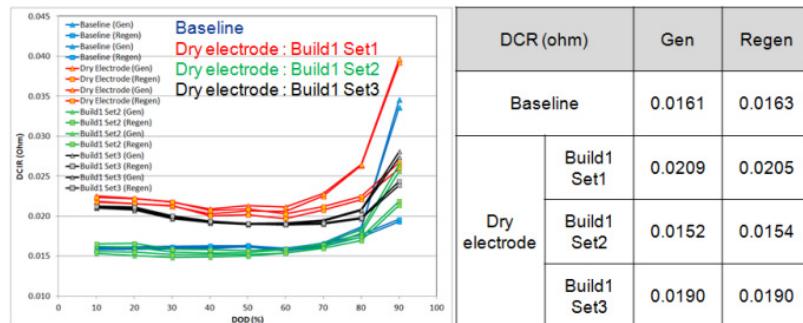
performance to 100% DOD is lower than that of baseline electrodes as shown in Figure III - 75.



**Figure III - 75: Non-NMP electrodes evaluation:**  
black: baseline, red: dry cathode electrode and baseline anode, blue: baseline cathode and dry anode electrode, green: dry cathode and dry anode, purple: aqueous cathode and baseline anode

We believe that the major contributors to the low performance of the dry processed electrodes are the higher loading weight and lower porosity, specifically smaller pore size diameter. Bound by program schedule and customized equipment limitation, we have optimized the current dry electrode designs to match that of the baseline cells under HPPC test protocol 3Ah dry electrode cells from Build 1 Set 2 electrode design produced a 15.2 mohm DC impedance using a 10 sec generation pulse. This performance is better than the baseline cells (16.1 mohm) as shown in Figure III - 76.

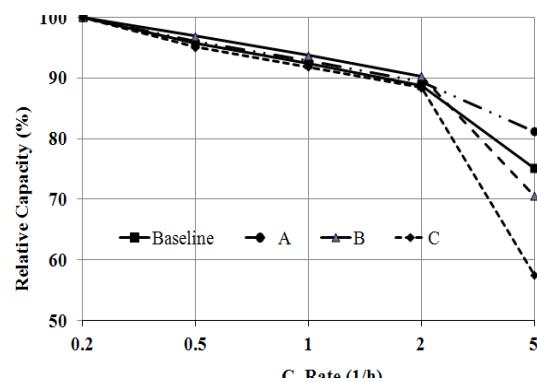
These results demonstrate the attractiveness of dry electrode process technology and its potential to match wet electrode coating technology once process and formulation optimization is achieved.



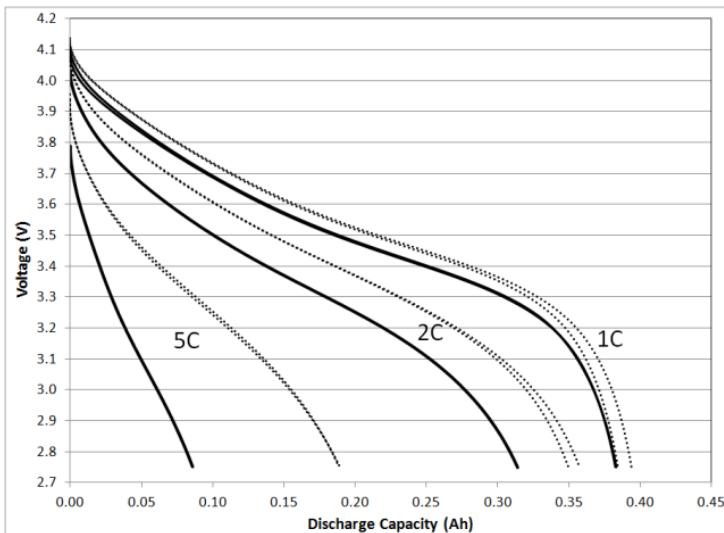
**Figure III - 76: HPPC test result:** blue: baseline, red: build 1 set 1 dry electrode, green: build 1 set 2 dry electrode, black: build 1 set 3 dry electrode

**Direct Coated Separator.** Three technologies (A, B, and C) were developed to incorporate the separator as a component of the electrodes. The implementation of the separator on the electrodes has positive implications on production speed and cost within the production process. The three technologies are currently investigated with lab scale electrodes. Technology A displayed better performance compared to baseline and other technologies as shown in Figure III - 77.

The results of technology A for integration have shown better performance at high current rate capability test as shown in Figure III - 78.



**Figure III - 77: Rate capability of separator technologies**



**Figure III - 78: Single layer pouch cell rate capability, solid line: dry electrodes with baseline separator, dotted line: dry electrodes with A technology**

Technology A is very promising. We are concentrating to reduce variations and to improve the self-discharge rate.

- Fast formation for integrated cells.
- 15Ah final integrated cell development and delivery.

## Conclusions and Future Directions

In summary, the team has evaluated the technologies in the area of non-NMP coating, direct coated separator, and fast formation and developed technology integrated cell design and processes. The 15Ah baseline cells performed according to expectations.

During the second phase of this program, the integration of these advanced manufacturing technologies was achieved for 3Ah cells. We have identified and are working to solve the technical barriers for performance and process improvement.

The key future directions are listed as following:

- 3Ah interim integrated cell development and delivery for evaluation.
- Final cost model including advanced technologies.
- Process development for pilot scale production of dry electrode and direct coated separator.
- Process development for integration.

## FY 2013 Publications/Presentations

1. Merit award poster presentation (5/13/2013)

## III.C.2 Ultraviolet Curable Binder Lithium Ion Battery Project (Miltec UV)

**John Tabacchi, NETL Manager**  
Contractor: Miltec UV International, LLC

Primary Contact:

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Start Date: October 1, 2011

Projected End Date: October 1, 2014



### Introduction

The objective of this project is to reduce lithium ion battery electrode manufacturing costs by 50% by replacing thermal drying of solvent-based binders with ultraviolet (UV) or electron beam (EB) curable binders. The project goal is to demonstrate that battery cells made from UV or EB cured electrode coatings perform equal to or greater than equivalent cells made from solvent based binders.

Previously identified UV and EB curable binders and associated curing technology will be shown to reduce the time required to cure electrode coatings from tens of minutes to less than one second. This revolutionary approach can result in dramatic increases in process speeds and significantly reduced capital costs (a factor of 10 to 20) and operating costs, reduced energy requirements and reduced environmental concerns and costs due to the virtual elimination of volatile organic solvents and associated solvent dryers and recovery systems. Multiple lithium ion battery cells will be fabricated using various approaches to UV and EB curing technology; performance of the cells will be evaluated; and analytical testing will be used to further improve the performance of the cells. Eventual cells made with UV/EB curable binders will be submitted to the DOE for independent testing and performance verification. Commercialization of UV/EB technology will lead to greater market penetration of HEVs, PHEVs and EVs as well as significantly reducing the environmental intrusion associated with the manufacturing processes.

### Progress and Current Status

During FY 2013, Miltec UV researchers formulated UV curable binders (patents pending) and used them to successfully make lithium ion battery anode and cathode coatings. These coatings have been applied at thicknesses up to 100 microns and successfully cured at speeds up to 200 feet per minute (FPM). Electrode coatings have been made which retained physical integrity after being immersed in pure electrolyte at elevated temperatures for extended periods. Coin cells have been made using UV curable binder anodes and cathodes and tested. The initial charge/discharge and first 50 cycles for two such coin cells are shown later in this section. The long term cycling performance of full cells made with a conventional anode and UV curable binder cathodes are shown below. Anodes have also been fabricated using UV curable binder and tested in half cells. The initial charge/discharge results for one such test is shown below. These efforts culminated in the delivery of 18 Interim cells made with UV curable binder anodes and cathodes with the goal of having performance equal to or greater than conventional cells.

A slot die coater and reel to reel conveyor have been installed on a Miltec UV multiple lamp UV curing system. The system is capable of accommodating a 10" current collector foil and an 8" coating width and is capable of coating and curing at speeds up to 200 fpm.

**Interim Cell Evaluation and Test.** The major part of the efforts during FY2013 has focused on research and development to improve and verify the adhesion, chemical stability, and other qualities of selected UV and EB curable binders leading to the delivery of 18 Interim cells for independent evaluation. These efforts are described below.

Figure III - 79 shows the initial charge discharge performance for a baseline cell. Figure III - 80 shows the initial charge/discharge performance of a half cell made with a cathode using UV curable binder and Figure III - 81 the cycling performance to 50 cycles. The active material is NMC and the coating is 87% NMC, 5% Carbon, 8% Binder (by weight); cured at 100 FPM; and 50 microns coating thickness. Full cells using these same UV curable binder coatings have completed long term cycling and the results of one full coin cell are shown in Figure III - 82. The initial charge and discharge tests for a UV cured anode are shown in Figure III - 83.

The Interim cells are 500 mAh pouch cells prepared by ANL. The cells coatings were comprised of 87% active material, 5% carbon and 8% binder. Cell test plans which include the testing limits and specifications for the interim cell validation tests such as voltage and current limits, state of charge, charging, and temperature recommendations, number of test sequences, and other appropriate test conditions were delivered simultaneously with the 18 Interim cells. These tests are based upon full cell configuration using PHEV test procedure based on the USABC test profile

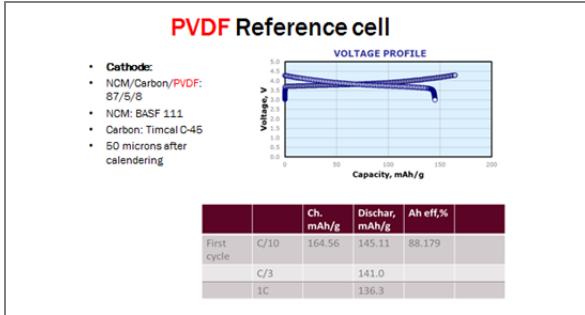


Figure III - 79: Reference cell

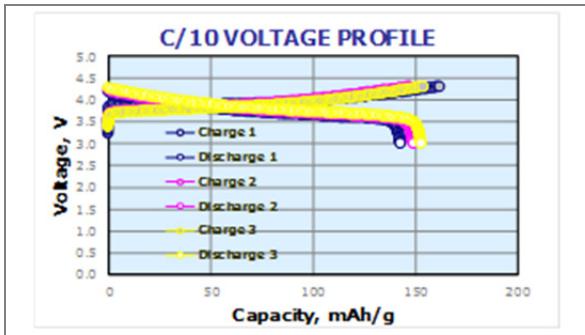


Figure III - 80: Initial charge and discharge

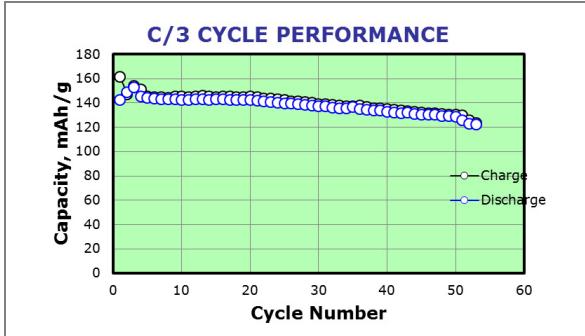


Figure III - 81: 50 cycle performance

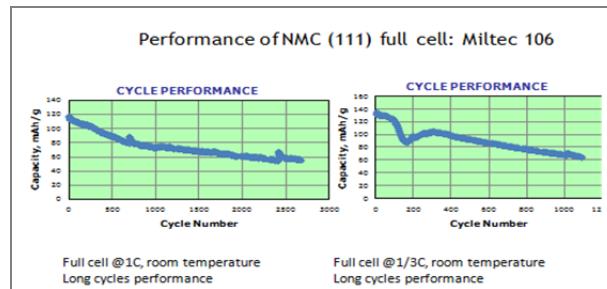


Figure III - 82: Full cell 1000+ cycle 1C and 1/3C data demonstrate UV cathode binder is durable and electrochemically stable

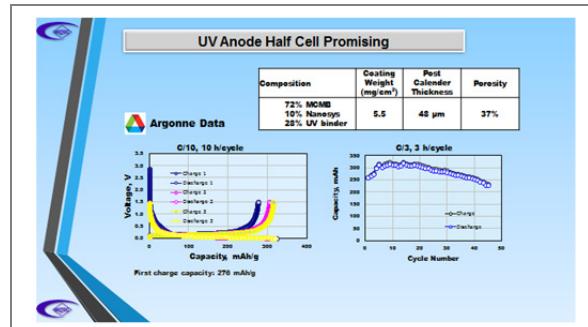


Figure III - 83: Half cell 1/3C data for anode with UV cured binder

### Planned Work for FY2014

During FY2014, research and development efforts will continue on the application of UV/EB cured binders in the fabrication of lithium ion battery anodes and cathodes. Optimum binder/anode and cathode material combinations will be subjected to testing in half coin cells, full coin cells, and full pouch cells during FY2014. Miltec UV will prepare and deliver 18 final design pouch cells to DOE for independent validation testing. The Miltec UV curing system and slot die coater will be operated and performance evaluated for both anode and cathode fabrication with a desired goal of demonstrating 150-200 feet per minute successful coating and UV curing of electrodes.

## III.C.3 High Capacity Alloy Anodes (Applied Materials)

### John Tabacchi, NREL Project Manager

Grant Recipient: Applied Materials, Inc.

### Sergey Lopatin, Project Director/Principal Investigator

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Phone: (408) 235-4742; Fax: (408) 235-6863  
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#### Subcontractors:

Lawrence Berkeley National Laboratory  
Oak Ridge National Laboratory  
FMC Lithium Division  
Navitas Systems  
Nissan Technical Center North America

Start Date: October 1, 2011

Projected End Date: September 30, 2014

### Objectives

- Develop and demonstrate the feasibility of depositing alloy anode materials at high deposition rates.
- Characterize, evaluate, and optimize the resulting electrodes using pouch cells and demonstrate the low cost potential of the new manufacturing methodology.

### Technical Barriers

Cycle life of alloy based anodes is one of the main issues that limit their viability. We are working closely with our partners (subcontractors) to understand the underlying issues leading to the low cycle life of these anodes and then make necessary process changes to meet requirements.

### Technical Targets

- Demonstrate high capacity Li-ion battery cell anodes that are capable of achieving an energy density of at least 500 Wh/l and a power density of at least 500 W/l.
- Demonstrate cycle life (300-1,000 cycles at 80% depth of discharge), calendar life (5-10 years), and durable cell construction and design capable of being affordably mass produced.

### Accomplishments

- Development of electro-deposition module which allows for 3D-porous structure formation in a single prototype tool for both 3D Cu collector and 3D CuSnFe alloy anode.
- Development of modular technological steps for forming 3-3.5 mAh/cm<sup>2</sup> cells including process methodology for Graphite coating by water soluble process to achieve adhesion to the 3D-porous structures. Testing rate performance in half-cell assembly vs. Li demonstrated capacity retention advantages up to 25-27% at 2C and 3C-rates.
- Testing baseline pouch cell assembly. Porous 3D electrodes were assembled in single layer pouch cells with  $\text{Li}_{1-x}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}]O_2$  (NMC) cathodes. The retention capacity for 3DCu/Graphite vs. NMC was measured 81.8% at 1310 cycles. Projection from these data is that the baseline cell is capable of over 1,400 cycles at capacity retention of 80% at C/3 rate.
- Eighteen cells comprised the program's 1st deliverable sent to Idaho National Laboratory (INL) for further evaluation.
- Development of 3DCuSnFe nano-structure alloy anode. Coulombic efficiency (CE) is improved by grain size reduction, pre-lithiation, and mitigation with combining alloy with Graphite.
- Extending 3D electrode concept to the high loading 3DCuSnFe/Graphite alloy electrodes and testing interim pouch cell. Capacity retention of 76.2% at 1280 cycles was demonstrated. These data show that the interim cell is capable of 985 cycles at 80% capacity retention at C/3 rate.



### Introduction

Applied Materials is working on a new class of Li battery anodes with high capacity based on an innovative micro-cell porous 3DCu-Li alloy structure. Micro-cell 3DCu-Li alloy architecture of controlled thickness forms continuous highly conductive Cu pathways for electrons through the full electrode. The technology holds great potential for electric vehicle lithium-ion batteries. The electrode structure also has a very large surface to volume ratio to contact with Li-ion

electrolyte. The porous 3DCu can accommodate the volumetric expansion during electrochemical cycling and contributes to long cycle life. The improved electrodes are assembled into prismatic battery cells and tested to demonstrate the feasibility of producing Li-ion batteries with the target energy density.

## Approach

Experimental development focused on initial electro-deposition module which allows for 3D-porous structure formation. Baseline processes have been developed for (a) 3DCu current collector and (b) for graphite coating using a water soluble process. Extending the baseline electrode concept to the high loading 3DCuSnFe/graphite alloy electrodes should allow a) low resistivity at the electrode/current collector interface, b) fast charge transfer at the electrode/electrolyte interface, and c) alloy expansion and contraction mitigated by reduced alloy grain size with Fe addition.

Modular technological steps were developed for forming 3-3.5 mAh/cm<sup>2</sup> cells (Figure III - 84).

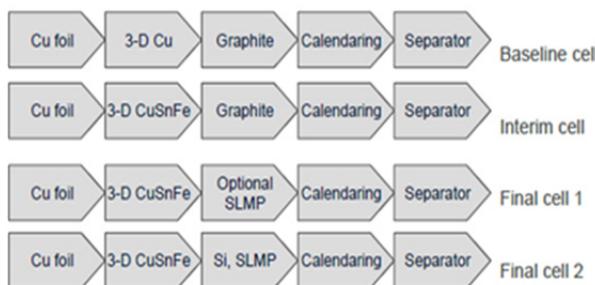


Figure III - 84: Schematic diagram of process flows for manufacturing baseline cells, interim cells and final cells with 3D current collector and alloy anodes

## Results

**3D Cu Current Collector Material.** Baseline processes have been developed for (a) 3DCu current collector and (b) for graphite coating using a water soluble process. Scanning Electron Microscopy (SEM) images of 3DCu/graphite structures showed crack-free coating. 3DCu/graphite baseline cell material was studied before and after calendaring. 3DCu remained unchanged with no mechanical damage as result of calendaring. Testing rate performance in half-cell assembly vs. Li demonstrated capacity retention advantages up to 25-27% at 2C and 3C-rates.

**Baseline Cell Testing.** 30-38 mAh single layer baseline full cells using 3DCu/graphite vs. NMC (Figure III - 85), have been assembled and shipped to INL for testing according to the USABC PHEV manual.



Figure III - 85: Single layer pouch cells (SLP) made with 3D structure electrode. Eighteen cells have been shipped to INL for testing

For the pre-tested cell, the capacity retention was 81.8% at 1310 cycles. Projection from these data is that the baseline cell is capable of over 1400 cycles at 80% capacity retention at C/3 rate (Figure III - 86).

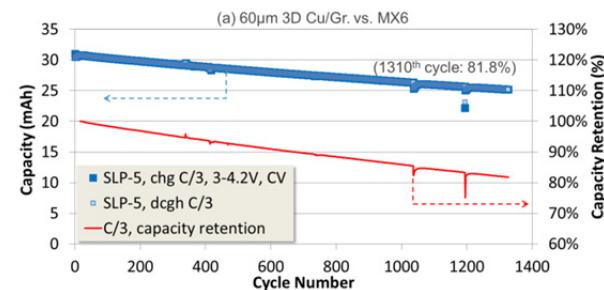
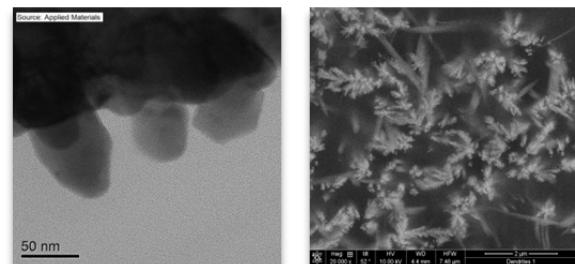


Figure III - 86: Cycling test results for baseline cell: 3DCu/Graphite vs. NMC. Projection for capacity retention over 80% is >1400 cycles

**3D CuSnFe Nano-Size Grain Material.** Electrochemical deposition has been developed for forming ~50 nm grains (Figure III - 87a) of alloy anode from Cu<sub>6</sub>Sn<sub>5</sub>(Fe). Connected nano-size grains form a conductive network of porous active material on Cu foil (Figure III - 87b).



a) ~50 nm grain size

b) conductive network  
Figure III - 87: a) TEM and b) high resolution SEM images of the 3DCuSnFe Material

Coulombic efficiency (CE) of the alloy electrodes has been improved (Figure III - 88) by following techniques: grain size reduction, pre-lithiation, and combining alloy with graphite. Dense and porous versions of CuSnFe alloy depositions with thickness between 25-50 microns were developed. These 3D CuSn(Fe) electrodes were fabricated by using electroplating from acidic solutions. The mass loading, chemical composition, porosity, and thickness were controlled to obtain  $\sim 1.5 \text{ mAh/cm}^2$ . These alloy electrodes were then coated with graphite to obtain 3-3.5  $\text{mAh/cm}^2$ . Samples were evaluated at ORNL, LBNL and Nissan TCNA in cell assemblies with different electrolytes (Figure III - 88). Improving CE was observed in electrolytes containing fluoroethylene carbonate (FEC) in the composition.

**Interim Cell Development.** Full cells including 3DCuSnFe/graphite vs. NMC have been assembled and tested. Modular technological steps were developed for forming 3-3.5  $\text{mAh/cm}^2$  cells including a methodology for graphite coating via a water soluble process to achieve adhesion to the 3DCuSnFe structures. Graphite was coated on 3D alloy of different loadings: 1, 1.5, 2 and 3  $\text{mAh/cm}^2$  for the 3DCuSnFe alloy. Assembly and testing of graphite coated 3D alloy electrodes showed results of 1280 cycles having high CE (Figure III - 89 and Figure III - 90). Capacity retention of 76.2% at 1280 cycles was demonstrated.

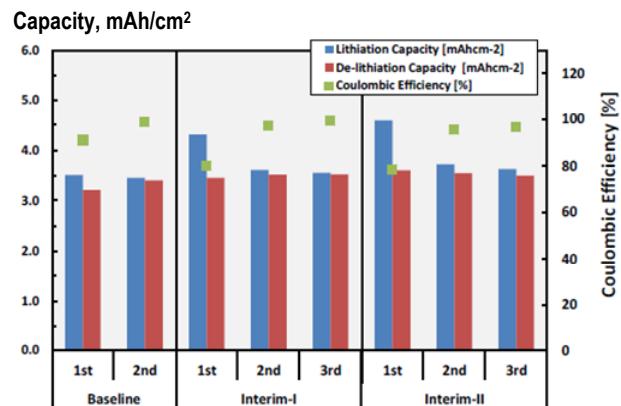


Figure III - 88: Half-cell capacity and CE vs. cycle number; for 3-3.5  $\text{mAh/cm}^2$  cells; baseline with 3DCu/graphite and interim I, interim II including the 3DCuSnFe/graphite material with 30% thickness reduction

Applied Materials and project partners continue to develop these cells in order to improve the cycling capability and energy density of the system. The second deliverable, eighteen interim cells, will be delivered to INL for further testing at the completion of formation protocol development including anode-cathode matching.

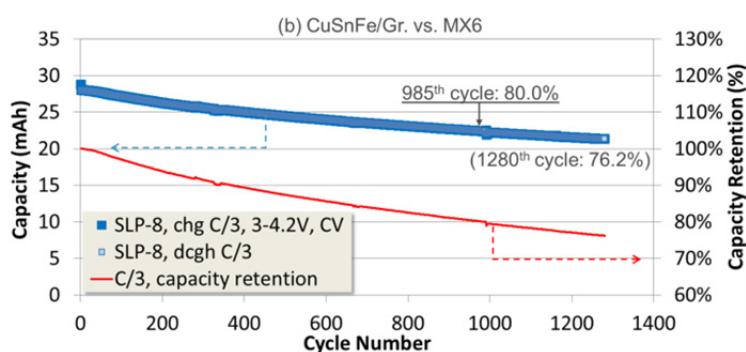
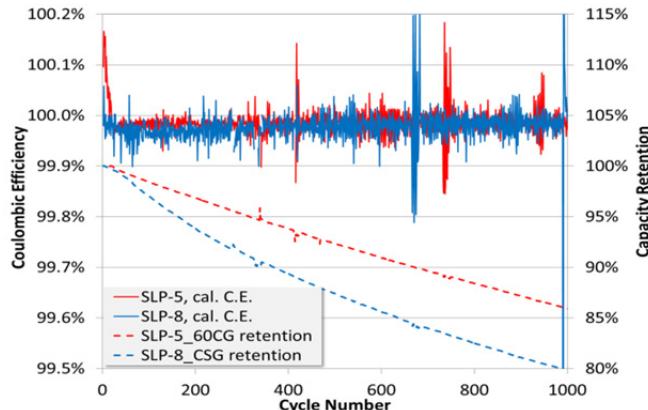


Figure III - 89: Cycling test results for interim cell: 3DCuSnFe/Graphite vs. NMC. Measured capacity retention over 80% is  $\sim 1000$  cycles



**Figure III - 90: Comparative analysis of CE and capacity retention of cycling test results for baseline and interim cells: SLP-5 3DCu/Graphite vs. NMC and SLP-8 3DCuSnFe/Graphite vs. NMC**

Experimental cells including coatings of 3DCuSnFe with Si were assembled and are being tested. Results will be included in the next technical progress report. The third deliverable, twenty four final cells, will be delivered after further cell optimization at the completion of the program.

Current results show that more optimizations for the cell formation protocol, ratio of alloy anode to graphite and for alloy pre-lithiation are necessary.

### FY 2013 Publications/Presentations

1. Presentation at the 2012 DOE Annual Peer Review Meeting, Arlington, VA.
2. Presentation at the 2013 Applied Materials Annual Engineering Technology (ET) Conference, Santa Clara, CA.

### Conclusions and Future Directions

Assembling and testing full prismatic cells with 3D current collectors resulted in CE over 99.96% at cycles 1000-1400. Projection from the data is that the baseline cell with 3DCu/graphite anode is capable of >1,400 cycles at capacity retention of 80% at C/3 rate, and that the interim cell with 3DCuSnFe/Graphite anode is capable of 985 cycles at the same conditions.

Development of 3DCuSnFe nano-structure alloy anode resulted in half-cell and full cell electrode thickness reduction. CE was improved by grain size reduction, pre-lithiation, and combining the alloy with graphite.

Equipment design concept and laboratory scale chamber prototype were developed. Plating module concept incorporated capability to form 3D structure on both sides of the Cu foil. The individual module designs as well as module integration concepts will be fine-tuned. This will allow Applied Materials and project partners to produce the interim and final sets of cell deliverables for the program. These cells will incorporate the most optimal alloy anode composition.

Applied Materials and project partners would like to continue development of the alloy anode to further improve the cycling performance. This development allows the benefits of the 3D CuSnFe alloy to be utilized in a higher energy density system.

## III.C.4 Innovative Manufacturing and Materials for Low Cost Lithium Ion Batteries (Optodot)

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Subcontractor: Optodot Corporation

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Subcontractors:  
Madico Inc., Woburn, MA  
Dow Kokam, LLC, Lee's Summit, MO  
University of Rhode Island (URI), Kingston, RI  
Ashland Inc., Wayne, NJ

Start Date: October 1, 2011  
Projected End Date: September 30, 2014

### Objectives

- Demonstrate technology that reduces the cell or battery inactive component weight, volume, and/or cost by at least 20% (goal of at least 40%), while maintaining overall cell or battery performance.
- Design, develop, optimize and improve the separator, current collectors, electrolyte, termination materials, and cell casing used for manufacturing lithium ion batteries.
- Develop a simpler and faster battery coating and assembly process.

### Technical Barriers

At least a two-fold reduction in the cost of manufacturing lithium-ion batteries is needed for widespread adoption of electric vehicles. Even though improvements in the battery anode and cathode materials will provide significant cost reduction, it is difficult to achieve this overall two-fold level of cost reduction from incremental improvements of the current generation of battery inactive components and of battery coating and assembly processes.

### Technical Targets

- Develop a high performance cell that reduces the combined cost of the battery inactive components of separator, current collectors,

electrolyte, termination materials, and casing by at least 20%.

- Demonstrate a manufacturing process based on new inactive components that provides high performance cells while reducing the coating and assembly cost by at least 20%.

### Accomplishments

- Developed new versions of 8 micron thick ceramic separator layers with an all-nanoporous design and a very narrow pore size distribution with a 30 nm average pore diameter.
- Using the Argonne National Lab(ANL) battery cost model, cost savings from the 8 micron ceramic separator component including the reduced usage of electrolyte were estimated to be greater than 20% for the inactive components of the cell. This estimated saving meets the cost reduction objectives of this project from the thinner ceramic separator alone.
- 3 micron thick copper and aluminum current collector layers were coated onto anode/separator and cathode/separator coated stacks, respectively, and showed good cycling and conductivity. A low cost proprietary process was developed for coating the 3 micron thick copper current collection layer.



### Introduction

Optodot has proposed to develop a new set of battery inactive components and a new battery coating and assembly process. These innovative materials and manufacturing process are based on the use of a thinner, safer, and lower cost ceramic separator. The proposed work comprises development of advanced ceramic separator, current collector, and electrolyte materials and of advanced battery stack coating and current collection methods. A new system of edge termination and cell casing will be developed for use with these coated anode and cathode stacks. The thinner ceramic separator enables the use of lower cost and more thermally stable electrolytes. Wider and higher speed industrial coaters will be utilized to make the coated battery electrode stacks to obtain the cost benefits of at least a five-fold increase in coating output. The new battery manufacturing process eliminates the expensive

conventional assembly equipment to precisely interleave the electrodes with free standing separators.

### Approach

Optodot will characterize the performance and cost of the inactive components and assembly process of current baseline cells. Starting with a thinner ceramic separator layer for this project, Optodot and its subcontractors will overcoat this separator with conventional anode and cathode layers. Optodot will design and develop thinner and lower cost current collector layers for the anode and cathode electrodes before coating a second anode or cathode layer. Optodot is also developing a cell termination and casing system for use in making and demonstrating high performance 2 Ah cells. With its subcontractors, Optodot is working to develop a lower cost and more thermally stable electrolyte that functions well with the much thinner ceramic separator and coated battery stack. Optodot and its subcontractors will demonstrate and document the acceptable performance and overall cost reduction of these improved inactive components for lithium ion batteries and of the simpler and faster coating and assembly processes. A cost analysis report will document the cell cost reduction achieved compared to the cost of current baseline cells.

### Results

The capability of overcoating the electrodes onto an 8 micron thick ceramic separator layer without penetration of the pigments of the electrode into the separator and without damage to the electrode/separator coated stack during calendering was demonstrated in FY2012. This 8 micron ceramic separator is 40% porous with a narrow pore size distribution centered at 30 nm.

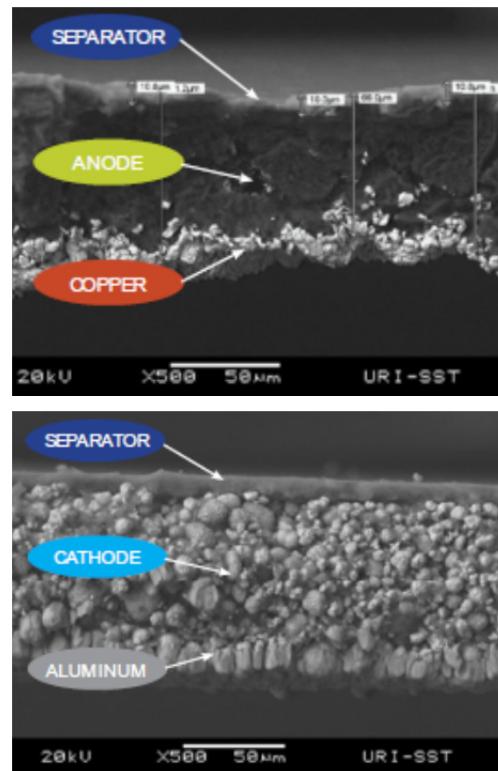
The use of an 8 micron nanoporous ceramic separator as the layer on which the electrodes and current collector layers are coated to form anode and cathode coated stacks provides significant cell cost savings of 20-25% of the inactive components of the cell, using the ANL battery cost model. The cost savings are derived from the use of the much thinner separator, a reduction in the usage of the electrolyte due to the thinner separator, and cell cost reduction in \$/kWh from the much thinner separator that allows more active material to be used in the cell.

The ceramic separator layers and the release substrates of this project have excellent stability to the heat and stress of the electrode coating process, as demonstrated during the machine coating of the electrodes and subsequent calendering of the electrode/separator stacks. Safety- and cell performance-related features of the ceramic separator layer include

dimensional stability of less than 0.5% shrinkage at 220°C, much greater compression strength than plastic separators, excellent thermal conductivity and heat dissipation, excellent cycling rate capability and low resistance from the much thinner ceramic separator, and non-flammability.

Metal current collector layers and edge connections are being incorporated into the electrode/separator coated stacks to produce the full anode and cathode coated stacks. Considerable progress was made in developing a low cost proprietary process for coating 3 micron copper metal layers as the anode current collector layer with an electrical conductivity of about 0.5 ohms/square. The estimated cost savings for this copper current collector layer is about 40% with a large weight savings compared to the existing copper foils used as the substrate for coating the anodes.

Figure III - 91 shows cross-sections of anode and cathode coated stacks of this project. Small cells made with these coated stacks showed good cycling and high and low temperature performance.



**Figure III - 91: Anode electrode stack and cathode electrode stack**

The new separator and current collector layers of this project are generic and compatible for use with various anode, cathode, and electrolyte materials as improved cell materials become available.

Since the much thinner ceramic separator provides more flexibility and latitude in the selection of

electrolytes that provide a suitable conductivity, URI is working on more stable and flame retardant electrolytes to use in the cells of this project.

Work was done in FY2013 to eliminate coating-related defects in the coated electrode stacks, and to scale up the machine coating of the ceramic separator layer to a full production width using slot die coating application. This project is ready to make the anode and cathode coated stacks on machine coaters and to assemble them into 2 Ah cells. From this, the estimated cell cost savings from coating at wider widths and higher line speeds and with a simpler cell assembly process will be determined.

### Conclusions and Future Directions

- Meeting the performance requirements of at least 20% improved cost, volume and weight for the key inactive components of Li-ion cells

and developing a low cost next generation manufacturing process will help meet the DOE goals of cost reduction to \$270/kWh by 2017 for PHEVs and to \$125/kWh by 2022 for EVs.

- The use of the 8 micron thick ceramic separator alone meets the project's > 20% cost improvement objective for the inactive components, while providing 10% lighter batteries and the safety of a ceramic separator with very high dimensional stability at 220°C.

### FY 2013 Publications/Presentations

1. 2013 DOE Annual Peer Review Meeting Presentation

## III.D Advanced Materials and Processing (Funded by FY 2008 DOE FOA)

### III.D.1 Protection of Lithium (Li) Anodes Using Dual Phase Electrolytes (Sion Power)

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Grant Recipient: Sion Power Corporation

**Yuriy Mikhaylik, Principal Investigator**

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Start Date: October 1, 2009

Projected End Date: September 30, 2014

#### Objectives

The objective of this project is to develop a unique electrolyte providing two liquid phases having good Li conductivity, self-partitioning and immiscibility, serving separately the cathode and anode electrodes. Introduce dual-phase electrolyte into Li-S cells and demonstrate improved cycling and thermal stability.

#### Technical Barriers

Barriers addressed for EV application

- Specific Energy >250 Wh/kg
- Thermal stability, safety
- Cycle Life

#### Technical Targets

Introduce dual-phase electrolyte into 250 mAh cell format. Perform full scale USABC test evaluation and abuse tolerance test and demonstrate improvement of specific energy > 250 Wh/kg, cycle life >100 cycles and cells thermal stability – increasing the runaway temperature to >165°C.

#### Accomplishments

Phases 1 and 2 of the Project were successfully completed.

Phase 3 of the Dual-Phase project was synchronized with Sion's ARPA-E project to develop Protected

Lithium Anode (PLA) for the Li-S system which ended on September 30, 2013.

The ARPA-E project resulted in development of an advanced PLA structure including ceramic/polymer protective layer and gel-electrolyte layer. The main function of the gel-electrolyte polymer was immobilizing the anode part of the dual-phase electrolyte. Newly introduced PLA structure developed under ARPA-E added two new functions for gel-polymer:

- Surface for coating of advanced protective ceramic/polymer layer
- Carrier and substrate for finished PLA

The dual phase gel-electrolyte polymer was modified to meet the new requirements and to be fully integrated into the new PLA structure.

The first step of integration of Dual-Phase gel-electrolyte into PLA was a combination of gel-polymer layer and polymer layer developed for ceramic/polymer structure. These two layers were combined with vacuum deposited lithium and tested in the laboratory in 0.25Ah cells. A new structure test confirmed improved thermal stability (no runaway) at temperatures exceeding metallic lithium's melting point.



#### Introduction

Achieving the DOE cell performance targets for electric vehicle application will require improved Li anode chemical stability (safety), cycle-ability and capacity. It also requires higher cell-level specific energy and the ability to be manufactured at high volume. To meet the DOE targets Sion Power is developing a unique electrolyte providing lithium protection and cell thermal stability.

#### Approach

Sion Power's approach is to develop an electrolyte consisting of two liquid phases having good Li conductivity, self-partitioning and immiscibility, serving separately the cathode and anode electrodes. This self-

partitioning dual-phase electrolyte will enable us to tailor electrolyte composition at each electrode to provide the optimum chemical stability. This innovative approach was applied to stabilize a high energy metallic lithium anode. While this approach could be generally applied to any Li metal or Li-ion rechargeable cell, SION Power uses a Lithium-Sulfur rechargeable battery system to apply two liquid phases concept.

## Results

Li-S cells were produced with vacuum deposited Li anodes coated with two polymer layers: gel-electrolyte polymer and another polymer designed to support the ceramic/polymer protective layer. The cells were discharged and charged at C/5 and C/8 respectively. The cells generated specific energy in the range 260 -310 Wh/kg. Cycling behavior is shown in Figure III - 92.

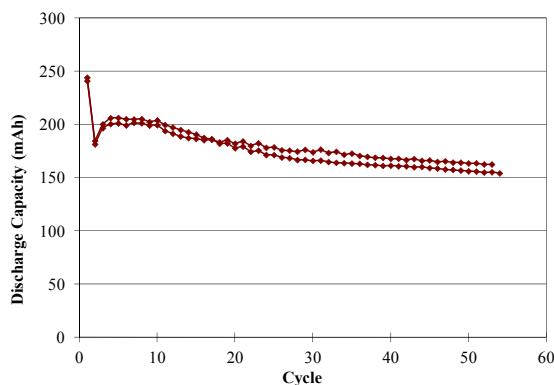


Figure III - 92: Discharge capacity vs cycle for Li-S cells with two polymer layers on the vacuum deposited lithium anode

A subset of cells were stopped after the 10<sup>th</sup> charge and were subjected to thermal ramp test shown in Figure III - 93. The cells did not show signs of thermal runaway at temperatures exceeding lithium metal's melting point (+181°C). In fact, cell thermal stability at temperatures over 200°C was limited by the packaging material showing loss of mechanical integrity and noisy signal in Figure III - 93.

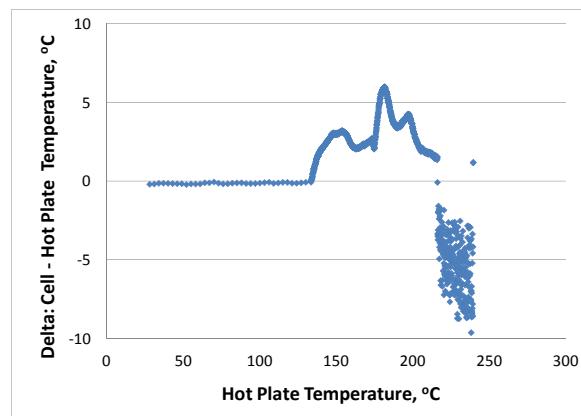


Figure III - 93: Cell thermal ramp test at 5°C/min. Fully charged cell after 10 cycles

## Conclusions and Future Directions

The next step is integration of this dual-phase electrolyte into the newly introduced advanced protected lithium anode ceramic/polymer structure and completion of Phase 3 goals: 250 mAh format production cells manufacturing, full scale USABC test performance evaluation and abuse tolerance test and improvement demonstration by making the cell more thermally stable – specifically increasing the runaway temperature to >165°C.

## III.D.2 New High-Energy Nanofiber Anode Materials (NCSU)

Bruce Mixer, NETL Project Manager

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Start Date: September 15th, 2009

Projected End Date: November 15th, 2013

### Introduction

- **Objective:** Use electrospinning technology to integrate dissimilar materials (silicon and carbon) into novel composite nanofiber anodes, which simultaneously have large energy density, high power capability, reduced cost, and improved abuse tolerance.



### Progress and Current Status

Achieving the DOE anode targets for advanced lithium-ion batteries will require novel material manufacturing technologies that can produce anodes with large energy density, high power capability, reduced cost, and improved abuse tolerance. In previous project years, we have used electrospinning technology (combined with carbonization) to synthesize a novel type of Si/C composite nanofiber anode (Figure III - 94), combining the advantageous properties of silicon (high storage capacity) and carbon (long cycle life). The nanofiber structure allowed the anode to withstand repeated cycles of expansion and contraction. Si/C composite nanofibers were electronically conductive and provided effective conductive pathways in electrodes. In addition, composite nanofibers formed a desirable porous electrode structure, thereby leading to fast Li-ion transport. Results demonstrated that anodes made of Si/C composite nanofibers were able to deliver high capacity and long cycle life.

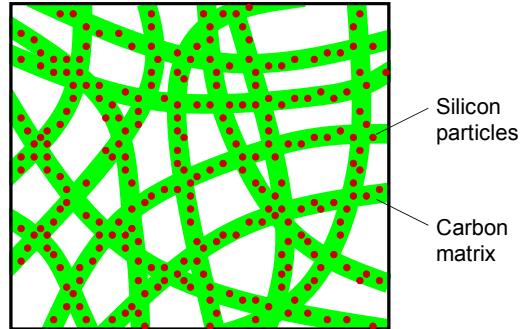


Figure III - 94: Schematic of composite nanofiber anode

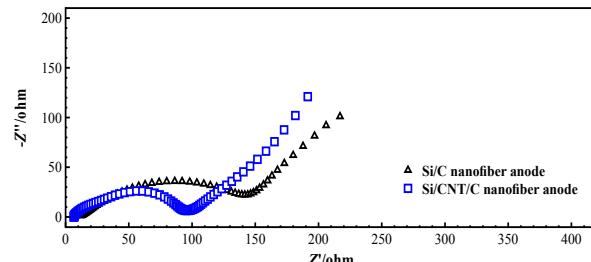
In this project year, we utilized several novel approaches to further improve the overall performance of Si/C composite nanofiber anodes. The following are two examples:

#### Improvement of C-rate Performance by

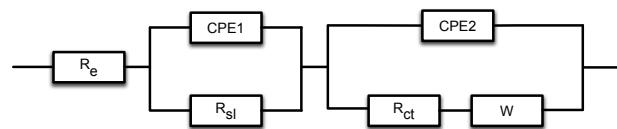
**Employing Carbon Nano Tube (CNT).** In order to obtain Si/C composite nanofiber anodes with improved C-rate performance, we employed CNTs to increase the electrode conductivity. Si/CNT/C composite nanofibers were prepared by electrospinning 15 wt% Si/0.75 wt% CNT/PAN precursor. These electrospun nanofibers were firstly stabilized in air environment at 280°C for 5 h (heating rate: 5°C/min) and then carbonized at 800°C for 2 h in argon atmosphere (heating rate: 2°C/min) to form Si/CNT/C composite nanofibers. In the previous project year, we studied the charge-discharge profiles of Si/CNT/C composite nanofiber anodes.

Figure III - 95 displays the impedance spectra of Si/C and Si/CNT/C composite nanofiber anodes. Both spectra show one depressed semicircle in the high and intermediate frequency range and a straight line in the low frequency range, corresponding to the migration within the surface layer, interfacial charge transfer process, and lithium diffusion in the electrode, respectively. With the addition of CNTs, the diameter of the depressed semicircle decreases, which indicates a decrease in charge transfer resistance. Figure III - 96 shows the corresponding equivalent circuit. Here,  $R_e$  is the electrolyte resistance of the cell,  $R_{sl}$  the resistance of ions transferring through the surface layer in the high frequency range,  $R_{ct}$  the charge transfer resistance in intermediate frequency region. Warburg impedance ( $W$ ) corresponds to the diffusion process of lithium ions within the electrode in the low frequency range. Constant phase element (CPE) other than ideal capacitor is introduced due to the porous nature of the composite nanofiber anodes. The results of impedance analysis are listed in Table III - 15. The addition of CNTs does not

have significant influence on the  $R_e$  and  $R_{sl}$  values. However, the  $R_{ct}$  value decreases from 167 to 90  $\Omega \cdot \text{cm}^2$  after the introduction of CNTs, indicating that Si/CNT/C composite nanofiber anodes might have better reaction kinetics during electrochemical cycling than Si/C composite nanofiber anodes.



**Figure III - 95:** Nyquist plots of Si/C and Si/CNT/C composite nanofiber anodes



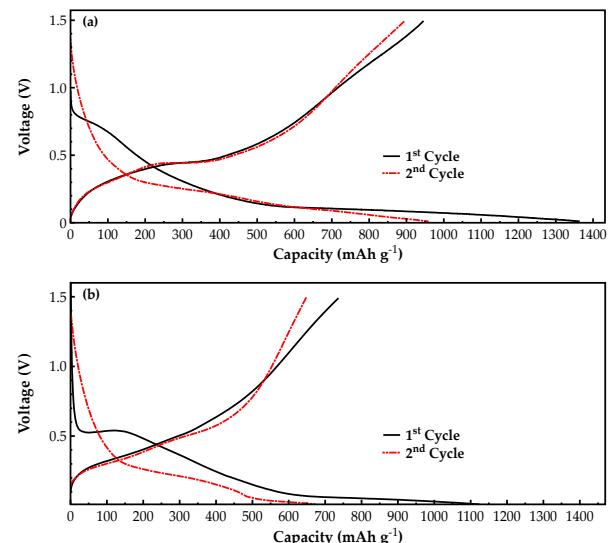
**Figure III - 96:** Equivalent circuit of Si/C and Si/CNT/C composite nanofiber anodes

**Table III - 15:** AC impedance analysis results of Si/C and Si/CNT/C nanofiber anodes

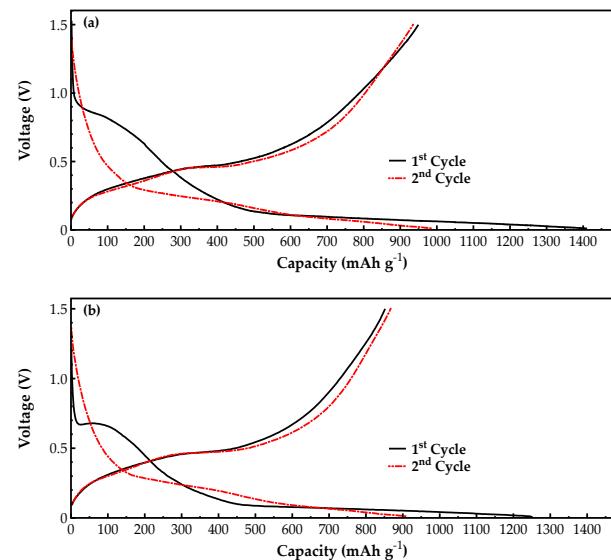
Electrodes	$R_e$ ( $\text{ohm} \cdot \text{cm}^2$ )	$R_{sl}$ ( $\text{ohm} \cdot \text{cm}^2$ )	$R_{ct}$ ( $\text{ohm} \cdot \text{cm}^2$ )
Si/C	9.00	15.29	167.72
Si/CNT/C	8.15	19.47	90.68

Galvanostatic charge-discharge experiments were carried out to evaluate the electrochemical performance of Si/C and Si/CNT/C composite nanofiber anodes. Figure III - 97 shows galvanostatic charge-discharge curves of Si/C nanofiber anodes under current densities of 50 and 300 mA/g. At the first cycle, when the current density is 50 mA/g, the Si/C nanofibers show a specific charge capacity of approximately 1363 mAh/g and discharge capacity of 947 mAh/g, respectively, corresponding to a Coulombic efficiency of 69.4%. When the current density is 300 mA/g, the Si/C nanofibers show a specific charge capacity of 1,123 mAh/g and discharge capacity of 736 mAh/g, respectively, corresponding to a Coulombic efficiency of 65.5%. The galvanostatic charge-discharge curves of Si/CNT/C nanofiber anodes under two different current densities are shown in Figure III - 98. At the first cycle, when the current density is 50 mA/g, the Si/CNT/C nanofibers show a specific charge capacity of 1,410 mAh/g and discharge capacity of 976 mAh/g, respectively, corresponding to a Coulombic efficiency

of 69.2% (Figure III - 98a). It is seen in Figure III - 98b that at the first cycle, the specific charge and discharge capacities of the Si/CNT/C nanofibers under 300 mA/g are 1,248 and 852 mA/g, respectively, corresponding to a Coulombic efficiency of 68.3%. The results indicate there is the relatively small degradation of capacity with the increase of current density. Here, the capacities were calculated based on the total weight of Si, CNFs and carbon nanofiber matrix.

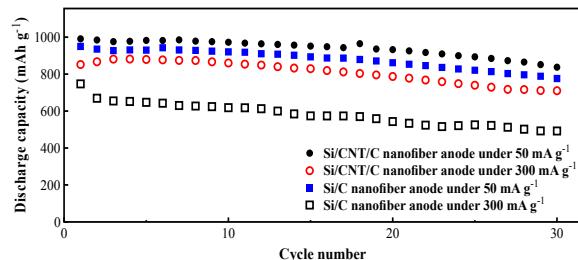


**Figure III - 97:** Galvanostatic charge-discharge curves of Si/C nanofiber anodes under different current densities: (a) 50  $\text{mA g}^{-1}$ , and (b) 300  $\text{mA g}^{-1}$



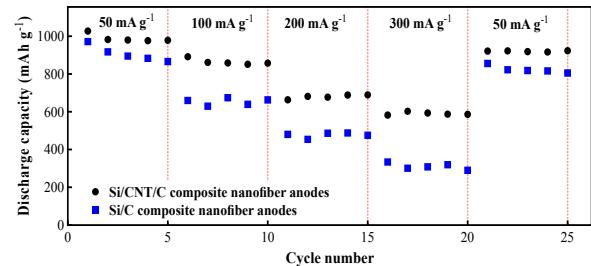
**Figure III - 98:** Galvanostatic charge-discharge curves of Si/CNT/C composite nanofiber anodes under different current densities: (a) 50  $\text{mA g}^{-1}$ , and (b) 300  $\text{mA g}^{-1}$

Figure III - 99 compares the cycling performance of Si/C and Si/CNT/C composite nanofiber anodes under two different current densities. It is seen that under 50 mA/g and at the 30th cycle, the discharge capacities are 775 and 837 mA/g, respectively, for Si/C and Si/CNT/C nanofiber anodes. The corresponding capacity retentions are 81.6 and 84.5%, respectively. At a current density of 300 mA/g, after 30 cycles, the discharge capacities are 492 and 710 mA/g, respectively, for Si/C and Si/CNT/C nanofiber anodes. The corresponding capacity retentions are 64.9 and 83.3%, respectively. Results indicate that at both current densities, the Si/CNT/C nanofiber anode have greater capacity retention than the Si/C nanofiber anode.



**Figure III - 99: Cycling performance comparison of Si/C and Si/CNT/C composite nanofiber anodes under different current densities**

The comparison of rate capacities of Si/C and Si/CNT/C nanofiber anodes is shown in Figure III - 100. The discharge capacity of the Si/C nanofiber anode decreases rapidly with increase in current density. However, the capacity decrease of the Si/CNT/C nanofiber anode is much slower. Even at a high current density of 300 mA g<sup>-1</sup>, a relatively high capacity value of 602 mA/g is still achieved with the Si/CNT/C nanofiber anode. The capacity of Si/CNT/C nanofiber anode almost rebounds back to the original value when a low current density of 50 mA/g was applied again after 20 cycles. This demonstrates the excellent stability of the Si/CNT/C nanofiber anode under various charge/discharge conditions. The enhanced C-rate performance is mainly due to the use of well-dispersed CNTs. Because of their high aspect ratio and high conductivity, the dispersed CNTs can effectively form a conducting pathway throughout the composite nanofibers even at low concentrations.



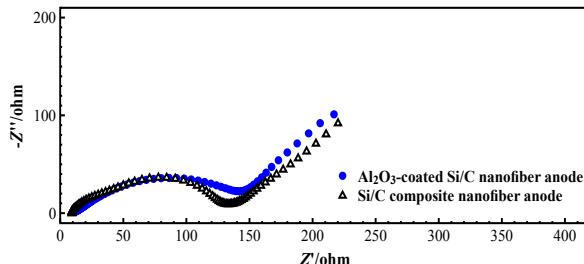
**Figure III - 100: Rate capabilities of Si/C and Si/CNT/C composite nanofiber anodes**

The results demonstrated that the electrochemical performance of Si/CNT/C nanofibers, especially the capacity retention and rate capability, has been improved significantly, which can be ascribed to the enhanced electrical conductivity of composite nanofibers. The unique morphology and structure of the one-dimensional conductive nanofibrous composite are beneficial to improve the electrochemical behavior of Si/CNT/C composite nanofibers. The incorporation of CNTs further enhances the electrochemical efficiency. These factors lead to Si/CNT/C composite nanofiber anode with high reversible capacity, good cycling performance, and excellent rate capability.

**Improvement of Cycling Performance by Employing ALD Alumina Coating.** In order to improve the cycling performance of Si/C composite nanofiber anodes, atomic layer deposition (ALD) was employed to coat the fiber surface. ALD is a unique technique for the deposition of conformal and homogenous thin films. In this study, we coated Si/C composite nanofibers with Al<sub>2</sub>O<sub>3</sub> by the ALD method. The purpose was to control the stability of the solid electrolyte interphase (SEI) by employing the Al<sub>2</sub>O<sub>3</sub> coating layer to prevent side reactions between the electrode and the electrolyte. The ALD process of alumina was performed on the surface of Si/C nanofiber electrodes using tri-methyl aluminum (TMA) and H<sub>2</sub>O as precursors at 120°C.

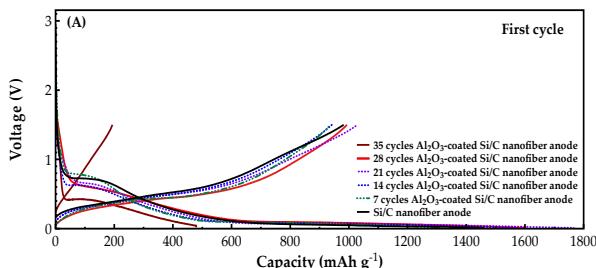
Figure III - 101 displays the impedance spectra of Si/C and ALD Al<sub>2</sub>O<sub>3</sub>-coated Si/C composite nanofiber anodes prepared with an ALD cycle number of 28. Both spectra show one depressed semicircle in the high and intermediate frequency range and a straight line in the low frequency range, corresponding to the migration within the surface layer, interfacial charge transfer process, and lithium diffusion in the electrode, respectively. The ionic conduction of the SEI film is a result of the migration of solvated Li ions through the micro-pores of SEI since the dried SEI itself is neither electronically nor ionically conductive. Hence, higher interfacial resistance corresponds to a more compact and more stable SEI. As shown in Figure III - 101, the addition of ALD Al<sub>2</sub>O<sub>3</sub> coating results in an increased semicircle diameter, *i.e.*, increased charge

transfer resistance. This means the SEI structure has become more compact and less conductive by the introduction of ALD  $\text{Al}_2\text{O}_3$  coating.



**Figure III - 101:** Nyquist plots of Si/C and  $\text{Al}_2\text{O}_3$ -coated Si/C nanofiber anodes (ALD cycle number = 28)

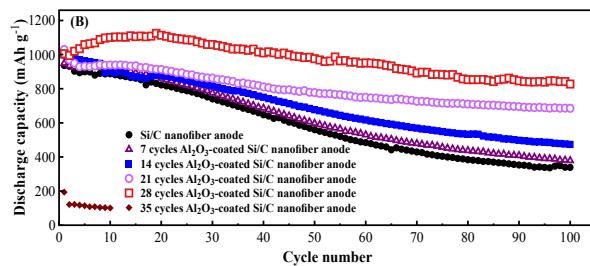
Galvanostatic charge-discharge tests were carried out within a voltage window of 0.02 – 1.5 V to evaluate the electrochemical performance of Si/C and  $\text{Al}_2\text{O}_3$ -coated Si/C composite nanofibers. Figure III - 102 shows galvanostatic charge-discharge curves of Si/C and  $\text{Al}_2\text{O}_3$ -coated Si/C composite nanofibers under 50 mA g<sup>-1</sup>. When the ALD coating cycle number is 35, the resultant  $\text{Al}_2\text{O}_3$ -coated Si/C composite nanofibers exhibit no useful capacity. This means that an  $\text{Al}_2\text{O}_3$  coating layer of 35 ALD cycles is too thick and blocks lithium diffusion. As shown in Figure III - 102, all other uncoated and  $\text{Al}_2\text{O}_3$ -coated Si/C composite nanofibers show reversible capacities of greater than 900 mA/g in the first cycle.



**Figure III - 102:** Galvanostatic charge-discharge curves of Si/C composite nanofiber anodes and  $\text{Al}_2\text{O}_3$ -coated Si/C composite nanofiber anodes

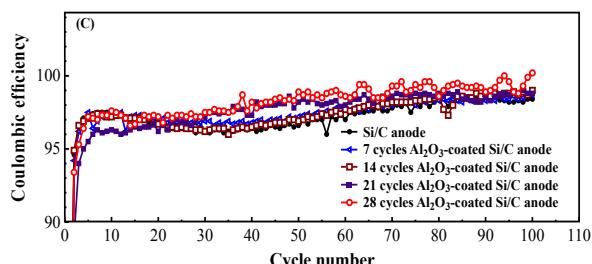
Figure III - 103 shows the cycling performance of uncoated and  $\text{Al}_2\text{O}_3$ -coated Si/C composite nanofibers. It is seen that at the 100th cycle, the discharge capacities are 338.8, 378.8, 473.5, 685.1 and 827.3 mA/g, respectively, for composite nanofibers with 0, 7, 14, 21, and 28 ALD cycles. The corresponding capacity retentions are 36.1, 39.8, 47.4, 66.5 and 82.3%, respectively. When the ALD coating cycle number is 7 or 14, the cycling performance of  $\text{Al}_2\text{O}_3$ -coated Si/C nanofibers is comparable to that of the uncoated Si/C nanofibers. When the ALD coating cycle number is 21, the capacity fades slower than that of uncoated Si/C nanofibers and shows an increased capacity retention of

66.5% at the 100th cycle. When the ALD coating cycle number is 28, the capacity exhibits the highest stability and the capacity retention at the 100th cycle increases significantly from 36.1% to 82.3%, compared to that of uncoated Si/C nanofibers. However, when the ALD coating cycle number further increases to 35, the capacity is lower than 200 mA/g and fades very quickly. These results demonstrate that  $\text{Al}_2\text{O}_3$ -coated Si/C composite nanofibers prepared with an ALD cycle number of 28 have the most stable cycling performance. The enhanced cycling performance is mainly due to the protective effect of conformal ALD alumina coating which could improve the mechanical integrity and prevent the side reactions between the electrode and the electrolyte. To achieve the enhanced cycling performance, it is important to select an appropriate ALD  $\text{Al}_2\text{O}_3$  coating thickness, which is a critical parameter for determining the electrochemical performance of the  $\text{Al}_2\text{O}_3$ -coated composite nanofibers.



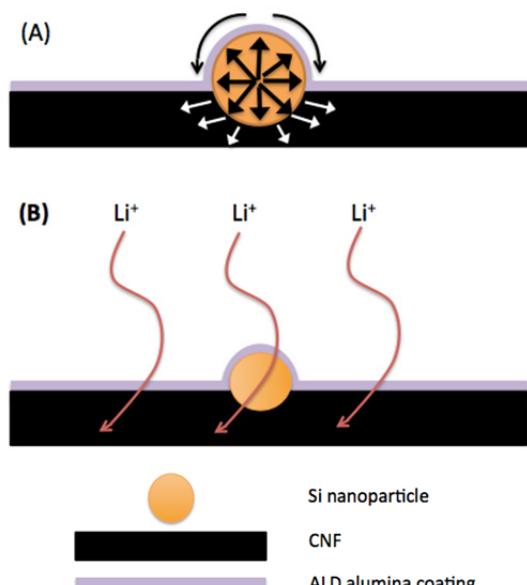
**Figure III - 103:** Cycling performance of Si/C composite nanofiber anodes and  $\text{Al}_2\text{O}_3$ -coated Si/C composite nanofiber anodes

Figure III - 104 compares the Columbic efficiencies of Si/C and  $\text{Al}_2\text{O}_3$ -coated Si/C composite nanofiber anodes during cycling. It is seen that  $\text{Al}_2\text{O}_3$ -coated Si/C composite nanofibers prepared with 28 ALD cycles deliver the highest Columbic efficiency of 99.9% at the 100th cycle, corresponding to a 1.5% point improvement compared to that of uncoated Si/C composite nanofibers. Similar to the enhanced cycling performance, the improved Columbic efficient can be mainly attributed to the ultrathin conformal ALD  $\text{Al}_2\text{O}_3$  coating, which minimizes the side reactions between the electrode and the electrolyte.



**Figure III - 104: Coulombic efficiencies of Si/C composite nanofiber anodes and  $\text{Al}_2\text{O}_3$ -coated Si/C composite nanofiber anodes**

ALD  $\text{Al}_2\text{O}_3$  coating tunes the electrochemical performance of Si-based anode materials from both physical and chemical aspects, as shown in Figure III - 105. Firstly, the ALD  $\text{Al}_2\text{O}_3$  coating has strong physical/mechanical restrain effects on the Si/C composite nanofibers since the coating might transfer the stress of Si nanoparticle expansion from radial direction to in-plane restrain when the Si nanoparticle is partly exposed on the surface. As a result, due to the presence of disordered carbon structure or voids, the buffer effect of carbon matrix could be well realized by restricting the expansion of silicon to the carbon nanofiber (Figure III - 105A). Secondly, the ALD  $\text{Al}_2\text{O}_3$  coating may act as a barrier for further side reactions between the electrode and the electrolyte (Figure III - 105B). The role of a chemical barrier combined with the reasonable mechanical properties makes the  $\text{Al}_2\text{O}_3$  coating an artificial but strong and stable SEI-like structure to improve the cycling performance and Columbic efficiency of Si-based anode.



**Figure III - 105: Schematic of (A) Physical/Mechanical, (B) Chemical protective effect of the ALD  $\text{Al}_2\text{O}_3$  coating**

The above are just two examples of the approaches that we used in the project year to improve the overall performance of Si/C composite nanofiber anodes. This year's results demonstrate that we have achieved the project objective of using electrospinning technology to integrate dissimilar materials (silicon and carbon) into novel composite nanofiber anodes, which simultaneously have large energy density, high powder capability, reduced cost, and improved abuse tolerance.

### FY 2013 Publications/Presentations

1. Kun Fu, Leigang Xue, Ozkan Yildiz, Shuli Li, Hun Lee, Ying Li, Guanjie Xu, Lan Zhou, Philip D. Bradford, and Xiangwu Zhang, "Effect of CVD Carbon Coatings on Si@CNF Composite as Anode for Lithium-ion Batteries," *Nano Energy*, 2, 976-986, 2013.
2. Shuli Li, Leigang Xue, Kun Fu, Xin Xia, Chengxin Zhao, and Xiangwu Zhang, "High-performance Sn/Carbon Composite Anodes Derived from Sn(II) Acetate/Polyacrylonitrile Precursors by Electrospinning Technology," *Current Organic Chemistry*, 17, 1448-1454 (2013).
3. Leigang Xue, Kun Fu, Ying Li, Guanjie Xu, Yao Lu, Shu Zhang, Ozan Toprakci, and Xiangwu Zhang, "Si/C Composite Nanofibers with Stable Electric Conductive Network for Use as Durable Lithium-Ion Battery Anode," *Nano Energy*, 2, 361-367 (2013).
4. Ying Li, Guanjie Xu, Yingfang Yao, Leigang Xue, Shu Zhang, Yao Lu, Ozan Toprakci, and Xiangwu Zhang, "Improvement of Cyclability of Silicon-Containing Carbon Nanofiber Anodes for Lithium-Ion Batteries by Employing Succinic Anhydride as an Electrolyte Additive," *Journal of Solid State Electrochemistry*, 17, 1393-1399 (2013).
5. Leigang Xue, Guanjie Xu, Ying Li, Shuli Li, Kun Fu, Quan Shi, and Xiangwu Zhang, "Carbon-Coated Si Nanoparticles Dispersed in Carbon Nanotube Networks as Anode Material for Lithium-Ion Batteries," *ACS Applied Materials & Interfaces*, 5, 21-25 (2013).
6. Ying Li, Guanjie Xu, Leigang Xue, Shu Zhang, Yingfang Yao, Yao Lu, Ozan Toprakci, and Xiangwu Zhang, "Enhanced Rate Capability by Employing Carbon Nanotube-Loaded Electrospun Si/C Composite Nanofibers as Binder-Free Anodes," *Journal of Electrochemical Society*, 160, A528-A534 (2013).
7. Xiangwu Zhang, "A Nanofiber Approach to Advanced Energy Storage," Department of Fiber Science and Apparel Design at Cornell University, Ithaca, New York, March 2013.

8. Kun Fu, and Xiangwu Zhang, “Flexible and Binder-Free Design: Nonwoven Structure Based Si Materials as Anodes for Lithium-Ion Batteries,” The 8th Annual NC State University Graduate Student Research Symposium, Raleigh, NC, March 2013.
9. Xiangwu Zhang, “Advanced Nanofibrous Energy-Storage Materials,” 2nd Annual World Congress of Advanced Materials-2013 (WCAM-2013), Suzhou, China, June 2013.
10. Xiangwu Zhang, “A Nanofiber Approach to Advanced Energy Storage,” The 5th International R&D Brokerage Event in Textiles and Clothing, Bursa, Turkey, April 2013.

## III.D.3 Internal Short Circuits in Lithium-Ion Cells for PHEVs (TIAX)

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Start Date: May 2010

Projected End Date: May 2013

### Objectives

- Develop an improved understanding of the conditions under which a thermal runaway will occur in a Li-ion cell.
- Use modeling to determine the threshold conditions for thermal runaway following an internal short circuit.
- Identify design factors for cells that can reduce propensity for thermal runaway.
- Identify and analyze opportunities for prevention of internal short circuits, or intervention/mitigation before they can cause thermal runaway.

### Technical Barriers

On rare occasions, Li-ion cells experience thermal runaway during normal charge/discharge cycles because of internal short-circuits; we term such incidents “field-failures.” Even though such incidents are rare, the potential consequences can be very serious. Safety technologies currently employed in Li-ion cells, such as positive thermal coefficient current limiting devices (PTC), current interrupt devices (CID), shut-down separators, etc., have not prevented thermal runaway due to internal shorts in commercial Li-ion cells. Development of new safety technologies is hindered by the rarity of field-failures in Li-ion cells, and the current incomplete understanding of field-failures. In this program, we fabricate Li-ion cells with various means to stimulate or develop appropriate internal shorts in order to study the effect of cell design variables, and cell-level materials choices. This improved understanding will help identify and evaluate technologies that enhance the safety of PHEV Li-ion batteries.

### Technical Targets

- Develop guidelines that will enable the development of technologies for a safe battery.
- Establish a facility for fabricating Li-ion cells to (1) study the effect of cell materials and cell design parameters on thermal runaway, (2) compare to TIAX’s Li-ion cell finite element analysis (FEA) model predictions, and (3) validate FEA model.
- Establish an experimental facility that permits testing the efficacy of technologies developed to mitigate safety incidents that occur in the field.
- Select and test approaches to enhance Li-ion battery safety using validated model and experimental data.

### Accomplishments

- Set-up fully functional cell prototyping facility with capability to fabricate high-quality multi-Ah cells.
- Adapted method for stimulating thermal runaway to cells fabricated on our prototyping line.
- Conducted experiments to induce thermal runaway of custom-built Li-ion cells under a range of external heat transfer conditions.
- Validated FEA model for simulating thermal runaway of Li-ion cells by fitting experimental thermal runaway data.
- Demonstrated ability to stop the progression to thermal runaway by adjusting the rate of heat transfer out of the cell.



### Introduction

Concerns regarding the safety of Li-ion batteries could severely limit their use in PHEVs, and undermine the prospects for realizing the appealing benefits of PHEVs. Recent highly-publicized safety incidents and the ensuing widespread recalls of Li-ion batteries used in laptops and cell phones have elevated such concerns. In these safety incidents, called field-failures, Li-ion batteries operating under otherwise normal conditions undergo what appear to be spontaneous thermal runaway events, with violent flaming and extremely high temperatures. These field-failures cause significant damage to cells, packs and devices, and sometimes to

their surroundings. Because a typical PHEV pack would be significantly larger than a typical laptop pack, the consequences of a field-failure in a PHEV pack could be far more severe than would be the case for a laptop pack, and may occur far more frequently.

Although it is well-recognized that the commercial viability of Li-ion technology in PHEVs is dependent on avoiding spontaneous occurrence of such incidents on board vehicles, it is clear but less well-recognized that the safety technologies currently employed in commercial Li-ion batteries for portable electronic applications are inadequate with respect to such incidents. Furthermore, there are currently a variety of standard safety-related technologies to guard against abuse of the Li-ion battery. However, field-failures have occurred despite the presence of these technologies in cells and packs. There is also no adequate test for the type of field-failure that presents the basic safety issue for Li-ion.

Given that field-failures occur in a manner that is not effectively addressed by any of the standard safety measures currently used in Li-ion batteries, and that there is no test currently available that can identify these cells before they undergo field-failure, it is clear that a fundamentally new approach is required to develop technologies that will prevent these rare but profoundly destructive safety incidents caused by internal short circuits in PHEV cells.

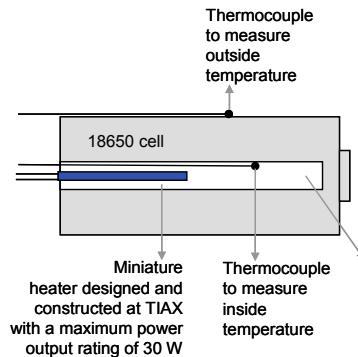
## Approach

Our approach to developing guidelines for safe PHEV pack design is to employ an FEA model to determine the conditions under which thermal runaway of PHEV-size cells occurs and can be suppressed. The FEA model is first validated using thermal runaway data on 18650 cells. Thermal runaway was induced in an 18650 cell by introducing a miniature heater into the center of the cell through a hole drilled at the bottom of the can. This approach allowed us to simulate local, spot heating of the cell, akin to an internal short. These cells were custom-built on our cell prototyping line with a range of design variations (including active materials) and were tested under a range of external heat transfer conditions in a custom-built wind tunnel. Here we describe our work in validating the FEA model, as well as initial experimental data in suppressing thermal runaway.

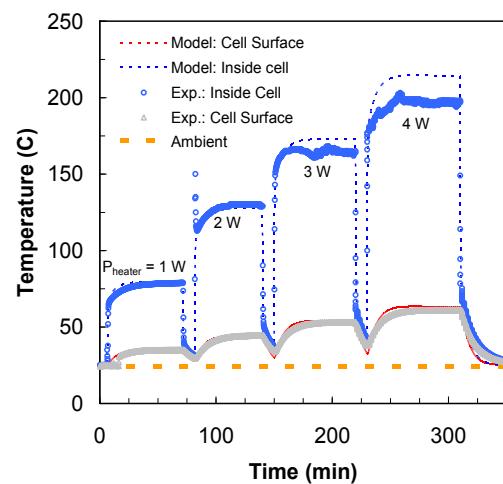
## Results

**Cell thermal parameters.** The heater method employed for estimating the thermal parameters for the 18650 cells is described in Figure III - 106. Temperature measurements inside the cell and at the cell surface were

made for different heater powers (Figure III - 107). By fitting the model to these time-dependent data, we were able to estimate/verify the thermal parameters for the cell (Figure III - 107).



**Figure III - 106: Schematic of experimental set-up to simulate internal short heat release in a cylindrical cell by using a miniature heater inserted in cell core. The heater power and external rate of heat transfer can be independently controlled**



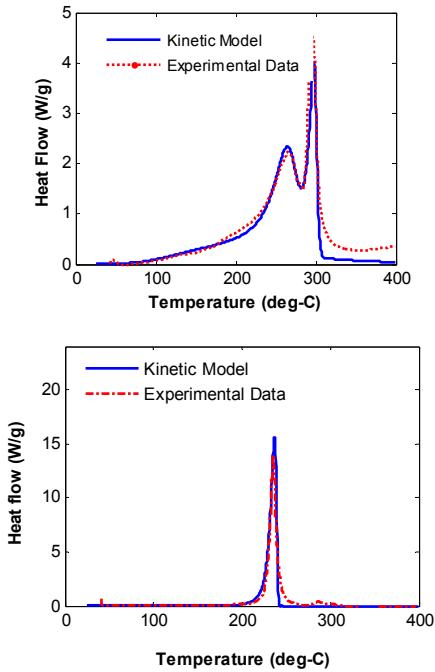
**Figure III - 107: Cell thermal properties, including specific heat and thermal conductivity were estimated/verified through heater experiments. Figure shows measured internal and cell surface temperatures for different heater power levels. Model fits are also shown. The cell was completely discharged prior to the experiment**

**Heat release kinetics from active materials.** Kinetics of heat release from the anode and cathode active materials are key inputs for any thermal runaway model of Li-ion cells. We developed representative models for heat release kinetics by fitting *ex situ* Differential Scanning Calorimeter (DSC) data for charged anode and cathode active materials used in our 18650 cells (Figure III - 108). These kinetic sub-models were then used in our FEA model for thermal runaway simulations.

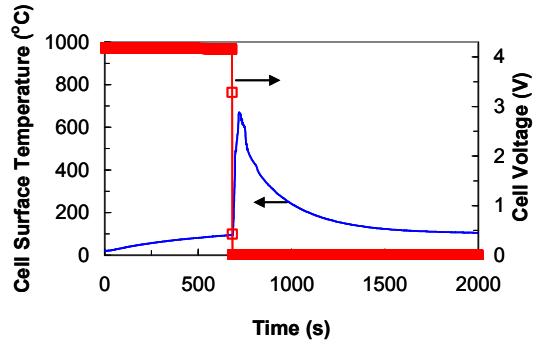
**Thermal runaway of Li-ion cells.** We induced thermal runaway by internally heating fully charged (4.2

V) 18650 cells using the heater method. Representative thermal runaway data are shown in Figure III - 109. In this test, the cell surface temperature initially rises slowly due to the internal heating. At ~680 s (cell surface temperature of 110 °C), there is a sharp drop in the cell voltage and thermal runaway ensues as indicated by the rapid rise in cell surface temperature. The measured cell temperature in this experiment exceeded 700°C. Separate experiments have confirmed that the sharp drop in cell voltage is due to an internal hard short. This phenomenon will be discussed in detail in a future publication.

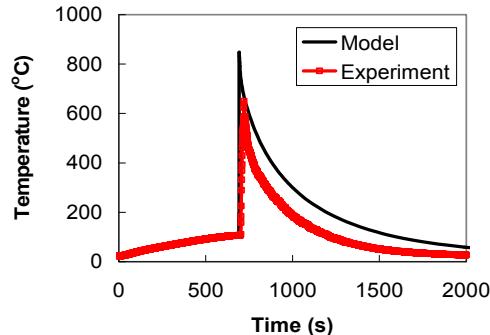
**Model fit to the thermal runaway data.** Figure III - 110 shows a comparison of the model fit to the experimental data from Figure III - 109. The only parameter adjusted was the power dissipated in the hard short. The model is able to determine the time and cell surface temperature at which thermal runaway occurs. We attribute the slight disagreement in the peak temperature between the model and the experiment to the experimental observation that the cell vents during thermal runaway, expelling electrolyte and active material mass, which is not yet taken into account in our model.



**Figure III - 108:** Kinetic models for heat generation were developed by fitting experimental DSC data for the materials used in our cells. Top plot shows fit to charged anode (graphite) data and bottom plot the fit to the charged cathode (NCA) data. The scan rate for the DSC measurement was 5°C/min

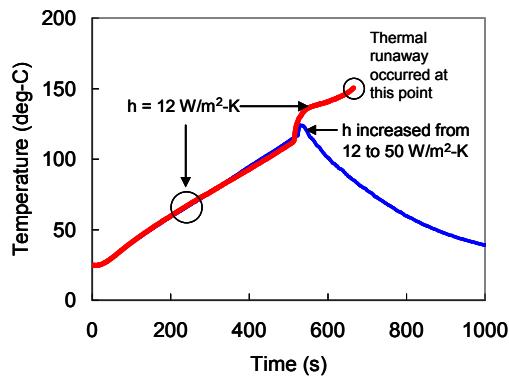


**Figure III - 109:** Experimental thermal runaway data from the heater experiment. The heater power was ~10 W and the external heat transfer coefficient was ~15 W/m<sup>2</sup>-K (low-level air flow past the cell)



**Figure III - 110:** Experimental thermal runaway data from the heater experiment. The heater power was ~10 W and the external heat transfer coefficient was ~15 W/m<sup>2</sup>-K

**Effect of ambient conditions on thermal runaway.** Previous *model* calculations had shown that increasing the heat transfer coefficient would prevent progression to thermal runaway. As shown in Figure III - 111, *experimental data* show that increasing the heat transfer coefficient from 12 W/m<sup>2</sup>-K (no air flow past the cell) to 50 W/m<sup>2</sup>-K (substantial air flow past the cell) when the cell surface temperature exceeded 130°C suppressed thermal runaway as predicted by the model.



**Figure III - 111: Experimental data demonstrating the benefit of increased heat transfer coefficient ( $h$ ) in suppressing thermal runaway. When  $h$  was maintained at  $\sim 12 \text{ W/m}^2\text{-K}$ , thermal runaway occurred at  $\sim 700 \text{ s}$  (cell surface temperature  $\sim 150^\circ\text{C}$ ). Temperatures higher than  $150^\circ\text{C}$  are not reported because the thermocouple was dislodged when the cell experienced thermal runaway, but we visually observed flames and a red-hot cell surface. In a subsequent experiment,  $h$  was increased from  $\sim 12 \text{ W/m}^2\text{-K}$  to  $\sim 50 \text{ W/m}^2\text{-K}$  when the surface temperature exceeded  $130^\circ\text{C}$ , resulting in cell cool down and suppression of thermal runaway. Identical cells were used in the two experiments**

## Conclusions and Future Directions

Collection and analysis of thermal runaway data under controlled conditions on custom-built 18650 cells have allowed us to validate an FEA model. Using the validated model, we are simulating thermal runaway in a large PHEV Li-ion cell following an internal short. Sensitivity analyses will help further elucidate the conditions that influence thermal runaway following an internal short circuit. We will derive some general guidelines for safe cells and packs from these simulations.

## FY 2013 Publications/Presentations

Portions of this work were presented at:

1. 30<sup>th</sup> International Battery Seminar and Exhibit, Ft. Lauderdale, FL, March 2013.
2. 224<sup>th</sup> Electrochemical Society Meeting, San Francisco, CA, October 2013

## III.E Small Business Innovative Research Projects

### Brian Cunningham

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Start Date: Ongoing

Projected End Date: Ongoing

### Objectives

Use the resources available through the Small Business Innovation Research (SBIR) and Small Business Technology Transfer (STTR) programs to conduct research and development of benefit to the Energy Storage effort within the Vehicle Technologies Program Office.



### Introduction and Approach

The Energy Storage effort of the Vehicle Technologies Program Office supports small businesses through two focused programs: Small Business Innovation Research (SBIR) and Small Business Technology Transfer (STTR). Both of these programs are established by law and administered by the Small Business Administration. Grants under these programs are funded by set aside resources from all Extramural R&D budgets; 2.7% of these budgets are allocated for SBIR programs while 0.35% for STTR grants. These programs are administered for all of DOE by the SBIR Office within the Office of Science. Grants under these programs are awarded in two phases: a 6-9 month Phase I with a maximum award of \$150K and a 2 year Phase II with a maximum award of \$1M. Both Phase I and Phase II awards are made through a competitive solicitation and review process.

The Energy Storage team participates in this process by writing a topic which is released as part of the general DOE solicitation. In FY12, the Energy Storage team decided to broaden its applicant pool by removing specific subtopics and allowing businesses to apply if their technology could help advance the state of the art

by improving specific electric drive vehicle platform goals developed by the DOE with close collaboration with the United States Advanced Battery Consortium.

**Phase II Awards Made in FY 2013.** Under the SBIR/STTR process, companies with Phase I awards that were made in FY 2012 are eligible to apply for a Phase II award in FY 2013.

Two Phase II grants were awarded in FY 2013 from ten Phase I grants that were conducted in FY 2012.

**Applied Spectra, Inc., (Fremont, CA 94538-6410).** This project will develop a bench top optical sensor for direct real-time measurements of the chemical composition of battery materials and electrode/electrolyte interfaces with depth resolution down to the nanometer range. This development will enable capabilities to improve domestic manufacturing of Li-ion batteries with higher yield and improved performance.

**XG Sciences, Inc., (Lansing, MI 48911-4224).**

This project will develop a low cost high energy silicon/graphene anode for use in extended range electric vehicle applications.

**Phase I Awards Made in FY 2013.** Three Phase I grants were awarded in the Summer of FY 2013.

**Navitas Systems, LLC, (Woodridge, IL 60517-4795).** This project will develop a low cost and high capacity silicon based anode for lithium-ion batteries. This will result in new battery technology capable of reducing the cost and extending the range of electric vehicles. This addresses the two key barriers that are limiting electric vehicle adoption.

**Pneumaticoat Technologies, LLC, (Westminster, CO 80021-3523).** This project will implement a low-cost, lean-manufacturing approach to providing safety and stability to lithium-ion battery materials using a nanotechnology-enabling coating solution. Expected outcomes are higher retained performance under extreme conditions using statistical experimental designs, and a roadmap toward rapid commercialization and domestic production of next generation Li-ion battery materials.

**TIAx, LLC, (Lexington, MA 02421-3102).** This project will develop a high voltage cathode material that improves the energy efficiency and mileage of HEVs and PHEVs, while also making it possible to charge PHEVs more quickly.