

**Applied Battery Research for Transportation  
(B&R No. VT-1102000)**

**Progress Report  
for  
Third Quarter FY 2011**

**Contributions from  
Argonne National Laboratory  
Army Research Laboratory  
Brookhaven National Laboratory  
Idaho National Laboratory  
Jet Propulsion Laboratory  
Lawrence Berkeley National Laboratory  
NAVSEA Carderock  
Oak Ridge National Laboratory  
Sandia National Laboratories**

**August 2011**

## **Applied Battery Research for Transportation Program Third Quarter Progress Report for FY 2011**

This quarterly progress report describes the activities to be conducted in support of DOE's Applied Battery Research for Transportation (ABR) Program. This program focuses on helping the industrial developers to overcome barriers for Li-Ion batteries for use in plug-in hybrid electric vehicles (PHEVs). In its goal of developing low-emission high fuel economy light-duty HEVs and PHEVs, the FreedomCAR and Fuels Partnership established requirements for energy storage devices in these applications. The Vehicle Technologies Program at DOE has focused the efforts of this applied battery R&D program on the PHEV application.

Through the FreedomCAR and Fuels Partnership, DOE is currently supporting the development of advanced Li-Ion batteries with industry for HEV, PHEV, and EV applications. The industrial developers have made significant progress in developing such batteries for HEV applications and there are new challenges associated with developing viable battery technologies for the PHEV application, especially when targeting the 40-mile all electric range. In addition to the calendar life, abuse tolerance, and cost challenges that exist for Li-Ion batteries in the HEV application, now the issue of providing sufficient energy within the weight and volume requirements becomes a huge challenge, as does cycle life. Also, the abuse tolerance and cost challenges become even greater. The Applied Battery Research for Transportation program is directed at assisting the industrial developers to identify the major factors responsible for the technical barriers and to find viable cost-effective solutions to them. The goal is to facilitate the development of low-cost cell chemistries that can simultaneously meet the life, performance, abuse tolerance, and cost goals that have been established by the FreedomCAR and Fuels Partnership.

The ABR Program is organized into three main tasks to address these issues for PHEVs:

- (1) Battery Cell Materials Development—focuses on research, development, and engineering of advanced materials and cell chemistries that simultaneously address the life, performance, abuse tolerance, and cost issues.
- (2) Calendar & Cycle Life Studies—deals with understanding the factors that limit life in different Li-Ion cell chemistries, which are used as feedback to Task 1. This task also deals with the establishment and operation of in-program cell fabrication capabilities for use in these life studies.
- (3) Abuse Tolerance Studies—deals with understanding the factors that limit the inherent thermal and overcharge abuse tolerance of different Li-ion cell materials and chemistries, as well as developing approaches for enhancing their abuse tolerance.

A list of the projects is given in the table, with the individual reports compiled in the Appendix.

Organization	AMR Project ID	AOP Project ID	Title	PI/Contact Point	Page Number
			<b>Task 1: Battery Cell Materials Development</b>		
ANL	ARRA VT076		Materials Scale-Up Facility	Gregory Krumdick	6
ANL	ARRA VT076	IV. E.1.1	Process Development and Scale up of Advanced Cathode Materials	Gregory Krumdick	11
ANL	ARRA VT076	IV. E.1.2	Process Development and Scale up of Advanced Electrolyte Materials	Gregory Krumdick	14
ANL	ES015	1.1A	Engineering the High Energy Cathode Material	Khalil Amine	17
ANL	ES016	1.1B	New High Energy Gradient Concentration Cathode Material	Khalil Amine	20
ANL	ES017	1.1F	Design and Evaluation of High Capacity Cathode Materials	Christopher Johnson	24
ANL	ES019	1.1G	Development of High-Capacity Cathode Materials with Integrated Structures	Sun-Ho Kang	27
ANL	ES020	1.1C	Developing High Capacity, Long Life anodes	Khalil Amine	30
ANL	ES022	1.1I	Develop Improved Methods of Making Intermetallic Anodes	Andrew Jansen	33
ANL	ES023	1.1H	Development of Novel Electrolytes & Additives for PHEV Applications	Dan Abraham	35
ARL	ES024		High Voltage Electrolytes for Li-ion Batteries	Richard Jow	38
ANL	ES025	1.1D	Development of Advanced Electrolyte Additives	Zhengcheng Zhang	42
JPL	ES026		Electrolytes for Use in High Energy Li-Ion Batteries with Wide Operating Temperature Range	Marshall Smart	45
INL	ES027		Novel Phosphazene Compounds for Enhancing Electrolyte Stability and Safety of Lithium-ion Cells	Kevin Gering	52
ANL	ES028	1.1E	Streamlining the Optimization of Lithium-Ion Battery Electrodes	Wenquan Lu	58

Organization	AMR Project ID	AOP Project ID	Title	PI/Contact Point	Page Number
			<b>Task 1: Battery Cell Materials Development</b>		
ANL	ES028	1.3	Screen Electrode Materials, Electrolytes, and Additives	Wenquan Lu	60
LBNL	ES029	1.2.2	Scale-up and Testing of Advanced Materials from the BATT Program	Vincent Battaglia	63
ANL	ES112	1.2C	Functionalized Surface Modification Agents to Suppress Gassing Issue of Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> Based Lithium Ion Chemistries	Khalil Amine	65
ANL	ES113	1.1L	Development of High Voltage Electrolyte for Lithium Ion Battery	Zhengcheng Zhang	67
ANL	ES114	1.2D	Spherical Carbon Anodes Fabricated by Autogenic Reactions	Vilas Pol	70
ANL	ES115	1.1V	Synthesis and Development of High-Energy and High-Rate Cathode Materials from Ion-Exchange Reactions	Christopher Johnson	74
NAVSEA-Carderock	ES038		High Energy Density Ultracapacitors	Patricia Smith	77
ANL		1.1X	Paper Study on Continuous Process for Making Gradient Concentration Cathode Material	Gregory Krumdick	81
ANL		1.1K'	Transition Metal Precursors for High Capacity Cathode Materials	Ilias Belharouak	84
			<b>Task 2: Calendar &amp; Cycle Life Studies</b>		
ANL	ARRA VT075		Prototype Cell Fabrication Facility	Andrew Jansen	88
ANL	ARRA VT077		Post-Test Facility	Ira Bloom	90
ANL	ES030	2.1	Fabricate PHEV Cells for Testing and Diagnostics in Cell Fabrication Facility	Andrew Jansen	94
ANL	ES031	2.2B	Model Cell Chemistries	Dennis Dees	97

Organization	AMR Project ID	AOP Project ID	Title	PI/Contact Point	Page Number
			<b>Task 2: Calendar &amp; Cycle Life Studies</b>		
ANL	ES032	2.3A	Diagnostic Evaluation of Lithium Battery Cells and Cell Components	Dan Abraham	100
ANL	ES032	2.3B	Structural Investigations of Layered Oxides for PHEV Applications	Dan Abraham	104
LBNL	ES033	1.1.1 and 2.4.1	Electrochemistry Diagnostics of Baseline and New Materials	Robert Kostecki	107
BNL	ES034		Diagnostic Studies to Improve Abuse Tolerance and life of Li-ion batteries	Xiao-Qing Yang	110
ORNL	ES039		In-situ characterization and diagnostics of mechanical degradation in electrodes	Claus Daniel	113
ANL	ES111	2.2A	Battery Design Modeling	Kevin Gallagher	118
			<b>Task 3: Abuse Tolerance Studies</b>		
ANL	ES035	3.1	Develop & Evaluate Materials & Additives that Enhance Thermal and Overcharge Abuse	Khalil Amine	121
SNL	ES036	3.2	Abuse Tolerance Improvements	Chris Orendorff	124
LBNL	ES037	1.2.1	Overcharge Protection for PHEV Batteries	Guoying Chen	127

## **APPENDIX**

### **Individual Project Progress Reports**

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number:** ARRAVT076

**June, 2011 update**

**Project Title:** Materials Scale-Up Facility

**Project PI, Institution:** Gregory Krumdick, Argonne National Laboratory

**Collaborators (include industry):**

Barton Malow, Design Build Subcontractor

**Project Start/End Dates:** start: 4/1/2010; end: 3/31/2012

**Objectives:** The objective of this project is to design and build a pilot-scale battery-materials production facility (Materials Engineering Facility) to scale up bench-scale battery chemistries and produce bulk quantities of new materials for evaluation in prototype cells to enable quick turnaround validation of new materials chemistries. Such a facility is a key missing link between the bench-scale development of battery technology and high-volume manufacturing of large-format advanced batteries for transportation applications. One of the primary contributing factors to the lack of a significant domestic Li-ion battery manufacturing capability is the lack of adequate facilities to enable the research community to produce quantities of materials for prototype cells to enable quick-turnaround validation screening of new materials chemistries throughout the R&D process.

**Approach:** To enable the process development and scale-up of new battery materials, the facility is planned to have:

- Suitable space – The Materials Engineering Facility will contain high hazard Group H-Occupancy labs to accommodate the larger volumes of hazardous materials used as processes are scaled up.
- Modular process equipment – The facility and equipment design will incorporate modular equipment to enable quick change out of unit operations, as required for a range of materials process R&D.
- Analytical lab for materials analysis – A dedicated analytical lab to characterized materials during scale up allows for rapid process optimization and can also provide materials quality assurance analysis.
- Staff experienced in process scale-up R&D – Scientists and engineers trained and experienced in process development and scale up are a critical component to the program.

The approach to achieve the facility plan is to:

- Establish conceptual design of facility (CDR), Establish Design Build contract for facility.
  - Following the principals of the DOE Project Management Process.
- Establish interim scale-up labs during the design and construction of the facility.

- To allow for the scale up of battery materials to begin now.
- Prepare the environmental and safety plans and NEPA for the facility construction and interim labs.
- Begin work in interim labs to demonstrate that scaling is possible.

**Milestones:**

Materials Engineering Facility Construction

Milestone / Deliverable	Description	Date	Status
Milestone 1	Complete full facility design (CDR)	10/1/2010	COMPLETED 8/19/2010
Milestone 2	Award full facility construction contract	2/1/2011	COMPLETED 11/22/2010
Deliverable 1	Open interim facility (3 facilities) 2 opened 9/17/10, 1 opened 6/13/11	9/30/2010	COMPLETED 9/17/2010
Deliverable 2	Complete full facility construction	2/1/2012	
Deliverable 3	Open full facility	3/31/2012	

Interim Facilities and Equipment

Milestone / Deliverable	Description	Date	Status
Milestone 1	Interim facility equipment purchased & installed (3 facilities)	12/31/2010	COMPLETED 9/17/2010
Milestone 2	Production scale-up facility equipment purchased & accepted	12/31/2011	No Funding Allocated
Deliverable 1	Interim facility open (3 facilities) 2 opened 9/17/10, 1 opened 6/13/11	9/30/2010	COMPLETED 9/17/2010
Deliverable 2	Full facility open	3/31/2012	

**Financial data:**

Total project duration: 24 mo.

Construction funds for facility: \$3.3M

Capital equipment for process and analytical equipment: \$2.5M

**Progress towards construction milestones:**

- The environmental and safety plans and NEPA for the facility construction and interim labs have been approved.
- First Construction milestone completed – 8/19/2010
  - Jacobs Engineering drafted the Conceptual Design Report and Fire Protection Assessment
- Second Construction milestone completed – 11/22/2010
  - Design Build contract was awarded to Barton Malow
    - Preliminary design has been submitted
    - Final design has been submitted, reviewed and comments returned
    - Contractor is on schedule for delivery of Approved for Construction submittal
    - Demolition work has begun (floor saw cutting for drains)



**Figure 1.** Materials Engineering Facility Construction Site – June 21, 2011

**Progress towards interim facilities and equipment milestones:**

- Electrolyte materials scale up lab – fully operational
  - Equipment has been delivered and installed
- Battery materials analytical lab – fully operational
  - Equipment has been delivered and installed
- Cathode materials scale up – partially operational
  - 4L reactor system is fully functional
  - 20L reactor system is being installed
  - Powders hood has been ordered

### Capital equipment delivery status

Item	Status
Cilas Particle size analyzer	Delivered
Netzsch TGA-DSC-MS	Delivered
Agilent GC-MS	Delivered
Agilent ICP-MS	Delivered
Bruker FTIR	Delivered
Bruker XRD	Delivered
Powrex Vertical mixer	Delivered
NGK Batch furnace	Delivered
Nissin Particle classifier	Delivered
GL Filtration washer dryer 1	Delivered
GL Filtration washer dryer 2	Delivered
Physical Electronics XPS	Delivered

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number:** IV.E.1.1 (ARRAVT076)

**June, 2011 update**

**Project Title:** Process Development and Scale up of Advanced Cathode Materials

**Project PI, Institution:** Gregory Krumdick, Argonne National Laboratory

**Collaborators (include industry):**

Young-Ho Shin, Argonne National Laboratory

Kaname Takeya, Argonne National Laboratory

**Project Start/End Dates:** start: 10/1/2010; end: 9/30/2011

**Objectives:** The objective of this task is to conduct process engineering research for scale-up of Argonne's next generation high energy cathode materials. These materials will be based on NMC chemistries and may include lithium rich technology, layered-layered and possibly layered-spinel classes of cathode materials. The current multistep batch processes, capable of producing approximately 2 kg of material per week using a 4L reactor will be optimized and scaled up. Scaling up the process involves modification of the bench-scale process chemistry to allow for the semi-continuous production of material, development of a process engineering flow diagram, design of a mini-scale system layout, construction of the experimental system and experimental validation of the optimized process. A flexible processing system will be designed, built and operated to produce multiple batches for prototype testing. The design basis for scale-up will be based on a 20L reactor capable of producing a 10 kg batch of cathode materials per week.

**Approach:** Next generation cathode materials have been developed at the bench scale by a number of researchers focusing on developing advanced lithium ion battery materials. Process engineers will work with these researchers to gain an understanding of the materials and bench-scale processes used to make these materials and then scale-up and optimize the processes. Standard chemical engineering unit operations will be utilized to develop flexible systems that will be enable scaling of a wide range of next generation high energy cathode materials. Initial work will be based on NMC based processes, but may include lithium rich technologies and layered-layered and layered-spinel classes of cathode materials.

**Schedule and Deliverables:** Engineering and construction of a cathode materials mini-pilot scale system is expected to be completed by the end of FY 2011. Deliverables will include scaled materials for independent testing, publications and a topical report.

**Financial data:**

Total project duration: 12 mo.

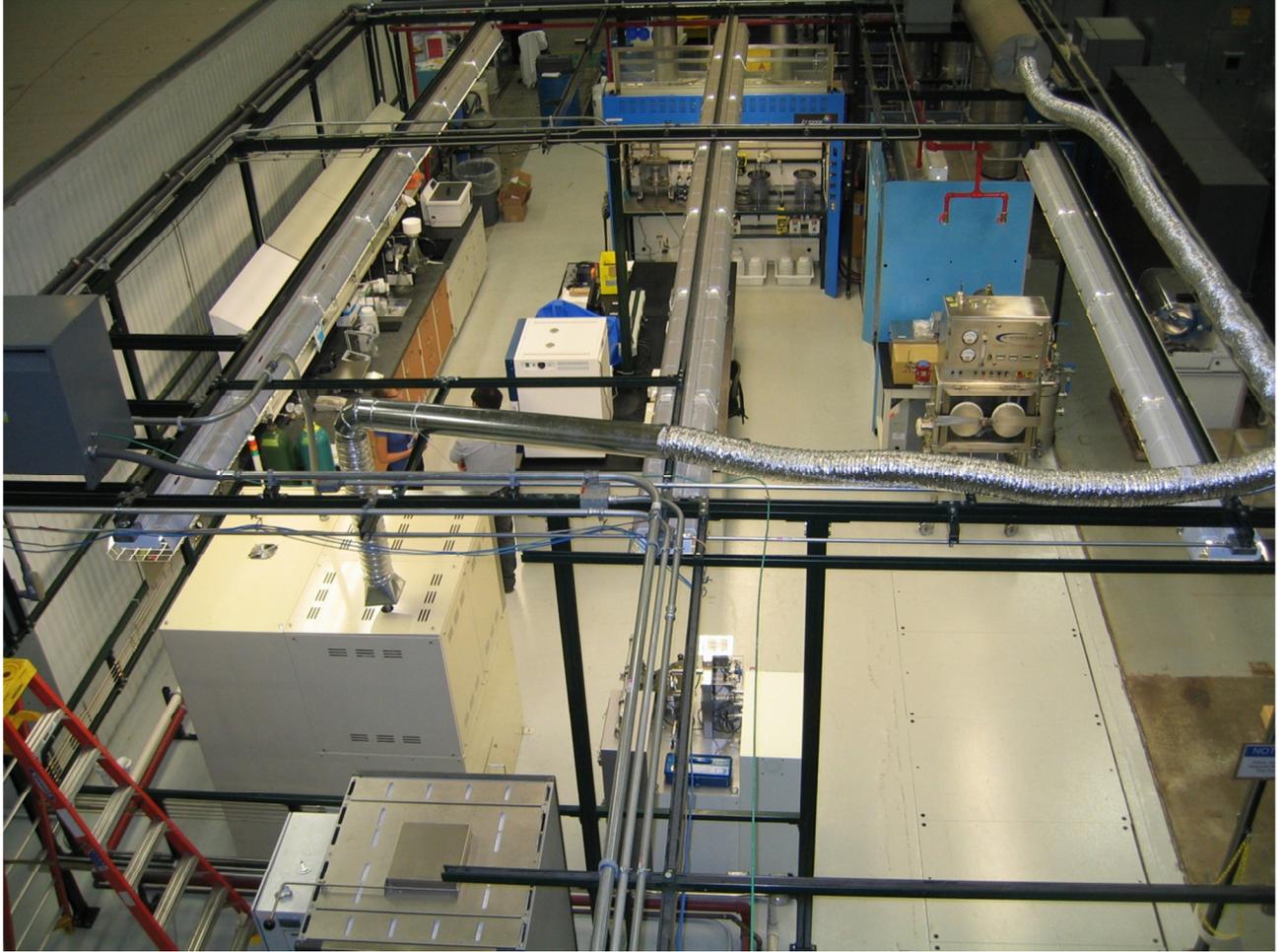
Staff and M&S: \$700K

**Progress towards deliverables:** A flexible processing system for the production of 10 kg batches of cathode materials was designed and all primary equipment for the processing unit operations has been ordered. Equipment has been delivered and is in the process of being installed. Young Ho Shin from Korea was selected to lead the scale up efforts and started work at Argonne on 5/2/2011. Young Ho has begun an assessment on the process engineering of the first cathode material selected to scale,  $\text{Li}_{1.14}\text{Mn}_{0.57}\text{Ni}_{0.29}\text{O}_2$ . Work Planning and Control documentation has been prepared for lab operations and a safety review of lab operations has been scheduled for mid-July.

Status of major equipment items for the interim cathode materials lab.

Item	Status
4L & 20L transparent co-precipitation reactors	Delivered
Filter-washer-dryer	Delivered
Vertical mixer	Delivered
Shaker mixer	Delivered
Batch furnace	Delivered
Rotor mill	Delivered
Jaw crusher	Delivered
Air classifier	Delivered
Heater circulator	Delivered
Compressor	Delivered
Powders hood	Ordered

**Figure 1. Interim Cathode Materials Lab, June 30, 2011**



## **TASK 1**

### **Battery Cell Materials Development**

**Project Number:** IV.E.1.2 (ARRAVT076)

**June, 2011 update**

**Project Title:** Process Development and Scale up of Advanced Electrolyte Materials

**Project PI, Institution:** Gregory Krumdick, Argonne National Laboratory

**Collaborators (include industry):**

Krzytof Pupek, Argonne National Laboratory

Trevor Dzwiniel, Argonne National Laboratory

**Project Start/End Dates:** start: 10/1/2010; end: 9/30/2011

**Objectives:** The objective of this task is to conduct process engineering research for scale-up of Argonne's new electrolyte and additive materials. Advanced electrolytes and additives are being developed to stabilize the interface of lithium ion batteries by forming a very stable passivation film at the carbon anode. Stabilizing the interface has proven to be key in significantly improving the cycle and calendar life of lithium ion batteries for HEV and PHEV applications. Up to this point, these advanced electrolytes and additives has only been synthesized in small batches. Scaling up the process involves modification of the bench-scale process chemistry to allow for the semi-continuous production of materials, development of a process engineering flow diagram, design of a mini-scale system layout, construction of the experimental system and experimental validation of the optimized process. The mini system will be assembled utilizing an existing synthesis reactor system. Electrolyte materials produced will be analyzed to confirm material properties and for quality assurance.

**Approach:** Scaling up of the electrolyte process for semi-continuous mini-pilot-scale production involves modification of the bench-scale process chemistry, development of a process engineering flow diagram, design of a mini-scale system layout, construction of the experimental system and experimental validation of the optimized process. Process engineers will work with these scientists to gain an understanding of the materials and bench-scale processes used to make these materials and then scale-up and optimize the processes. Standard chemical synthesis unit operations will then be utilized to develop flexible systems that will be enable scaling of a wide range of electrolyte/electrolyte additives. The system will be assembled utilizing an existing synthesis reactor system. Electrolyte/electrolyte additives materials produced will be analyzed to confirm material properties and for quality assurance

**Schedule and Deliverables:** Engineering and construction of an electrolyte materials mini-pilot scale system is expected to be completed by the end of FY 2011. Deliverables will include scaled materials for independent testing, publications and a topical report.

**Financial data:**

Total project duration: 12 mo.

Staff and M&S: \$300K

**Progress towards deliverables:**

Engineering and construction of an electrolyte materials lab was completed in November, 2010. Work has begun on the process scaling-up the following electrolyte materials:

Redox shuttles ANL-RS2 & ANL-RS6

Electrolytes 1NM3 & 2SM3

**Milestones:**

MILESTONE	DATE	STATUS	COMMENTS
Establish electrolyte scale-up lab	9/30/2010	Completed	
<b>ANL-RS2 – Scale up work completed</b>			Kilogram quantities available
Select CSE material to scale	10/1/2010	Completed	
Assess scalability of CSE process	10/18/2010	Completed	
WP&C documentation approved	11/1/2010	Completed	
Develop and validate scalable process chemistry (10g bench scale)	12/1/2010	Completed	
First process scale-up (100g bench scale)	12/23/2010	Completed	
Second process scale-up (1000g pilot scale)	03/04/2011	Completed 02/21/2011	1,576 g produced in a single batch, purity > 99.9%.
<b>1NM3 – Scale up work completed</b>			Kilogram quantities available
Select CSE material to scale	11/01/2010	Completed	
Assess scalability of CSE process	11/15/2010	Completed	
WP&C documentation approved	12/23/2010	Completed	
Develop and validate scalable process chemistry (10g bench scale)	02/18/2011	Completed	
First process scale-up (100g bench scale)	03/11/2011	Completed 03/09/2011	130 g produced in a single batch, purity >99.9%. Single fractional distillation delivered high purity product.
Second process scale-up (1000g pilot scale)	05/13/2011	Completed 05/17/2011	3,360 g produced in a single batch, purity >99.95%.
<b>2SM3 – Scale up work completed</b>			Kilogram quantities available
Select CSE material to scale	01/07/2011	Completed	
Assess scalability of CSE process	01/14/2011	Completed	
WP&C documentation approved	03/07/2011	Completed	

Develop and validate scalable process chemistry (10g bench scale)	04/28/2011	Completed	Requires double fractional distillation to achieve purity >99.5%. Difficult to handle in a small scale.
First process scale-up (100g bench scale)	05/20/2011	Completed 05/26/2011	Single fractional distillation yield material with purity 99.7 %. The reaction in 250 g (total reagents) scale exhibited very strong exothermic effect not observed on 10 g scale. The process needs to be re-designed.
Develop and validate scalable process chemistry (10g bench scale)	06/03/2011	Completed	A modified procedure has been developed that allows full control of thermal effect of the reaction. The new procedure was validated in 25g scale reaction.
Second process scale-up (1000g pilot scale)	06/24/2011	Completed 06/24/2011	1,477 g produced in a single batch, purity > 99.9%.
<b>ANL-RS6</b>			
Select CSE material to scale	01/07/2011	Completed	
Assess scalability of CSE process	01/14/2011	Completed	
WP&C documentation approved	03/14/2011	Completed	
Develop and validate scalable process chemistry (10g bench scale)	05/06/2011	Completed	Requires multiple crystallizations to achieve purity greater than 99%. We are still working to simplify/optimize the process.
First process scale-up (100g bench scale)	06/03/2011	Completed 05/26/2011	113 g produced in a single batch, purity 99.17%
Second process scale-up (1000g pilot scale)			The reagents for kilo scale reaction have been ordered.

# TASK 1

## Battery Cell Materials Development

**Project Number: 1.1A (ES015)**

**Project Title:** Engineering of high energy cathode material

**Project PI, Institution:**

Khalil Amine (Argonne National Laboratory)

**Collaborators (include industry):**

Huiming Wu (ANL); Ilias Belharouak (ANL); Ali Abouimrance (ANL); Y.K. Sun (Hangyang University); Toda Corporation, USA & Japan; BASF, USA & Germany; University of Colorado

**Project Start/End Dates:**

October 1, 2008 /September 30, 2014

**Objectives:**

Enable the Argonne high energy composite layered cathode  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNiO}_2$  for 40 miles PHEV

- Capacity of over 250 mAh/g
- High packing density ( 2.2~2.4g/cc)
- Good rate capability
- Excellent cycle and calendar life
- Excellent abuse tolerance

**Approach:**

- Optimize suitable composition and engineer the material to improve rate capability for PHEV applications
- Optimize synthesis process to obtain high packing density
- Explore surface modification to enable high rate and long cycle life at high voltage (4.6 V)

**Milestones:**

Characterize the Kg level Co-free high energy cathode material ( $\text{Li}_{1.2}\text{Ni}_{0.3}\text{Mn}_{0.6}\text{O}_{2.1}$ ) in detail.

Investigate the core reason why the material shows the good electrochemical performances with reproducibility. (On going)

Use BET, high solution SEM, etc to determine the primary particles and second particles, also the pore size, and pore density on a single second particles. Understand the relationship between the physical properties with electrochemical performance. Guide to improve the materials' tap density for further study. (On going)

Optimize the preparation process and material composition to improve the tap density of the cathode material (On going)

**Financial data:**

- Total project funding
- DOE share: \$300K

**PROGRESS TOWARD MILESTONES**

After developing Kg level high energy cathode material ( $\text{Li}_{1.2}\text{Ni}_{0.3}\text{Mn}_{0.6}\text{O}_{2.1}$ ) for the cell build, our focus was on understanding the core reason why the material shows the good electrochemical performances with reproducibility and building the relationship between the physical properties with electrochemical performance.

Some physical properties of cathode material has been tested and recorded in the Table 1 with data from the electrochemical performance. The surface area is much high (about  $5.5 \text{ m}^2/\text{g}$ ) than most of commercial layered cathode material, such as  $\text{LiCoO}_2$ , NMC. The average size of second particles is about  $10 \mu\text{m}$  (D50), but the tap density is about  $1.8 \text{ g}/\text{cm}^3$ . We know the second particles are formed by the primary particles (about  $100 \text{ nm}$ ). A cross section of one particle was performed to investigate any sign of void volume within the particle. Fig. 1 shows the cross section of the high energy material with a formula  $\text{Li}_{1.2}\text{Ni}_{0.3}\text{Mn}_{0.6}\text{O}_{2.1}$ . Over all, the inside of the particle is very uniform with high porosity and small primary particles of about  $14 \text{ nm}$ , These result explain the high surface are observed in these material as shown by BET. The calculated porosity on a single second particle is about 16.5%, which means we still have enough space to decrease the porosity and improve the tap density for the cathode material.

We are optimizing the composition (Lithium amount) to improve the tap density, this work is ongoing now. Furthermore, we still need to optimize the preparation process. The target is decrease the primary particle size and pore size inside of the second particles.

standard notation ( $\text{Li}_x\text{M}_y\text{O}_z$ )	$\text{Li}_{1.14}\text{Mn}_{0.57}\text{Ni}_{0.29}\text{O}_2$
composite notation	$0.33\text{Li}_2\text{MnO}_3 \cdot 0.67\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$
<b>PHYSICAL PROPERTIES</b>	$\text{Li}_{1.2}\text{Ni}_{0.3}\text{Mn}_{0.6}\text{O}_{2.1}$
particle size (micrometer)	D50: 10
BET ( $\text{m}^2/\text{g}$ )	5.5
Tap density ( $\text{g}/\text{cc}$ )	1.8
conductivity ( $\text{S}/\text{cm}$ )	
surface treatment	no
<b>Half cell</b>	
Average voltage (V)	3.66 (C/15), 3.64 (C/3)
Capacity (mAh/g)	238 (C/15), 217 (C/3)
first cycle efficiency (%)	86 (C/15)
energy density (Wh/kg)	874 (C/15), 791 (C/3)
voltage window (V)	4.6-2.0
capacity retention(%)	

Figure 1 Cross-section SEM images of  $\text{Li}_{1.2}\text{Ni}_{0.3}\text{Mn}_{0.6}\text{O}_{2.1}$

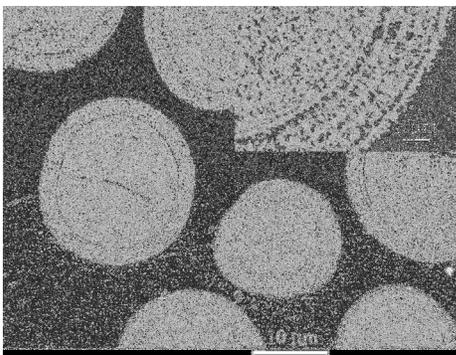


Table 1 The physical property and electrochemical performance of  $\text{Li}_{1.2}\text{Ni}_{0.3}\text{Mn}_{0.6}\text{O}_{2.1}$

**Publications, Reports, Intellectual property or patent application filed this quarter.  
(Please be rigorous, include internal reports--invention records, etc.)**

No publications, reports, or patents were submitted this quarter.

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number:** 1.1B (ES016)

**Project Title:** New High Energy Gradient Concentration Cathode Material

**Project PI, Institution:** Khalil Amine, Argonne National Laboratory

**Collaborators (include industry):** Gary Koenig and Ilias Belharouak, Argonne National Laboratory; Prof. Yang-Kook Sun, Hanyang University; ECPRO; TODA

**Project Start/End Dates:** October 1, 2008-September 30, 2014

**Objectives:** Develop a high energy cathode material for PHEV applications that provides over 200 mAh/g reversibly capacity, good rate capability, excellent cycle and calendar life, and good abuse tolerance. The cathode material capacities being investigated have capacities exceeding 200 mAh/g, which exceeds that of the NMC baseline.

**Approach:** Our approach is to develop a general synthetic method to tailor the internal composition gradient in cathode particles. This will be achieved by depositing a gradual composition gradient throughout particles to suppress stress during lithium intercalation and diffusion. We also aim to further enrich materials in Mn at the surface to enhance safety.

#### **Milestones:**

- a) Develop a model to predetermine the concentration gradient in particles produced via co-precipitation. This is necessary to have reproducibility of synthesized cathode materials. Complete.
- b) Develop a process for precursors with a gradient in transition metal composition that was enriched in manganese. Manganese enriched materials have shown excellent safety and cycle life. Complete.
- c) Demonstrate in a proof-of-principle experiment that precursors could be synthesized with predetermined compositional profiles. Complete.
- d) Demonstrate high capacity (>200 mAh/g) in final materials produced using the gradient precursors. On schedule
- e) Demonstrate that a tailored relative transition metal composition at the surfaces of gradient particles influences safety and cycle life. Complete.

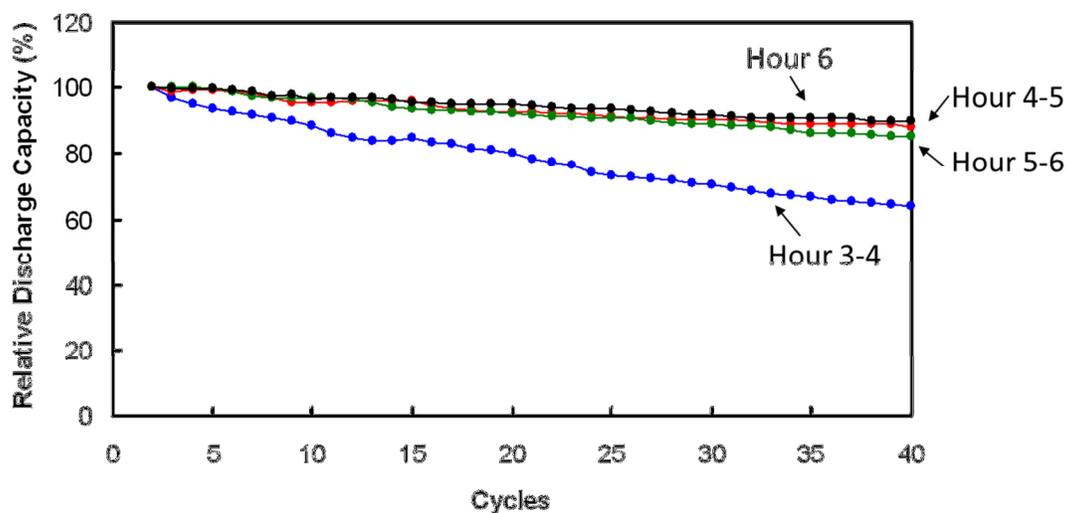
- f) Develop hydroxide co-precipitation process at Argonne and implement gradient concentration materials in hydroxide process to achieve higher tap density particles and larger relative core nickel concentrations for increased rate capability. On schedule.

**Financial data:** \$300K/year

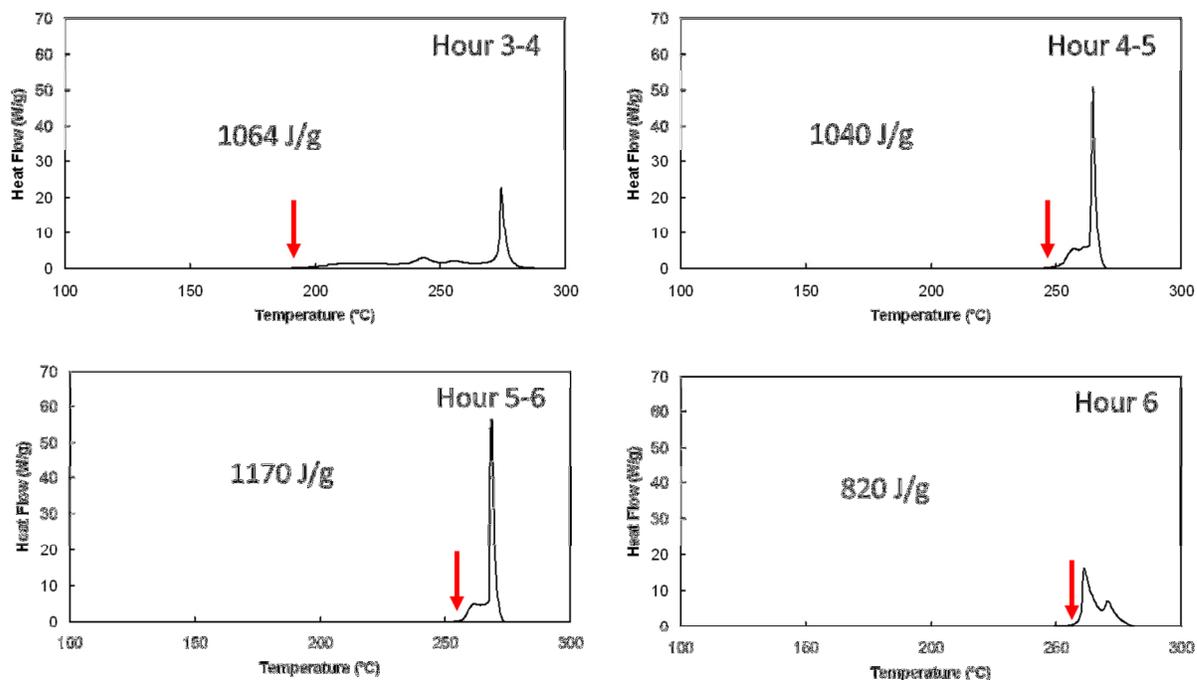
#### PROGRESS TOWARD MILESTONES (1 page)

- a) Model was completed in Q1.
- b) Initial synthesis was completed in Q1.
- c) Proof-of-principle gradient demonstration completed in Q2.
- d) Gradient materials routinely have ~190-200 mA-h/g capacity at low (~C/10) rates. Efforts are being made to further increase capacities and improve rate capability by moving to higher relative Ni compositions in the core of individual particles.
- e) The influence of having tailored gradient particles with a Mn-enriched particle surface on the cycle life and safety of a Li-ion battery was studied by using the discharge capacity fade in Li-ion half cells (Figure 1) and differential scanning calorimetry (DSC, Figure 2). Gradient precursors were collected at different times in the process (Hour 3-4, Hour 4-5, Hour 5-6, and Hour 6) and lithiated with the same Li-to-transition metal ratios. While all of these materials have gradients in internal composition (as confirmed with EDXS on internal particle cross sections), particles collected at later times have an increasingly thicker Mn-enriched shell. As can be seen in Figure 1, the particles from the earliest time (Hour 3-4) result in cathodes with a significant capacity fade relative to all the other materials, indicating that the Mn-enriched shell is not of a sufficient thickness. Also of note is that the particles collected at later times did not have progressively increasing capacity retentions, which indicates that there was not a significant advantage to going to an increasingly thick Mn-enriched shell beyond a certain threshold. DSC data was also consistent with a threshold thickness providing a significant safety advantage (Figure 2). The onset temperature for an exothermal event for the materials from the earliest collection time was at less than 200°C, while the materials from later collection times had similar onset temperatures that were all above 250°C. These DSC results are consistent with the Mn-enriched shell delaying the onset of an exothermal event, which indicates that they would have advantages in terms of safety in a Li-ion cell. The results above, when combined, indicate that a Mn-enriched shell provides cycle life and safety advantages to Li-ion cathodes, even when they are all gradient materials. The shell seems to have a threshold thickness beyond which increasing thickness does not provide additional benefits, meaning that fine-tuning of this shell thickness will be an important

design parameter. We are carefully studying our materials to determine the threshold thickness, and whether it varies with different relative transition metal compositions.



**Figure 1.** Relative discharge capacity during the first 40 cycles of Li half cells with cathodes comprised of active materials that were made using gradient precursors collected during different times (Hour 3-4 (blue), Hour 4-5 (red), Hour 5-6 (green), Hour 6 (black)). All final cathode materials had the same relative Li-to-transition metal ratios, and later times correspond to a thicker Mn-enriched shell.



**Figure 2.** Differential scanning calorimetry (DSC) profiles for gradient cathode materials collected during different times. All final cathode materials had the same relative Li-to-transition metal ratios, and later times correspond to a thicker Mn-enriched shell. DSC was performed on cathodes harvested from Li-half cells charged to 4.6 V.

f) We are currently developing the hydroxide co-precipitation process to add the possibility of increasing Ni compositions in the core. We have preliminary synthesis of a precursor with nominal composition  $\text{Ni}_{0.9}\text{Mn}_{0.1}(\text{OH})_2$  which will serve as our baseline material.

**Publications, Reports, Intellectual property or patent application filed this quarter.**

## TASK 1

### Battery Cell Materials Development

**Project Number:** 1.1F (ES017)

**Project Title:** Development of High-Capacity Cathode Materials (Design and Evaluation of Novel High Capacity Cathode Materials)

**Project PI, Institution:** Christopher Johnson, Argonne National Laboratory

**Collaborators (include industry):**

Prashant Kumta, University of Pittsburgh  
Sun-Ho Kang, Argonne National Laboratory  
Wenquan Lu, Argonne National Laboratory  
Michael Thackeray, Argonne National Laboratory  
Industrial Collaborator – unnamed at this point

**Project Start/End Dates:** October 2008 / September 2014

**Objectives:** The project objective is to design, evaluate and screen high-capacity cathodes that will provide high-energy for transportation batteries. Novel electrode materials are needed in order to advance the field and push the limits of state-of-art technology into new cathode systems. To satisfy the energy requirements of batteries for 40 mile all-electric mode in plug-in hybrid electric vehicles (PHEV), we are focusing on novel systems that can maximize the available energy density, but also try to utilize inexpensive materials, such as inherently safe oxides of Fe V, and Mn that possess high-capacities, and operate at low voltage to promote long life.

**Approach:** In this approach we utilize the high capacity  $\text{MnO}_2$  (308 mAh/g),  $\text{Li}_{1.2}\text{V}_3\text{O}_8$  (LVO; 372 mAh/g), and  $\text{V}_2\text{O}_5$  (442 mAh/g) charged cathode materials together with a high lithium containing material,  $\text{Li}_5\text{FeO}_4$  (LFO) that are co-blended in the cathode. The LFO is used to prelithiate the anode during the first charge, which introduces cyclable lithium into the cell. When these cells are combined with high-capacity Si anode materials, then high-energy density cells are possible > 400 Wh/kg. We will optimize LFO, the evaluation of dopants, coatings, and gain understanding of the release of lithium during the first charge. In addition, the electrochemistry of  $\text{LiV}_3\text{O}_8$  (LVO),  $\text{V}_2\text{O}_5$ , and  $\text{MnO}_2$  will be improved. The optimization of the charged LVO and  $\text{MnO}_2$  material is important to improve the energy density and power of the cathode.

**Milestones:** Materials will be produced and tested that will show progressively improved properties as the project moves forward.

(a) Synthesize new materials, September 2011, (on-schedule)

(b) Characterize electrochemical properties of synthesized materials, September 2011, (on-schedule)

- Demonstrate high-rate of 200 mAh/g @ C rate, from LVO or  $\text{V}_2\text{O}_5$ ; September 2011, (on-schedule)

- Employ LFO as an additive in conventional composite ‘layered-layered’ cathodes to improve full-cell coulombic efficiency over long-term cycling.

(c) Evaluate Si anodes to pair with blended LFO and composite ‘layered-layered’ cathodes in full cell, June 2011, (delayed until September 2011)

- Li half cells with Si-C composites were completed. Data is necessary for cell balancing with LVO-LFO cathodes. This will be done in the next quarter. The first source of Si-C did not work in Li half cells, so we are procuring Argonne-developed Si-graphene.

(d) Initiate measurement of thermal properties of charged material in DSC, June 2011, (delayed until September 2011)

**Financial data:** \$300K

### PROGRESS TOWARD MILESTONES

(a) 1. While LFO is an interesting lithium-releasing material with high capacity above 800 mAh/g, there are other high-lithia ( $\text{Li}_2\text{O}$ ) containing oxides such as  $\text{Li}_8\text{CeO}_6$  (734 mAh/g), and  $\text{Li}_8\text{SnO}_6$  (792 mAh/g). These fall into a class of known structure types, and have been successfully synthesized (XRD of  $\text{Li}_8\text{SnO}_6$  below (Fig. 1)). Electrochemical testing is underway. An objective is to make these materials directly reversible as high-capacity cathodes (no oxygen loss).

2.  $\text{CrVO}_4$  will be synthesized as a charged cathode and will be evaluated in a Li half cell. Theoretical capacity for 3 multiple electrons transferred (V +5 to +3; Cr +3 to +2) is 482 mAh/g.

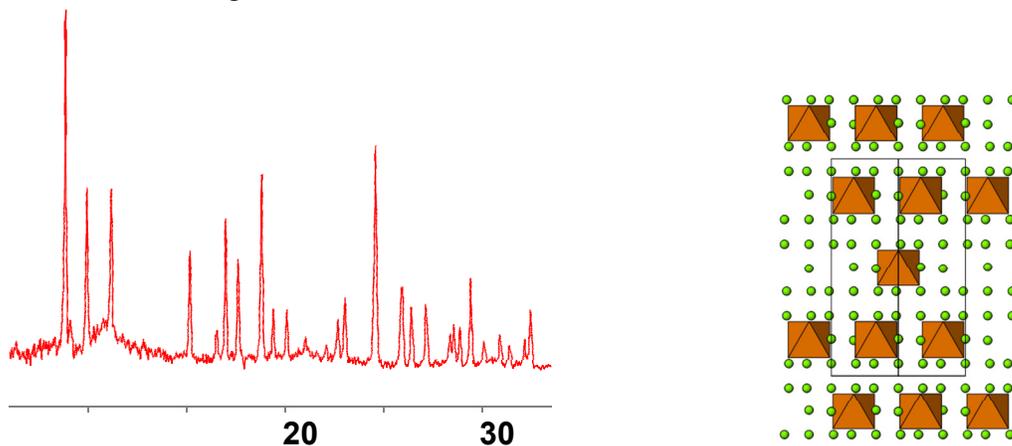


Fig. 1. (left) XRD pattern of  $\text{Li}_8\text{SnO}_6$ , (right) structural perspective of  $\text{Li}_8\text{SnO}_6$  (Li – green;  $\text{SnO}_6$  orange octahedral); many channels are available for Li diffusion.

(c) Initial cycling with Li/Si anode half-cells showed poor performance and cannot be used in the cell chemistry. Cycling results of a Si-graphene/LFO-LVO or Si-graphene/LFO-composite ‘layered-layered’ cell will be reported in the next quarterly.

(d) Thermal properties of the charged materials synthesized in milestone (a) are planned, once a system is chosen and optimized.

**Publications, Reports, Intellectual property or patent application filed this quarter.**

No presentations, publications, reports, or patents were submitted this quarter.

## TASK 1

### Battery Cell Materials Development

**Project Number:** 1.1G (ES019)

**Project Title:** Development of High-Capacity Cathode Materials with Integrated Structures

**Project PI, Institution:** Sun-Ho Kang, Argonne National Laboratory

**Collaborators (include industry):**

Donghan Kim, Argonne National Laboratory  
Keving Gallagher, Argonne National Laboratory  
Michael Thackeray, Argonne National Laboratory  
Yang Shao-Horn, Massachusetts Institute of Technology  
Chris Carlton, Massachusetts Institute of Technology  
Hanwha Chemical

**Project Start/End Dates:** October 2009/September 2014

**Objectives:** The objective of this work is to develop Li- and Mn-rich cathode materials with integrated structures that promise low cost and good thermal stability and show improved first-cycle efficiency (>85 %) while maintaining high capacity (~240 mAh/g) and good rate capability ( $\geq 200$  mAh/g at C/1 rate). The target performance values are 240 mAh/g of reversible capacity with >85 % first cycle efficiency. If successfully developed, energy density of a cell coupled with graphite would be ~460 Wh/kg (assuming 300 mAh/g graphite, 3.7 V nominal).

**Approach:** Layer-layer composite cathode materials,  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$  (M=Ni,Co,Mn) deliver high capacity of ~240 mAh/g. However, the materials have drawbacks such as low first-cycle efficiency and poor power performance. We will continue to exploit the concept of embedding spinel component into the layer-layer structure to improve the first-cycle efficiency and rate performance. We will also continue to explore the blending of  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$  with high-power cathode to improve the impedance characteristics at low SOC. We have chosen  $\text{LiFePO}_4$  as the high-power cathode. We have extended our research to studying of voltage decaying and Mn dissolution issues of  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ .

**Milestones:** Project deliverables and decision points. Milestones should clearly show progress towards your project objectives, including overcoming issues, and should clearly support achieving a significant improvement in cell energy density, safety, and/or cost. If your material or couple has known issues, please address some or all of them in your milestones.

- (a) Chemical composition optimization (on schedule)
- (b) Characterization of integrated structural feature using analytic techniques (on schedule)
- (c) Blending of  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$  with high power cathode materials (on schedule)
- (d) Identification of performance degradation mechanism of  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$  materials (on schedule)

**Financial data:** \$400K

## PROGRESS TOWARD MILESTONES

### (a) Summary of work in the past quarter related to milestone (a).

In order to improve the structural stability and thermal safety characteristics of  $\text{Li}_x\text{Mn}_{0.65}\text{Ni}_{0.35}\text{O}_y$  chemistry, cation- and anion substitutions have been tried using magnesium and fluorine, respectively. Among various cathode compositions,  $\text{Li}_{1.25}\text{Mn}_{0.65}\text{Ni}_{0.33}\text{Mg}_{0.02}\text{O}_y$  material showed the best rate capability and highest initial capacity with improved first-cycle efficiency (89%), as shown in Figure 1a. However, cycling performance test revealed some capacity fading as shown in Figure 1b. Surface modifications using  $\text{Li-Ni-PO}_4$  and  $\text{AlF}_3$  are being carried out to enhance the cycling performance. In addition, electrochemical characterizations in a full cell configuration are being carried out.

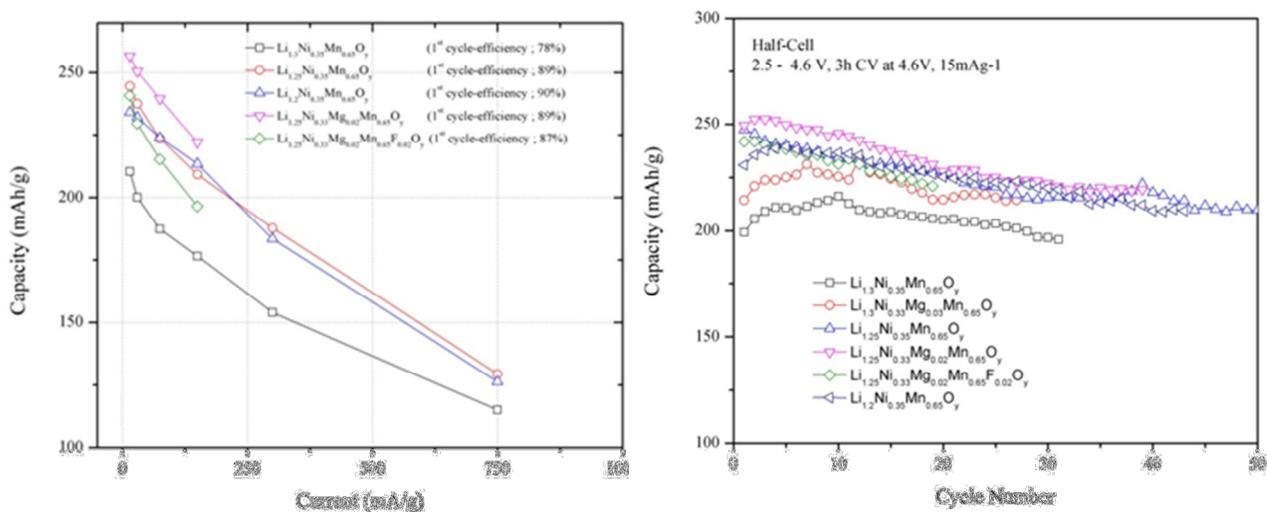


Figure 1. (a) rate capability test, and (b) cycle performance of lithium half cells containing  $\text{Li}_x\text{Mn}_{0.65}\text{Ni}_{0.35-x}\text{Mg}_{x0.02-y}\text{F}_y$  cathode materials.

### (b) Summary of work in the past quarter related to milestone (b).

Structural changes in  $\text{Li}_{1.2}\text{Mn}_{0.75}\text{Ni}_{0.25}\text{O}_y$  after extensive cycling (50 cycles) between 4.95 and 2.0 V in a lithium cell have been studied using high-resolution transmission electron microscope (HRTEM), the result of which is shown in Figure 2. According to the Fast

Fourier Transform (FFT) analysis, the significant portion of the material has  $\text{LiM}_2\text{O}_4$ -type spinel structure. Additionally, Figure 2 shows that the lattice fringes in the material are highly distorted. It is clear that the material contains several dislocations. The inset in Figure 2 highlights one the dislocation. The burgers vector corresponds to the  $(111)_{\text{Spinel}}$  planes of the material, possibly indicating oxygen loss.

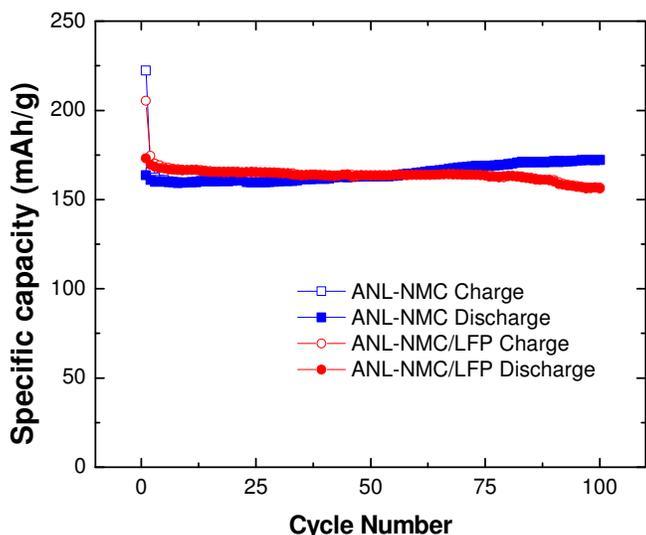


Figure 2. A phase contrast TEM image of cycled cathode material

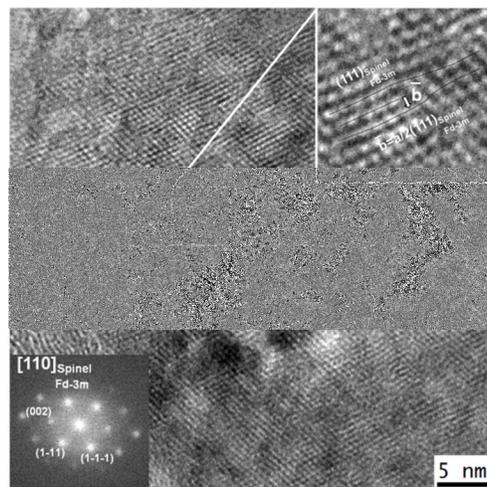


Figure 3. Full cell cycling at C/1 rate, 2-4.5V, C/10 cutoff at 4.5V.

**(c) Summary of work in the past quarter related to milestone (c)**

Cycling performance of the blended cathode (80 wt% of ANL-NMC with 20 wt%  $\text{LiFePO}_4$ ) was examined in a full cell configuration using Mag-10 anode. The cells were cycled at 1C rate at 2.0-4.5 V. The blended cathode cell exhibits good cycling stability. With significantly enhanced pulse power characteristics at low SOC (reported previously) and good cycling performance, the concept of blending of high-capacity and high-power cathodes with proper active voltage windows has been proved to work. Further optimization is under way.

**(d) Summary of work in the past quarter related to milestone (d)**

Various experiments to identify the origin of voltage decay of  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$  cathodes upon cycling have been carried out. High-voltage ( $>4.4$  V vs.  $\text{Li/Li}^+$ ) and high-temperature cycling accelerated the voltage decay. Correlation between voltage decay and structural change during cycling will be examined using various analytic techniques.

**Publications, Reports, Intellectual property or patent application filed this quarter. (Please be rigorous, include internal reports--invention records, etc.)**

K. G. Gallagher et al., “ $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$  blended with  $\text{LiFePO}_4$  to achieve high energy density and pulse power capability,” J. Power Sources, in press.

# TASK 1

## Battery Cell Materials Development

**Project Number: 1.1C (ES020)**

**Project Title:** Developing High Capacity, Long Life anodes

**Project PI, Institution:** K. Amine, and A. Abouimrane, Argonne National Laboratory

**Collaborators (include industry):**

- D. Dambournet, I. Belharouak, (CSE/ANL).
- P. Chupas, K. Chapman, Y. Ren Advanced Photon Source, (APS/ANL).
- Z. Fang (University of Utah).
- FMC, Northwestern University,

**Project Start/End Dates:** October 1<sup>st</sup>, 2009/September 2014

**Objectives:**

- Develop new advanced high energy anode materials with long life and improved Safety for PHEV and EV applications
- Develop a low cost synthesis methods to prepare high energy anodes
- Full structural and electrochemical characterizations of the prepared anode materials.
- Demonstrate the applicability of these anodes in half and full cells systems.

**Approach:**

- $\text{MO-Sn}_x\text{Co}_y\text{C}_z$  ( $\text{MO}=\text{SiO}, \text{SiO}_2, \text{SnO}_2, \text{MoO}_2, \text{GeO}_2$ ) anode materials were selected for investigation as high energy anode based on the following criteria:
  - $\text{Sn}_x\text{Co}_y\text{C}_z$  alloys are known to provide a capacity of 400-500mAh/g for hundreds of cycles.
  - MO anodes are known to provide more than 1000 mAh/g with poor cycleability.
  - The formation of  $\text{Sn}_x\text{Co}_y\text{C}_z$  and MO composite could lead to the increase in the capacity, reduce the amount of cobalt in the material and improve the cycleability as  $\text{Sn}_x\text{Co}_y\text{C}_z$  play the role of buffers against the volume expansion of MO.
  - This anode system is more safer than the graphite and possess low potentials in the range of 0.3-0.75V (expect high voltage cells when combined with high cathodes)

**Milestones:**

- 1- Explore the  $\text{M}_a\text{O}_b\text{-Sn}_x\text{Co}_y\text{C}_z$  system where  $\text{M}=\text{Si}, \text{Sn}, \text{Mo}, \text{Ge}$  (in term of electrochemistry, material structure investigation, binders effect); (2011-2012)
- 2- Prepare materials with at least 600 mAh/g capacity with cycleability more than hundred cycles (2011-2012);

- 3- Identify the best material in term of cost, voltage output, cycling performance, and deliverable capacity (2011-2012);
- 4- Prepare a scalable amount of anode material ( ~ 200 grams) with 600 mAh/gas capacity for 100 cycles (2012);
- 5- Deliver a full cell battery (coin cell configuration) with a least 420 Wh/kg energy density (when combined with NMC) (2013-2014);

**Financial data:** Project budget/year, amount subcontracted if appropriate  
300K/year

### PROGRESS TOWARD MILESTONES (1 page)

**(a) Summary of work in the past quarter related to milestone (1)**

First, we study various compositions of oxide alloys composite  $M_aO_b-Sn_xCo_yC_z$  system (where M= Si, Sn, Mo, Ge). These materials deliver a capacity between 400 and 900 mAh/g. For example, we investigate the lithium insertion and de-insertion in 50wt% SiO-50wt%  $Sn_{30}Co_{30}C_{40}$  anode material. A quasi plateau located below 0.6V appears in the first discharge curve (Figure 1) and a capacity of about 1430 mAh/g was obtained under 50mA/g current rate. During the discharge a capacity of 90 mAh/g was observed before reaching the voltage of 0.75V which can be attributed to the formation solid electrolyte interphase (SEI) layer, which consists of ethyleneoxide- based oligomers, LiF,  $Li_2CO_3$ , and lithium alkyl carbonate ( $ROCO_2Li$ ). The first cycle charge discharge reversibility of this material is about 79%. After the 1<sup>st</sup> cycle, the curves of each cycle are similar in shape, indicating that the electrode reactions become more reversible and a capacity ~ 700 mAh/g was sustained for hundred cycles under the current rate of 300mAh/g. (En schedule)

**(b) Summary of work in the past quarter related to milestone (2)**

We have successfully prepared three anodes materials based  $M_aO_b-Sn_xCo_yC_z$  (where MO: SiO,  $MoO_3$ ,  $GeO_2$ ). A capacity between 600 and 800 mAh/g for more than 100 cycles was sustained (see Fig. 1&2). The three anode materials exhibit a tap density of 1.9, 2.6 and 2.7 g/cc which is much higher than that of the graphite (0.8-1.1g/cc). A higher volumetric energy density is expected for batteries based this new anode system.

**(c) Summary of work in the past quarter related to milestone (3)**

Composite materials based  $SnO_2$  and SiO oxide have a low cost raw materials but in the case of  $SnO_2-Sn_xCo_yC_z$  system the voltage profile is much higher than SiO- $Sn_xCo_yC_z$  system. Composite material based  $MoO_3$  delivers a higher capacity with medium cost price. We are planning to prepare SiO- $Sn_xFe_yC_z$  as anode material. The use of iron instead of cobalt will reduce the anode material price. (En schedule) “The progress to this milestone is achieved at 50%”

Provisional patent application “Anode materials for lithium batteries: ANL-IN-10-013”

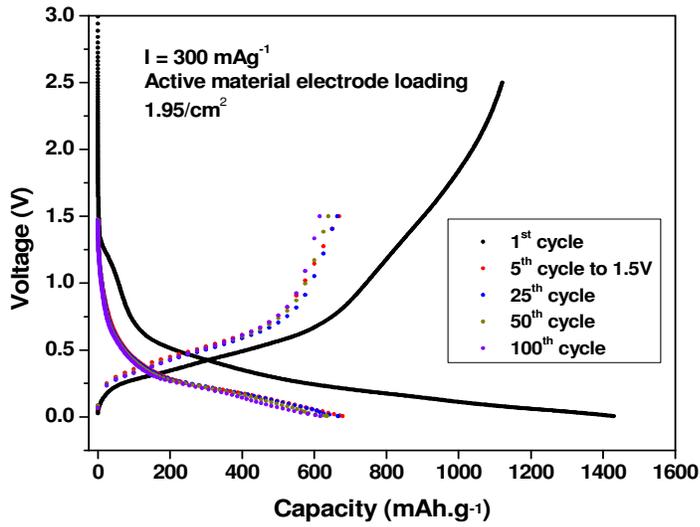


Figure 1: Voltage profile of Li/50wt% SiO-50wt% Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub> half-cell at the 1<sup>st</sup>, 5<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup> and 100<sup>th</sup> cycles.

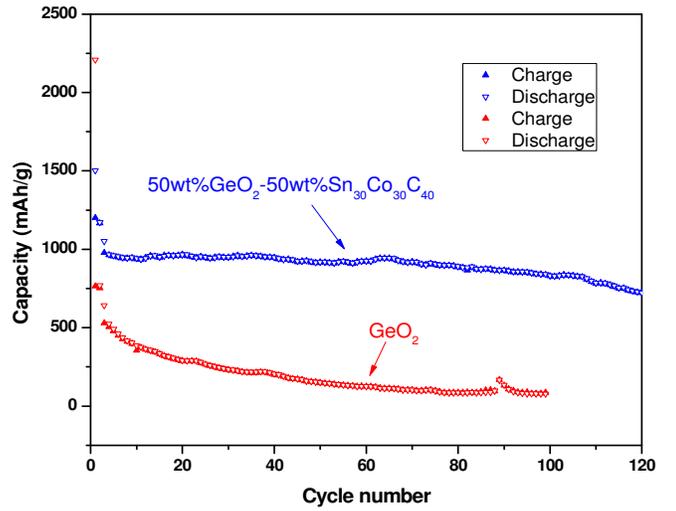


Figure 2: cycleability of Li/50wt% GeO<sub>2</sub>-50wt% Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub> and Li/GeO<sub>2</sub> half-cell.

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number:** 1.1I (ES022)

**Project Title:** Develop Improved Methods of Making Intermetallic Anodes

**Project PI, Institution:** Andrew Jansen, Argonne National Laboratory

**Collaborators (include industry):**

Dileep Singh, Argonne National Laboratory

Jack Vaughey, Argonne National Laboratory

Wenquan Lu, Argonne National Laboratory

**Project Start/End Dates:** October 2008 / September 2014

**Objectives:** The objective of this work in FY2011 is to produce an intermetallic electrode that can achieve over 200 cycles while retaining 80% of its initial capacity. Likely solutions to these problems will involve the proper choice of binders and methods of controlling the particle size and morphology during production, and during repeated cycling.

**Approach:** The general approach is to explore alternative methods of making electrodes based on intermetallic alloys, which suffer from severe volume expansion upon lithiation. Earlier work in this task showed that the choice of binders and additives in the electrode did not improve the poor cycle life. This work was done for a relatively large particle of 10 microns. Efforts were then directed to determine the ideal particle size to minimize particle cracking during cycling. This work indicated that the alloy particle must be submicron in size. A contract was established with Wildcat Discovery Technologies to make  $MCu_5Sn_5$  alloy powders that are near 400 nm. These powders were received in the summer of 2010. This year's effort is devoted to characterizing the performance of these smaller particles in new electrode studies.

**Milestones:**

- (a.) Determine influence of lithium on mechanical properties of alloy. February 2011, (Complete)
- (b.) Determine influence of particle size on cycle life, September 2011, (On schedule)
- (c.) Obtain cycle life of 200 cycles with 80% capacity retention, September 2011, (Delayed)

**Financial data:** \$300K

### **PROGRESS TOWARD MILESTONES**

**(a) Summary of work in the past quarter related to milestone (a).**

This work was completed; see Q1 report.

**(b) Summary of work in the past quarter related to milestone (b)**

More half cells were made with electrodes based on the new smaller alloys from Wildcat Discovery Technologies. While the primary particle size is near 400 nm, many of these particles are agglomerated into secondary particles. More energetic milling and mixing is being used to break up these particles during the slurry making process. Work is centered on the  $\text{Cu}_5\text{Sn}_6$  and  $\text{FeCu}_5\text{Sn}_5$  alloys.

**(c) Summary of work in the past quarter related to milestone (c)**

Variations in the amount of carbon black and PVDF binder are being studied. The influence of the lower cutoff voltage is also being assessed. To date, no effective means of extending the cycle life to 200 cycles has been achieved. It is hoped that improved slurry processing and electrode composition and processing will improve the cycle life. But, it is possible that the poor cycle life could be due to the larger surface area (higher activity) of the smaller particles, or the primary particles are still too large, or copper displacement is preventing re-alloying. Effort will also be directed to other classes of binders (cellulose and polyimide).

**Publications, Reports, Intellectual property or patent application filed this quarter. (Please be rigorous, include internal reports--invention records, etc.)**

A. N. Jansen, J. A. Clevenger, A. M. Baebler, J. T. Vaughey, "Variable temperature performance of intermetallic lithium-ion battery anode materials", *J. Alloys and Compounds*, **509**(13), 4457 – 4461 (2011).

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number:** 1.1H (ES023)

**Project Title:** Development of Novel Electrolytes & Additives for PHEV Applications

**Project PI, Institution:** Daniel Abraham, Argonne National Laboratory

**Collaborators (include industry):**

G. Cheng, Argonne National Laboratory

B. Lucht, University of Rhode Island

Alex Wei, Purdue University

Kang Xu, Army Research Laboratory

**Project Start/End Dates:** October 2008 / September 2014

**Objectives:** The performance, calendar-life, and safety characteristics of Li-ion cells are dictated by the nature and stability of the electrolyte and the electrode-electrolyte interfaces. Desirable characteristics for these electrolytes include stability in the 0 to 5V vs. Li range, excellent lithium ion conductivity, wide temperature stability range, non-reactivity with the other cell components, non-toxicity and low cost. Our goal is to develop novel electrolytes and electrolyte additives to meet the cost, calendar life and safety requirements of batteries for PHEV applications.

**Approach:** Our approach is to (i) develop novel electrolytes that include glycerol carbonate (GC), and derivatives thereof, (ii) examine a wide variety of electrolyte additives that can provide multiple benefits in terms of cell life, reduction of initial capacity loss, and better safety by protecting both electrode surfaces, (iii) investigate the use of ionic liquids, and mixtures of ionic liquids and carbonate solvents, to enable high-safety batteries. Our approach is to synthesize a series of GC derivatives, and systematically examine their performance in lithium-ion cells aiming to gain an understanding of the relationship between organic functional groups and cell performance. In addition, systematic examination of other novel compounds, which can be used as electrolyte solvents or as additives to conventional electrolytes, is being pursued based on studies of their oxidation and reduction potentials, binding affinity to Li-ion, etc.

**Milestones:**

- (a.) Synthesize the methyl ester, methyl carbonate, and other derivatives of glycerol carbonate, September 2011, (on schedule)
- (b.) Examine/evaluate the performance/cycling behavior of the GC-derivative compounds, both as co-solvents and as electrolyte additives, September 2011, (on schedule)

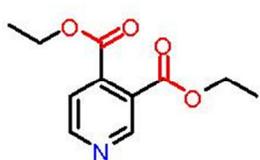
(c.) Continue evaluation of family of heteroaromatics substituted carboxylic ester-based compounds that have been identified as electrolyte additives, September 2011, (on schedule)

**Financial data:** \$300K

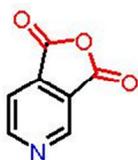
## PROGRESS TOWARD MILESTONES

We have successfully prepared several derivatives of GC, including methyl ester, alkyl ethers etc.. We have demonstrated that both the oxide-positive and graphite-negative electrodes can be cycled in methyl ester derivative of GC. Tests of other alkyl ether derivatives of GC are currently in progress. We have also identified the next generation of GC derivatives that show promise either as electrolyte solvents or as additives, and have established collaboration with Prof. Alexander Wei at Purdue University, to synthesize these compounds.

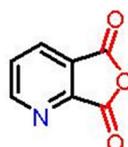
Furthermore, we have discovered a new family of heteroaromatics substituted carboxylic ester-based compounds that have been identified as electrolyte additives. Some examples of N-containing heteroaromatic-substituted carboxylic esters are shown below.



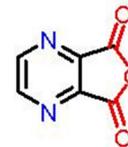
3,4-diethyl pyridine  
Carboxylate (3,4-DEPC)



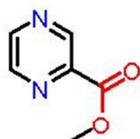
3,4-pyridinedicarboxylic  
anhydride (3,4-PyDCA)



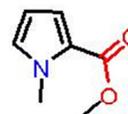
3,4-pyridinedicarboxylic  
anhydride (2,3-PyDCA)



2,3-pyrazinedicarboxylic  
anhydride(2,3-PzDCA)



Methyl-2-Pyrazinecarboxylate (2-MPzC)



Methyl-1-methylpyrrole-2-carboxylate (MPC)

The effect of the above compounds, as additives to the Gen2 electrolyte, is shown below.

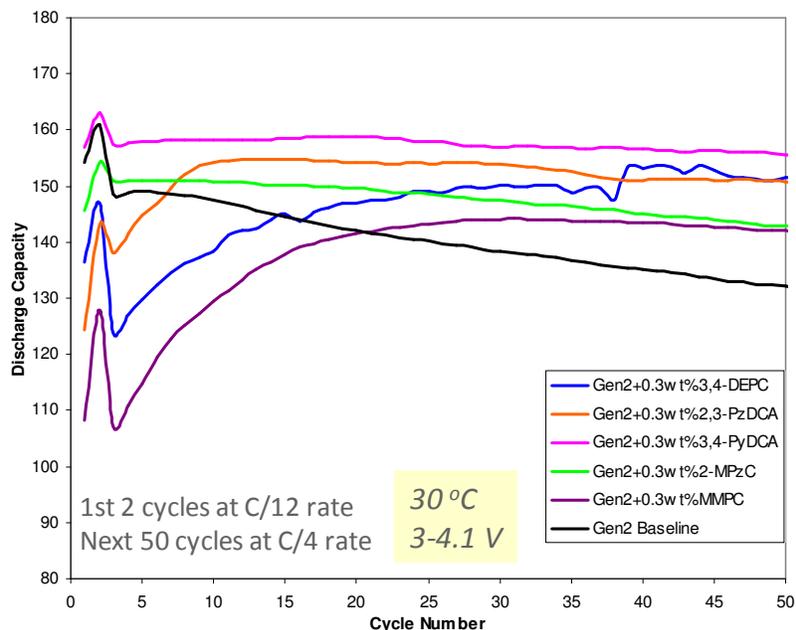


Fig. 1. Cycling data from NCA(+)//Graphite(-) cells comparing effects of various additives with that of the baseline Gen2 electrolyte.

Small amounts (0.3 wt%) of 3,4-DEPC, 2,3-PzDCA, 3,4-PyDCA, 2-MPzC and MMPC addition to Gen2 electrolyte improves capacity retention. 3,4-PyDCA seems to be the best candidate in the group in terms of minimal initial capacity loss. Surprisingly, the cell with 0.3wt% 2,3-PyDCA showed an abnormal first cycle and died during the second cycle; this effect was reproducible and was observed in three different cells. It is evident that small structural changes cause significant impact on initial cycling behavior. The SEI generated by the various additives is expected to bear signatures of the corresponding lithium-additive complexes. Stronger SEI/Li<sup>+</sup> interaction may cause higher impedance. The “initial induction period” reflects changes in SEI characteristics during cycling.

**Publications, Reports, Intellectual property or patent application filed this quarter.**

No publications, reports, or patents were submitted this quarter.

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number:** ES024

**Project Title:** High Voltage Electrolytes for Li-ion Batteries

**Project PI, Institution:** T. Richard Jow/Kang Xu, U.S. Army Research Laboratory

**Collaborators (include industry):** Dr. Jan L. Allen, Dr. Oleg Borodin, Dr. Arthur von Cresce, Army Research Laboratory; Y. F. Lam, U. of Maryland; Grant Smith, Lidan Xing, U. of Utah; K. Amine, D. Abraham, D. Dees, ANL

**Project Start/End Dates:** June 2008 / May 2011

**Objectives:** Develop high voltage electrolytes that enable the operation of 5 V Li Ion Chemistry. With a 5-V high voltage electrode materials and a capacity similar to that of the state-of-the-art cathode, the energy density will be increased more than 25% than that of the state-of-the-art Li-ion batteries for HEV/PHEV. Our other objective is to identify factors that limit the charge-discharge rate of Li-ion batteries especially at low temperatures.

**Approach:** Three approaches were taken.

1. Sulfone based solvents approach
  - a. Synthesize and characterization of unsymmetric sulfones for lower viscosity
  - b. Synthesize and characterization of unsaturated sulfones for higher reactivity with potential for forming protective layer on cathodes
2. Carbonate based solvents approach
  - a. Search additives that would decompose and form protective interface on cathode
  - b. Formulate electrolytes using fluorinated phosphate ester as additives for the state-of-the-art electrolytes
3. Computational effort
  - a. Understand oxidative stability of solvents/electrolytes
  - b. Understand reactive pathways of additives and electrolytes
  - c. Develop ability to predict and design electrolyte components

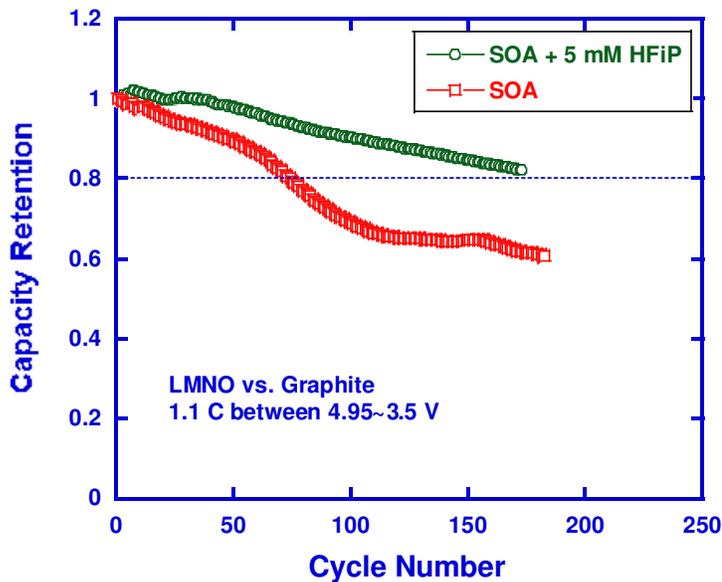
**Milestones:**

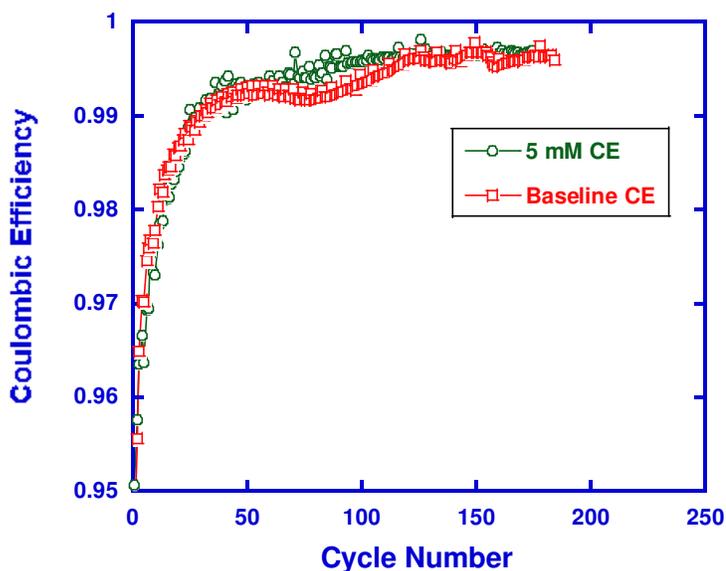
- (a) Explored additives that passivates cathode surfaces at high voltages, (Dec 2010)
- (b) Diagnostic studies: surface characterization and SEI chemistry (Dec 2010)
- (c) Evaluate electrolytes with additives in both half cells and full cells (May 2011)
- (d) Understand reactive pathways of electrolyte components through computational effort (May 2011)
- (e) Surface characterization and SEI chemistry studies (May 2011)

**Financial data:** \$200,000/year

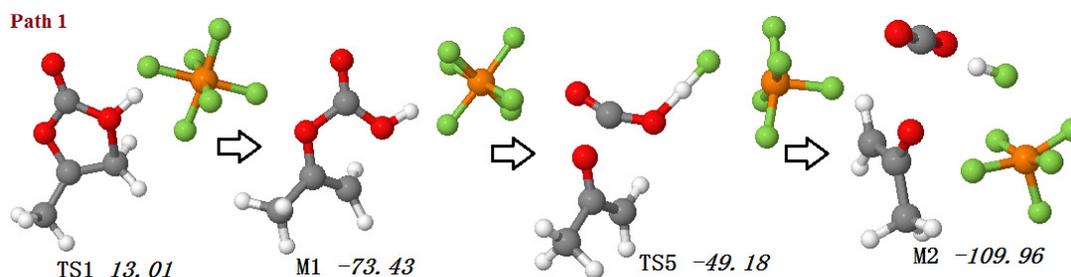
## PROGRESS TOWARD MILESTONES

(a) **Cycling of high voltage electrolytes in full cells made of high voltage  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode and graphite anode:** Both  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode and graphite anode were provided by Argonne National Laboratory. The state-of-the-art electrolyte made of 1.2 m  $\text{LiPF}_6$  in EC:EMC (3:7 wt. ratio) was used as a baseline electrolytes. The high voltage electrolyte was made of the baseline electrolyte with 5 mM HFiP as an additive. The capacity retention and the coulombic efficiency of a full cell cycling at room temperature in both the baseline and the high voltage electrolyte are shown in the following two figures, respectively. The capacity retention for the cell cycled in high voltage electrolyte is 80% after 175 cycles. This is an improvement over 60% capacity retention for the cell cycled in the baseline electrolyte. The coulombic efficiency of the cycling reaches 99.5% for the cell cycling in the high voltage electrolyte.





(b) **Solvent oxidative decomposition reactions in the presence of anions from Density Functional Calculations:** The presence of anion influences the oxidation stability limits (see Q1 2011 quarterly report). Investigation of the influence of anions ( $\text{PF}_6^-$ ,  $\text{ClO}_4^-$ ) on the oxidative decomposition reaction of propylene carbonate (PC) were completed using density functional theory (DFT) in collaboration with Lidan Xing and Grant Smith from University of Utah. DFT calculations were performed in gas phase (dielectric constant  $\epsilon=1$ ) and in the implicit solvent using polarized continuum model (PCM) with  $\epsilon=20.5$ . It has been found that the presence of  $\text{PF}_6^-$  and  $\text{ClO}_4^-$  anions significantly reduces PC oxidation stability, stabilizes the PC-anion oxidation decomposition products and changes the order of the oxidation decomposition paths. The primary oxidative decomposition products of PC- $\text{PF}_6^-$  and PC- $\text{ClO}_4^-$  were  $\text{CO}_2$  and acetone radical that would react to form an oligo(ethylene carbonate). Formation of HF and  $\text{PF}_5$  was observed upon the initial step of PC- $\text{PF}_6^-$  oxidation while  $\text{HClO}_4$  formed during oxidation of PC- $\text{ClO}_4^-$ . The most probable reaction path for the initial decomposition of the oxidized PC/ $\text{PF}_6^-$  complex using PCM,  $\epsilon=20.4$  is shown below along with the energies in kJ/mol for the transition states (TS1 and TS5) and minima (M1 and M2) It illustrates formation of  $\text{CO}_2$  and acetone radical that would recombine with another acetone radical to form ethylene carbonate dimer. The pathway with the second lowest barrier for the PC- $\text{PF}_6^-$  oxidative ring opening resulted in a formation of fluoro-organic compounds suggesting that these toxic compounds could form at elevated temperatures under oxidizing conditions. Detailed discussion of these results is given in the manuscript submitted to *J. Phys. Chem. A* Xing, L.; Borodin, O.; Smith, G. D.; Li, W. "A Density Function Theory Study of the Role of Anions on the Oxidative Decomposition Reaction of Propylene Carbonate".



**Publications, Reports, Intellectual property or patent application filed this quarter.**

1. Xu, K., Cresce, A. "Interfacing electrolytes with electrodes in Li-ion batteries." *J. Mater. Chem.*, **21**, 2011, 9849, 10.1039/c0jm04309e.
2. Xu, K., Cresce, A. Electrolytes in support of 5V Li ion chemistry, US PTO application #12952354.
3. Allen, J. L.; Jow, T. R.; Wolfenstine, J., "Improved Cycle Life of Fe-substituted LiCoPO<sub>4</sub>", to appear in *J. Power Sources*, 2011.
4. Xing, L.; Borodin, O.; Smith, G. D.; Li, W. "A Density Function Theory Study of the Role of Anions on the Oxidative Decomposition Reaction of Propylene Carbonate," submitted to *J. Phys. Chem. A*.

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number:** 1.1D (ES025)

**Project Title:** Development of Advanced Electrolyte Additives

**Project PI, Institution:** Zhengcheng (John) Zhang, Argonne National Laboratory

**Collaborators (include industry):** Khalil Amine, Lu Zhang, Yan Qin, Zonghai Chen, and Ali Abouimrane

**Project Start/End Dates:** 10/01/2008~09/30/2014

**Objectives:** The objective of this work is to develop new electrolytes and associated additives that could bring additional features to the state-of-the-art lithium-ion battery electrolyte to meet the requirements of EV and PHEV applications.

**Approach:** The approach for development novel electrolyte and additives consists of three phases. The first phase is to screen and evaluate novel electrolyte and additive candidates using DFT theory and relative sample test procedures. Certain criteria are needed to make the screening list. In the second phase, thorough evaluation and mechanism analysis will be conducted to the promising candidates to gain the insights of their superior performance. In the third phase, based on the knowledge earned, new design of promising electrolytes and additives should be proposed and organic synthesis will be involved to make these compounds. Evaluations will certainly give feedback to our designs and thus leading to modifications and even more new designs.

#### **Milestones**

- (a) Generate screening list based on the semi empirical rules and establish valid and quick screening procedures, Mar. 2011, (Complete).
- (b) Run the screening procedures to find promising additives that could bring superior features to lithium-ion cell system, Sep. 2012, (On schedule).
- (c) Evaluate and analyze the interesting additives to further understand the possible mechanism and give feedbacks to screening list, Sep. 2012, (On schedule).

**Financial data:** \$200K/FY2011

PROGRESS TOWARD MILESTONES (1 page)

#### **(a) Summary of work in the past quarter related to milestone (a).**

Degree of unsaturation of chemical structures is regarded as one criterion for making screening list. Chemicals with high degree of unsaturation always have cyclic structure and double bonds, which could be beneficial to the SEI formation process. The screening process consists of formation, impedance measurements, and fast cycle test at elevated

temperature. A series of new maleic anhydride derivatives and a bicycle structure compound, as shown in Fig 1, have been screened.

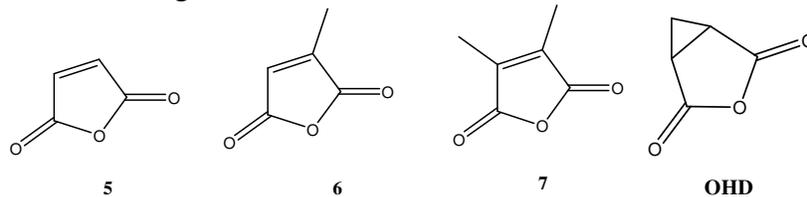


Fig.1, Structures of succinic anhydride derivatives (5-7) and bicycle structure additive (OHD)

**(b) Summary of work in the past quarter related to milestone (b)**

Fig 2 is the impedance results of cells containing none or 1w% of A5-A7. Despite the previous reported improved capacity retention, the impedance, however, is increased at least twice compared with that of Gen 2 cells without additive either before or after the cycling. Fig 4 is the differential capacity profiles of the cells with none and 1w% additive OHD. No perceptible difference could be observed. With 0.2 w% of OHD additive, the cell showed dramatic improvements in capacity retention. In this case, the impedance of the cell with OHD additive (Fig 5) remains almost similar to that with no additive. This result is very encouraging since the DSEI formed during the polymerization of OHD is thin but yet very effective.

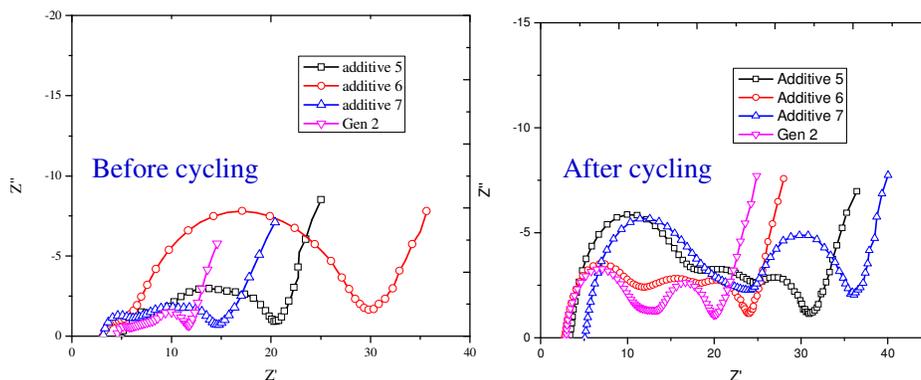


Fig 2. AC impedance profile of MCMB-1028/Li<sub>1.1</sub>[Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>]<sub>0.9</sub>O<sub>2</sub> coin cells in 3E7EMC/PF12 with or without 1 wt% additives(5-7). The cells were charged to 3.8 V. The charge rate was 1C.

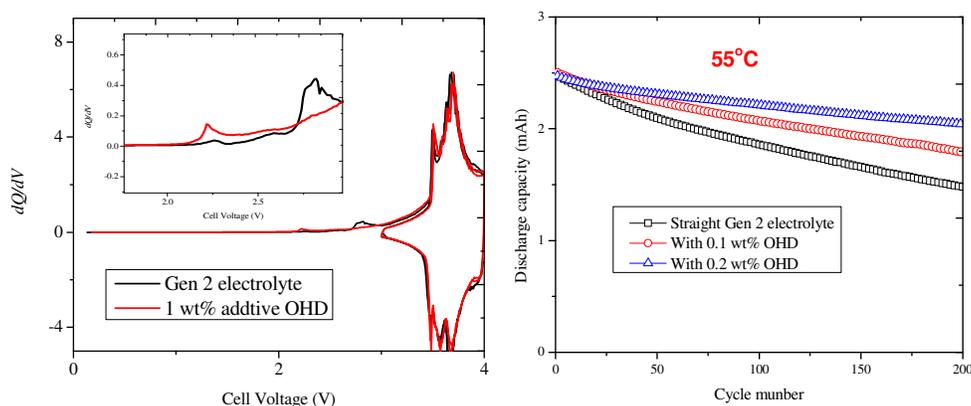


Fig 4. (a) Differential capacity profiles of MCMB/NCM cells, electrolyte: 1.2M LiPF<sub>6</sub> EC/EMC 3/7+1% additive; (b) Capacity retention of MCMB/NCM cells cycled between 2.7 and 4.2V at 55 °C in electrolyte of 1.2M LiPF<sub>6</sub> EC/EMC 3/7 with no and various amount of additive OHD.

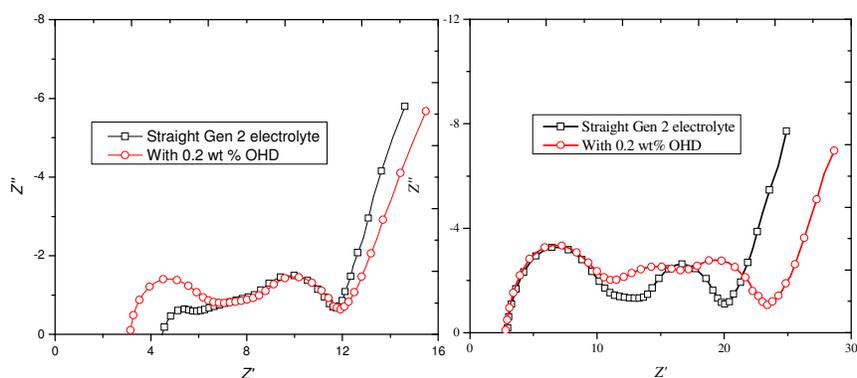


Fig 5. AC impedance profiles of MCMB-1028/Li<sub>1.1</sub>[Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>]<sub>0.9</sub>O<sub>2</sub> coin cells in 3E7EMC/PF12 with none or 0.2 wt% additive (OHD). The cells were charged to 3.8 V. The charge rate was 1C.

### (c) Summary of work in the past quarter related to milestone (c)

A new OHD additive was isolated and its performance was investigated in a full cell. This additive when added in the electrolyte at 0.2wt%, shows significant improvement in cycling at 55°C compared to the cell without additive. Unlike the maleic anhydride derivatives, the new OHD additive shows no significant increase the initial interfacial impedance of the cell.

We will focus in the next quarter to understand and characterize the SEI film obtained from the polymerization of this additive.

**Publications, Reports, Intellectual property or patent application filed this quarter. (Please be rigorous, include internal reports--invention records, etc.)**

Lu Zhang, Zhengcheng Zhang, Khalil Amine, “NON-AQUEOUS ELECTROLYTE FOR LITHIUM-ION BATTERIES”, invention report, ANL-IN-10-39;

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number: ES026**

**Project Title: Electrolytes for Use in High Energy Li-Ion Batteries with Wide Operating Temperature Range**

**Project PI, Institution: Marshall Smart, Jet Propulsion Laboratory, California Institute of Technology**

**Collaborators (include industry):** (1) University of Rhode Island (Prof. Brett Lucht) (Analysis of harvested electrodes, on-going collaborator), (2) Argonne Nat. Lab (Khalil Amine) (Source of electrodes, on-going collaborator), (3) LBNL (John Kerr, Li Yang) (Evaluation of novel salts), (4) Loker Hydrocarbon Institute, USC (Prof. Surya Prakash) (Fluorinated Solvents and novel salts), (5) A123 Systems, Inc. (Electrolyte development, on-going collaborator), (6) Quallion, LCC. (Electrolyte development, on-going collaborator), (7) Yardney Technical Products (Electrolyte development, on-going collaborator), (8) Saft America, Inc. (Collaborator, industrial partner under NASA program), (9) NREL (Smith/Pesaran)(Supporting NREL in model development by supplying data).

**Project Start/End Dates:** Start Date: Oct 1, 2009, Projected End Date: September 30, 2014

#### **Objectives:**

- Develop a number of advanced Li-ion battery electrolytes with improved performance over a wide range of temperatures (-30 to +60°C) and demonstrate long-life characteristics (5,000 cycles over 10-yr life span).
- Improve the high voltage stability of these candidate electrolyte systems to enable operation up to 5V with high specific energy cathode materials.
- Define the performance limitations at low and high temperature extremes, as well as, life limiting processes.
- Demonstrate the performance of advanced electrolytes in large capacity prototype cells.

**Approach:** The development of electrolytes that enable operation over a wide temperature range, while still providing the desired life characteristics and resilience to high temperature (and voltage) remains a technical challenge. To meet the proposed objectives, the electrolyte development will include the following general approaches: (1) optimization of carbonate solvent blends, (2) use of low viscosity, low melting ester-based co-solvents, (3) use of fluorinated esters and fluorinated carbonates as co-solvents, (4) use of novel “SEI promoting” and thermal stabilizing additives, (5) use of alternate lithium based salts (with USC and LBNL). Many of these approaches will be used in conjunction in multi-component electrolyte

formulations (i.e., such as the use of low viscosity solvents and novel additives and salts), which will be targeted at improved operating temperature ranges while still providing good life characteristics.

The candidate electrolytes are characterized using a number of approaches, including performing ionic conductivity and cyclic voltammetry measurements, and evaluating the performance characteristics in experimental ~ 400 mAh three electrode cells. Initially, cells will be fabricated with either (a) MCMB /LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> or (b) graphite/LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> electrode couples, and later evaluated with high voltage systems. Other chemistries can be evaluated depending upon availability from collaborators. In addition to performing charge/discharge characterization over a wide range of temperatures and rates on these cells, a number of electrochemical characterization techniques will be employed, including: (1) Electrochemical Impedance Spectroscopy (EIS), (2) DC linear (micro) polarization, and (3) Tafel polarization measurements. The electrochemical evaluation in proven three electrode test cells enables electrochemical characterization of each electrode (and interface) and the identification of performance limiting mechanisms. Electrodes are easily harvested from these test cells and samples will be delivered to collaborators (i.e., URI and LBNL). In addition to evaluating candidate electrolytes in spirally wound experimental cells, studies will be performed in coin cells, most notably in conjunction with high voltage cathode materials.

Performance testing of prototype cells containing candidate advanced electrolytes will be performed and evaluated under a number of conditions (i.e., assessment of wide operating temperature capability and life characteristics). JPL has on-going collaborations with a number of battery vendors and also has the capabilities to perform extensive testing. Typical prototype cells that will be considered include (i) Yardney 7 Ah prismatic cells, (ii) Quallion prismatic cells (0.300Ah size), and (iii) A123 2.2 Ah cylindrical cells. Cells will be procured and obtained through on-going collaborations

**Milestones:**

<b>Month/Year</b>	<b>Milestone</b>
<b>Sept. 2011</b>	Milestone A: Prepare and characterize experimental laboratory cells containing Gen-2 electrolytes and identify performance limiting characteristics at different temperatures.
<b>Sept. 2011</b>	Milestone B: Demonstrate improved performance of first generation electrolyte over a wide temperature range compared with the baseline electrolyte (i.e., 1 M LiPF <sub>6</sub> in EC:DEC 1:2), especially at -30°C, in experimental and prototype cells

**Financial data:**

Total project funding:

- 875K total (~ 175K/year)
- Contractor share = 0K

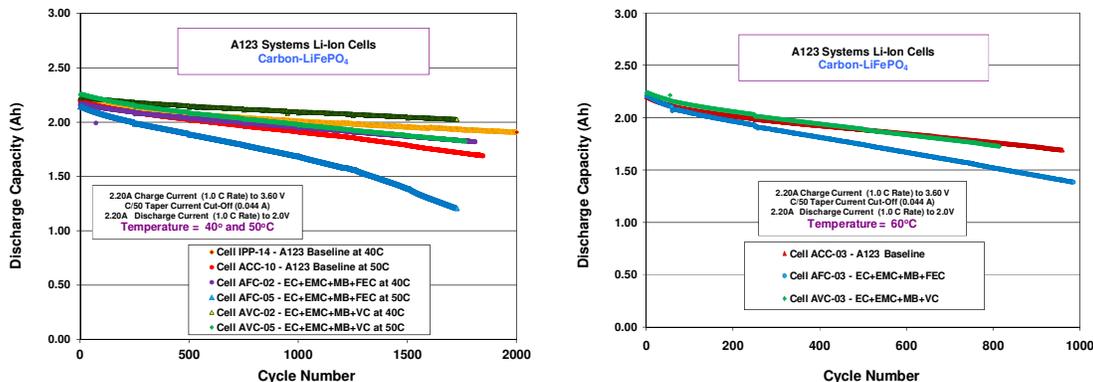
Funding received:

- FY'09 = 0 K
- FY'10 = 175K
- FY'11 = 175K

**Accomplishments and Progress toward Milestones:**

We continue to investigate wide operating temperature range electrolytes that contain based solvent, such as methyl propionate and methyl butyrate. To these systems we have employed the use of electrolyte additives with the intent of providing improving the high temperature resilience and cycle life performance, while still delivering improved low temperature performance. We have focused upon formulations consisting of  $\text{LiPF}_6$  in ethylene carbonate (EC) + ethyl methyl carbonate (EMC) + methyl propionate (MP) or methyl butyrate (MB) (20:20:60 vol %) with and without electrolyte additives, including lithium oxalate, mono-fluoroethylene carbonate (FEC), vinylene carbonate, and lithium bis(oxalate) borate (LiBOB). The identification of these esters, as well as the optimization of their concentrations in EC+EMC-based solutions, was based upon studies with MCMB-LiNiCoO<sub>2</sub> and LiNiCoAlO<sub>2</sub> systems.

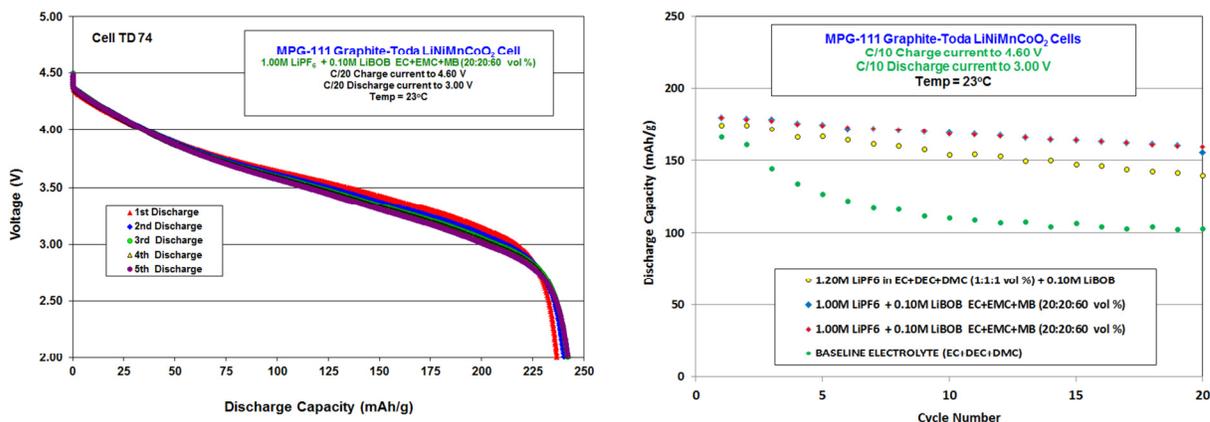
In the recent quarter, we have continued to evaluate the performance of a number of A123 cells that have incorporated methyl butyrate-based electrolytes investigated under the program (i.e., specifically 1.20M  $\text{LiPF}_6$  in EC+EMC+MB (20:20:60 vol %) + 4% FEC and 1.20M  $\text{LiPF}_6$  in EC+EMC+MB (20:20:60 vol %) + 2% VC). As reported previously, we have performed discharge rate characterization over a wide temperature range (-60 to +20°C) using a number of rates (ranging from C/20 to 11.4C rates). Excellent performance was demonstrated with over 90% of the room temperature capacity being delivered at -40°C at a 11.2C discharge rate (57-59 Wh/kg under these conditions). These systems have also been observed to support up to 10C rates at temperatures as low as -50°C and C rates at -60°C. We also continue to evaluate the cycle life performance of these systems up to temperatures as high at 60°C. Excellent performance has been obtained at ambient temperature. When cells were evaluated at 40°C and 50°C, as shown in Fig 1a, good performance was observed, with the cells containing the 1.20M  $\text{LiPF}_6$  in EC+EMC+MB (20:20:60 vol %) + 2% VC electrolyte behaving comparably to the baseline system, and the FEC containing variant displaying increased capacity fade. This same trend was also displayed when cells were cycled at 60°C, as illustrated in Fig.1b. As shown, the cells containing the MB-based electrolyte with VC delivered comparable performance to the baseline chemistry.



**Figure 1:** Cycle life performance of LiFePO<sub>4</sub>-based A123 cells containing various electrolytes at +40°C and +50°C (Figure A) and +60°C (Figure B). C rate charge and discharge (2.0V to 3.60V).

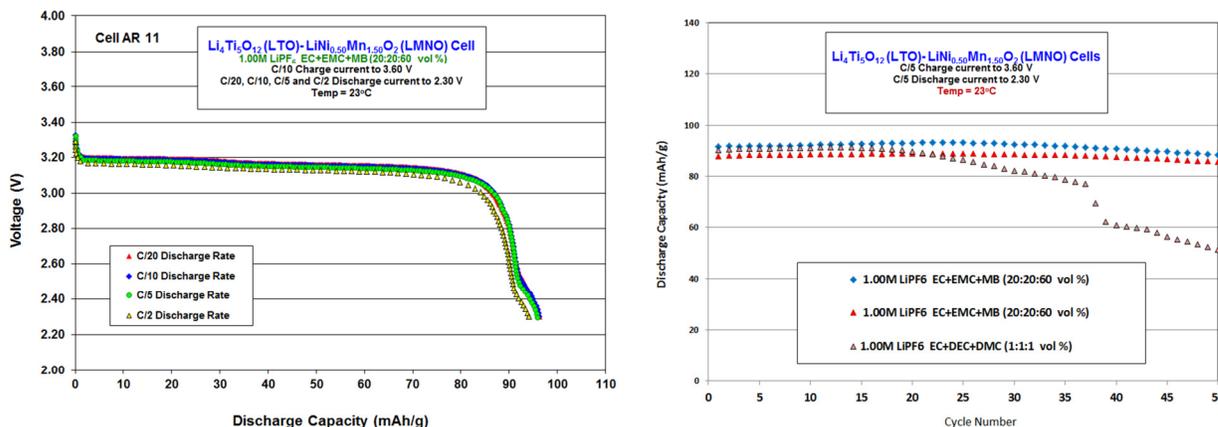
Continued efforts have been focused upon investigating the effect of using additional lithium electrolyte salts in conjunction with LiPF<sub>6</sub> to serve as electrolyte additives, with the intent of improving the high temperature resilience of the cells. Specifically, we have studied electrolytes that contain LiBOB, lithium hexafluoro isopropoxide, and a lithium malonate borate-based salt (LiDMMDFB) developed by LBNL and the URI (Li Yang, John Kerr, and Brett Lucht). With MCMB-LiNiCoO<sub>2</sub> cells containing these electrolytes, we have performed the electrochemical evaluation (i.e., EIS, linear and Tafel polarization), discharge rate characterization, and exposure to high temperature. These electrolyte additives have been investigated in various formulations, including both ester based and all carbonated-based electrolytes.

In the recent quarter, we have focused upon evaluating various ester-based electrolytes in conjunction with high voltage cathode materials. For example, we have investigated the performance of a number of electrolytes with the MPG-111 graphite/Toda LiNiMnCoO<sub>2</sub> system. It should be noted that emphasis was placed upon utilizing commonly used carbonaceous anode materials, rather than lithium metal, to establish the compatibility of the electrolyte systems. As shown in Fig. 2, good reversibility was observed with methyl butyrate-based electrolytes, with over 230 mAh/g capacity delivered (based on active cathode material). When a number of cells were subjected to 100% DOD cycling using C/10 rates (4.60V to 3.0V), cells containing a methyl-butyrate based solution containing LiBOB as an electrolyte additive outperformed the baseline all carbonate-based blend.



**Figure 2:** Formation cycling at 23°C of a cell containing MPG-111 graphite and Toda LiNiCoMnO<sub>2</sub> (C/20 rates, 2.0 to 4.60V) (Fig. 2A) and 100% cycle life performance of MPG-111 graphite and Toda LiNiCoMnO<sub>2</sub> cells containing various electrolytes (Fig. 2B).

Recent work has also focused upon developing a number of wide operating temperature range electrolytes that operate well with the high voltage LiNi<sub>0.50</sub>Mn<sub>1.50</sub>O<sub>2</sub> (LMNO) cathode. A number of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO)/LiNi<sub>0.50</sub>Mn<sub>1.50</sub>O<sub>2</sub> (LMNO) cells were fabricated with electrodes provided by Argonne National Lab. Preliminary results with a methyl butyrate electrolyte solutions are very encouraging, with comparable formation characteristics and rate capability observed, as shown in Fig. 3A. Furthermore, when the cells were subjected to 100% cycle life testing, the cells containing the methyl butyrate-based electrolyte outperformed the all carbonate-based blend, as shown in Fig. 3B. Current efforts are focused upon evaluating the effectiveness of utilizing various electrolyte additives with these electrolytes to improve the cycle life performance of this system, while also providing the capability to operate over a wide temperature range. Furthermore, these efforts will also be extended to other high voltage systems recently received from Argonne (i.e., LiNiCoMnO<sub>2</sub>) and similar materials obtained from in-house programs.



**Figure 3:** Formation cycling at 23°C of a cell containing MPG-111 graphite and Toda LiNiCoMnO<sub>2</sub> (C/20 rates, 2.0 to 4.60V) (Fig. 2A) and 100% cycle life performance of MPG-111 graphite and Toda LiNiCoMnO<sub>2</sub> cells containing various electrolytes (Fig. 2B).

Future work will involve continuing the investigation of the use of additives in conjunction with ester-based wide operating temperature range electrolytes evaluated with different electrode chemistries, with a focus upon (i) assessing other candidate additives, (ii) studying the high temperature and cycle life degradation modes, (iii) correlating electrochemical trends with performance, and (iv) identifying performance limiting aspects at extreme temperatures. Future work will also focus upon the use of fluorinated esters, especially with high voltage systems, including trifluoroethyl butyrate, ethyl trifluoroacetate, and trifluoroethyl acetate. Effort will also be devoted to demonstrating these systems in prototype cells, such as in LiFePO<sub>4</sub>-based cells (A123), LiNiCoAlO<sub>2</sub> cells (Quallion), and LiNiCoO<sub>2</sub> cells (Yardney).

## Publications:

1. N. Leifer, M. C. Smart, G. K. S. Prakash, L. Gonzalez, L. Sanchez, P. Bhalla, C. P. Grey, and S. G. Greenbaum, “<sup>13</sup>C Solid State NMR Study of SEI Formation in Carbon Lithium Ion Anodes Cycled in Isotopically Enriched Electrolytes Suggests Unusual Breakdown Products”, *J. Electrochem. Soc.*, **158** (5), A471-A480 (2011).
2. M. C. Smart and B. V. Ratnakumar, “Effect of Cell Design Parameters on Lithium Plating in Lithium-Ion Cells”, *J. Electrochem. Soc.*, **158** (4), A379-A389 (2011).
3. F. C. Krause, M. C. Smart, R. V. Bugga, and G. K. S. Prakash, “The use of fluorinated electrolyte in lithium-ion batteries for improved safety in human-rated aerospace and terrestrial applications”, 241<sup>st</sup> American Chemical Society National Meeting and Exposition, Anaheim, CA, March 28, 2011.
4. M. C. Smart, B. V. Ratnakumar, W. C. West, and E. J. Brandon, “Primary and Secondary Lithium Batteries Capable of Operating at Low Temperatures for Planetary Exploration”, Lunar Superconductor Applications, 1<sup>st</sup> International Workshop, Houston Texas, March 3-5, 2011.

5. M. C. Smart and B. V. Ratnakumar, "Electrolytes for Wide Operating Temperature Range Lithium-Ion Cells", US Patent Application, 13/161,387, June 15, 2011.

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA).

## TASK 1

### Battery Cell Materials Development

**Project Number:** ES027

**Reporting Period:** FY 2011 Q3

**Project Title:** Novel Phosphazene Compounds for Enhancing Electrolyte Stability and Safety of Lithium-ion Cells

**Project PI, Institution:** Kevin L. Gering, INL

**Collaborators (include industry):** Michael T. Benson (INL), Mason K. Harrup (INL), Harry W. Rollins (INL), Sergiy V. Sazhin (INL), Khalil Amine (ANL), Chris Orendorff (SNL), Princess Energy Systems, Dow Chemical

**Project Start/End Dates:** Jan. 2009/Ongoing

**Objectives:** For 2011 our objective is to establish viability of our new classes of phosphazene materials for use in lithium-ion cell electrolytes, considering both conventional voltage ranges (4.2V) and higher voltage electrode couples (4.5-5V).

Comprising this overall work are the following focus areas:

- ◆ Synthesize novel solvents for Li-ion cells that are safer alternatives to volatile organics.
- ◆ Gain understanding of molecular-scale interactions between phosphazenes and other electrolyte components.
- ◆ Determine what phosphazene structures are more tolerant to high and low voltage, and to high temperatures.
- ◆ Determine the effect of phosphazenes on SEI films, cell performance, and cell aging in general, using ABR-relevant electrode couples.

This collective effort will enable us to engineer advanced electrolyte materials for more robust lithium-ion cells.

**Approach:** The INL is leveraging this work based on interdepartmental synergy between a well-established battery testing program and its foremost experts in phosphazene chemistry that are producing new classes of novel compounds for use in lithium-ion batteries. As such, the INL is strongly positioned to approach primary targets for ABR electrolyte development while maintaining historical knowledge of phosphazene chemistry and related applications.

This work is split under four primary tasks: solvent synthesis, characterization, DFT modeling, and lithium-ion cell testing. Upfront issues are

- ◆ voltage stability (CV)
- ◆ flammability (flash point)
- ◆ transport properties (viscosity, conductivity)
- ◆ chemical compatibility with the cell environment
- ◆ molecular interactions (solvent-ion)
- ◆ temperature stability
- ◆ lithium salt solubility

Coin cell testing covers issues of formation, interfacial impedance, polarization testing, and aging, using our compounds as electrolyte additives (1-10%). We investigate the performance of our electrolytes with two electrode couples: LNMO/LTO and NMC/Carbon.

For cell testing the general protocol is: formation cycling (C/10 @ 3), EIS, followed by a matrix of C/10, C/3, C/1, and 3C, all at 30 °C. Testing concludes with 3C cycling at 55 °C to determine how electrolyte additives affect high temperature tolerance. Final EIS is optional.

**Milestones (cumulative over FY 2011):**

	<b>= Activity completed in reporting period</b>
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<b>Milestone</b>	<b>Status</b>	<b>Date</b>
<b>a.</b> Synthesis of Fluorinated Phosphazene series (FM1,2,3)	completed	March 2011
<b>b.</b> Synthesis of Gen1 Ionic Liquid Phosphazene (PhIL-1)	completed	Feb. 2011
<b>c.</b> Synthesis of newer SM series (SM 5,6,7)	completed	October 2010
<b>d.</b> Development of improved voltammetry techniques for SEI characterization.	completed	December 2010
<b>e.</b> DFT simulations of selected phosphazenes regarding interaction with lithium ions	completed	Feb./March 2011
<b>f.</b> Thermal stability testing of blends with SM6 and SM7	completed	March 2011
<b>g.</b> Cell testing using LNMO/LTO and NMC/Carbon* couples: characterization of capacity and impedance attributes	completed	March 2011
<b>h.</b> Cell testing using LNMO/LTO and NMC/Carbon* couples: aging studies	In Progress	
<b>i.</b> Synthesis of newer FM series and second-generation Ionic Liquid Phosphazenes	In Progress	
<b>j.</b> Abuse testing of INL Phosphazene compounds at SNL	Under planning	

*Various supporting characterization and cell testing will be ongoing throughout FY 2011.*

\* Initial set of NMC/Carbon electrodes received from SNL were not calendared. We repeated the experimental matrix for calendared sets of this electrode couple and provide updated performance data below.

**Financial data:** Funding Received: FY 10: \$ 400K; FY 11: \$ 400K (none under subcontract)

## **PROGRESS TOWARD MILESTONES**

(a, b) Completed 2011 Q2.

(c) Completed 2011 Q1.

(d) Completed 2011Q1.

(e) Completed 2011 Q2.

(f) Completed 2011 Q2.

(g) Completed 2011 Q2.

(h) Coin cell testing of INL electrolyte formulations. We have compared behavior of the NMC/Carbon electrode couple, looking at uncalandared versus calandared laminates (Fig. 1). Trends can be inferred from EIS data that are tied to reduced porosity in the calandared case (Fig. 2). We also continue to test coin cells at 55 °C and a 3C rate to determine if the phosphazene compounds prolong cell life at these mildly abusive conditions. Initial indications are that the phosphazenes act to prolong cell life at elevated temperature. We will conclude this work in Q4 and report on the efficacy of our INL additives.

(i) Synthesis targets are being used to generate newer generations of FM and phosphazene-based ionic liquid (PhIL) compounds. Synthetic efforts continued to make a series of related PhIL electrolyte solvents, producing two phosphazene RTILs. One compound was synthesized, purified, and elementary characterization was completed. This compound was then transformed into a RTIL through a quaternization step, and was turned over to colleagues for blending with the baseline electrolyte and coin cell testing. Another target compound was synthesized, purified, and elementary characterization was completed. The quaternization scheme for this compound is being optimized. A new route was devised to form PhILs based on alternate functional groups, resulting in synthesis of INL PhIL-4; the precursor molecule has been synthesized and work to transform this neutral precursor species into a RTIL is in progress.

(j) Abuse testing of INL Phosphazene compounds at SNL. Discussions between INL and SNL have been held to plan delivery of INL electrolyte systems to SNL for thermal ramp studies to determine how INL additives help to mitigate (delay) the onset of thermal runaway. In Q4 INL will send sufficient electrolyte to SNL to perform such studies with 18650 cells, possibly using the NMC/carbon couple.

## **Publications, Reports, Intellectual property**

- S. V. Sazhin, M. K. Harrup, K. L. Gering, “Characterization of low-flammability electrolytes for lithium-ion batteries”. J. Power Sources, v. 196 (2011) 3433-3438.

- Sergiy V. Sazhin, Mason K. Harrup, Harry W. Rollins, Kevin L. Gering, “Investigation of Phosphazene-based Low Flammability Electrolytes for PHEV Batteries”, Pacific Power Source Symposium, January 10-14, 2011. (Waikoloa, HI).

Intellectual property documentation of newer phosphazene compounds is progressing, and all such INL invention disclosures to date have been elected by the INL primary contractor.

Fig. 1

# Cell Testing, Capacity Attributes (NMC/Carbon)

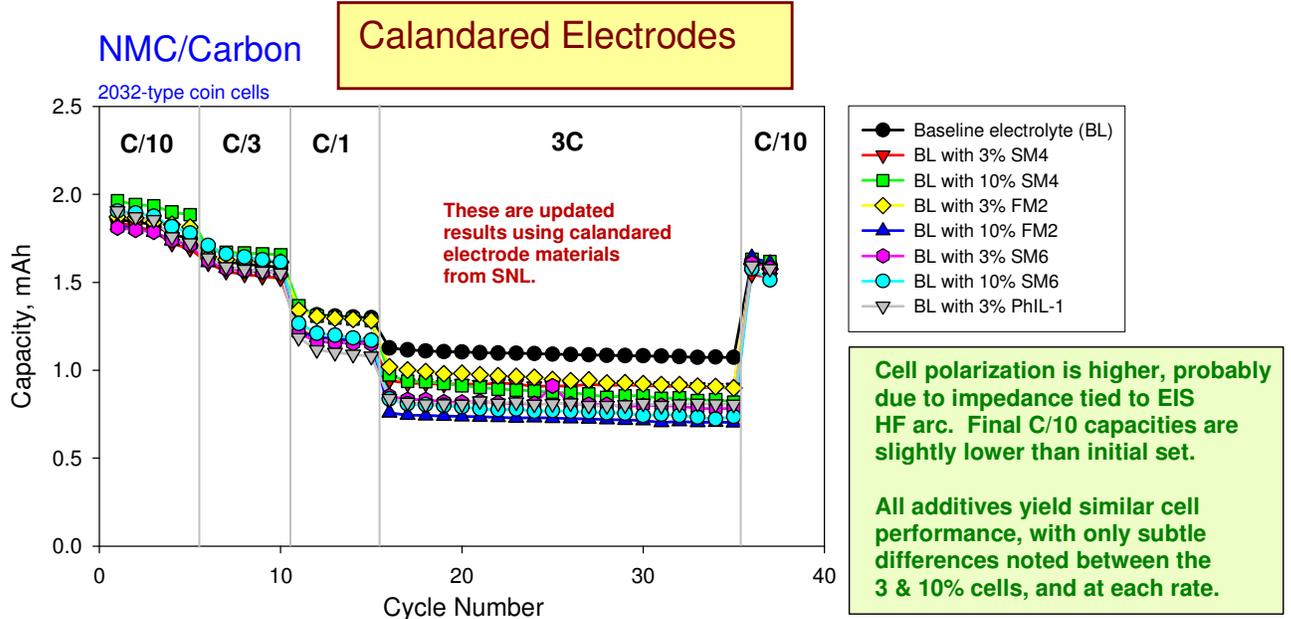
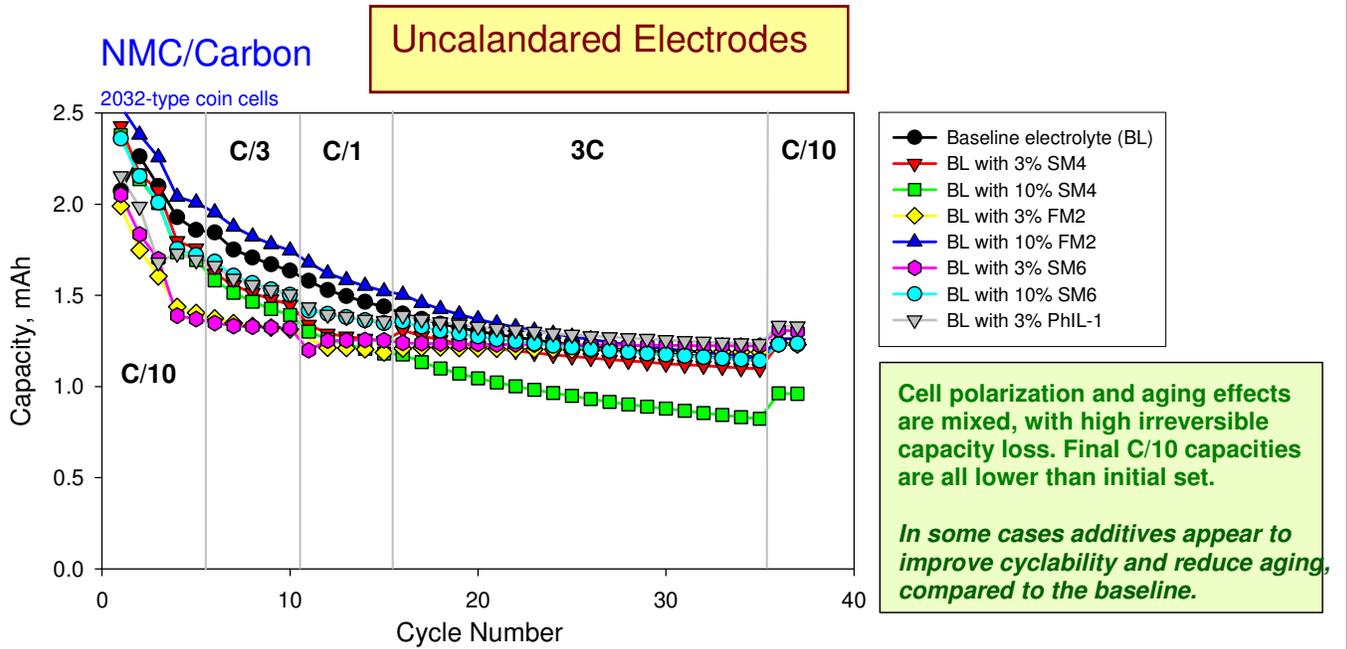
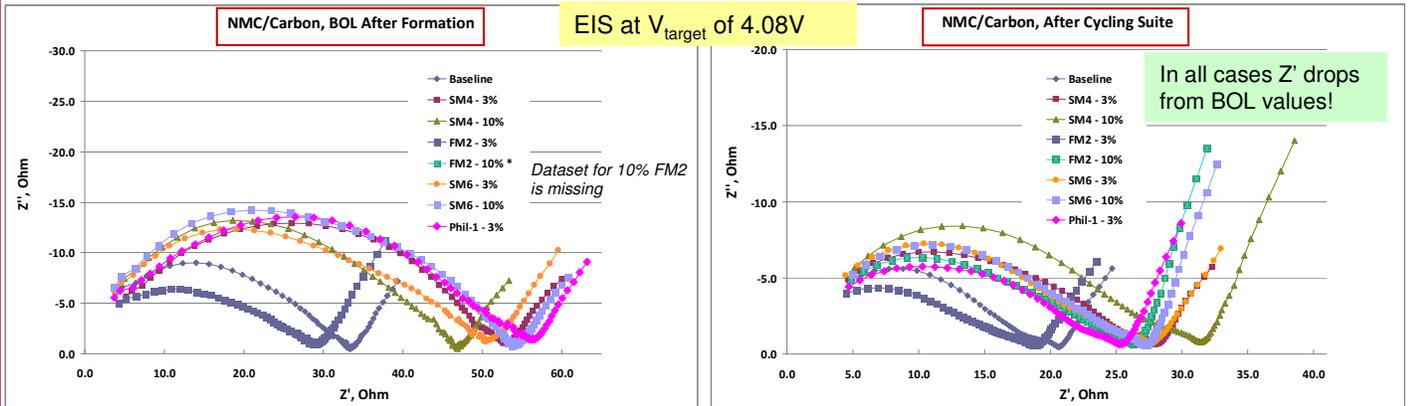


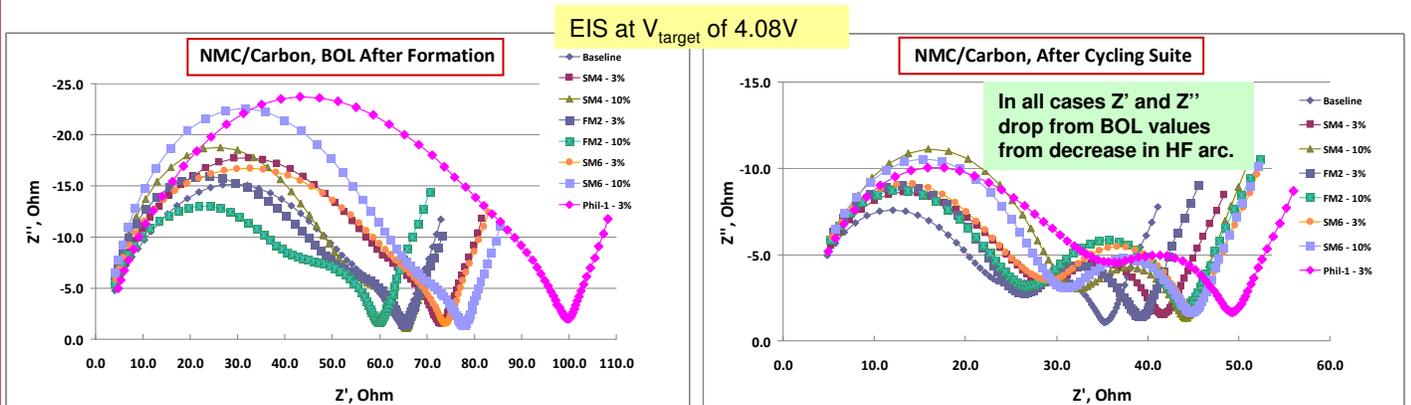
Fig. 2

# Cell Testing, EIS Attributes (NMC/Carbon)

## Uncalandered Electrodes



## Calandered Electrodes



# TASK 1

## Battery Cell Materials Development

3<sup>rd</sup> Quarter Report, Apr. ~ Jun. 2011

**Project Number:** 1.1E (ES028)

**Project Title:** Streamlining the Optimization of Lithium-Ion Battery Electrodes

**Project PI, Institution:** Wenquan Lu and Sun-Ho Kang, Argonne National Laboratory

**Collaborators (include industry):**

Dennis Dees, Argonne National Laboratory

Jai Prakash, Illinois Institute of Technology

**Project Start/End Dates:** October 2008 / September 2014

**Objectives:**

To establish the scientific basis needed to streamline the lithium-ion electrode optimization process.

- To identify and characterize the physical properties relevant to the electrode performance at the particle level.
- To quantify the impact of fundamental phenomena associated with electrode formulation and fabrication (process) on lithium ion electrode performance.

**Approach:**

The initial focus of this effort will be on optimizing the electronic conductivity of the electrode. The factors affecting the distribution of binder and conductive additive throughout the composite matrix will be systematically investigated at the particle level, as well as their effect on overall electrode performance. Modeling simulations will be used to correlate the various experimental studies and systematically determine their impact on the overall electrode performance.

**Milestones:**

- (a) The percolation point of uncoated  $\text{LiFePO}_4$  cathode materials was determined.
- (b) The electrochemical performance of  $\text{LiFePO}_4$  electrode with 7wt.% carbon black was investigated.

**Financial data:** \$300K

### **PROGRESS TOWARD MILESTONES**

In this work, high resistive cathode materials, uncoated  $\text{LiFePO}_4$  was used as test vehicle due to its poor electronic conductivity. The conductive additive and binder effects will be more profound. The percolation theory was adopted to look for the percolation point for this specific cathode material.

- (a) Electronic conductivity of uncoated  $\text{LiFePO}_4$  and carbon black was tested. The percolation point was determined using percolation theory.
- (b) 7wt.% carbon black and 7wt.% PVDF binder was used for uncoated  $\text{LiFePO}_4$  cathode material with good electrochemical performance.

**(a) Summary of work in the past quarter related to milestone (a).**

Electronic conductivity of uncoated  $\text{LiFePO}_4$  and carbon black blend was measured. The full S curved was obtained and the 2wt% carbon black was found to reach the percolation point from interpolation of the percolation theory. The conductivity of blend levels off when the carbon black composition is higher than 7wt.%.

**(b) Summary of work in the past quarter related to milestone (b)**

Electrochemical performance of uncoated  $\text{LiFePO}_4$  with 7wt.% CB and 7wt.% PVDF was investigated. The promising results were obtained at low rate with this specific composition.

**Publications, Reports, Intellectual property or patent application filed this quarter.  
(Please be rigorous, include internal reports--invention records, etc.)**

# TASK 1

## Battery Cell Materials Development

3<sup>rd</sup> Quarter Report, Apr. ~ Jun. 2011

**Project Number:** 1.3 (ES028)

**Project Title:** Screen Electrode Materials, Electrolytes, and Additives

**Project PI, Institution:** Wenquan Lu, Argonne National Laboratory

**Collaborators (include industry):**

Andrew Jansen, Argonne National Laboratory

Dennis Dees, Argonne National Laboratory

Jai Prakash, Illinois Institute of Technology

**Project Start/End Dates:** October 2008 / September 2014

**Objectives:**

- To identify and evaluate low-cost cell chemistries that can simultaneously meet the life, performance, abuse tolerance, and cost goals for Plug-in HEV application.
- To enhance the understanding of advanced cell components on the electrochemical performance and safety of lithium-ion batteries.
- Identification of high energy density electrode materials is the key for this project.

**Approach:**

Base upon battery design model developed by Argonne, the specific capacities of cathode and anode materials should be above 200mAh/g and 400mAh/g, respectively, to meet PHEV requirements set by USABC.

Since there is no commercial available electrode materials can meet PHEV energy requirements, the electrode material candidates will be required from both battery materials companies and research institutes. The promising materials will be evaluated under the controlled process and standard test procedures derived from the “Battery Test Manual for Plug-in Hybrid Electric Vehicles” by INL 2010. In addition, thermal properties of the electrode materials will be studied.

Other battery components for lithium ion batteries, such as electrolyte and additives, separators, binder, conductive additives, and other relevant materials, will also be investigated accordingly.

**Milestones:**

Materials have been investigated in 3<sup>rd</sup> Quarter:

- a) Electrodes evaluation ( $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  from Toda,  $\text{LiNiCoMnO}_2$  from Toda and graphite from ConocoPhillips) from Saft for high voltage electrolyte development.

- b) Evaluation of the electrodes made for 2<sup>nd</sup> cell build at Argonne.
- c) 2<sup>nd</sup> batch redox shuttle (3.8V vs. Li/Li<sup>+</sup>) from ES (ANL).

**Financial data:** \$350K

## **PROGRESS TOWARD MILESTONES**

Electrodes made of a high energy composite material,  $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.37}\text{Co}_{0.24}\text{Mn}_{0.39}\text{O}_2$  (Toda Kogyo, Japan), by Saft was obtained and tested in this quarter. The obtained electrochemical performance was consistent with the results of material screening and electrode fabricated by Cell Fabrication Facility at Argonne. Other than high energy composite material, Electrodes made of  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  from Toda and graphite from ConocoPhillips were also evaluated. These electrodes, together with previous high voltage spinel (LNMO) and lithium titanium oxide (LTO) made by Enerdel, are interchangeable in terms of anode/cathode capacity ratio (about 1.2) except LTO electrode, which has less capacity.

In support of battery built, the electrodes made for 2<sup>nd</sup> cell built at Argonne by Cell Fabrication Facility was evaluated. The cathode material was provided by H. Wu, which was screened in the last quarter. The anode material was provided by ConocoPhillips, which was also screened in the past. The electrochemical performance was investigated and no difference was noticed compared to the screening results.

In support of battery material scale up activities at ES (ANL), 2<sup>nd</sup> batch redox shuttle (RS2) was received and investigated in terms of its electrochemical performance. No performance difference was obtained compared two batches.

### **(a) Summary of work in the past quarter related to milestone (a).**

Half cells using  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ,  $\text{LiNiCoMnO}_2$  composite from Toda and graphite from ConocoPhillips have been investigated. The specific capacity of each material was consistent with previous screening results. Except LTO, all the electrodes, including the high voltage spinel (LNMO), are interchangeable in terms of capacity ratio, which allows the flexibility for high voltage electrolyte development. The cycle life of full cells of all three cathode materials, NCA, NCM, and LNMO were tested against A12 graphite. The NCA showed best capacity retention in 50 cycles, followed by high voltage spinel and  $\text{LiNiCoMnO}_2$  composite.

### **(b) Summary of work in the past quarter related to milestone (b)**

Cell Fabrication Facility at Argonne made electrodes using composite cathode,  $1/3\text{Li}_2\text{MnO}_3 \cdot 2/3\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ , from ANL (H. Wu) for 2<sup>nd</sup> cell build. Both half cells and full cells were tested in terms of specific capacity, HPPC, rate capability and cycling. Consistent results were obtained compared to previous screening results.

### **(c) Summary of work in the past quarter related to milestone (c)**

2<sup>nd</sup> batch (1500g) redox shuttle RS-2 from ES was tested using graphite/ $\text{LiFePO}_4$  cells. The same electrochemical performance was obtained compared to previous batch (100g).

Redox potential was determined to be around 3.8V depending on the current applied to the cell. Excellent overcharge protection (100% overcharge) was obtained using 6wt.% RS-2. We did notice that 9wt% RS-2 could not be obtained. It is speculated that the low solubility of 2<sup>nd</sup> batch RS-2 was caused by the low lab temperature. The solubility test of RS-2 was suggested.

**Publications, Reports, Intellectual property or patent application filed this quarter.  
(Please be rigorous, include internal reports--invention records, etc.)**

Enerdel and Saft Electrode Evaluation - HV electrolyte, internal report on high voltage spinel for high voltage electrolyte development, May 2011.

Investigation of RS2 Redox Shuttle by ES, internal report on redox shuttle scaled up at ES, Jun 2011.

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number:** 1.2.2 Electrode Material Development (ES029)

**Project Title:** Scale-up and Testing of Advanced Materials from the BATT Program

**Project PI, Institution:** Vincent Battaglia, LBNL

**Collaborators (include industry):** NEI Corp.; Nippon Denko Co., Ltd; G. Ceder, (MIT); A. Manthiram, (U.T.); K. Zaghieb (HydroQuebec)

**Project Start/End Dates:** October 1, 2009 / September 31, 2013

**Objectives:** In 2011 we expect to identify a NiMnO-spinel as the baseline material for the high-voltage electrolyte task. If the electrolyte developed as a result of this task is stable when in contact with the NMC material at higher voltages, then the theoretical cell energy storage capacity could be improved by 20%.

**Approach:** We will evaluate sources of  $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$  spinel for potential use in the high-voltage electrolyte effort of the ABR Program. We will utilize physical, chemical, and electrochemical techniques in this effort. An important consideration is that the spinel formulation allows the properties of the candidate electrolytes to be compared with minimal ambiguity as we make a selection. After a suitable spinel is selected, we will work on optimizing its formulation through the BATT Program and transfer the results to this project.

**Milestones:**

(a) Battery design, performance, and cycling characteristics of BATT materials will be reported on at the DOE Annual Merit Review (May 2011.) On schedule

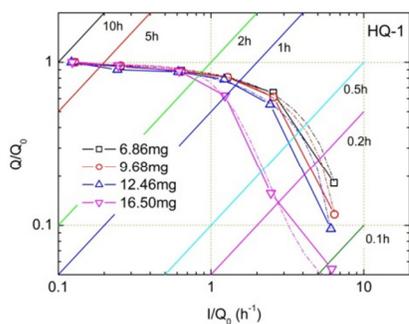
**Financial data:** \$240 k for FY11.

#### PROGRESS TOWARD MILESTONES

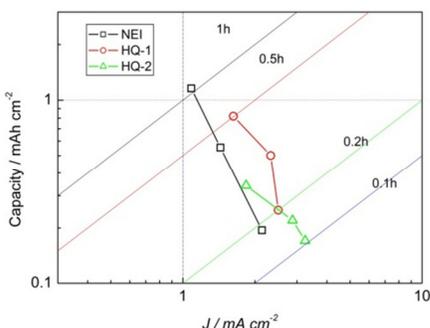
**(a) Summary of work in the past quarter related to milestone (a).**

During the third quarter of FY 2011, four samples of  $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$  were obtained from the BATT PI Karim Zaghieb of Hydro Quebec, namely: HQ-1, HQ-2, HQ-3, and HQ-4. Physical characterization of these materials included SEM, PSA, and BET. Through the SEM data, it was determined that the materials have different morphologies, from mossy to crystalline. The PSA data indicated that the average secondary particle size varies from 4.6 to 8.7 microns. The BET data indicated that the average surface area varies from 0.54 to 5.5  $\text{m}^2/\text{g}$ .

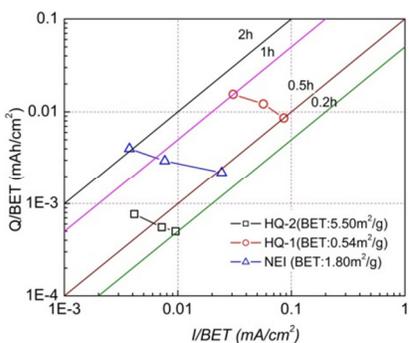
The materials were also tested for their electrochemical performance and compared to the baseline material supplied by NEI. The HQ materials demonstrated reversible discharge capacities between 95 and 116 mAh/g, substantially less than the discharge capacity of the NEI material of 128 mAh/g. Moreover, the HQ materials demonstrated 19 to 25% of their capacity at the 4.1 V plateau, which is considered to be due to a  $\text{LiMn}_2\text{O}_4$  spinel “impurity.” This is in comparison to the 7.3 % seen for the NEI material. All of the materials showed similar 1<sup>st</sup> cycle capacity efficiencies of 89%.



Electrodes of different active material loadings of HQ-1 and HQ-2 were evaluated for their rate performance and compared to similar electrodes prepared from the NEI material. (The two other HQ materials are still under testing.) The figure on top shows the rate performance of HQ-1 for different electrode thicknesses normalized by their capacity measured at  $C/10$ ,  $Q_0$ . The capacity shows a gradual decrease with increase in discharge rate just before a more rapid drop off at higher currents.



The figure in the center shows the area specific capacity of the materials *versus* the current density reached just prior to limitations related to the thickness of the electrodes. The graph shows that in general the two HQ materials have higher rate capability than the NEI material. Note that the material with the highest reversible specific capacity (NEI) delivers the lowest capacity at rate; also note that these are higher-rate electrodes than are needed for a 40-mile PHEV.



These data were then normalized for active surface area by multiplying the current and the capacity by the superficial area of the cell and the active material loading per  $\text{cm}^2$  and dividing by the BET measured surface area. The results are shown in the lower figure and indicate that the rate performance differences between the materials cannot be fully attributed to differences in surface area or particle size, and that the HQ-1 material appears to have intrinsically higher rate capability than the other two.

Once the rate performance tests are completed, the cells will be cycled at  $C/1$  to determine their cycling stability.

# TASK 1

## Battery Cell Materials Development

Quarter 3

**Project Number:** 1.2C (ES112)

**Project Title:** Functionalized Surface Modification Agents to Suppress Gassing Issue of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  Based Lithium Ion Chemistries (Mechanism of LTO Gassing and Potential Solutions)

**Project PI, Institution:** Yan Qin, Zonghai Chen and Khalil Amine, Argonne National Laboratory

**Collaborators (include industry):**  
EnerDel  
University of Colorado

**Project Start/End Dates:** October 2010 / September 2014

**Objectives:** The objective of this work is to investigate the gassing mechanism of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and to develop advanced technologies to solve this problem.

- Identify gassing mechanism.
- Identify and develop advanced technologies to eliminate the gassing issue.

**Approach:** The role of the salt in the gassing process has been investigated with examination of different salts. Now, we have identified the salt as the one of the key components responsible for gassing in addition to charged LTO and electrolyte. The additive which has been proposed to passivation the surface of the LTO in order to interrupt the reaction pathway of gassing has been tested to show positive outcome.

**Milestones:**

- (a.) The salt effect on the gassing has been investigated and identified. (On schedule)
- (b.) The additive proposed before has been tested and shown promising outcome. (On schedule)

**Financial data:** \$300K

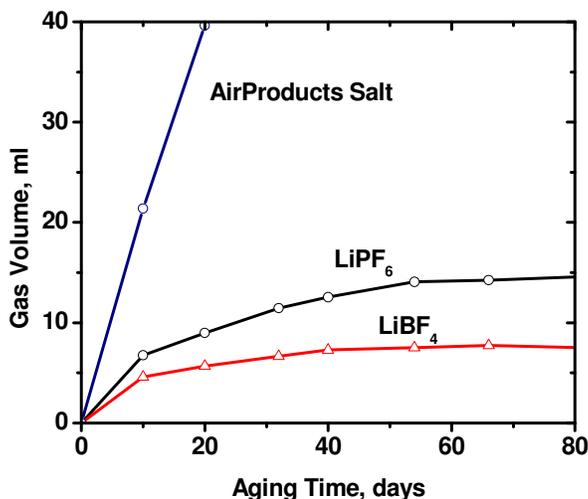
### PROGRESS TOWARD MILESTONES

A type of additives is proposed to passivation the surface of the LTO through interaction with the surface group of  $-\text{OH}$ .

**(a) Summary of work in the past quarter related to milestone (a).**

Previously, we have quantified the relation between  $Ti^{3+}$  and  $H_2$ , and also identified the carbonate solvents as the source of  $H^+$ . Now, we further revealed that the salt played an important role in the process. Three key components are now coming together to form an electron transfer pathway to enable the gas generation.

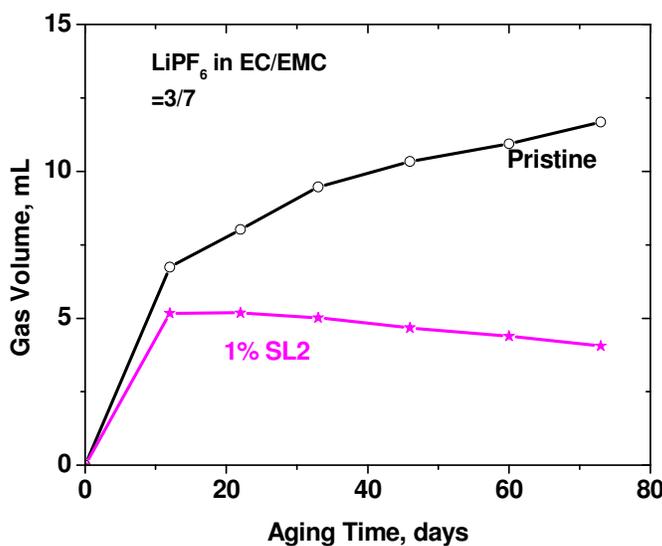
**Fig 1** shows the gas evolution progress for different lithium salts in PC:EMC:DEC:DMC = 1:1:1:1.  $LiBF_4$  produce less gas than  $LiPF_6$  and AirProducts Salt ( $LiB_{12}F_{12}$ ). The salt  $LiTFSI$  and  $LiBETI$  won't produce any gas, however, they have severer corrosion problem.



**(b) Summary of work in the past quarter related to milestone (b)**

Since the charged LTO surface is the place the reaction is taking place, additive is added to form a passivation film on the surface of LTO in order to shut off the reaction pathway.

**Fig 2** shows the effect of additive SL2 in reducing the gas. With addition of additive SL2 in the electrolyte, the gas amount is greatly reduced and stabilized over long period of time.



**Publications, Reports, Intellectual property or patent application filed this quarter. (Please be rigorous, include internal reports--invention records, etc.)**

No publications, reports, or patents were submitted this quarter.

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number:** 1.1L (ES113)

**Project Title:** Development of High Voltage Electrolyte for Lithium Ion Battery (High Voltage Electrolyte for Lithium Batteries)

**Project PI, Institution:** Zhengcheng Zhang, Khalil Amine, Argonne National Laboratory

**Collaborators (include industry):**

Ali Abouimrane, Argonne National Laboratory

Huiming Wu, Argonne National Laboratory

Wei Weng, Argonne National Laboratory

Kevin Gering, Idaho National Laboratory

EnerDel

**Project Start/End Dates:** October 2010 / September 2014

**Objectives:** The objective of this work is to develop an electrolyte with wide electrochemical window that can provide stable cycling performance for cathode materials that can charge above 4.5 V.

FY11's objective is to identify, synthesize and evaluate new solvent systems as possible candidates for high voltage electrolyte application.

**Approach:** Investigate new none carbonate solvent such as silane, sulfone, fluoro-ethers and fluoro-esters. The silane based electrolyte has high conductivity, low viscosity and good wetting capability. Sulfone based electrolyte has high voltage stability but high viscosity and poor wetting capability of electrode and separator. Exploring a hybrid electrolyte made of the mixture of the above solvents is the general approach.

**Milestones:**

(a.) Material synthesis, purification and formulation, September 2011, (On schedule)

(b.) Investigation of physical properties of the Silane/Sulfone hybrid electrolytes, September 2011, (Complete)

(c.) Complete initial evaluation of Silane/Sulfone hybrid electrolytes for LNMO/LTO chemistry, September 2011, (On schedule)

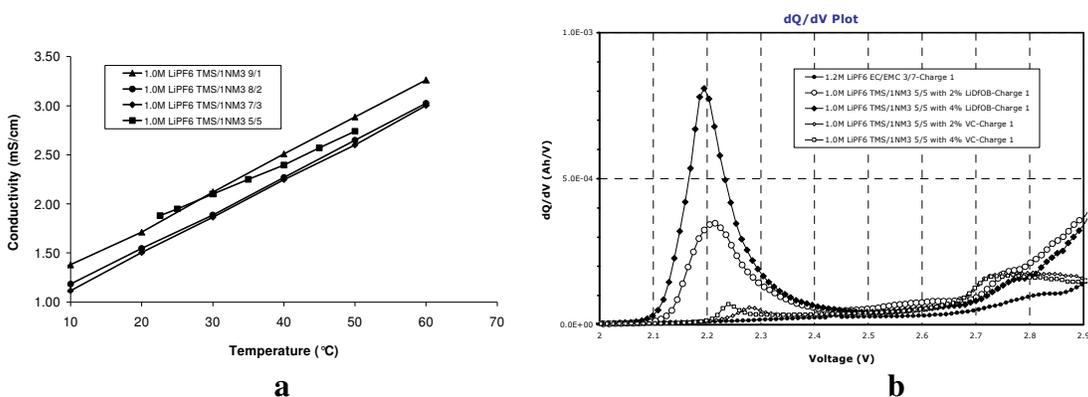
**Financial data:** \$200K

#### **PROGRESS TOWARD MILESTONES**

**(a) Summary of work in the past quarter related to milestone (a).**

Fig.1a shows the conductivities of mixed TMS/1NM3 electrolyte with 1.0M LiPF<sub>6</sub> salt concentration at various temperatures. Interestingly, the mixed electrolyte exhibited higher conductivity than their component electrolyte alone, indicating certain extent of molecular level synergetic effect. The TMS/1NM3 mixed electrolytes showed much higher conductivity of 2.0mS/cm at mixed ratios of 9:1 and 5:5 than at mixed ratios of 8:2 and 7:3. It is known that high polar and low viscosity molecules will facilitate the ion dissociation and transfer [7]. TMS has much higher dipole moment (4.35D), therefore it dominates the ion dissociation of the mixed solvent at high concentration. However, the lower viscosity of 1NM3 (1.4cP for 1NM3, 10.1cP for TMS at 30°C) will facilitate the ion transfer in the mixed solvent with low TMS concentration at ratio of 5:5. The TMS/1NM3 mixed electrolyte showed the optimal ambient conductivity of 2.0x10<sup>-3</sup> S/cm, which is slightly lower than the conventional carbonate based electrolytes.

Differential capacity profiles of the LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (NMC)/MCMB lithium-ion cells with various additive concentrations were illustrated in Fig.1b and only the initial data below 3.0 V during the first charge are shown to demonstrate the formation of the SEI film. The additive effects on the SEI formation can be clearly detected by the peaks at about 2.2 V. Although the intensity of the peaks at about 2.7-3.0V is independent of the additive and its concentration, the peaks at around 2.2V depends on the additive type and its amounts. Not observed for the cell without additives, the peak at 2.2 V is believed to result from the SEI layer formed by the decomposition of additives, which is evidenced by the increases of peak intensity with the increasing additives from 2% to 4% for both LiDfOB and VC. The best cycling performance was obtained with 2% ratio for both additives as shown in Fig.4, suggesting that the passivation film was optimized with t. More additive will lead to the significant change in the thickness of SEI layer and thus the high impedance of the cell.

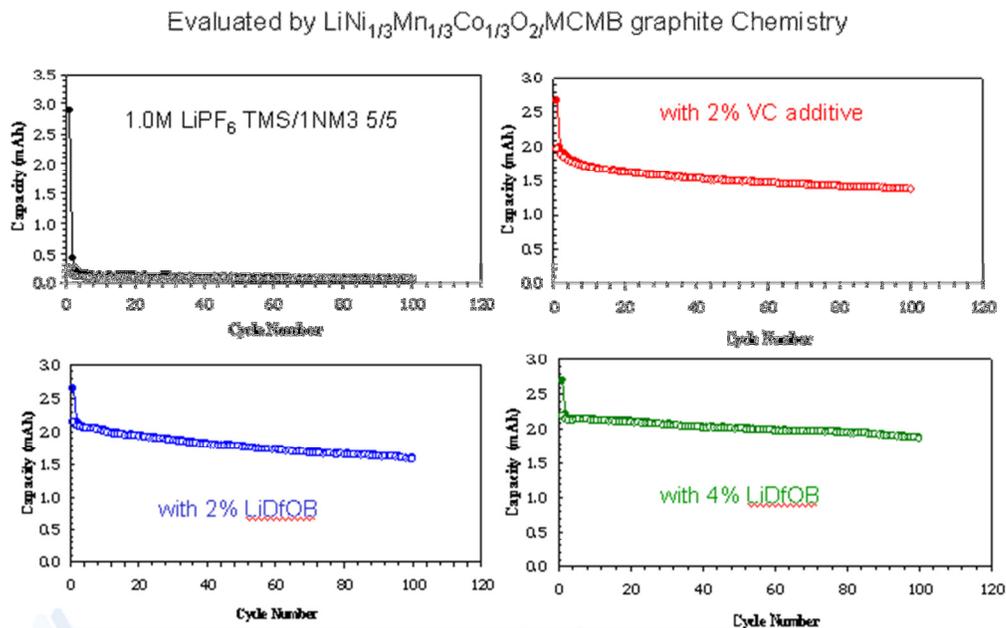


**Fig.1a.** Ionic conductivities versus temperature for 1.0M LiPF<sub>6</sub> TMS/1NM3 mixed electrolytes **Fig.1b.** Differential capacity profiles of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>/MCMB cells with different concentrations of additive in 1.0M LiPF<sub>6</sub> TMS/1NM3 5:5 electrolyte.

**(b) Summary of work in the past quarter related to milestone (b)**

The Sulfone and silane hybrid system can provide excellent performance in high voltage cathode/LTO cell. However this electrolyte is not compatible with the carbonaceous

anode. As shown in Fig.2a, no cycling behavior is observed using 1.0M LiPF<sub>6</sub> TMS/1NM3 5/5. When additive is added, the capacity retention of the cell is greatly improved with 4% LiDfOB showing the best results and indicating an integrated SEI formation on the surface of the graphite.



**Fig. 2a, 2b, 2c and 2d.** NMC/MCMB cell cycling performance using 1.0M LiPF<sub>6</sub> TMS/1NM3 with and without additives.

**(c) Summary of work in the past quarter related to milestone (c)**

Work on Fluorinated ether (D2) and ester (FEC) is ongoing. The focus is on optimizing the ration between these two solvents to increase both conductivity and dielectric constant. These electrolytes will be investigated using LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode coupled with Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> as anode and will be reported in the next report.

**Publications, Reports, Intellectual property or patent application filed this quarter. (Please be rigorous, include internal reports--invention records, etc.)**

Hybrid Electrolyte Patent-ANL-IN-09-039

## TASK 1

### Battery Cell Materials Development

**Project Number:** 1.2D (ES114)

**Project Title:** Spherical Carbon Anodes Fabricated by Autogenic Reactions

**Project PI, Institution:** Vilas G. Pol, Argonne

**Collaborators (include industry):** Michael Thackeray (Co-PI, Argonne), ConocoPhillips, Superior Graphite, General Motors

**Project Start/End Dates:** 1 October 2010/30 September 2011

#### **Objectives:**

The initial objective of this project is to prepare spherically-shaped- and other rounded carbon anode particles for HEVs, PHEVs and EVs by autogenic reactions to:

- 1) improve the abuse tolerance of carbon anodes without compromising capacity or power;
- 2) optimize autogenic processing conditions to enhance structural and electrochemical properties of the carbon products; and
- 3) evaluate electrochemical and thermal properties of the carbon materials.

The first objective of this phase of the project is to therefore to achieve a spherical carbon anode with comparable capacity (300mAh/g) and enhanced safety relative to graphite. A second objective would be to use autogenic reactions to prepare high capacity carbon-Si and carbon-Sn anode architectures that offer twice the capacity of graphite.

#### **Approach:**

- 1) Exploit autogenic reactions to prepare spherical carbon particles quickly and reliably;
- 2) Collaborate with industry to access high-temperature furnaces to increase the graphitic component in the carbon;
- 3) Optimize processing conditions and evaluate electrochemical properties;
- 4) Evaluate thermal stability/reactivity of lithiated carbon electrodes in electrolyte; and
- 5) Model current distribution around carbon spheres.

#### **Milestones:**

- (a) Establish collaborative interactions with ConocoPhillips, Superior Graphite and General Motors to gain access to high temperature (>2000 °C) furnaces – *New collaboration established with ConocoPhillips to heat samples to 2800 °C;*
- (b) Prepare carbon samples for ConocoPhillips – *Batches successfully prepared and heated - on going*
- (c) Evaluate electrochemical properties of heat-treated carbon samples in lithium half cells and full cells – *Sept. 2011 – on schedule*
- (d) Evaluate the relative physical, chemical and electrochemical properties of lithiated carbon spheres vs. lithiated graphite – *Sept 2011 – on schedule*

- (e) Compare models of current distribution around spherically-shaped and sheet-like (graphitic) carbon particles – *Sept 2011 – on schedule.*

**Financial data:** \$300K/year

#### PROGRESS TOWARD MILESTONES

**Milestone (a). Establish collaborative interactions with ConocoPhillips:**

Because of furnace problems at GM and the difficulty in accessing temperatures in excess of 2500 °C, a collaboration with ConocoPhillips has been established to assist us in this endeavor.

**Milestone (b). Prepare carbon samples for ConocoPhillips:**

A sample of autogenically-prepared carbon spheres was synthesized at 700 °C (SCP-700) and dispatched to ConocoPhillips. This sample was heated further to 2800 °C under argon for 1 hour and returned to Argonne, hereafter referred to as SCP-2800.

**Milestone (d). Evaluate the relative physical, chemical and electrochemical properties of lithiated carbon spheres vs. lithiated graphite:**

The physical properties of a SCP-2800 sample, in terms of its morphology, composition, density and structure were determined and compared with those of untreated SCP-700 and SCP-2400 samples, the latter sample having been heated under inert conditions at 2400 °C (Table 1).

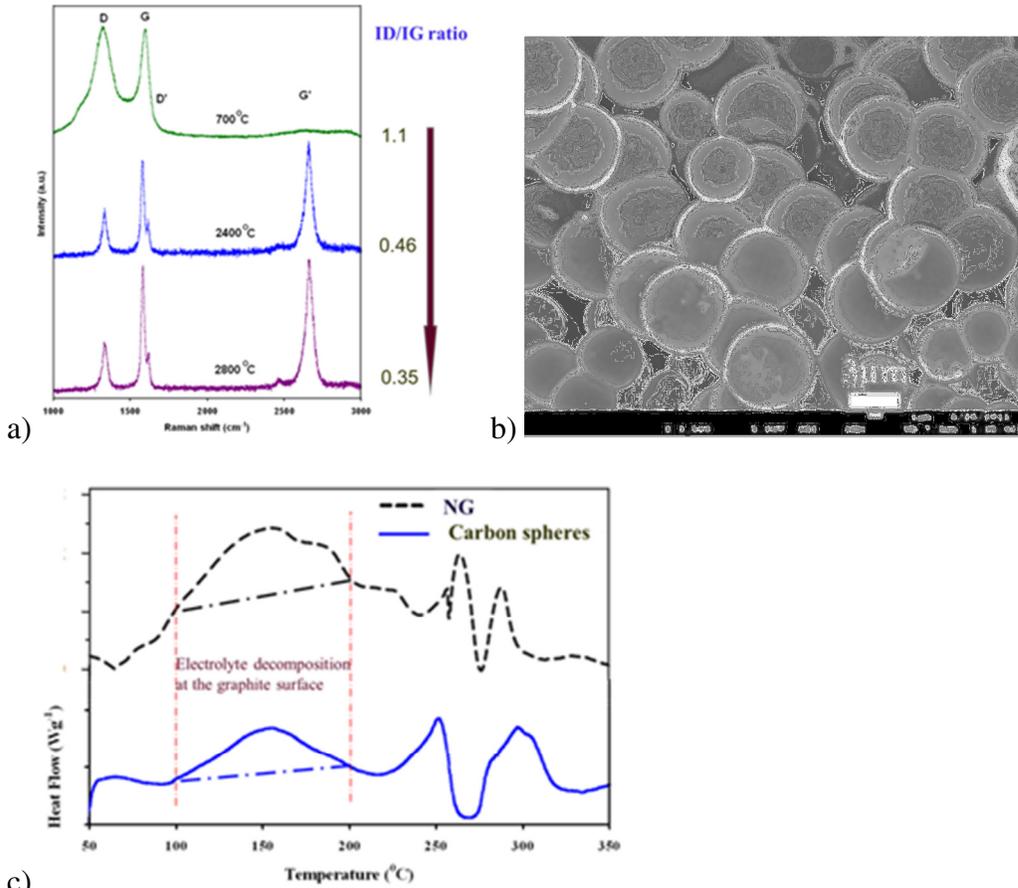
**Table 1.** Physical properties of SCP-700, SCP-2400 and SCP-2800 samples.

Spherical carbon	Density	Morphology	Raman ID/IG ratio
SCP-700	2.2 g/cm <sup>3</sup>	Spherical particles	1.1
SCP-2400 (1h)	2.1 g/cm <sup>3</sup>	Spherical particles	0.46
SCP-2800 (1h)	2.04 g/cm <sup>3</sup>	Fusion of spherical particles	0.35

The carbon spheres prepared at 700 °C are extremely hard and dense, having a true density equivalent to that of graphite (2.2 g/cm<sup>3</sup>). The true density of SCP-2800 is slightly lower, 2.04 g/cm<sup>3</sup>. By contrast, the tap density of all the carbon samples is less than 1 g/cm<sup>3</sup>, due to the difficulty of compacting the powders because of an apparent electrostatic charge between the particles. EDS analysis showed that the spheres consisted of >99% carbon; no other impurities were detected. The structural evolution of the carbon spheres, as a function of temperature, was monitored by Raman spectroscopy (Figure 1a); the ID/IG ratio decreases as a function of increasing heat-treatment, reflecting an increase in the graphitic character of the carbon spheres, as expected. The slight increase in the graphitic character of the SCP-2800 samples was also corroborated by powder X-ray diffraction.

Spherical carbon particles tend to fuse or sinter during heat treatment to 2800°C (Figure 1b).

An evaluation of the thermal stability and reactivity of lithiated SCP-2400 was carried out and compared with lithiated natural graphite (Figure 1c). Between 100 and 200 °C, approximately 380 J/g heat was generated due to breakdown of the SEI layer on the carbon spheres. This heat generation value was less than that observed for the lithiated natural graphite electrode (409 J/g), emphasizing the slight advantage that the carbon spheres may have with respect to safety.



**Figure 1.** a) Raman spectra of carbon spheres prepared at 700°C (top), 2400°C (middle) and 2800°C (bottom); b) Scanning electron micrograph of SCP-2800; and c) Differential scanning calorimetry curves of fully lithiated carbon spheres in the presence of electrolyte, compared to natural graphite (NG)

**Milestone (c). Evaluate electrochemical properties of heat-treated carbon samples:**

An electrochemical evaluation of SCP-2800 samples has recently been initiated. These data will be provided in the next report along with a comparison of the electrochemical properties of SCP-700 and SCP-2400 samples.

**Milestone (e). Compare models of current distribution around spherically-shaped and sheet-like (graphitic) carbon particles**

Dennis Dees is developing a model to ascertain the potential benefit of using carbon spheres vs. other forms of carbon with respect to suppressing lithium dendrite formation and enhancing the relative safety of lithium-ion cells with carbon sphere electrodes. This investigation is in progress and will be discussed in a later report.

**Publications, reports, talks, invention reports, patent applications.**

1. V. G. Pol, M. M. Thackeray, Autogenic reactions for fabricating lithium battery electrode materials, Proceedings of the 35<sup>th</sup> International Conference on Advanced Ceramics & Composites (ICACC), *in press* (2011).
2. M. M. Thackeray and V. G. Pol, Spherical Carbon Anodes Fabricated by Autogenic Reactions, Annual Merit Review, ABR, Washington, D.C. May 9-13 (2011)

## TASK 1

### Battery Cell Materials Development

**Project Number:** 1.1V (ES115)

**Project Title:** Synthesis and Development of High-Energy and High-Rate Cathode Materials from Ion-Exchange Reactions (Novel Composite Cathode Structures)

**Project PI, Institution:** Christopher Johnson, Argonne National Laboratory

**Collaborators (include industry):**

Sun-Ho Kang, Argonne National Laboratory

Wenquan Lu, Argonne National Laboratory

Stephen Hackney, Michigan Technological University

**Project Start/End Dates:** October 2010 / September 2016

**Objectives:** Ion-exchange reactions are used to make new cathode materials with high-energy and high-rate. The objective is to produce an optimized material that shows an improvement over the drawbacks of Argonne high-energy cathodes. These ion-exchange cathodes should thus demonstrate <10% irreversible capacity in the first cycle, > 200 mAh/g at a C rate, no alteration in voltage profile during cycling, lower cost, and improved safety.

**Approach:** We will synthesize, characterize, and develop new cathode materials that exploit the difference in sodium versus lithium cation radii and their respective coordination properties. Cathodes will be derived from layered sodium transition metal oxide precursors that contain modest amounts of lithium in the transition metal (TM) layer. The sodium in the precursor materials is then ion-exchanged with lithium to form layered composite oxide cathodes for lithium batteries. We will focus on electrode materials that contain redox active Ni, and low cost Mn and Fe transition metals

**Milestones:** Materials will be produced and tested that will show progressively improved properties as the project moves forward.

- (a) Synthesize new materials, September 2011, (on-schedule)
  - Optimize ion-exchange reaction conditions, June 2011 (completed)
- (b) Characterize electrochemical properties of synthesized materials, September 2011, (on-schedule)
  - Demonstrate high-rate of 200 mAh/g @ 2C rate, March 2011, (completed)
- (c) Characterize structure of materials, September 2011, (on-schedule)
  - Examine morphology of starting materials, and ion-exchange products, June 2011, (completed, and on-going)
- (d) Continue optimization of Na, Li and transition metal content ratios in materials, June 2011, (delayed – but on-schedule for Sept. 2011)
- (e) Initiate measurement of thermal properties of charged material in DSC, September 2011, (on-schedule)

**Financial data:** \$300K; \$50K subcontracted to Prof. S. Hackney (Michigan Technological University)

## **PROGRESS TOWARD MILESTONES**

(a) Optimization of Li ion-exchange reaction conditions for a set composition of the precursor  $(\text{Na}_{1.0}\text{Li}_{0.2}(\text{Ni}_{0.25}\text{Mn}_{0.75})\text{O}_y)$  material has been completed. Solvents tried were methanol, ethanol, and water. Methanol is the best solvent for the reaction together with a two-fold excess of LiBr. In addition, we found that a post-anneal temperature of 550 °C leads to the most favorable electrochemical response. Work is ongoing to improve this process.

(b) 1C rate of > 200 mAh/g is consistent even with various compositions. The water ion-exchanged sample showed inferior electrochemistry likely due to proton for lithium exchange.

(c) HRTEM now suggests that the ion-exchanged material consists of a repeating two-layer two-phase laminate structure that displays a natural super-lattice. Further, the data suggests a non-homogenous Ni-Mn distribution in the a/b plane. Ramifications of these findings will be considered. Finally, results of many electron diffraction patterns taken, surprisingly shows no spinel domains in the fresh as-prepared materials. Next we will interrogate cycled samples.

(d) The Mn/Ni ratio continues to be varied, and will be reported in the next quarter.

(e) Thermal properties of the charged materials in milestone (a) are on-going. Initial data shows the ion-exchange sample has 10% less heat evolved (4.6 V charged cathode) than a typical composite 'layered-layered' material:  $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiNi}_{0.44}\text{Co}_{0.25}\text{Mn}_{0.312}\text{O}_2$ . The onset temperature is also shifted about 30 °C higher (see Fig. 1).

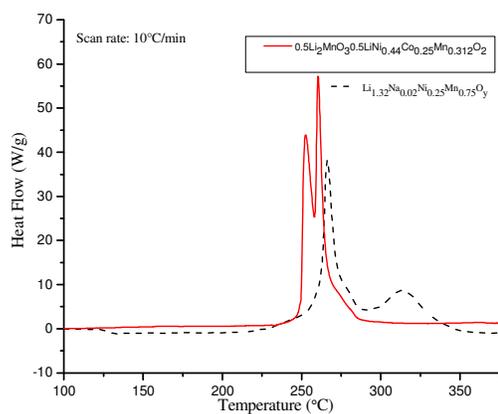


Fig.1. DSC output of 4.6 V charged ion-exchanged cathode versus an Argonne composite 'layered-layered' cathode:  $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiNi}_{0.44}\text{Co}_{0.25}\text{Mn}_{0.312}\text{O}_2$

**Publications, Reports, Intellectual property or patent application filed this quarter.**

No presentations, publications, reports, or patents were submitted this quarter.

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number:** ES038

**Project Title:** High Energy Density Ultracapacitors

**Project PI, Institution:** Patricia Smith, NAVSEA-Carderock

**Collaborators:** Thanh Tran and Thomas Jiang (NAVSEA-Carderock), Michael Wartelsky (SAIC), Steven Dallek (Spectrum Technologies), Deyang Qu (University of Mass., Boston), Steve G. Greenbaum (Hunter College of CUNY), and Jae Sik Chung (PCTest)

**Project Start/End Dates:** FY09 to FY12

**FY11 Objectives:** Improve low temperature energy density of lithium ion capacitor (LIC) by 25% (in comparison to 1<sup>st</sup> generation LIC cells). Assess safety of present LIC technology.

#### **Approach:**

Identify candidate high-performance electrolyte compositions via technical discussions with battery manufacturers and DOE investigators and from literature reports. Evaluate most promising systems by fabricating and cycling pouch cells in the temperature range from 25°C to -30°C. Evaluate the thermal stability of electrode materials, electrolytes, and cell design using differential scanning calorimetry (DSC) and accelerating rate calorimetry (ARC). Investigate the effect of negative electrode carbon graphitization on cell performance and thermal stability. Identify optimal carbon pore size for low temperature performance.

#### **Milestones:**

- (a) Safety and performance evaluation of 1<sup>st</sup> generation LIC cell technology (March 2011). Status: Complete
- (b) Identification of negative electrode material that exhibits high reversible capacity, high power capability, and good low temperature performance. (June 2011). Status: Initiated
- (c) Identification of high-performance, low-temperature electrolyte (July 2011). Status: In progress
- (d) Safety and performance evaluation of 2<sup>nd</sup> generation LIC cell technology (September 2011). Status: In progress

**Financial data:** Project budget/year, amount subcontracted if appropriate  
FY10: \$350K, Funding Expensed 1Q FY11: \$35,324.00 (FY10 carry-over funding.)

## Progress Toward Milestones:

Second generation, 2,000F LIC cells were obtained from JM Energy for performance and safety evaluation. A cell was transferred to a glove box and the electrodes harvested. Three-electrode pouch cells, containing positive and negative harvested electrodes and a lithium ion reference electrode, were fabricated. A lithium reference electrode was used to determine the relative contribution of the positive and negative electrodes to impedance rise during low-temperature operation. The positive electrode was mainly responsible for cell impedance as shown in Figure 1. As the temperature of the cell was lowered from 25°C to -30°C, the contribution of the positive electrode to the overall cell impedance decreased whereas the contribution of the negative decreased. (Table I).

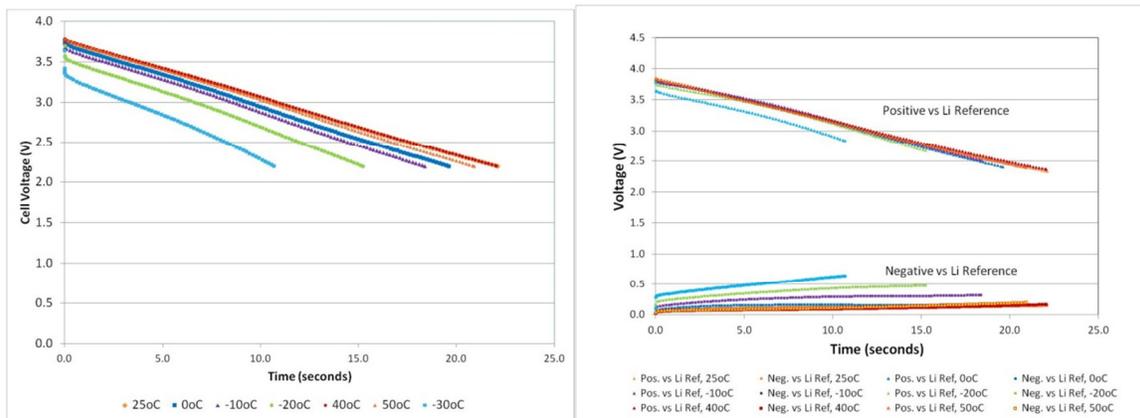


Figure 1. The 25<sup>th</sup> voltage discharge profiles of a three-electrode pouch cell cycled at constant current (1mA/cm<sup>2</sup>). The cell was cycled 25 times at 50°C, 40°C, 25°C, 0°C, -10°C, -20°C, and -30°C.

Table I. Contributions of Individual Electrodes to Cell Polarization

Temperature (°C)	% Voltage Drop Attributed to Positive Electrode	% Voltage Drop Attributed to Negative Electrode
25	94	6
-10	82	18
-20	72	28
-30	59	41

The safety evaluation of the second generation LIC capacitor developed by JM Energy was initiated. The second generation cell contains an electrolyte and electrode design that is different from that of the first generation cells. Fully-charged, 2,000F second generation LIC cells were evaluated using accelerating rate calorimetry (ARC) method and the test results are shown in Figure 2. Calorimetric methods such as ARC or differential scanning calorimetry (DSC) can provide valuable insights regarding thermal behavior of specific cell designs and individual cell materials. This information may identify future LIC cell designs and material selections that are more tolerant of electrical and mechanical abuse conditions.

The ARC investigation results revealed that self-heating of the second generation JM Energy LIC cell begins at approximately 105°C as shown in Figure 2. Based on ARC and DSC experiments previously conducted on the first generation cells and individual cell components, the exothermic reaction at 105°C is tentatively assigned to the decomposition of the SEI film formed on the negative electrode. The sharp increase in temperature at 120°C is tentatively assigned to the reactions of the charged anode and electrolyte and the reaction of the charged anode with binder. At 210°C, the cell vent opened and the cell temperature reached over 400°C. Efforts in the next quarter will focus on performing DSC experiments to confirm these results.

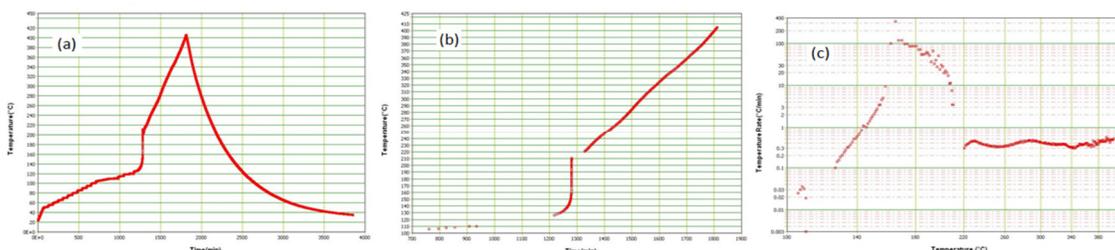


Figure 2. Results of ARC experiment conducted on a second generation, 2,000F lithium-ion capacitor, (a) Calorimeter/LIC temperature profile, (b) LIC self-heating profile, (c) LIC self-heating rate profile.

During the initial charge of a lithium-ion battery, lithium ions migrate from the positive (lithiated metal oxide electrode) to the negative (carbon electrode). This process cannot be utilized when charging a lithium ion capacitor since the positive electrode (activated carbon) is not lithiated. Employing a charging process similar to that of lithium ion batteries would result in a depletion of the  $\text{Li}^+$  ions and reduce cell power capability. In order to mitigate the problem, LIC cells are therefore “pre-doped” at the manufacturer’s facility using a sacrificial lithium electrode. This process results in the formation of a SEI layer that is expected to influence cell performance as it does in a lithium-ion battery.

Half cells containing JM Energy negative electrodes (first generation) and a lithium ion counter electrode were fabricated to compare the reversible and irreversible capacity of JM Energy’s generation 1 and generation 2 electrolytes. As shown in Figure 3, both electrolytes gave high reversible capacity: 383 mAh/g for first generation and 394 mAh/g for second generation. The irreversible capacity was determined as 151 mAh/g or 28% of full capacity for first generation electrolyte and 167 mAh/g or 30% of full capacity for second generation electrolyte.

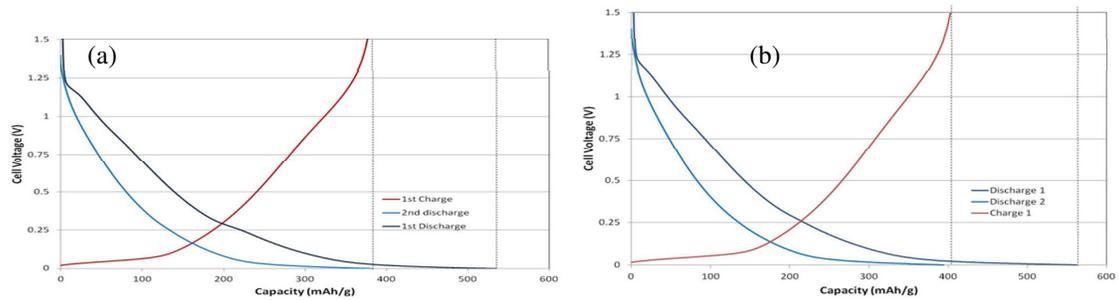


Figure 3. The voltage profiles of JM Energy's negative carbon electrode cycled in: (a) 1<sup>st</sup> generation electrolyte consisting of 1.2M LiPF<sub>6</sub> in EC:PC:DEC (3:1:4 by volume), and (b) 2<sup>nd</sup> generation electrolyte whose composition is proprietary. Cells were cycled at 10 mA/g and a voltage window of 0.0V to 1.5V.

**Publications, Reports, Intellectual Property or Patent Application Filed this Quarter.**

P. Smith, T. Tran, and T. Jiang, "Lithium-Ion Capacitors - Performance Strengths, Limitations, and Future Directions", AABC Europe 2011, Mainz, Germany, 7 June 2011.

P. Smith, T. Tran, T. Jiang, S. Dallek, G. Zoski, J. Chung, M. Wartelsky, "Lithium-Ion Capacitors", Electrochemical Power Sources R&D Symposium, Monterey, CA, 21 June 2011.

# TASK 1

## Battery Cell Materials Development

**Project Number:** 1.1.X

**Project Title:** Paper study on continuous process for making gradient concentration cathode materials

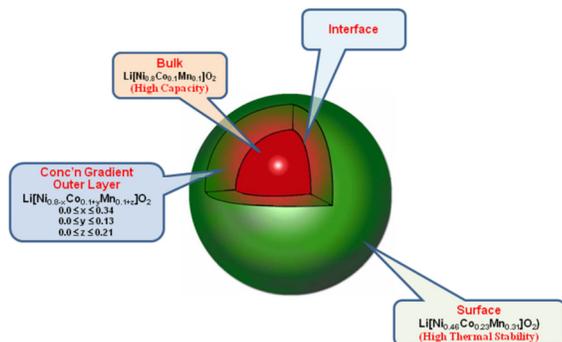
**Project PI, Institution:** Gregory Krumbick, Argonne National Laboratory

**Collaborators (include industry):**  
Young Ho Shin, Argonne National Laboratory

**Project Start/End Dates:** start: 10/1/2010; end: 9/30/2011

**Objectives:** The objective of the work is to determine economic feasibility of batch and continuous processes developed for the production of the newly develop new high energy functional cathode material based on Mn-Ni-Co layered oxide system for 40 miles PHEV. This material has the potential of offering high capacity of over 220mAh/g at 4.4V with excellent cycle and calendar life and excellent abuse tolerance.

**Approach:** We propose to analyze the current method for making the gradient concentration cathode material and to apply process engineering to scale this batch process to the 1-10kg and 10-100kg scale and to determine if a continuous process was feasible. An economic analysis will be conducted on all processes.



**Figure 1.** Schematic of positive electrode particle with Ni-rich core surrounded by concentration-gradient out layer.

### Deliverables:

- Detailed batch process for the production of 1-10kg batches of gradient concentration cathode material
- Economic analysis of the 1-10kg batch process

- Detailed batch process for the production of 10-100kg batches of gradient concentration cathode material
- Economic analysis of the 10-100kg batch process
- Detailed process for the continuous production of gradient concentration cathode material
- Economic analysis of the continuous process

At the recommended funding level, the study is expected to be completed in 1 year. Deliverables will include a final topical report which will include proposed process scale-up designs and an economic analysis of the proposed process.

**Financial data:**

Total project duration: 12 mo.

Staff: \$100K

**Progress towards Deliverables:**

Successful completion of this task requires the skills of an experienced process scale up materials engineer with extensive experience in battery materials development. While this task was initially going to be assigned to Dr. Kaname Takeya, due to other obligations, Dr. Takeya's available time working at Argonne was reduced and he was unable to devote time to this project. In addition to the current task, we were searching for an individual who would be responsible for the scale-up of other advanced lithium ion battery materials and chemistries in our cathode materials group and have located Dr. Young-Ho Shin from Hanwha Chemical in Daejeon, Korea to fill this role. Dr. Shin has extensive experience in cathode materials process scale up as well as pilot scale development and operations.

Dr. Shin was offered a staff position on 12/23/2011 and Argonne's HR department initiated the process to obtain an H1 visa. Dr. Shin received final visa approval on 4/1/2011. Dr. Shin started work at Argonne on 5/2/2011.

As assessment of the current process for the synthesis of the gradient concentration cathode material was started. A preliminary table of unit operations was developed (Table 1).

Target material : Mn-Ni-Co layered oxide		Lab. experiment Optimization is uncompleted		Process improvement Re-optimization is necessary for new system
Reactant preparation	Ni-Sulfate / Mn-Sulfate	0.6M / 1.2M	Fixed	Increased concentration
	Na <sub>2</sub> CO <sub>3</sub> / NH <sub>4</sub> OH	2.0M / 0.2M	Fixed	
Co-precipitation	Agitation speed	1000rpm	Fixed	Re-optimized
	pH control	7.88~8.01	Fixed	Re-optimized
	Reaction temp.	55°C	Fixed	Re-optimized
	Residence time	x	x	Optimized
	Precursor yield	x	x	Monitored
	Wastewater treatment	x	x	Reuse or treatment
	Min. secondary nucleation	x	x	New process design
Slurry washing	Impurity (Na/S) control	10 times	Fixed	Optimized
	Wastewater treatment	x	x	Reuse or treatment
Slurry filtration	Glass system with filter	10µm	Fixed	Conditions
Slurry drying	Box furnace in air	95°C, 20hrs	Fixed	Conditions
Sieving / classification	Hand sieving	~50µm	Fixed	Mechanical sieving
Mixing with Li <sub>2</sub> CO <sub>3</sub>	Ball milling	~48hrs	Fixed	Set-up equip. & condition
Calcination	Temperature profile	~850°C, 40hrs	Fixed	Re-optimized
Sieving / classification	Hand sieving	~50µm	Fixed	Mechanical sieving
	total yield	x	x	Monitored

**Table 1.** Unit operations for the synthesis of the gradient concentration cathode material

## TASK 1

### Battery Cell Materials Development

**Project Number:** 1.1K'

**Project Title:** Transition Metal Precursors for High Capacity Cathode Materials

**Project PI, Institution:** Ilias Belharouak, Argonne National Laboratory

**Collaborators (include industry):** D. Wang, G. Koenig, G. Krumdick, K. Takeya, Argonne National Laboratory.

**Project Start/End Dates:** January 1, 2011-September 30, 2014

**Objectives:** Develop a better correlation between the electrochemical properties of a high capacity material and its structural, morphological, and physical properties.

**Approach:** Carbonate is developed to prepare the precursors that will serve to produce high capacity cathode materials  $\text{Li}_{1+t}(\text{Ni}_x\text{Co}_y\text{Mn}_z)_{1-t}\text{O}_2$  ( $t \geq 0$ ,  $x+y+z=1$ ). A comparative study using the three routes (carbonate, hydroxide, and oxalate) will be made at the level of the materials morphology, physical characteristics, and electrochemical properties.

#### **Milestones:**

- a) Synthesis of  $(\text{Ni}_{0.3}\text{Mn}_{0.7}\text{CO}_3)$  carbonate precursor using a continuous stirred tank reactor (CSTR) continued. (Completed).
- b) Structural, physical, and chemical characterizations of  $(\text{Ni}_{0.3}\text{Mn}_{0.7}\text{CO}_3)$  continued. (Completed).
- c) The electrochemical performance of the final lithiated cathode materials is investigated (On schedule).

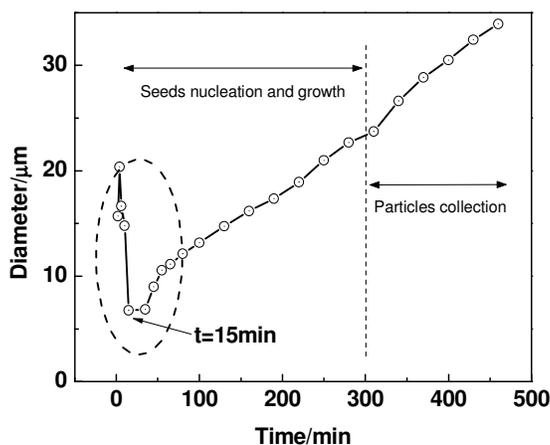
**Financial data:** \$300K/year, \$250K received in FY11.

#### **PROGRESS TOWARD MILESTONES**

Transition metal carbonate ( $\text{Ni}_{0.3}\text{Mn}_{0.7}\text{CO}_3$ ) was co-precipitated as the precursor for Li- and Mn-enriched composite materials. The optimal pH range for synthesis of  $\text{Ni}_{0.3}\text{Mn}_{0.7}\text{CO}_3$  in a continuous stirred tank reactor (CSTR) at the pilot scale was predicted by taking into account the chemical equilibriums between the products and reactants. The nucleation and growth of precursor particles were investigated during the CSTR process by monitoring particle size distributions, particle morphologies, chemical compositions, and structures with time. It was found that in the early stage of co-precipitation both the particle size distribution and the chemical composition were not homogeneous; a lead time of about 5 hours under our experiment conditions was necessary to achieve the uniformity in particle shape and chemical composition. The

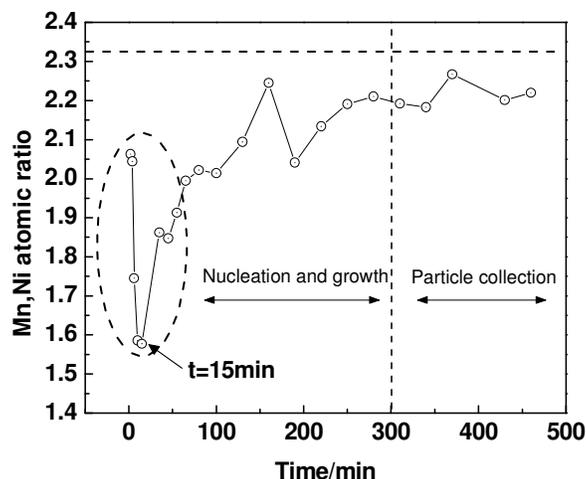
latter was not altered during extended times of co-precipitation; however, a continuous growth of particles resulting in relatively large particles ( $D_{50} > 30 \mu\text{m}$ ).

Fig. 1 shows the evolution of the average particle size ( $D_{50}$ ) with time. During the first 35 min of the reaction,  $D_{50}$  decreased from 20 to 8  $\mu\text{m}$ . Thereafter,  $D_{50}$  increased almost linearly during the rest of the experiment. The calculated growth rate of the average diameter was 3.4  $\mu\text{m}$  per hour. During the collection time, the average size of the particles increased from 24  $\mu\text{m}$  (300 min) to 34  $\mu\text{m}$  (460 min). As a result, the individual particles grew in mass, even though the feeding rate was kept constant during the co-precipitation. The possible explanation is that some additional nucleation sites were available at the surface of the freshly formed particles for further growth.



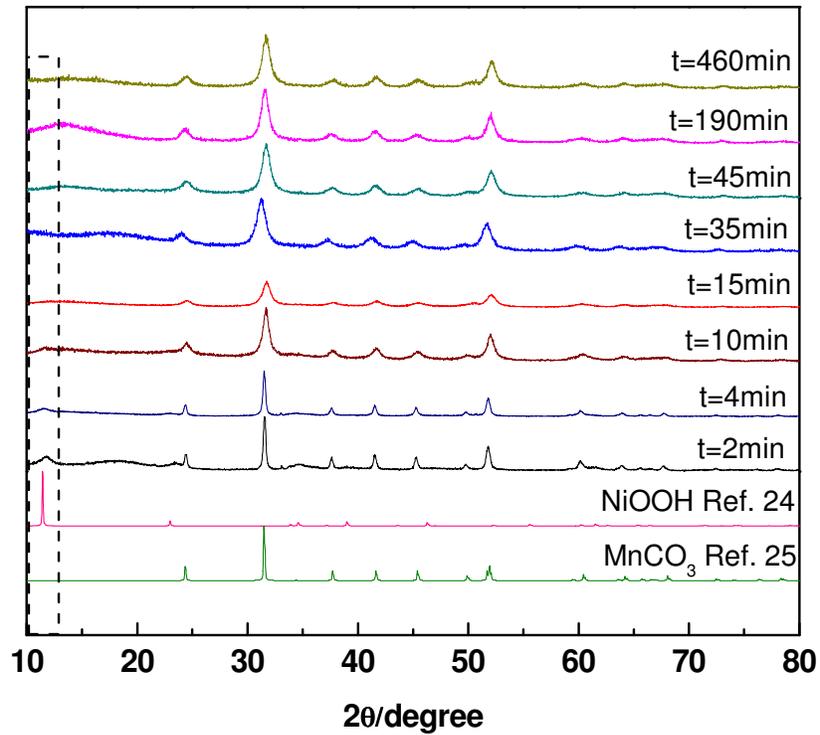
**Fig. 1. Average particle size ( $D_{50}$ ) evolution as a function of time**

Fig. 2 shows the compositions measured using EDXS obtained on particles collected during the co-precipitation reaction. Our qualitative analysis of the transition metals showed that the Mn/Ni atomic ratio fluctuated with time early in the process and then became more stable after 5 hours of reaction. The horizontal dotted line in Fig. 2 shows the nominal Mn/Ni atomic ratio expected under our experimental conditions. A huge deviation of the nominal and measured Mn/Ni atomic ratio was apparent at the beginning of the co-precipitation reaction. As time increased, the Mn/Ni atomic ratio increased and then approached the desired ratio after 5 hours of co-precipitation. For this reason, the precursor particles that were selected for the electrochemical study were collected after 5 hours of co-precipitation. Quantitatively, ICP analysis was used to determine the chemical composition of the precursor collected after 5 hours. In this case, the Mn/Ni ratio was 2.37 which is very close to 7:3 nominal ratio.



**Fig. 2. EDXS of samples collected at different reaction times**

X-ray diffraction provided further structure and phase information of the samples collected during the nucleation and growth processes (Fig. 3). It can be seen that the main component of the precipitates was carbonates; however, at an early stage, the small broad peak at  $2\theta = 11.6^\circ$  was consistent with the formation of nickel oxyhydroxide impurity. This peak became less important for the subsequent sample and finally disappeared after 15 min. At the beginning of the co-precipitation, NiOOH formed because it is thermodynamically much more stable than  $\text{NiCO}_3$  and also because the possibly localized high pH value within the reactor favors the formation of the hydroxide. At the early stage of the reaction a competition between the hydroxide and carbonate co-precipitation may have occurred because of the likelihood of fluctuations in pH and transition metal concentration inside the reactor. The peak signature of the observed nickel oxyhydroxide was very broad possibly due to the nano-character of the crystallites of the co-precipitated phase. Thereafter, as the solution became more homogeneous, the pH in the CSTR reactor stabilized, and therefore, the carbonate co-precipitation process dominated the reaction and give rise to the production of spherical carbonate precursor particles. Since the particles formed before 5 hours were less homogeneous in chemical composition and morphology, they were not used as the precursor for the preparation of the cathode material.



**Fig. 3. X-ray diffraction patterns of samples from different collection times**

**Publications, Reports, Intellectual property or patent application filed this quarter.**

Growth Mechanism of  $\text{Ni}_{0.3}\text{Mn}_{0.7}\text{CO}_3$  Precursor for High Capacity Li-Ion Battery Cathodes.

Dapeng Wang, Ilias Belharouak, Gary M. Koenig Jr., Guangwen Zhou, and Khalil Amine

J. Mater. Chem., 2011, 21 (25), 9290 – 9295.

## **TASK 2**

### **Calendar & Cycle Life Studies**

**Project Number:** ARRAVT075

**Project Title:** Prototype Cell Fabrication Facility

**Project PI, Institution:** Andrew Jansen and Dennis Dees, Argonne National Laboratory

**Collaborators (include industry):**

Ilias Belharouak, Argonne National Laboratory

Wenquan Lu, Argonne National Laboratory

Bryant Polzin, Argonne National Laboratory

John Vaughey, Argonne National Laboratory

**Project Start/End Dates:** April 2010 / May 2011

**Objectives:** The objective of this work is to identify and purchase several key pieces of equipment that will greatly enhance Argonne's ability to conduct vital preparation and diagnostic studies on advanced prototype lithium-ion cells, thereby supporting a DOE-EERE funded cell fabrication facility at Argonne.

**Approach:** The approach for this project is to utilize the extensive in-house expertise at Argonne available to identify, purchase, and install the equipment critical to the support and operation of the Argonne prototype lithium-ion cell fabrication facility.

**Milestones:**

(a.) Equipment identified and orders placed. August 2010, (Complete)

(b.) Equipment delivered and installed. December 2010, (Complete)

**Financial data:** \$1,000K in FY2010

#### **PROGRESS TOWARD MILESTONES**

**(a) Summary of work in the past quarter related to milestone (a).**

This milestone is complete. A list of all equipment is given below.

- Prototype cell testing and formation equipment
- Environmental chambers and ovens
- X-ray powder diffractometer
- Accelerating rate calorimeter (ARC) system
- Inert atmosphere glove box
- Multi-channel electrochemical test station and impedance analyzer
- Instron materials testing instrument

**(b) Summary of work in the past quarter related to milestone (b).**

All equipment has been delivered and installed, completing this milestone and the project.

**Publications, Reports, Intellectual property or patent application filed this quarter.  
(Please be rigorous, include internal reports--invention records, etc.)**

No publications, reports, or patents were submitted this quarter.

## TASK 2 Calendar & Cycle Life Studies

**Project Number:** ARRAVT077

**Project Title:** Post-Test Facility

**Project PI, Institution:** Ira Bloom/Argonne National Laboratory

**Collaborators (include industry):** < none >

**Project Start/End Dates:** start: 4/1/2010; end: 12/31/2011

**Objectives:** Establish a facility for the post-test examination of aged batteries. Post-test characterization of these materials can provide additional information, which, previously, could be only inferred. Physical, spectroscopic, metallographic, electrochemical tests will be used to aid the further improvement of a given technology by further elucidating failure modes.

**Approach:** Renovate and existing laboratory space to accommodate the needs of the new facility. Purchase a glove box, spectroscopic, microscopy, electrochemical and metallographic equipment for the tests to be performed. Use the experience and techniques developed in DOE's applied battery program in a standardized fashion, similar to the performance test protocols.

### **Milestones:**

Item	Due date	Status
Complete design for post-test laboratory construction	7/30/2010	Complete
Start construction of post-test laboratory	9/30/2010	Late start date: 12/2/2010
Post-test laboratory construction complete	3/31/2011	Delayed (vide infra)
Post-test equipment identified	7/30/2010	Complete
Issue solicitation for glove box and equipment	9/30/2010	Complete
Complete construction of post-test facility	12/31/2011	On schedule

### **Financial data:**

Total project duration: 21 mo.

Laboratory modifications \$300K/6 mo.

Equipment: \$2000K/17 mo.

### **PROGRESS TOWARD MILESTONES**

The overall design of the laboratory is shown in Fig. 1. The design shows the approximate placement of the major pieces of equipment.

An existing laboratory is being modified to accommodate the new facility. The existing laboratory was completely demolished and was brought up to current building codes. Most of the construction is complete, as shown in Fig. 2. There are support services (gas, water and electric) for some of the analytical equipment which still have to be installed. Consequentially, it is expected that construction will be completed by mid-August.

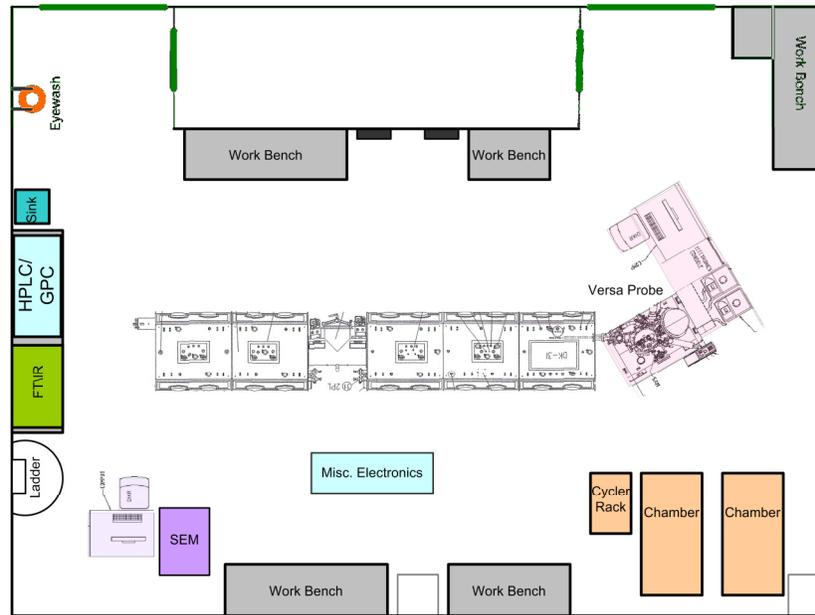


Fig. 1. Overall design of the post-test facility. The large, open area at the top of the figure is not part of the post-test facility. The VersaProbe X-ray photoelectron spectrometer (XPS) was purchased with funds from other sources.



Fig. 2. Photographs of the Post-Test Facility nearing completion. Clockwise from upper left: glovebox being installed; the VersaProbe XPS being aligned to the glovebox; and the scanning-electron microscope being calibrated.

Establishing the post-test facility will require procuring many pieces of equipment. The progress is shown in Table 1.

Table 1. Status of equipment purchases.

Equipment	Purchased?	Delivered?
Custom glovebox	Y	Y
FT-IR	Y	Y
Raman	Y	Y
Metallography equipment (saws, polishers, grinders, etc.)	Y	Y
Optical microscope	Y	Y
Electrochemical Impedance Spectroscopy (8-ch frequency analyzer and potentiostat)	Y	Y
Low-vacuum SEM	Y	Y
XPS	Y	Y
HPLC/GPC	Y	N-delivery is expected during the week of July 25
Coin cell cyclers	Y	Y
Environmental chambers	Y	Y

## **TASK 2**

### **Calendar & Cycle Life Studies**

**Project Number:** 2.1 (ES030)

**Project Title:** Fabricate PHEV Cells for Testing & Diagnostics in Cell Fabrication Facility

**Project PI, Institution:** Andrew Jansen and Bryant Polzin, Argonne National Laboratory

**Collaborators (include industry):**

Dennis Dees, Argonne National Laboratory  
Sun-Ho Kang, Argonne National Laboratory  
Wenquan Lu, Argonne National Laboratory

**Project Start/End Dates:** October 2008 / September 2014

**Objectives:** The objective of this work is to speed the evaluation of novel battery materials from the ABR and BATT programs, as well as from universities and the battery industry. The main objective in FY11 is to develop the capability to fabricate in-house pouch and 18650 cells in Argonne's new dry room facility.

**Approach:** Promising new exploratory materials are often developed in small coin cells, which may or may not scale up well in large PHEV battery designs. For this reason, pouch cells or rigid cells such as 18650's will be used for proofing of new materials in the capacity range of 0.4 to 2 Ah. Subcontracts will be established with battery developers to produce these cells. Concurrent to the fabrication of PHEV cells by battery developers, Argonne will develop the capability to fabricate pouch cells and 18650 cells in Argonne's new dry room facility. Once in-house cells are deemed to be reliable, the developer subcontracts will be reduced.

**Milestones:**

- (a.) All electrode and cell making equipment installed and approved for operation, December, 2011 (Completed)
- (b.) First cell build using advanced materials in pouch cell, March, 2011 (Completed)
- (c.) Second cell build using Argonne's advanced materials in pouch cell, May, 2011 (Delayed)
- (d.) First cell build using 18650 cell making equipment, September 2011, (On schedule)

**Financial data:** \$740K

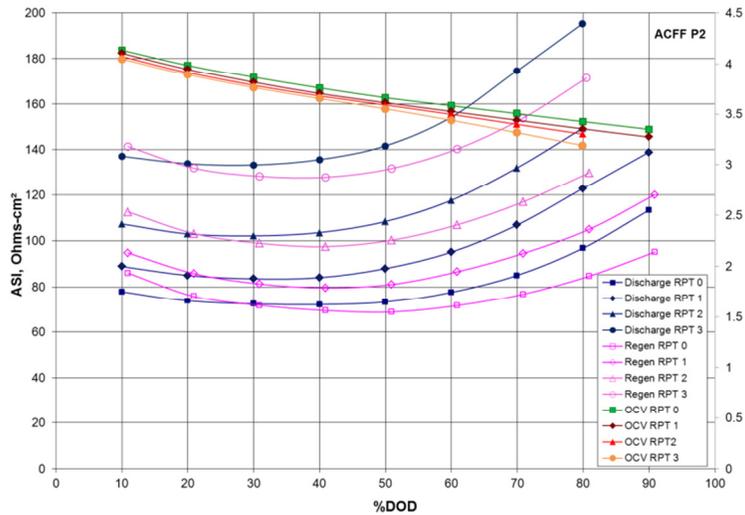
#### **PROGRESS TOWARD MILESTONES**

**(a) Summary of work in the past quarter related to milestone (a).**

Modifications were made to several pieces of equipment to enhance safety and operation in the dry room, with final approval to operate all equipment granted in February, 2011.

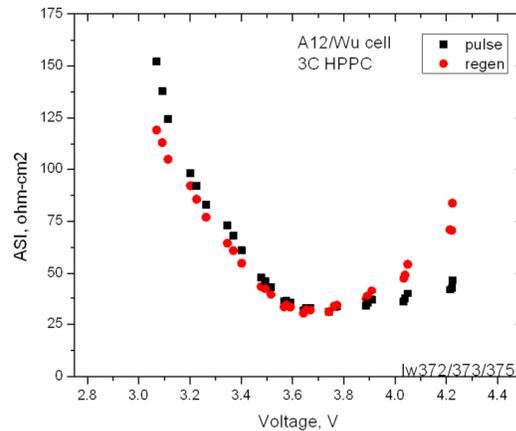
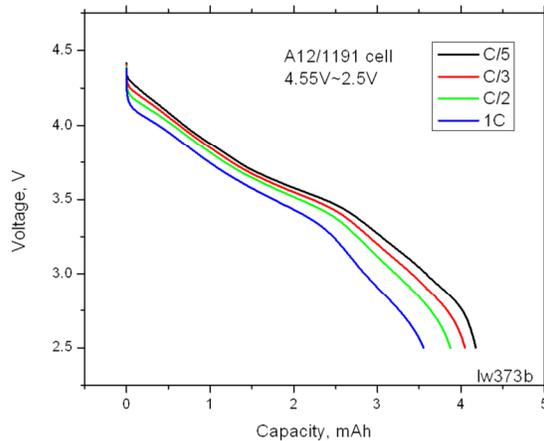
**(b) Summary of work in the past quarter related to milestone (b)**

Single-sided and double-sided electrodes were made with Toda' high energy cathode material, HE5050 ( $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.10}\text{Mn}_{0.55}\text{O}_2$ ), and with ConocoPhillips CGP-A12 high energy graphite. Over a dozen pouch cell assemblies were made with these advanced electrodes, seven of which were filled with electrolyte and then subjected to formation cycling and electrochemical performance characterization cycling. These cells performed well and were delivered to the EADL for independent verification and life testing. EADL completed testing of the first batch of Toda HE5050 cells at the end of June. A typical summary of one of these pouch cells is shown in the figure below. The cells were taken off test due to impedance rise. No further cells were made with this chemistry; more may be made in the future depending on recommendations from Diagnostics and Post-test Analysis.



**(c) Summary of work in the past quarter related to milestone (c)**

Huiming Wu (Argonne) produced 2 kg of his high-energy NMC cathode ( $\text{Li}_{1.2}\text{Ni}_{0.3}\text{Mn}_{0.6}\text{O}_{2.1}$ ) in several batches. Single-sided and double-sided electrodes were made on the A-Pro coater and validated by the Materials Screening. These results were good and are shown below. At least a dozen pouch cells are scheduled to be made in July in the Cell Fabrication Facility.



**(d) Summary of work in the past quarter related to milestone (d)**

Received the additional 18650 cell parts and the matching can holders for the groover and electrolyte filler equipment. Will begin electrode slitting trials in August.

**Publications, Reports, Intellectual property or patent application filed this quarter. (Please be rigorous, include internal reports--invention records, etc.)**

A poster abstract titled “DOE’s Cell Fabrication Facility” was submitted to the 5<sup>th</sup> International Conference on Polymer Batteries and Fuel Cells to be held at Argonne on August 1-5, 2011.

“High-Energy Electrode Investigation for Plug-in Hybrid Electric Vehicles”, Wenquan Lu, Andrew Jansen, Dennis Dees, Paul Nelson, Nicholas R. Veselka, and Gary Henriksen, J. Power Sources, 196, 2011, 1537-1540.

## TASK 2 Calendar & Cycle Life Studies

**Project Number:** 2.2B (ES031)

**Project Title:** Model Cell Chemistries (Electrochemistry Cell Model)

**Project PI, Institution:** Dennis Dees and Kevin Gallagher, Argonne National Laboratory

**Collaborators (include industry):**

Daniel Abraham, Argonne National Laboratory

Sun-Ho Kang, Argonne National Laboratory

Andrew Jansen, Argonne National Laboratory

Wenquan Lu, Argonne National Laboratory

Kevin Gering, Idaho National Laboratory

**Project Start/End Dates:** October 2008 / September 2014

**Objectives:** The objective of this work is to correlate analytical diagnostic results with the electrochemical performance of advanced lithium-ion battery technologies for PHEV applications.

- Link experimental efforts through electrochemical modeling studies.
- Identify performance limitations and aging mechanisms.

**Approach:** Electrochemical modeling studies are utilized to elucidate transport, reaction, and thermodynamic phenomena in advanced lithium-ion cell chemistries. This work builds on earlier successful characterization and modeling studies in extending efforts to new PHEV technologies. The challenges center on expansion of the data base and enhancement of the modeling capabilities.

**Milestones:**

- (a.) Advance development of PHEV focused electrochemical models in support of programmatic goals. September 2014, (On schedule)
- (b.) Identify new differential algebraic equation solver package with enhanced capabilities and complete conversion of existing models to newly adopted package. September 2011, (On schedule)
- (c.) Complete implementation and initial testing of full SEI growth model. December 2012, (On schedule)
- (d.) Initiate parameter estimation of high-energy NMC/graphite system. March 2012, (On schedule)

**Financial data:** \$400K/year

### PROGRESS TOWARD MILESTONES

**(a) Summary of work in the past quarter related to milestone (a).**

A three-dimensional electrochemical model, developed earlier this year to examine primary-secondary active particle microstructure and properties affecting impedance, was modified to study spheroid shaped particles. To simplify the studies three types of overall particle shapes were examined spherical (adopted in original modeling study with an aspect ratio = 1), potato ( $1 < \text{aspect ratio} < 4$ ), and saucer ( $1 < \text{aspect ratio} < 4$ ). As an initial test case for this model, the spherical-particle-shaped carbon anode material being developed in this program was examined. An approximate sloping voltage discharge curve was estimated from half-cell cycling data with the graphitized material. A reasonable estimate was made for the diffusion coefficient of lithium through the carbon, based on previous work on graphite negative electrodes. Initial studies were conducted assuming isotropic transport properties, an assumption that can be changed for examining highly graphitized material. The core of the particle was considered dense and a relatively thin shell was added with limited porosity to account for the measured surface area.

Initial simulations with the three particle shapes were conducted with all particles having the same volume and active area. The particle impedances are given in Figure 1 for a ten minute step in potential applied to each of the particles. In general, the transport of lithium through the electrolyte around the particle is much faster than the solid-state transport of lithium through the carbon. This combined with the relatively high interfacial impedance makes the current distribution across the active area relatively uniform, despite changes in the particle shape. For short times, the impedance of all three particle shapes is similar. As the time increases, the concentration gradients reach further into the particles and the shorter diffusion length of the non-spherical particles is advantageous. These simulations are continuing by examining the impact of anisotropic solid-state diffusion coefficients.

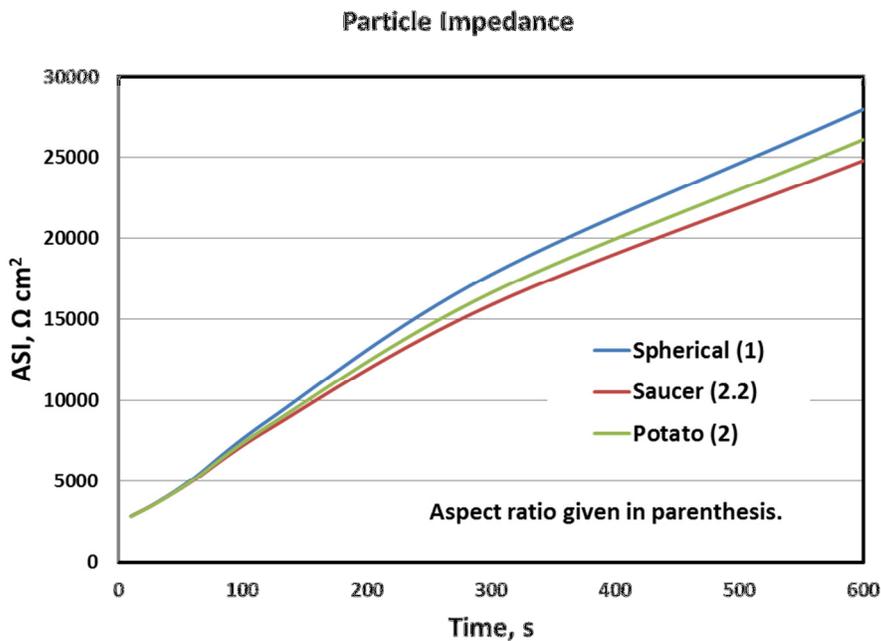


Figure 1 Impact of particle shape on performance.

**(b) Summary of work in the past quarter related to milestone (b)**

This project has been continually challenged by finding efficient ways to solve increasingly complex electrochemical cell models. A new differential algebraic equation solver package (PSE gPROMS) is being adopted to solve a wide variety of cell studies at the required level of complexity. Parameter estimation is always a serious challenge when dealing with the complex phenomenological modeling being used in this project. Previous effort used a “hand-fit” approach where the modeler systematically varied parameters to find a “best-fit” to the eye of the user. The new software package being implemented has parameter estimation algorithms and statistical assessment of the solution. Parameter estimations for new chemistries in both the DC and AC versions of the model will be streamlined enabling greater speed in modeling chemistries being evaluated in the ABR program. We have set-up the parameter estimation for the DC model and begun evaluating some of the previous values used.

**(c) Summary of work in the past quarter related to milestone (c)**

Work is progressing on implementing the SEI growth model necessary to understand power and energy fade in future Li-ion cell builds. Differing negative electrode aging behavior between Gen 2 to Gen 3 is being examined to establish a baseline set of parameters. The deposition of cations (Mn, Ni, Co, Fe, Li etc) into the solid-electrolyte interphase is known to accelerate capacity fade; although, the exact mechanism has yet to be proven. We suggest that the mobility of the negative charge carrier in the SEI (assuming  $t_- > 0$ ,  $t_+ + t_- = 1$ ) is the limiting factor for capacity fade during calendar-life testing at moderate and high states of charge. The reduction of cations to metals under certain conditions will lead to an enhanced mobility of negative charge in the SEI. It is not clear whether this effect is constrained to the immediate proximity of the metal center. Regardless, the mobility of the negative charge carrier in the SEI will be higher than without the deposited cation. Current model development involves inclusion of the appropriate equations to capture this side reaction that may govern an interplay between the cathode and anode.

**(d) Summary of work in the past quarter related to milestone (d)**

While on schedule, initiating work on this Milestone is dependent on the completion of Milestones (b) and (c), as well as generation of high-energy NMC/graphite Li-ion cell data by the diagnostics and testing area.

**Publications, Reports, Intellectual property or patent application filed this quarter. (Please be rigorous, include internal reports--invention records, etc.)**

No publications, reports, or patents were submitted this quarter.

## **TASK 2**

### **Calendar & Cycle Life Studies**

**Project Number:** 2.3A (ES032)

**Project Title:** Diagnostic Evaluation of Lithium Battery Cells and Cell Components

**Project PI, Institution:** Daniel Abraham, Argonne National Laboratory

**Collaborators:**

M. Bettge, J. Bareno, G. Cheng, S.-H. Kang, M. Balasubramanian, B. Polzin, A. Jansen, D. Dees, W. Lu, Argonne National Laboratory

J.G. Wen, M. Sardela, S. MacLaren, R. Haasch, I. Petrov, University of Illinois at Urbana-Champaign

B. Lucht, University of Rhode Island

**Project Start/End Dates:** October 2008 / September 2014

**Objectives:** Various electrochemical couples are being examined for use in lithium-ion cells for PHEV applications. The objective of this study is (1) to identify factors that contribute to cell performance and performance degradation (capacity fade, impedance rise) on long-term storage/cycling of these various electrochemical couples; (2) to recommend solutions that improve performance and minimize performance degradation of materials, electrodes, and cells.

**Approach:** Every component in a cell – positive and negative electrodes, separator, electrolyte – is examined to gain an understanding of cell performance and performance degradation. We typically employ electrochemical and physicochemical techniques. Our electrochemical measurements are conducted in various cell configurations that include coin cells, pouch cells, and reference electrode cells. Our physicochemical examinations employ a combination of spectroscopy, microscopy, diffraction and chemical analysis techniques that include scanning and transmission electron microscopy, electron energy loss spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, Fourier Transform Infrared spectroscopy, and Nuclear Magnetic Resonance spectroscopy.

**Milestones:**

- (a.) Complete accelerated aging studies of PHEV baseline cells, March 2011, (met milestone)
- (b.) Complete diagnostic examination of PHEV baseline cells and cell constituents, September 2011, (on schedule)
- (c.) Initiate characterization and aging experiments on electrodes and electrode constituents identified for the next set of ABR PHEV cells, September 2011, (on schedule)

**Financial data:** \$300K

## PROGRESS TOWARD MILESTONES

### (a) Summary of work in the past quarter related to milestone (a).

Cells with the PHEV baseline chemistry contain  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ -based positive electrodes, Mag10 Graphite-based negative electrodes, Celgard 2325 separator, and EC:EMC (3:7, by wt.) + 1.2M  $\text{LiPF}_6$  (baseline) electrolyte. The performance of as-prepared cells was characterized using a series electrochemical charge-discharge cycling and impedance experiments. The cells were then cycle-life aged at 45°C; capacity and impedance data were obtained periodically to characterize performance degradation. Our accelerated aging tests on the PHEV baseline cells are now complete.

### (b) Summary of work in the past quarter related to milestone (b).

In a previous quarterly report we indicated that cells with the PHEV-baseline chemistry show capacity fade and impedance rise on accelerated aging. We showed that cell performance degradation is greater for wider voltage cycling windows; i.e., when a larger proportion of the  $\text{Li}^+$  inventory is shuttled between the electrodes. Herein, we report data from our reference electrode studies.

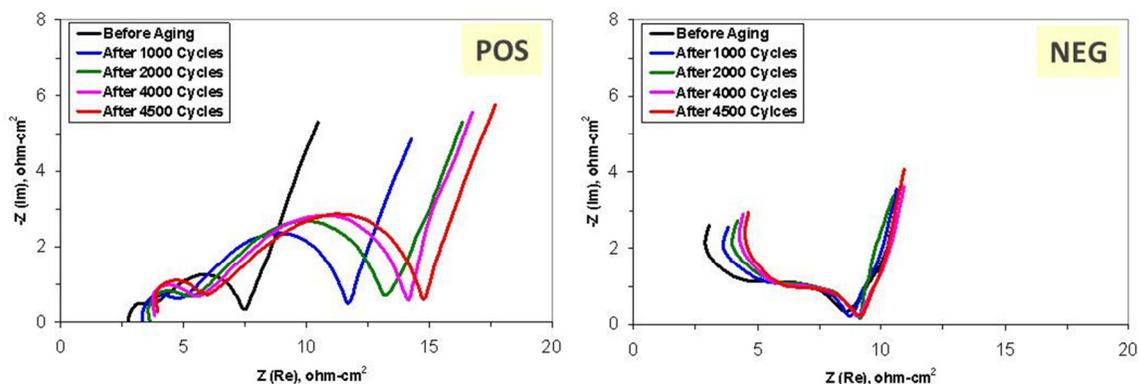


Fig. 1. AC impedance data obtained on a cell containing a Li-Sn reference electrode

Figure 1 shows AC impedance data obtained on a cell that underwent 4000 cycles between 3.6 and 4.0V, then 2000 cycles between 3.3 and 4.0V at a C/1 rate at 45°C. The full cell data (not shown) indicated that cell impedance increases on aging. Data from cells with a Li-Sn reference electrode showed that negative electrode contribution is minimal (see Fig. 1). The impedance rise arises mainly at the positive electrode, and can be attributed to processes (i) at the electrode-electrolyte interface (mid-frequency arc) and (ii) within oxide bulk (Warburg diffusion tail – *data not shown*).

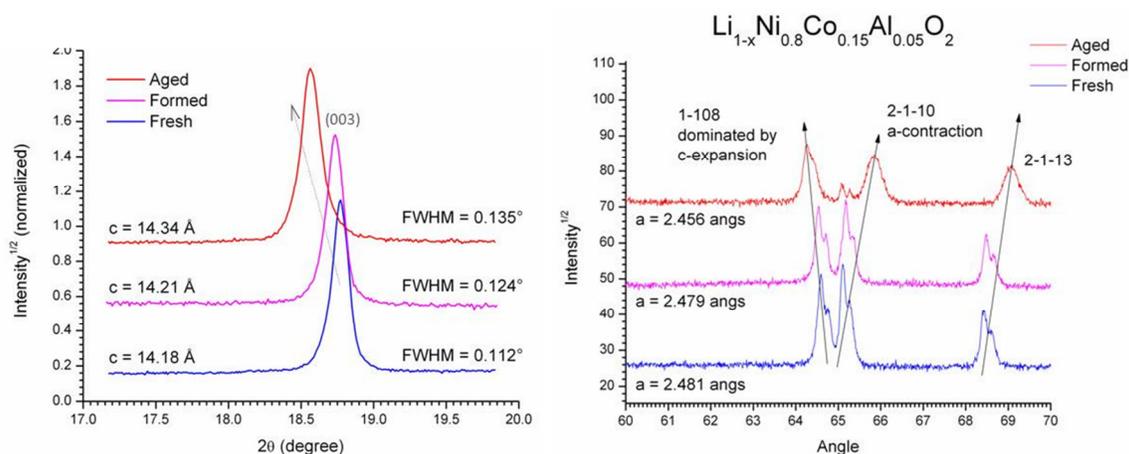


Fig. 2. X-ray diffraction data obtained on the positive electrode

To determine the source of impedance rise we conducted experiments on positive electrodes that were harvested from various full cells. Figure 2 contains XRD data on positive electrode samples harvested from “Formed” and “Aged” full cells discharged to  $< 2V$ . The measured peak shifts indicate c-axis expansion and a-axis contraction on aging. These data indicate that the aged samples contain Li-deficient oxides. The observed changes in the bulk oxide structure indicate Li-loss from the oxides, which is consistent with the capacity loss displayed by the cells.

**(c) Summary of work in the past quarter related to milestone (c)**

We have initiated experiments with electrodes and electrode constituents for ABR-1 cells. Figure 3 is an example of one such dataset. It shows electrochemical cycling data obtained on a cell containing HE5050(+)//Li electrodes cycled in the 2 – 4.7V window, at 30 °C, at a rate of 9.9 mA/gm. (HE5050 =  $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ ). The data indicate changes in the voltage profile during cycling – this “depression” of the voltage profile, seen on both charging and discharging, is significant during the early cycles and slows with cycle number. This behavior appears to be triggered by changes to the oxide structure during the first charge cycle and is believed to result from phase changes in the oxide.

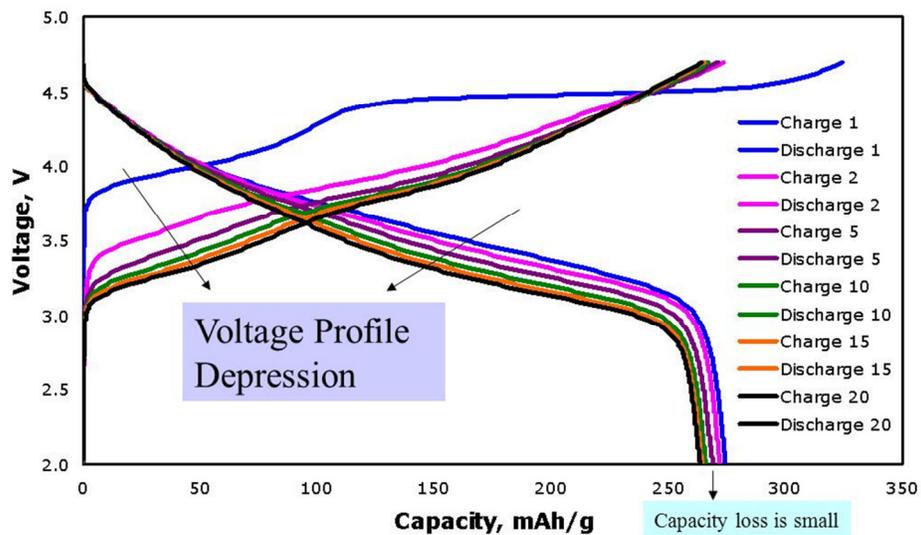


Fig. 3. Electrochemical cycling data obtained on a cell containing HE5050(+)//Li electrodes.

**Publications, Reports, Intellectual property or patent application filed this quarter. (Please be rigorous, include internal reports--invention records, etc.)**

No publications, reports, or patents were submitted this quarter.

## TASK 2

### Calendar & Cycle Life Studies

**Project Number:** 2.3B (ES032)

**Project Title:** Structural Investigations of Layered Oxides for PHEV Applications

**Project PI, Institution:** Daniel Abraham, Argonne National Laboratory

**Collaborators (include industry):**

J. Bareno, S.-H. Kang, M. Balasubramanian, Argonne National Laboratory

J.G. Wen, M. Sardela, S. MacLaren, I. Petrov, University of Illinois at Urbana-Champaign

**Project Start/End Dates:** October 2008 / September 2014

**Objectives:** The structure and structural rearrangements in Mn-based oxides, which high-capacities when cycled at high-voltages, have a significant effect on cell performance, calendar-life, and safety. Our goal is to obtain a detailed structural understanding of the  $\text{Li}_{1+a}(\text{Mn}_x\text{M}'_z)\text{O}_2$  family of materials: M' is typically Ni and/or Co, but other elements such as Fe, Cr, and Al, are also being studied. Our experiments are designed to answer some of the following questions: (i) What are the local atomic arrangements in the as-prepared oxides and how are these arrangements influenced by composition? (ii) What are the charge compensation mechanisms during electrochemical cycling? (iii) What phase transformations result on cycling/aging? How does this affect the oxide's capacity and rate performance?

**Approach:** A multi-institution effort is underway to synthesize, characterize, and model these complicated oxide structures. After synthesis, and initial examination of oxide electrochemical performance, we conduct both *exsitu* and *insitu* X-ray absorption spectroscopy (XAS) measurements that provide information on oxidation states, coordination number around the transition metal (TM) elements, and changes in these parameters during electrochemical cycling. The XAS study is complemented by Analytical Electron Microscopy (AEM), which includes high angle annular dark field electron microscopy to examine the crystal structure and electron energy loss spectroscopy to examine composition variations at near-atomic spatial resolutions. Our initial studies are on  $\text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2$ , which is a model compound to study the structure of  $\text{Li}_{1+a}(\text{Mn}_x\text{M}'_z)\text{O}_2$  materials being considered for PHEV applications.

**Milestones:**

- (a.) Complete structural study of as-prepared  $\text{Li}(\text{Li}_{0.2}\text{Mn}_{0.4}\text{Co}_{0.4})\text{O}_2$ , March 2011, (met milestone)
- (b.) Initiate structural study of cycled  $\text{Li}(\text{Li}_{0.2}\text{Mn}_{0.4}\text{Co}_{0.4})\text{O}_2$ , March 2011, (on schedule)

**Financial data:** \$300K

## PROGRESS TOWARD MILESTONES

### (a) Summary of work in the past quarter related to milestone (a).

The work related to milestone (a) is complete; we reported on it in a previous quarterly. In summary, the as-prepared  $\text{Li}(\text{Li}_{0.2}\text{Mn}_{0.4}\text{Co}_{0.4})\text{O}_2$  samples revealed the coexistence of monoclinic  $\text{Li}_2\text{MnO}_3$ -like and rhombohedral  $\text{LiCoO}_2$ -like crystal structures. After examination of our data we concluded that the sample contains well integrated  $\text{LiCoO}_2$  and  $\text{Li}_2\text{MnO}_3$  areas arranged as dendritic nanoclusters.

### (b) Summary of work in the past quarter related to milestone (b).

Analytical electron microscopy (AEM) and X-ray absorption spectroscopy (XAS) of cycled  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  samples are in progress.

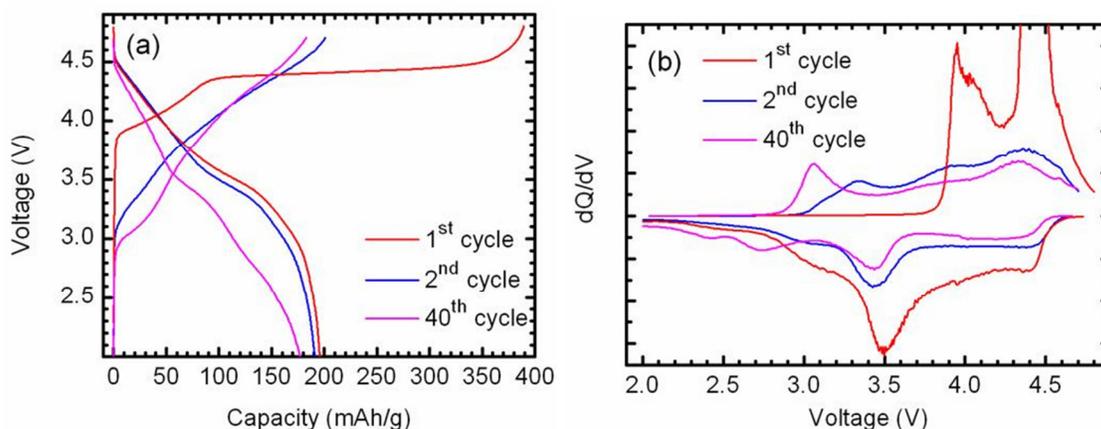


Fig. 1 a) Charge-discharge profiles and (b) corresponding  $dQ/dV$  plots of  $\text{Li}(\text{Li}_{0.2}\text{Mn}_{0.4}\text{Co}_{0.4})\text{O}_2$  vs. Li cell between 2 and 4.7V.

Figure 1 shows charge-discharge cycles for the first, second and 40<sup>th</sup> cycle, carried between 2.0 V and 4.7 V vs. Li. The long plateau is observed during the first charge cycle is believed to result from a crystal structure change that includes the evolution of oxygen from the sample. A depression of the voltage profile is observed on extended cycling.

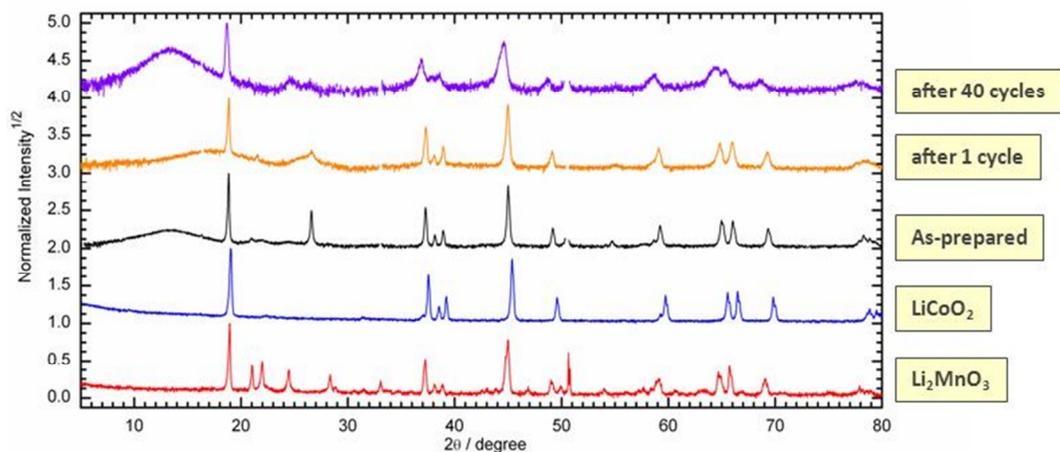


Fig. 2. X-ray diffraction data on  $\text{Li}(\text{Li}_{0.2}\text{Mn}_{0.4}\text{Co}_{0.4})\text{O}_2$  samples. Data from  $\text{LiCoO}_2$  and  $\text{Li}_2\text{MnO}_3$  are shown for comparison.

X-ray diffraction (XRD) data provide information on long-range (average) structure of crystal lattice. Figure 2 presents a comparison of XRD spectra from  $\text{Li}_2\text{MnO}_3$ , and  $\text{LiCoO}_2$  powder samples with  $\text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2$  laminates, both as-prepared, and after one and forty electrochemical cycles in a cell employing a Li anode. The cycled  $\text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2$  spectra present an overall shift to lower  $2\theta$  values, indicative of an increase in lattice parameters, and decreased crystal quality, as evidenced by reduced signal to noise ratio and broadened reflections. The data show no obvious evidence of new oxide phase formation after extended cycling. However, the graphite peak, evident at  $\sim 26.5^\circ$  in the as-prepared sample, shows significant broadening after the 1<sup>st</sup> cycle, and is not seen in the 40-cycle sample. The disappearance of the peak maybe related to the intercalation of  $\text{PF}_6^-$  ions into the graphite, which is an electron-conducting additive in the positive electrode.

**Publications, Reports, Intellectual property or patent application filed this quarter.**

No publications, reports, or patents were submitted this quarter.

## TASK 2

### Calendar & Cycle Life Studies

**Project Numbers:** 1.1.1 and 2.4.1 (ES033)

**Project Title:** Electrochemistry Diagnostics of Baseline and New Materials

**Project PI, Institution:** Robert Kostecki and Thomas Richardson, LBNL

**Collaborators (include industry):** ANL, BNL, INL, and SNL.

**Project Start/End Dates:** LBNL carried out diagnostics in the ATD Program since its 1999 inception, and the ABRT Program began October 2008

**Objectives:** (i) Enable increased cell specific energy by addressing the impact of high-voltage cathodes on the conducting carbon matrix. (ii) Determine the key factors that contribute to degradation mechanisms in PHEV test cells and individual cell components. (iii) Characterize SEI formation on model electrode surfaces to improve understanding of key interfacial phenomena in PHEV cells.

**Approach:** (i) Determine the mechanisms for carbon damage and retreat at high potentials. (ii) Investigate mitigating treatments, additives, and procedures. (iii) Use advanced *in situ* and *ex situ* spectroscopic and microscopic techniques in conjunction with standard electrochemical methods to characterize components harvested from fresh and tested PHEV cells, model thin-film cells, and special cells used to evaluate SEI formation processes. Surface optical spectroscopy (Raman, FTIR), scanning electron microscopy (SEM), atomic force microscopy (AFM), energy-dispersive x-ray analysis, and gas chromatography will be adapted (as needed) and applied to characterize fresh, formatted, and surface-modified high-energy composite cathodes and anodes.

**Milestones:** (i) Identify the mechanisms of carbon damage at high potentials, and investigate various approaches to preventing or reducing their effects (on schedule). (ii) Characterize specific interfacial, bulk-electrode, and electrolyte processes that may contribute to the electrode degradation modes, reduce high-rate performance, and/or induce a significant lithium inventory distortion in the cell, and thereby limit the cycle and calendar lifetimes of PHEV test cells (on schedule). (iii) Report progress on reduction of contact resistance growth in high-voltage cathodes (July 2010). Attend review meetings and present diagnostic results obtained in collaboration with ABR Program participants during FY 2011 (on schedule).

**Financial data:** FY 2011 diagnostics/materials funding \$600K

**Progress towards milestones:** In our previous reports we presented data showing that the electrochemical activity of a thin-film carbon electrode (from pyrolyzed polyimide precursor) toward electrolyte oxidation was dramatically diminished upon oxidation treatment at elevated temperatures. In an effort to evaluate the potential application of

this technology in high-voltage Li-ion cells, a common carbon black powder (Denka) was subjected to the same surface oxidation procedure. A small carbon sample was placed in a tubular furnace under a constant flow of nitrogen and heated to 900°C. When the temperature of the furnace reached 900°C, N<sub>2</sub> was replaced with CO<sub>2</sub>. After 1 hour, the CO<sub>2</sub> flow was stopped and nitrogen was introduced again while the furnace was allowed to cool down to room temperature.

BET surface area measurements of the pristine and the oxidized carbon powders were performed using nitrogen adsorption at -196°C. The BET surface areas of the pristine and oxidized samples were 50 m<sup>2</sup>/gr and 70 m<sup>2</sup>/gr, respectively. Unlike the case of the polyimide samples (the surface area increased from 35 m<sup>2</sup>/gr to >500 m<sup>2</sup>/gr), the surface area of the Denka black was increased by only 40%. This difference is likely due to a different structure and morphology of Denka carbon black as compared to the carbon film pyrolyzed from polyimide at 1000°C.

To evaluate the electrochemical properties of the heat-treated carbon black material, composite electrodes were prepared. 90% of carbon powder and 10% of PVdF were mixed in NMP for 12 hours. The resulting slurry was drop casted onto an aluminum current collector and allowed to dry at 80°C. The electrodes were then placed in a vacuum oven and dried at 120°C for 12 hours. A three-electrode cell was assembled with lithium-foil reference and counter electrodes, and filled with 1M LiPF<sub>6</sub>, EC:DEC (wt. 1:2). Cyclic voltammetry measurements were performed at a scan rate of 5 mV/sec.

Figures 1 and 2 show the CVs of the pristine and oxidized carbon black electrodes. The double layer capacities of the pristine sample and oxidized sample were 2 F/gr and 3 F/gr, respectively. This difference in capacitance is consistent with the 40% increase of surface area upon carbon oxidation treatment. The current at the anodic potential vertex is an excellent indication of the extent of electrolyte oxidation taking place at that potential. As can be seen from Figures 1&2, the anodic vertex current in the pristine carbon black is significantly higher compared to the oxidized sample. The difference in the anodic vertex current becomes more pronounced as the electrodes were polarized to higher anodic potentials. When the potential span was higher than 5 V, a cathodic peak appeared at 4.2 V (in both samples) and was attributed to the deintercalation of PF<sub>6</sub><sup>-</sup> anions.

Based on the results presented here, we postulate that carbon surface structure modification due to the oxidation process inhibits both electrolyte oxidation and anion intercalation. Interestingly, this deactivation effect is observed despite the significant surface area increase, which should produce the opposite current trend. It is likely that the presence of surface groups created during the oxidation treatment is responsible for improved electrolyte stability.

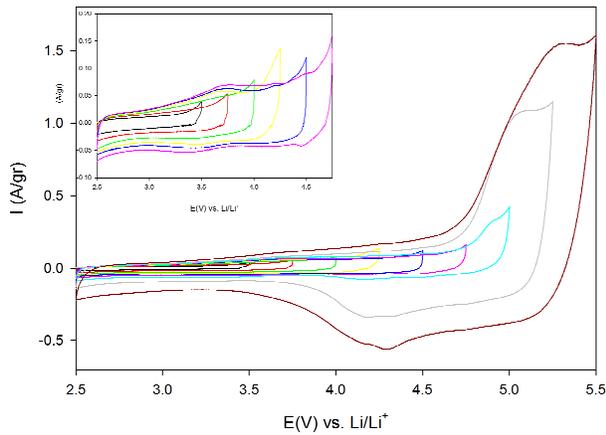


Figure 2. CV's of pristine Denka carbon black.

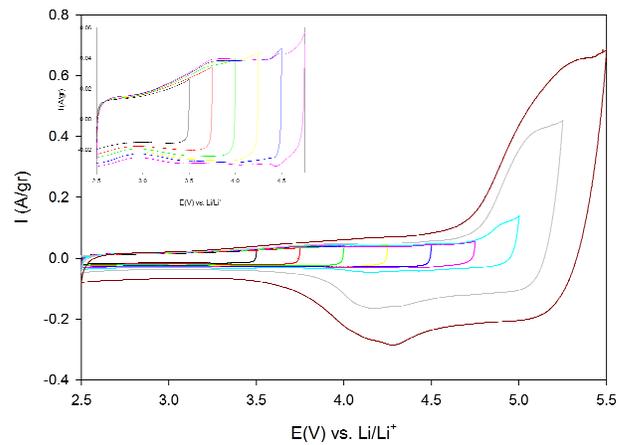


Figure 3. CV's of oxidized Denka carbon black. Inset, CV's of oxidized Denka carbon black up to 5V

## **TASK 2**

### **Calendar & Cycle Life Studies**

**Project Number: ES034**

**Project Title: Diagnostic Studies to Improve Abuse Tolerance and life of Li-ion batteries**

**Project PI, Institution: Xiao-Qing Yang and Kyung-Wan Nam, Brookhaven National Lab.**

**Collaborators (include industry):**

Argonne National Lab. (ANL), Oakridge National Lab. (ONL), University of Tennessee Beijing Institute of Physics (IOP, CAS), Korea Institute of Science and Technology (KIST)  
Hydro-Québec (IREQ), Duracell (P&G), Dow Chemical, GM R&D Center

**Project Start/End Dates: October 1, 2010-September 2011**

**Objectives:**

- Develop new diagnostic techniques with ability to distinguish bulk and surface processes, to monitor the degradation processes, to determine the effects of structural changes of electrode materials, the interfacial phenomena, and electrolyte decomposition on the cell capacity and power fading, as well as on the abuse tolerance for safety characteristic related issues.
- Using diagnostic techniques to evaluate and screen the new materials, material processing and modification procedures which are aimed to improve the performance, calendar and cycling life, and the abuse tolerance of lithium batteries for HEV, PHEV, and EV.

**Approach:**

- A combination of time resolved X-ray diffraction (XRD), in situ soft and hard X-ray absorption (XAS), in situ transmission electron microscopy (TEM) techniques during heating to study the thermal stability of the electrode materials.
- Apply the atomic layer deposition (ALD) technique for the surface modification of new cathode materials, using time resolved X-ray diffraction (XRD) to study the effects of surface modification on the thermal stability.
- In situ XRD, soft and hard XAS studies of new electrode materials during charge-discharge cycling to understand the power and energy density fading mechanism for longer cycling life of Li-ion batteries.
- Extended collaboration with other US and international academic institutions and US industrial partners.

**Milestones:**

(a) Complete the *In situ* XRD studies during charge-discharge cycling for Cr and F doped  $\text{LiMn}_2\text{O}_4$  spinel as high power cathode materials in collaboration with ANL. by April 2011, **Completed**. (b) Complete the Time resolved X-ray diffraction (TRXRD) studies of  $\text{ZrO}_2$  coated  $\text{LiAl}_{0.05}\text{Co}_{0.15}\text{Ni}_{0.8}\text{O}_2$  and  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cathode materials during heating by April 2011, **Completed**. (c) Report the results of in situ XRD studies of Cu or Ni doped  $\text{LiMn}_2\text{O}_4$  spinel as high voltage cathode materials in collaboration with Duracell (P&G) by September, 2011, **on schedule**. (d) Start in situ XAS and TR-XRD studies of  $\text{Li}_2\text{MnO}_3$ - $\text{LMO}_2$  type new cathode materials during cycling and heating by September, 2011, **on schedule**.

**Financial data:** \$350,000/year

### **Progress Toward Milestones:**

#### **(a) Summary of work in the past quarter related to milestone (a).**

This milestone has been completed

#### **(b) Summary of work in the past quarter related to milestone (b)**

Progress has been made toward the milestone (b): The Time resolved X-ray diffraction (TRXRD) studies of  $\text{ZrO}_2$  coated  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  and  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cathode materials during heating are underway. The results show that no significant improvement in thermal stability for the  $\text{ZrO}_2$  coated  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  samples in comparison with the uncoated ones, if no electrolyte is added. However, if the electrolyte is added, the  $\text{ZrO}_2$  coated samples show quite impressive improvement in thermal stability. This is a clear indication that the improvement of thermal stability by  $\text{ZrO}_2$  surface coating is originated by reducing the surface contact of the cathode material with the electrolyte. This milestone has been completed

#### **(c) Summary of work in the past quarter related to milestone (c)**

Progress has been made toward milestone (c). In situ XRD spectra of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  samples calcined at 700 °C and 800 °C by scientist at Duracell (P&G) have been collected during charge-discharge cycling at NSLS. The in situ XRD spectra in Figure 1 for the sample calcined at 700 °C shown that the capacity fading of this sample during cycling is correlated to the cycling induced structural deterioration. The Bragg peaks representing the residue of original phase can be clearly observed at the end of each charge (discharge) and the ranges of the lattice parameter change between the end of charge and discharge are decreasing with increasing cycling number, indicating the increasing of the inactive parts of the cathode materials upon cycling. In contrast, for the sample calcined at 800 °C, the charge-discharge curves plotted in Figure 2 showed very good capacity retention. The in situ XRD showed complete reversible structural changes during cycling with no original phase residue observed at the end of each charge (discharge). These results show the high crystallinity of the sample calcined at 800 °C is the key for superior cycling performance of the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  materials.

#### **(d) Summary of work in the past quarter related to milestone (d)**

Progress has been made toward the milestone (d): Preliminary results of in situ TR-XRD data of  $\text{Li}_2\text{MnO}_3$ - $\text{LMO}_2$  type new cathode materials during heating has been collected.

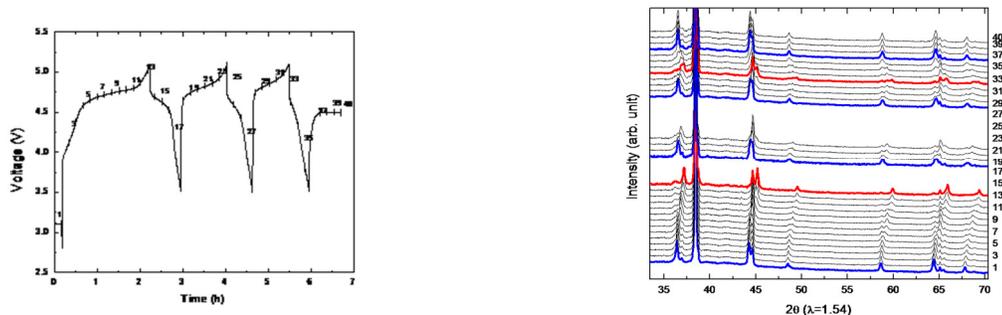


Figure 1: Charge-discharge curves and in situ XRD for  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  sample calcined at  $700\text{ }^\circ\text{C}$ .

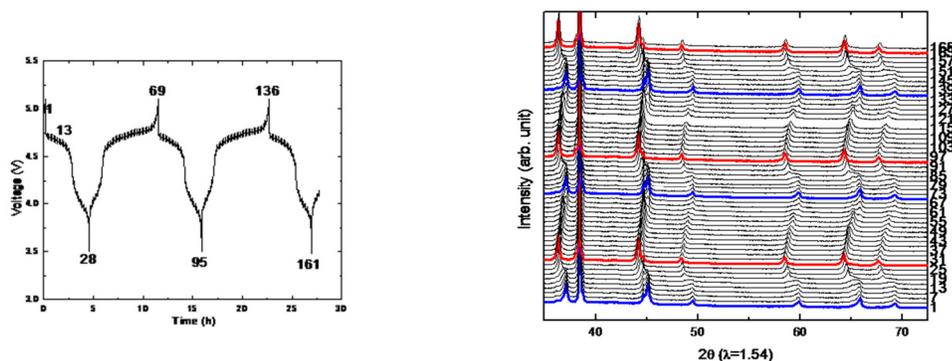


Figure 2: Charge-discharge curves and in situ XRD for  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  sample calcined at  $800\text{ }^\circ\text{C}$ .

#### Publications and presentations in this quarter:

1. X.J. Wang, X. Q. Yang, H. S. Lee, K. W. Nam, H. Li, and X. Huang, "The Synthesis and Characterization of New Additives and New Solvents for Lithium Battery Electrolytes", presented at the 2011 MRS Spring Meeting, April, 25-30, 2011, San Francisco, California, USA, **Invited**
2. Kyung-Wan Nam, Xiao-Jian Wang, Xiqian Yu, Enyuan Hu, Seong Min Bak, Kyung-Yoon Chung, and Xiao-Qing Yang, "Thermal Stability Study of Surface Modified Ni-based Cathode Materials using in situ- XRD, hard and soft X-ray Absorption Spectroscopy during Heating", presented at the 2011 MRS Spring Meeting, April, 25-30, 2011, San Francisco, California, USA.
3. X.J. Wang, C. Jaye, B. Zhang, Y.N. Zhou, K.W. Nam, H.Y. Chen, J.M. Bai, H. Li, X.J. Huang, D. Fischer, E.Y. Hu, and X.Q. Yang, "Investigation of Phase Transition Delay in  $\text{LiFePO}_4/\text{FePO}_4$  upon Charge Using Synchrotron Based X-ray Diffraction and Absorption Techniques", presented at the 2011 MRS Spring Meeting, April, 25-30, 2011, San Francisco, California, USA.
4. E.Y. Hu, Y. Lee, K-W. Nam, X.Q. Yu, X.J. Wang, and X.Q. Yang, "In situ X-ray absorption and diffraction studies of Ni and Fe substituted layer structured  $\text{Li}_2\text{MnO}_3$  based cathode material during electrochemical cycling", presented at the 2011 MRS Spring Meeting, April, 25-30, 2011, San Francisco, California, USA.

## **TASK 2**

### **Calendar & Cycle Life Studies**

**Quarterly report FY2011/03 – Performance period April 1 – June 30, 2011**

**Project Number:** ID39

**Project Title:** In-situ characterization and diagnostics of mechanical degradation in electrodes

**Project PI, Institution:** Claus Daniel, Oak Ridge National Laboratory (ORNL)

**Collaborators (include industry):**

University of Tennessee: Kevin Rhodes

ORNL: Melanie Kirkham, Robbie Meisner, Andrew Payzant, Chad Perish, Sergiy Kalnaus, Nancy Dudney, Zhili Feng, Xun-Li Wang, Ke An, David Wood

Argonne National Laboratory: Daniel Abraham

General Motors: Steve Harris, Yan Wu

Dow Kokam: Maneesh Bahadur, Erin O’Driscoll

**Project Start/End Dates:** August 2009 – September 2012

**Objectives:** Extend lifetime through understanding of mechanical degradation mechanisms and material design guidance. Improvement of capacity retention of MNO cathodes. Application of technique to be utilized by other ABR PIs and their materials.

**Approach:**

Electrode materials for lithium ion batteries (LIB) undergo many changes as they are cycled including lattice strain and particle fracture. The role of mechanical degradation overall LIB performance is not thoroughly understood but is likely to play an important role in the development of next generation active materials and cell design. However the progress of work in this is limited by current characterization techniques. A novel in situ technique that combines acoustic emission (AE) and X-ray diffraction (XRD) has been developed and tested on both anode and cathode materials.

AE has been utilized to detect, sort, and classify mechanical events such particle fracture inside of cycling LIBs. In order to directly correlate the observed fracture events with strain in the active materials special in situ methods of XRD can be utilized. A novel beryllium free in situ AE-XRD cell has been devised which uses a metalized Mylar or Kapton window to allow X-ray penetration during cycling in standard coin cell hardware. This provides a safe and inexpensive alternative to current in situ XRD methods. Polymer disks sputtered with a may be used in direct contact with anode materials while disks sputtered with aluminum can be used in contact with cathode materials. Studies using this combined technique will allow for further fundamental understanding of material degradation mechanisms and how they are correlated with capacity fade and cell failure.

**Milestones:**

- Adapt the AE-XRD technique to cathode materials and test – **In Progress (80% complete)**
- Adapt technique to be used on commercial batteries for state of health or expected life time measurement (e.g. during formation cycling) – **In Preparation**

**Financial data:**

\$300K/year; \$40K/year subcontract to UTK

**PROGRESS TOWARD MILESTONES****Status**

Our last quarter diagnostics work focused on in situ XRD to study the phase change behavior of  $\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4$  (MNO) and apply AE studies on this material (published in Rev. Sci. Instr. – accepted). We showed that at 4.7V, stepwise transformations between tetragonal spinel phases occurred as Ni was oxidized or reduced during charge and discharge respectively. At low potentials near 2.7V a Jahn Teller distortion was observed that creates a distorted spinel phase. AE experiments were conducted using the same MNO materials and cycling parameters as used this paper.

The total number AE hits recorded during each charge and discharge step are shown plotted with capacity in Figure 1. The most striking feature of this figure is that almost all of the AE activity occurring during charging when lithium is being removed from the MNO particles. As lithium is removed the particle surface comes under tension while the core experiences compression. This likely indicates that cracks are forming on the particle surface. Another interesting observation is that major AE activity is not observed until about the 7<sup>th</sup> cycle, peaks at the 11<sup>th</sup> cycle, and decreases thereafter. This indicates a fatigue type behavior where the material undergoes a pile up of dislocations and defects during the initial cycles which result in fracture after a critical point.

Figure 2 was created by binning the AE activity as a function of voltage over sets of 10 cycles. Here it clear that a majority of AE hits were detected in the 4.7V region where transition between the difference Ni oxidation states occurs. A significant population of AE hits was also detected in the low potential region near 2.7V which is related to the Mn Jahn Teller distortion. A minority group near 4.0V seems to correspond with the voltage plateau observed when cycling ordered MNO and may be related to material damage arising from cation reordering processes. The high potential AE group is most affected by cycle number and it peaks between 11-20 cycles before decreasing.

Thin film electrodes for lithium ion batteries (LIB) poses several attractive advantages over traditional composite electrodes including size and shape constraints, operating temperature range, and volumetric energy density. Tin is an attractive candidate for LIB anode applications due to its exceptional specific capacity, cascading voltage profile, safety, wide availability, and low cost. Tin thin film electrodes were sputtered onto the Ti current collector of an in situ XRD cell and were monitored continuously by XRD while cycling. A phase transformation from white tin, to  $\text{Li}_2\text{Sn}_5$ , to  $\beta\text{-LiSn}$ , to  $\text{Li}_{22}\text{Sn}_5$  was observed during lithiation with the same phases detected in reverse order during delithiation as shown in Figure 3. This represents the successful attempt to apply

this in situ XRD technique to thin film electrodes. This work sets the stage for future experiments to test the performance of thin films with different preferred orientations and surface coatings.

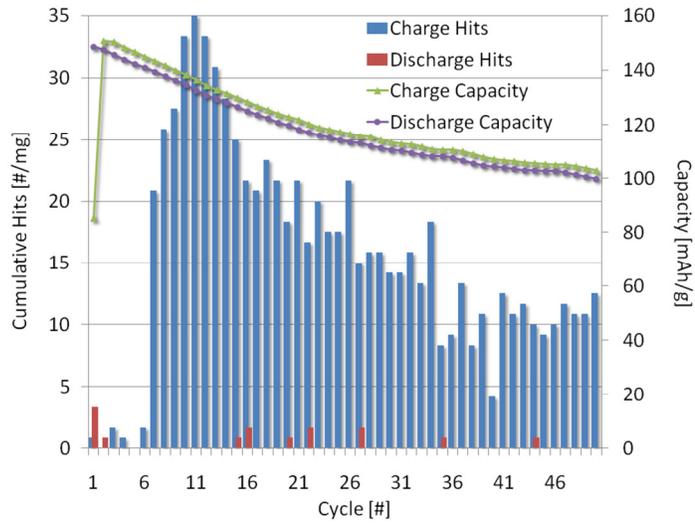


Figure 1: Bar graph of AE activity for each charge and discharge step. A clear majority of events were observed during charging and a fatigue type AE activity onset was seen.

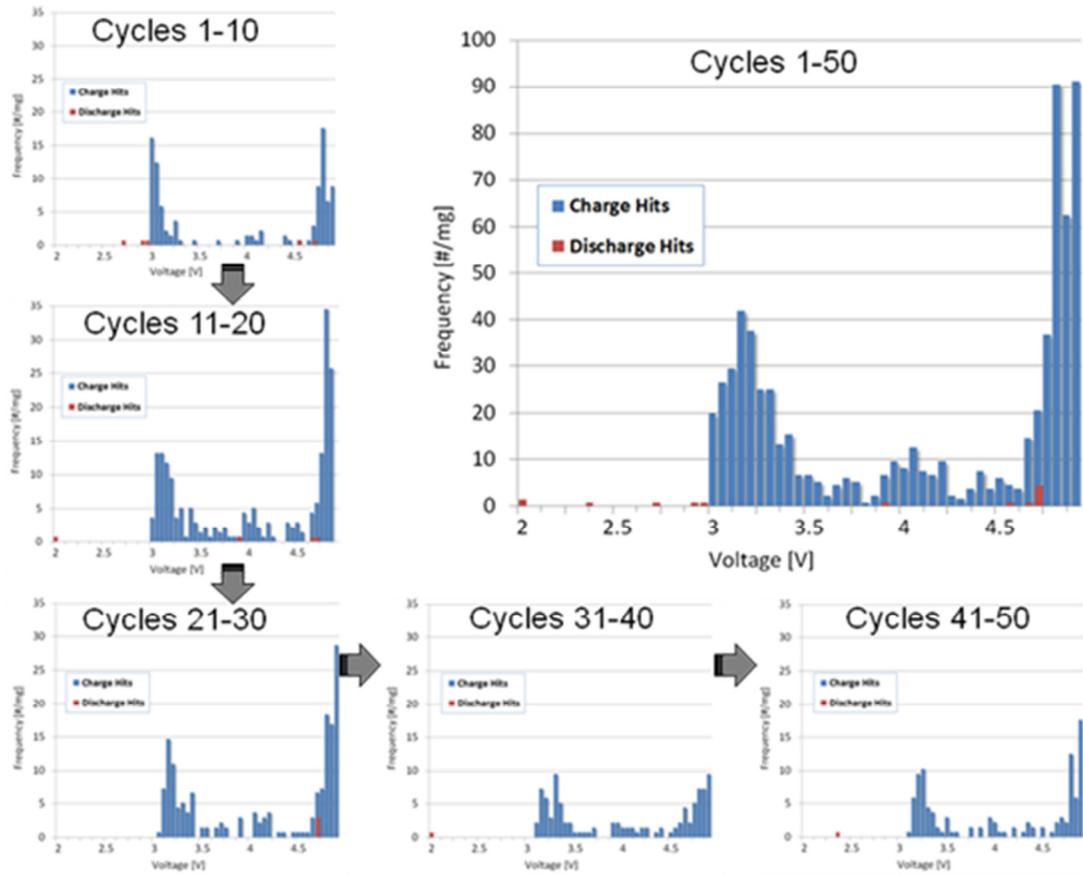


Figure 2: Bar graph of AE activity binned by cell potential. Three activity regions were noted including those related to Ni oxidation (4.7V), Mn Jahn Teller distortion (2.7V), and cation ordering (4.0V). The 4.7V group showed the most dependence on cycle number and is likely the source of the fatigue onset type behavior.

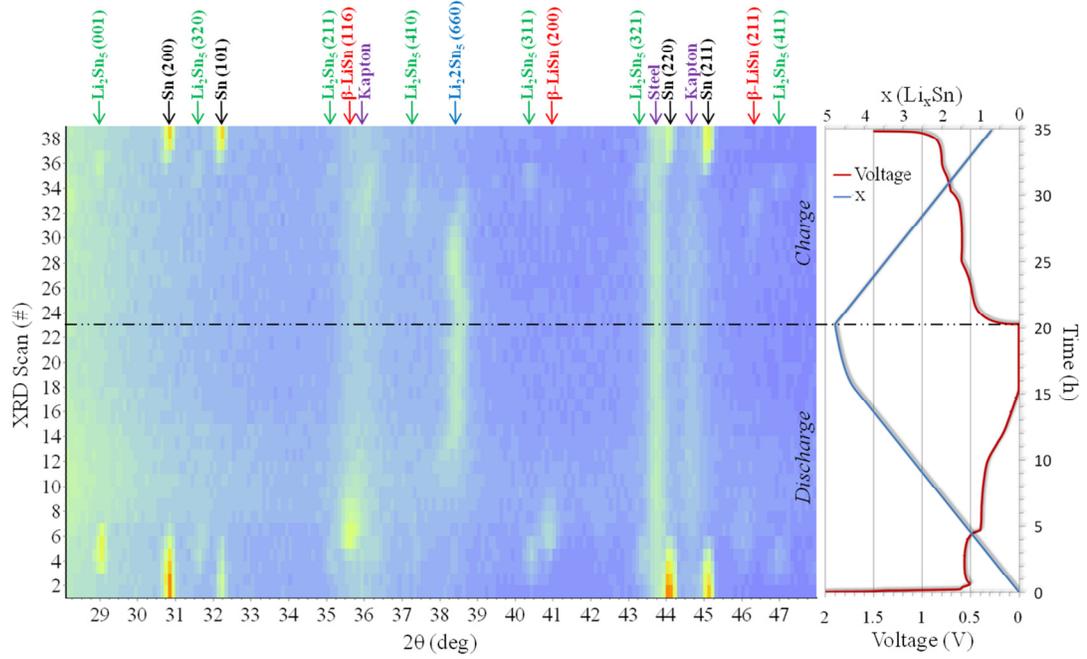


Figure 3: An isoplot of in situ XRD data collected during the cycling of a Sn thin film electrode. Clear transitions between the white tin,  $\text{Li}_2\text{Sn}_5$ ,  $\beta\text{-LiSn}$ , and  $\text{Li}_{22}\text{Sn}_5$  phases are seen.

## **TASK 2**

### **Calendar & Cycle Life Studies**

**Project Number:** 2.2A (ES111)

**Project Title:** Battery Design Modeling (PHEV Battery Cost Assessment)

**Project PI, Institution:** Kevin Gallagher, Dennis Dees, and Paul Nelson, Argonne National Laboratory

**Collaborators (include industry):**

Ira Bloom, Argonne National Laboratory

Dan Santini, Argonne National Laboratory

**Project Start/End Dates:** August 2010/ September 2014

**Objectives:** The objective of this task is to develop and utilize efficient simulation and design tools for Li-ion batteries to predict precise overall (and component) mass and dimensions, cost and performance characteristics, and battery pack values from bench-scale results. Through these means, researchers and manufacturers will be able to better understand the requirements in the material and battery design to reach DOE cost and specific energy goals.

**Approach:** Our approach is to design batteries based on power and energy requirements for any chosen cell chemistry and then feed this design into a cost calculation that accounts for materials & processes required. Coupling design and cost allows the user to quantify the impact of underlying properties on the total battery pack cost (cell chemistry, parallel cells, electrode thickness limits, P/E). Furthermore, the efficient nature of these calculations means that various scenarios may be characterized in a short time span – analysis limited by the user not the model.

**Milestones:**

- (a.) Produce version 1.0 of an efficient model for calculating battery design and cost for PHEVs as well as HEVs and EVs. January 2011 (Complete)
- (b.) Document model assumptions and methodology. January 2011 (Complete)
- (c.) Support EPA sponsored peer-review of model and modify model inputs or calculations in response to review. July 2011 (On schedule)
- (d.) Publically distribute model and report. September 2011 (On schedule)
- (e.) Initiate design and cost modeling of advanced Li-ion electrochemical couples. October 2011 (On schedule)

**Financial data:** \$300K/year

**PROGRESS TOWARD MILESTONES**

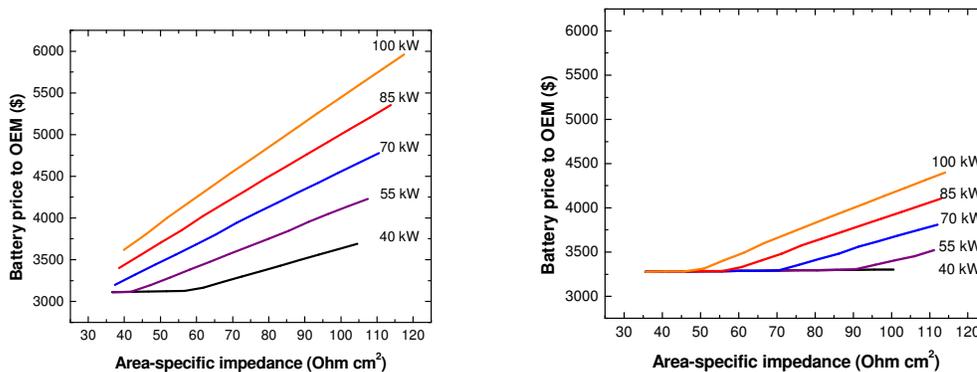
(a) **Creation of battery design and cost model v1.0: Completed January 2011**

(b) **Documentation of assumptions and methodology: Completed January 2011**

(c) **EPA peer-review:** Completed spreadsheet version of the Battery Performance and Cost model (BatPaC) based on public and private peer-reviews. Documentation of the changes by modifying the draft report is on pace to be completed by the end of the July. Completion of the model and report will represent a completed effort, for the current scope of work, to support the EPA's use of the BatPaC model in their rules making process.

(d) **Public distribution:** Meeting with Argonne's technology transfer office to set-up website interface and distribution plan.

(e) **Design & cost of advanced Li-ion:** One of the challenges to predicting the cost and energy density of materials not yet of commercial quality is in accurately accounting for the impedance of the chemistry. The 5V spinel,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_2$  (LNMO), and lithium- and manganese-rich transition metal oxide,  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$  (LMR-NMC), were the two advanced Li-ion cathode materials evaluated against a commercially available carbon-coated graphite anode (350 mAh/g and 95% first cycle efficiency). The area-specific impedance (ASI) was varied to analyze the sensitivity of the final price of the battery to electrode and cell performance. Two interesting conclusions may be drawn from this analysis. First, PHEV batteries based on LNMO / Gr are less sensitive to cell impedance. This insensitivity is a direct result of the high cell voltage, which tolerates higher overpotential while operating at the same level of efficiency as a couple based on a lower cell voltage. Second, the maximum achievable electrode thickness sets the minimum cost level for each system. Here, the LMR-NMC / Gr couple shows more attractive price behavior. The LMR-NMC / Gr couple is limited by the graphite electrode thickness while the LNMO / Gr couple is limited by the LNMO cathode thickness.



**Figure 1.** (Left) Price of 360 V 17 kWh LMR-NMC / Gr battery and (Right) 360 V 17 kWh LNMO / Gr battery as a function of ASI for different power levels (defined at  $[V/U] = 0.8$ ). The high voltage LNMO / Gr couple is less sensitive to the ASI but is more limited by the maximum allowable electrode thickness (100 microns assumed here).

**Publications, Reports, Intellectual property or patent application filed this quarter.  
(Please be rigorous, include internal reports--invention records, etc.)**

Sun-Ho Kang, Wenquan Lu, Kevin G. Gallagher, Sang-Ho Park, and Vilas G. Pol,  
“Study of  $\text{Li}_{1+x}(\text{Mn}_{4/9}\text{Co}_{1/9}\text{Ni}_{4/9})_{1-x}\text{O}_2$  Cathode Materials for Vehicle Battery  
Applications” *Journal of the Electrochemical Society* **158** (8) A936-A941 (2011).

## **TASK 3**

### **Abuse Tolerance Studies**

**Project Number:** 3.1 (ES035)

**Project Title:** Develop & evaluate materials & additives that enhance thermal & overcharge abuse

**Project PI, Institution:** Khalil Amine, Argonne National Laboratory

**Collaborators (include industry):** Zonghai Chen, Yang Ren, Yan Qin, Lu Zhang, Wenquan Lu, Sandia National Laboratory

**Project Start/End Dates:** 10/01/2008~09/30/2014

**Objectives:** Identify the role of each cell material/components in the abuse characteristics of different cell chemistries; Identify and develop more stable cell materials that will lead to more inherently abuse tolerant cell chemistries; Secure sufficient quantities of these advanced materials (and electrodes) & supply them to SNL for validation of safety benefits in 18650 cells.

**Approach:** Three-phase strategy is adopted for the thermal property improvement, including securing material, tests on cell components, and validation at cell level. In-house synthesis, commercial source and partners are used to secure materials, and various electrochemical and thermal analysis are conducted at cell components level in the second phase, and finally the thorough validation is executed at cell level. At the second and third phase, certain feedbacks can be obtained to phase one. For overcharge study, similar strategy is applied but in the first phase organic synthesis is the major source to secure materials. In addition, when feedbacks go to phase one, new design can be achieved using organic knowledge to improve the performance in certain aspect.

#### **Milestones**

- (a) Building in situ high energy X-ray diffraction techniques to investigate the failure mechanism of battery materials (finished);
- (b) Investigating the thermal decomposition of delithiated cathodes (on schedule);
- (c) Investigating the thermal decomposition of SEI layer on graphite (on schedule);

**Financial data:** \$300K/FY2011

PROGRESS TOWARD MILESTONES (1 page)

#### **(a) Summary of work in the past quarter related to milestone (a).**

Figure 1a shows the setup for in situ high energy X-ray diffraction during thermal ramping of a DSC sample. The material required for the experiment can be down to 1 mg, and one XRD pattern will be collected every 20 seconds. Figure 1b shows the interface of in-house software to process and visualize the in situ XRD data.

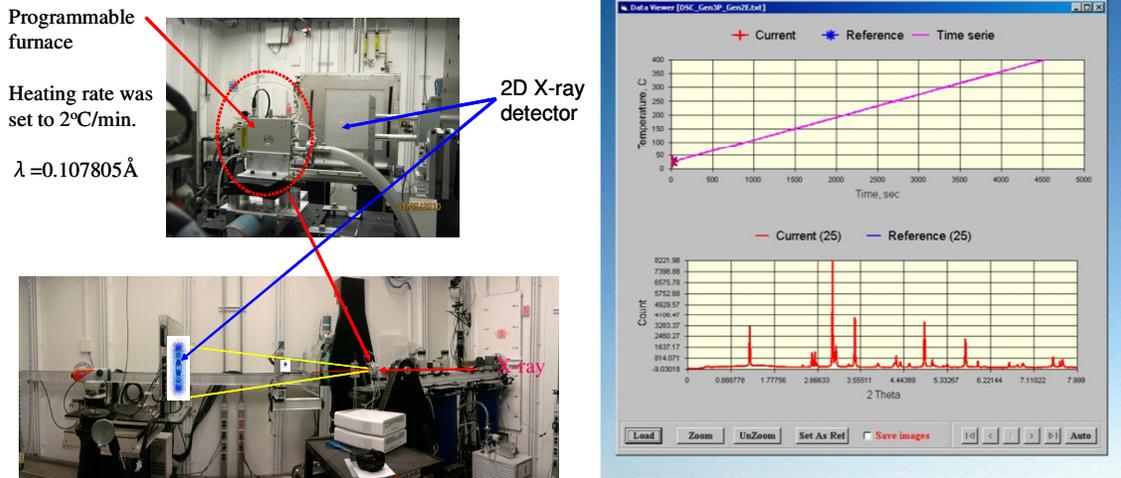


Figure 1 (a) picture of in situ XRD set up at APS; and (b) interface of in-house software for data processing and visualization.

**(b) Summary of work in the past quarter related to milestone (b)**

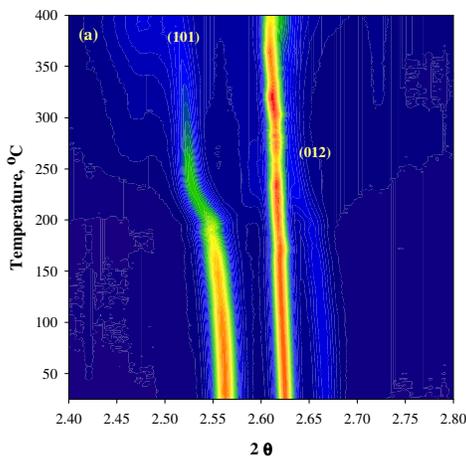


Figure 2 shows the 2D contour plot of in situ XRD data collected during the thermal decomposition of delithiated NMC (charged to 4.1 V). The characteristic peaks (101) and (012) for layer materials are labeled on Figure 2. It clearly shows that the material decomposed at about 180°C.

Figure 2 Contour plot of in situ XRD data during thermal decomposition of delithiated NMC that started to decompose at 180°C.

**(c) Summary of work in the past quarter related to milestone (c)**

The in situ XRD technique was also applied to study the thermal decomposition of solid electrolyte interface (SEI) as shown in Figure 3. The (002) peaks for graphite,  $\text{LiC}_{12}$ , and  $\text{LiC}_6$  are labeled on Figure 3. After fully intercalation, only  $\text{LiC}_6$  and  $\text{LiC}_{12}$  were presented in the anode electrode. When the temperature was below 110°C, only lattice expansion was observed for  $\text{LiC}_6$  and  $\text{LiC}_{12}$ , but no change on concentration. When the temperature was above 110°C, when SEI decomposition was triggered, the intensity of  $\text{LiC}_6$  and  $\text{LiC}_{12}$  decreased, and the diffraction peak of graphite appeared at about 250°C, when the SEI decomposition finished. It is clear that lithium was continuously consumed during SEI decomposition.

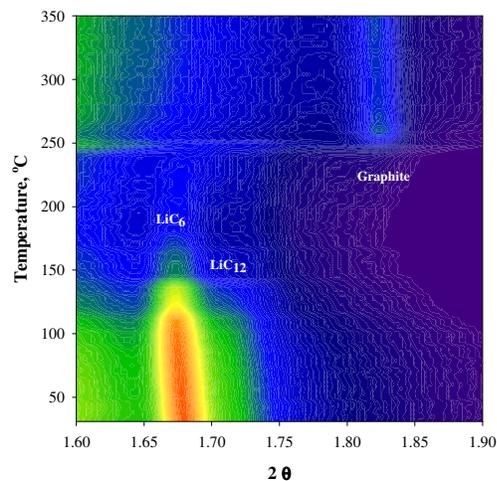


Figure 3 Contour plot of in situ XRD data during thermal decomposition of lithiated graphite.

**Publications, Reports, Intellectual property or patent application filed this quarter.  
(Please be rigorous, include internal reports--invention records, etc.)**

1. Zonghai Chen, Yan Qin, Yang Ren, Wenquan Lu, Christopher Orendorff, and Khalil Amine, Multi-scale Study of Thermal Stability of Lithiated Graphite, Energy & Environmental Science (in press), (2011).
2. Zonghai Chen, Andrew N. Jansen, Bill Casteel and K. Amine, Novel Functionalized Electrolytes for MCMB/Li<sub>1.156</sub>Mn<sub>1.844</sub>O<sub>4</sub> Lithium-Ion Cells, Energy & Environmental Science (in press), (2011).
3. Khalil Amine, Zonghai Chen, Z. Zhang, Jun Liu, Wenquan Lu, Larry Curtis, Yang-Kook Sun, Functional Electrolyte Additive for Long-Life High-Power Lithium-Ion Batteries, submitted to J. Mater. Chem., (2011).
4. Zonghai Chen, Yang, Ren, Yan Qin and Khalil Amine, Thermal Decomposition of Delithiated Cathode for Lithium-Ion Batteries, to be submitted to Energy & Environmental Science, (2011).

## **TASK 3**

### **Abuse Tolerance Studies**

**Project Number: 3.2 (ES036)**

**Project Title:** Abuse Tolerance Improvements

**Project PI, Institution:** Chris Orendorff, Sandia National Laboratories

**Collaborators (include industry):** ANL, INL, BNL, Univ. Hawaii, Binrad Industries, Physical Sciences Inc., A123

**Project Start/End Dates:** 10/1/2008-9/30/2012

**Objectives:** The objective of this work is to develop inherently abuse tolerant lithium-ion cell chemistries. This involves understanding the mechanisms of cell degradation and failure, determining the effects of new materials & additives on abuse response, and cell level abuse testing and cell characterization to quantify improvements

**Approach:** Materials to full cell characterization to determine inherent safety and reliability of the most advanced lithium-ion chemistries. Approaches include a suite of battery calorimetry techniques (microcal, DSC, TGA/TDA, isothermal, ARC), abuse tests (electrical, mechanical, thermal), and analytical diagnostics (electrochemical characterization, optical spectroscopy, mass spectrometry, computed tomography, electron microscopy, etc.)

**Milestones:**

- (a) The effect of cell age on thermal response (DUE 9/30/2011, on schedule)
- (b) LiF/ABA electrolyte development (ON GOING, on schedule)
- (c) Cell prototyping optimization (ON GOING, on schedule)
- (d) Overcharge shuttle evaluation in full cells (DUE 9/30/2011, on schedule)

**Financial data:** Total budgeted \$1.35M; received \$1.07M (from SNL); \$40K subcontract to Dan Doughty (Battery Safety Consulting); \$30K subcontract to Binrad Industries (pending)

**PROGRESS TOWARD MILESTONES (1 page)**

(a) **The effect of cell age on thermal response:** Initial targets for this work include determining the baseline thermal response of the Sanyo SA 1.25 Ah cells and age them to < 30% power fade (within the end-of-life criteria in the EV testing manual). SNL has completed ARC measurements on 10 fresh cells to determine baseline response for thermal variations (onset temperature, peak heating rate, total enthalpy, etc.). Results from these experiments show very little cell-to-cell variation in terms of their thermal parameters and in the total gas generation during runaway. At INL, cells were calendar aged to ~20% power fade (60 °C storage for 2 months). Data will be compiled and sent to

Univ. Hawaii (Dr. Bor Yann Liaw) in Q4 to perform numerical analysis of the cell-to-cell variations. Initial ARC work on the 20% power faded aged cells shows an increase in the exotherm onset temperature by ~10-20 °C (suggesting a thicker or stabilized SEI film), a decrease in the onset temperature for cathode decomposition by ~10 °C (suggesting destabilized cathode interface), and a decrease in the total peak heating rate by ~50% compared to the fresh cells (suggesting diminished reactivity of the aged cells). Measurements and analysis of the remaining cells will be completed in Q4 of FY11.

**(b) LiF/ABA electrolyte development:** SNL has previously shown the dramatic improvement in runaway response of NMC (40% Ni) cells with the LiF/ABA electrolyte. DSC results confirm the full-cell response, showing a ~50% reduction in total heat flow for the NMC (40:30:30) cathodes in LiF/ABA electrolyte compared to the same cathode in LiPF<sub>6</sub> EC:EMC. A similar trend is also observed for other NMC chemistries (1:1:1), however, only a ~15-20% reduction in total heat output is observed. This is consistent with the full cell ARC measurements where the 40% Ni NMC cathodes show a greater reduction in runaway enthalpy relative to the 33% Ni NMC cells. Measurements are currently underway using LiCoO<sub>2</sub> and NCA chemistries to elucidate the mechanism of this cathode passivation. Collaboration between SNL and BNL has been established and BNL is in the process of synthesizing more ABA molecules to provide to SNL for characterization. Moreover, contracts are currently in place with Binrad/Richmond Chemical to synthesize new ABA molecules in Q4.

**(c) Cell prototyping:** Worked to optimize our 18650 electrode coating and cell building to support abuse testing and materials evaluation efforts. In addition to 3M NMC/CP G8 cells, we have also moved forward with coating and optimization of CP A12 anodes, TODA NMC cathodes, and LFP cathodes to support the electrolyte thrust in ABR. Current cell building will support electrolyte development programs at INL (phosphazine), JPL (low temperature), ARL (high voltage), and ANL (shuttle additives) in FY11 Q4 and through FY12.

**(d) Overcharge shuttle evaluation in full cells:** Coordinated the overcharge testing work with ANL and have outlined a test plan for the shuttle in full cells which will include two cell populations: (1) cells built at SNL with LFP provided by ANL and (2) cells built at A123. Both populations will contain control and shuttle samples. Experiments to evaluate the shuttle in cells will include constant current overcharge, C/D overvoltage cycling, isothermal calorimetry, and ARC. LFP electrodes (LFP positive and CP A12 negative) have been coated (designed for 1.0 Ah 18650 cells), NDA is in progress between SNL and ANL (at ANL's request), verbal agreement with A123 to produce cells once materials have been received.

#### **Publications, presentations, reports, IP, etc.**

**C. J. Orendorff**, "A Materials Approach to Abuse Tolerance in Lithium-Ion Batteries" Space Power Workshop, Aerospace Corporation, El Segundo, CA, 4/21/2011

**C. J. Orendorff**, "Evaluation of Abuse Tolerance Improvements" DOE Annual Merit Review, Washington D.C., 5/9/2011

**C. J. Orendorff**, “A Materials Approach to Abuse Tolerance in Lithium-Ion Batteries”  
Dow Chemical (Invited), Midland, MI, 5/24/2011

**C. J. Orendorff**, “A Materials Approach to Abuse Tolerance in Lithium-Ion Batteries”  
Army TARDEC (Invited), Warren, MI, 5/25/2011

**C. J. Orendorff**, “A Materials Approach to Abuse Tolerance in Lithium-Ion Batteries”  
Detroit Chapter ECS (Invited), Southfield, MI, 5/25/2011

**C. J. Orendorff**, “A Materials Approach to Abuse Tolerance in Lithium-Ion Batteries”  
A123 Systems (Invited), Ann Arbor, MI, 5/26/2011

## **TASK 3**

### **Abuse Tolerance Studies**

**Project Number:** 1.2.1 (ES037)

**Project Title:** Overcharge Protection for PHEV Batteries

**Project PI, Institution:** Guoying Chen and Thomas Richardson, Lawrence Berkeley National Laboratory

**Collaborators:** Robert Kostecki, John Kerr, Vince Battaglia, Marca Doeff, Gao Liu, Yueguang Zhang (Molecular Foundry)

**Project Start Date:** March 2009

**Objectives:** Develop a reliable, inexpensive overcharge protection system. Use electroactive polymers for internal, self-actuating protection. Minimize cost, maximize rate capability and cycle life of overcharge protection for high-energy Li-ion batteries for PHEV applications.

**Approach:** Our approach is to use electroactive polymers as self-actuating and reversible overcharge protection agents. The redox window and electronic conductivity of the polymer will be tuned to match the battery chemistry for non-interfering cell operation. Rate capability and cycle life of the protection will be maximized through the optimization of polymer composite morphology and cell configuration.

**Milestones:**

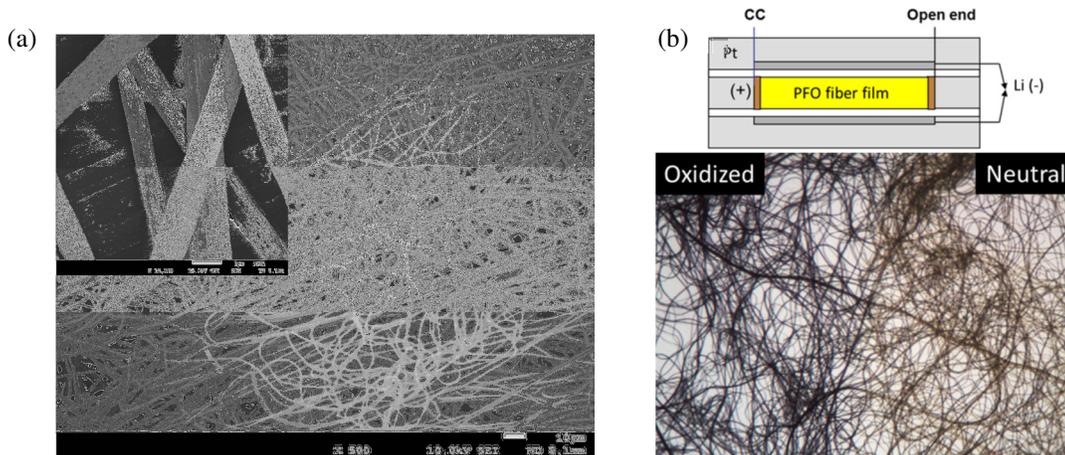
- (a) Report the properties of alternative high-voltage electroactive polymer candidates (July 2011). **Complete**
- (b) Report overcharge protection performance of modified polymer composite separators and cell configurations (September 2011). **On schedule**

**Financial data:** \$190K (FY2009), \$190K (FY2010), \$250K (FY2011)

#### PROGRESS TOWARD MILESTONES

We have shown that morphology has a large impact on polymer utilization, and that higher overcharge current densities can be sustained by electroactive polymer nanofibers. In this quarter, alternative approaches were explored to synthesize these fibers at low cost and large scale. Electrospinning is a technology commonly used by industry to produce polymer fibers from aqueous solutions. During the process, a solution is pumped into the syringe, and a high potential is applied between the spinneret and a grounded collector. The fluid overcomes the surface tension under the external electric field and forms a fine charged jet, which is further elongated by electrostatic repulsion to form fibers.

This process was successfully adapted to the synthesis of electroactive polymer fibers from organic solvents. Figure 1a shows poly[(9,9-dioctylfluorenyl-2,7-diyl)] (PFO) fibers collected on a Al substrate, obtained by electrospinning of a  $\text{CHCl}_3$  solution containing 3 wt% of the polymer. The fibers have an average diameter of 1  $\mu\text{m}$ , with 100 nm pores forming on the surface due to solvent evaporation. The presence of these relatively large-sized pores should improve electrolyte penetration, polymer utilization and rate capability during overcharge protection. The aspect ratio of the fibers can be easily tuned through the adjustment of synthesis conditions, such as applied voltage, solvent, solution concentration and feeding speed.



**Figure 1.** a) Morphology of porous PFO polymer fibers prepared by an electrospinning method, b) galvanostatic oxidation of the PFO fibers in 1M  $\text{LiPF}_6$  in 1:1 EC: PC. The image was taken under an optical microscope at 100x magnification.

Fibers were studied as charge carriers in Li-ion batteries by visual examination of oxidation and reduction processes in an *in situ* optical cell with PFO fiber-film as working electrode and Li metal as counter and reference electrodes. Figure 1b shows the cell configuration and a still image of the fibers during the passage of a steady state current of 40  $\mu\text{A}$ . Upon oxidation, the conduction front gradually moved from the positive electrode towards the end of the film. The color of the fibers changed from light yellow at neutral state to deep black upon oxidation, indicating an increase in electronic conductivity. A distinct boundary between the oxidized and the neutral PFO is clearly shown, suggesting that the inter-connection between fibers is sufficient to allow charge carriers to propagate across rather than only within individual fibers. Under current magnification, the volume change of the fibers was indiscernible.