

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

**Progress Report  
for  
First 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**

**April 2011**

## **Applied Battery Research for Transportation Program First 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	10
ANL	ARRA VT076	IV. E.1.2	Process Development and Scale up of Advanced Electrolyte Materials	Gregory Krumdick	12
ANL	ES015	1.1A	Engineering the High Energy Cathode Material	Khalil Amine	14
ANL	ES016	1.1B	New High Energy Gradient Concentration Cathode Material	Khalil Amine	17
ANL	ES017	1.1F	Design and Evaluation of High Capacity Cathode Materials	Christopher Johnson	20
ANL	ES018	1.1K	Evaluation of Li <sub>2</sub> MnSiO <sub>4</sub> Cathode	Ilias Belharouak	23
ANL	ES019	1.1G	Development of High-Capacity Cathode Materials with Integrated Structures	Sun-Ho Kang	26
ANL	ES020	1.1C	Developing High Capacity, Long Life anodes	Khalil Amine	29
ANL	ES022	1.1I	Develop Improved Methods of Making Intermetallic Anodes	Andrew Jansen	31
ANL	ES023	1.1H	Development of Novel Electrolytes & Additives for PHEV Applications	Dan Abraham	34
ARL	ES024		High Voltage Electrolytes for Li-ion Batteries	Richard Jow	37
ANL	ES025	1.1D	Development of Advanced Electrolyte Additives	Zhengcheng Zhang	41
JPL	ES026		Electrolytes for Use in High Energy Li-Ion Batteries with Wide Operating Temperature Range	Marshall Smart	43
INL	ES027		Novel Phosphazene Compounds for Enhancing Electrolyte Stability and Safety of Lithium-ion Cells	Kevin Gering	49

Organization	AMR Project ID	AOP Project ID	Title	PI/Contact Point	Page Number
			<b>Task 1: Battery Cell Materials Development</b>		
ANL	ES028	1.1E	Streamlining the Optimization of Lithium-Ion Battery Electrodes	Wenquan Lu	55
ANL	ES028	1.3	Screen Electrode Materials, Electrolytes, and Additives	Wenquan Lu	57
LBNL	ES029	1.2.2	Scale-up and Testing of Advanced Materials from the BATT Program	Vincent Battaglia	59
ANL	ES112	1.2C	Functionalized Surface Modification Agents to Suppress Gassing Issue of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Based Lithium Ion Chemistries	Khalil Amine	61
ANL	ES113	1.1L	Development of High Voltage Electrolyte for Lithium Ion Battery	Zhengcheng Zhang	63
ANL	ES114	1.2D	Spherical Carbon Anodes Fabricated by Autogenic Reactions	Michael Thackeray	66
ANL	ES115	1.1V	Synthesis and Development of High-Energy and High-Rate Cathode Materials from Ion-Exchange Reactions	Christopher Johnson	69
NAVSEA-Carderock	ES038		High Energy Density Ultracapacitors	Patricia Smith	72
ANL		1.1X	Paper Study on Continuous Process for Making Gradient Concentration Cathode Material	Gregory Krumdick	74
			<b>Task 2: Calendar &amp; Cycle Life Studies</b>		
ANL	ARRA VT075		Prototype Cell Fabrication Facility	Andrew Jansen	76
ANL	ARRA VT077		Post-Test Facility	Ira Bloom	78
ANL	ES030	2.1	Fabricate PHEV Cells for Testing and Diagnostics in Cell Fabrication Facility	Andrew Jansen	81
ANL	ES031	2.2B	Model Cell Chemistries	Dennis Dees	83

<b>Organization</b>	<b>AMR Project ID</b>	<b>AOP Project ID</b>	<b>Title</b>	<b>PI/Contact Point</b>	<b>Page Number</b>
			<b>Task 2: Calendar &amp; Cycle Life Studies</b>		
ANL	ES032	2.3A	Diagnostic Evaluation of Lithium Battery Cells and Cell Components	Dan Abraham	86
ANL	ES032	2.3B	Structural Investigations of Layered Oxides for PHEV Applications	Dan Abraham	89
LBNL	ES033	1.1.1 and 2.4.1	Electrochemistry Diagnostics of Baseline and New Materials	Robert Kostecki	92
BNL	ES034		Diagnostic Studies to Improve Abuse Tolerance and life of Li-ion batteries	Xiao-Qing Yang	95
ORNL	ES039		In-situ characterization and diagnostics of mechanical degradation in electrodes	Claus Daniel	98
ANL	ES111	2.2A	Battery Design Modeling	Kevin Gallagher	101
			<b>Task 3: Abuse Tolerance Studies</b>		
ANL	ES035	3.1	Develop & Evaluate Materials & Additives that Enhance Thermal and Overcharge Abuse	Khalil Amine	104
SNL	ES036	3.2	Abuse Tolerance Improvements	Chris Orendorff	107
LBNL	ES037	1.2.1	Overcharge Protection for PHEV Batteries	Guoying Chen	109

## **APPENDIX**

### **Individual Project Progress Reports**

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number: ARRAVT076**

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

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

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

**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)	9/30/2010	2 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	2 COMPLETED 9/17/2010
Milestone 2	Production scale-up facility equipment purchased & accepted	12/31/2011	FUNDING INADEQUATE
Deliverable 1	Interim facility open (3 facilities)	9/30/2010	2 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
  - Contractor is on schedule for preliminary design

**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 – under construction
  - Equipment delivery is expected 2/1/2011

Capital equipment delivery status

Item	Status
Cilas Particle size analyzer	Delivered
Netsch TGA-DSC-MS	Delivered
Agilent GC-MS	Delivered
Agilent ICP-MS	Delivered
Bruker FTIR	Delivered
Bruker XRD	Expected Delivery 1/30/2011
Powrex Vertical mixer	Expected Delivery 2/1/2011
NGK Batch furnace	Expected Delivery 2/1/2011
Nissin Particle classifier	Expected Delivery 2/1/2011

GL Filtration washer dryer 1	Expected Delivery 1/25/2011
GL Filtration washer dryer 2	Expected Delivery 1/25/2011
Physical Electronics XPS	Expected Delivery 7/1/2011

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number: IV.E.1.1**

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

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

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

**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 delivery is expected mid-February, 2011. Site preparation has begun, removal of unused equipment has been completed and utilities for cathode processing equipment are being installed. Candidates are being interviewed for a full time materials scale-up engineer for this project.

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

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

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number:** IV.E.1.2

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

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

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

**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 interim electrolyte materials lab was completed in November, 2010. Work has begun on the process scale up of the redox shuttle ANL-RS2 and the electrolyte solvent 1NM3.



Figures 1&2 Interim electrolyte materials lab

<b>ANL-RS2</b>		
Select CSE material to scale	10/1/2010	Completed
Assess scalability of CSE process	10/18/2010	Completed
WP&C safety 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)		In Progress
Second process scale-up (1000g pilot scale)		

Table 1: Redox shuttle ANL-RS2 schedule

<b>1NM3</b>		
Select CSE material to scale	11/01/2010	Completed
Assess scalability of CSE process	11/15/2010	Completed
WP&C safety documentation approved		In Progress
Develop and validate scalable process chemistry (10g bench scale)		
First process scale-up (100g bench scale)		
Second process scale-up (1000g pilot scale)		

Table 2: Electrolyte solvent 1NM3 schedule

# TASK 1

## Battery Cell Materials Development

**Project Number: 1.1A (ES-015)**

**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

**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 250mAh/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 (4.6V)

**Milestones:**

- Resolved the reproducibility problem of Co-free high energy material.
- Optimized the Ni/Mn ratio and varied lithium amount of the Argonne high energy composite layered cathode  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNiO}_2$  to achieve high capacity, good cycle and rate capability with high reproducibility (Completed)

**Financial data:**

Total project funding

- DOE share: \$300K

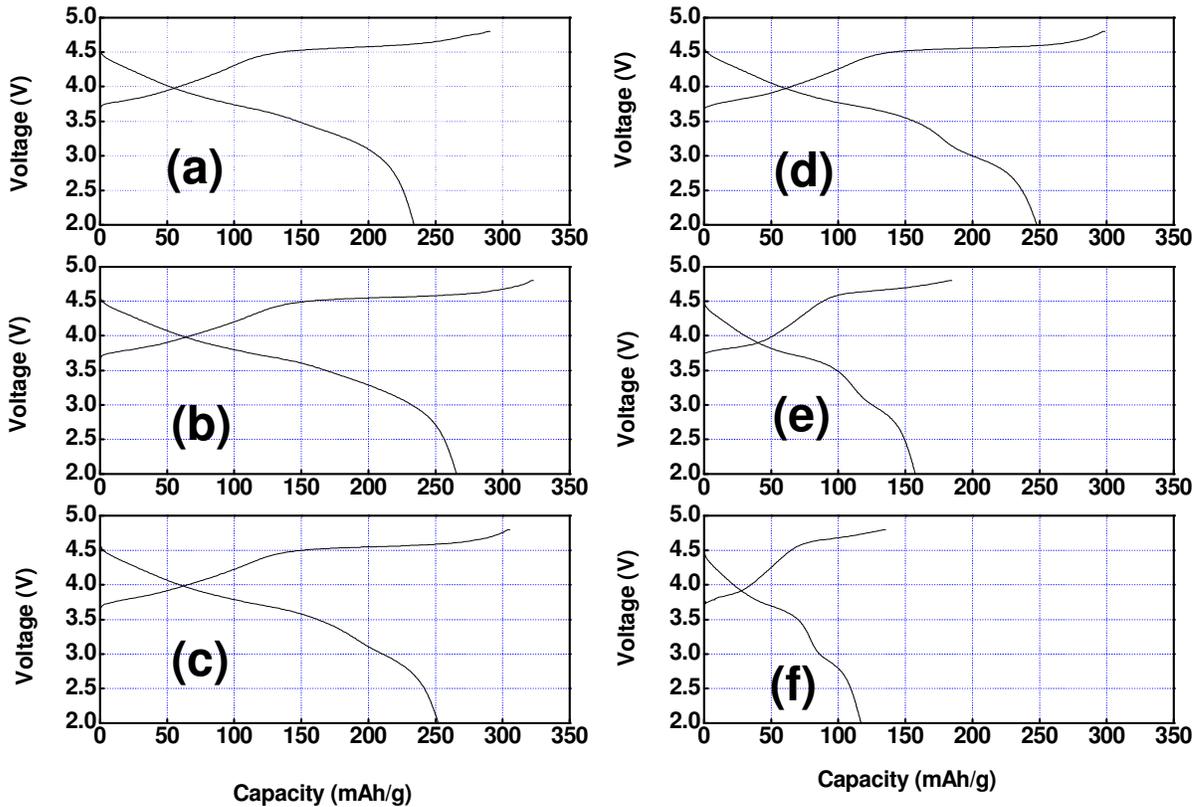
### PROGRESS TOWARD MILESTONES

In the past, our focus was on developing high-energy cathodes based on the layered lithium-rich nickel manganese oxide composite with a composition of  $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$  (Ni/Mn ratio = 1:3). This material shows a high packing density of 2.1 g/cc and a high capacity of 210 mAh/g at the 1 C rate. However, the good performance of this material was not easy to reproduce

We carried out extensive optimization of the Ni/Mn ratio and isolated a new composition,  $\text{Li}_{1.2}\text{Ni}_{0.3}\text{Mn}_{0.6}\text{O}_{2.1}$ , where Ni/Mn ratio is 1:2.

Figure 1 shows the charge and discharge capacities  $\text{Li}_{1.2+x}\text{Ni}_{0.3}\text{Mn}_{0.6}\text{O}_{2.1}$  with different lithium ratio. When the lithium amount  $x$  was fixed in the window range of 0.94 to 1.03, the obtained materials always delivered a high capacity of about 250 mAh/g, which means that the performance of  $\text{Li}_{1.2+x}\text{Ni}_{0.3}\text{Mn}_{0.6}\text{O}_{2.1}$  is not very sensitive to lithium excess as observed previously with  $\text{Li}_{1.2+x}\text{Ni}_{0.2}\text{Mn}_{0.7}\text{O}_{2.1}$ .

As a result, the high energy cathode composition  $\text{Li}_{1.2}\text{Ni}_{0.3}\text{Mn}_{0.6}\text{O}_{2.1}$  was found to be the optimum composition that delivers high capacity and good rate capability.



**Figure 1** Charge and discharge capacity of  $\text{Li}_{1.2+x}\text{Ni}_{0.3}\text{Mn}_{0.6}\text{O}_{2.1}$  (a:  $x=1.03$ , b:  $x=1.0$ , c:  $x=0.97$  d:  $x=0.94$ , e:  $x=0.91$  f:  $x=0.88$ )

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

1. H. M. Wu, I. Belharouak, Y.-K. Sun and K. Amine, Electrochemical performance of high capacity  $\text{Li}_{1.2}\text{Ni}_{0.3}\text{Mn}_{0.6}\text{O}_{2.1}$  cathode for lithium-ion batteries, Paper in preparation.
2. *H. Deng, I. Belharouak, C. S. Yoon, Y. K. Sun, K. Amine*, High Temperature Performance of Surface-Treated  $\text{Li-1.1}(\text{Ni}0.15\text{Co}0.1\text{Mn}0.55)\text{O-1.95}$  Layered Oxide, *J. Electrochem. Soc.*, 157 (10): A1035 (2010).
3. S. Y. Myung, K. Amine, Y. K. Sun, Surface modification of cathode materials from nano- to microscale for rechargeable lithium-ion batteries *J. Mater. Chem.*, 20 (34) 7074 (2010)

## **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; 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 manganese at the surface to enhance safety.

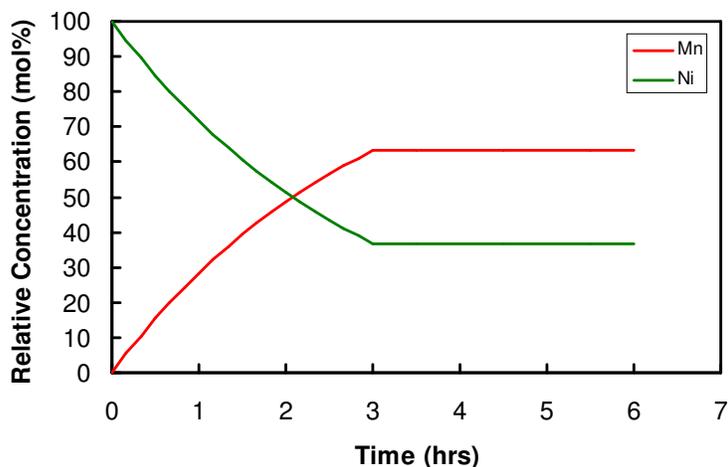
#### **Milestones:**

- 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. (Completed)
- 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. (Completed)
- c) Demonstrate in a proof-of-principle experiment that precursors could be synthesized with predetermined compositional profiles. (On schedule)
- 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. (On schedule)

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

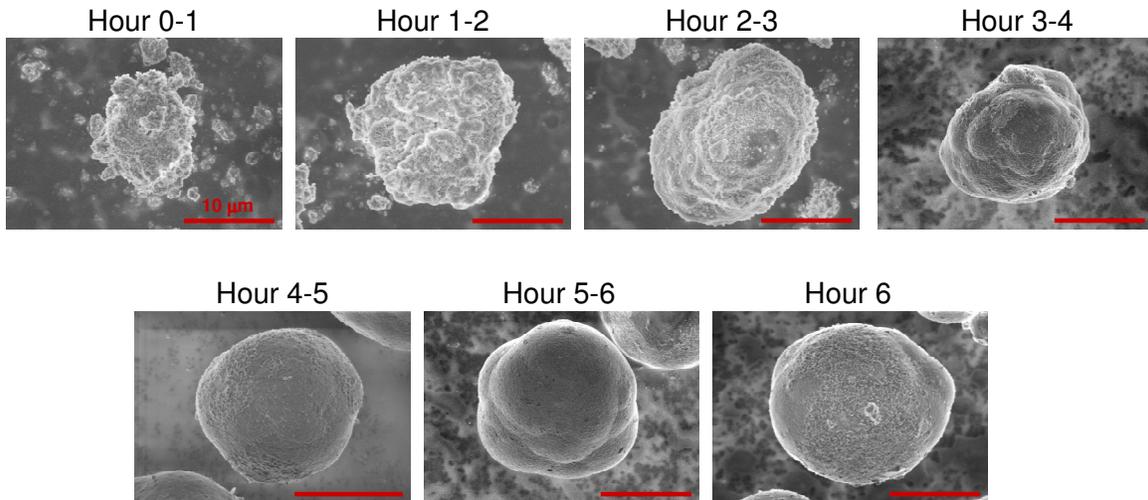
## PROGRESS TOWARD MILESTONES

a) The concentration profile of the transition metal feed to the reactor was calculated by assuming that the feed (nickel solution) was well-mixed. A sample calculated concentration profile of the relative transition metal composition is shown in Figure 1 below. This model has been applied to a variety of process conditions. Over the first 3 hours of the process, the Mn solution was fed to the Ni solution, leading to a gradually increasing composition of Mn (from 0% to 63.2%) fed to the reactor and a concurrent decrease in the Ni concentration (from 100% to 36.8%) in the feed. After 3 hours, a constant relative composition of the two transition metals is achieved.



**Figure 1.** Predetermined calculated concentration profile of relative transition metal composition in the feed to the reactor

b) The co-precipitation process was run using a CSTR and the experimental conditions to provide a relative transition metal concentration in the feed to the reactor shown in Figure 1. SEMs of particles collected from the reactor are shown below in Figure 2. Understanding the morphology and compositional changes in co-precipitated particles as a function of time is on schedule.



**Figure 2.** SEMs of particles collected from the CSTR in 1 hour intervals.

- c) Demonstration of internal concentration gradient is ongoing. SEM and EDXS measurements of internal cross-sections are in progress.
- d) Electrochemical cycling to determine material capacities are in progress.
- e) Safety and cycle life experiments are ongoing.

**Publications, Reports, Intellectual property or patent application filed this quarter.**  
G. M. Koenig, I. Belharouak, H. M. Wu, and K. Amine, *Electrochimica Acta*, **56**, 1426 (2011)

## 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)
  - Baseline materials synthesized, December 2010 (completed)
  - Optimize charged cathodes, December 2010 (completed)
  - Doped LFO synthesized, March 2011, (on-schedule)

- (b) Characterize electrochemical properties of synthesized materials, September 2011, (on-schedule)
  - Demonstrate capacity of 120 mAh/g with LVO December 2010, (completed)
  - Demonstrate high-rate of 200 mAh/g @ C rate, September 2011, (on-schedule)
- (c) Characterize structure of materials, March 2011, (on-schedule)
- (d) Evaluate Si anodes to pair with blended LFO, March 2011, (on-schedule)
- (e) Initiate measurement of thermal properties of charged material in DSC, September 2011, (on-schedule)

**Financial data:** \$300K

### PROGRESS TOWARD MILESTONES

- (a) LFO was successfully synthesized by an optimized reaction involving lithium hydroxide hydrate and iron oxide. The reaction is conducted in Ar at 700 C for 70 hours. LVO was synthesized with a coating of 3 wt.%  $\text{Al}_2\text{O}_3$  by a simple process.
- (b) The electrochemistry of cells were checked and the results are in Fig. 1.

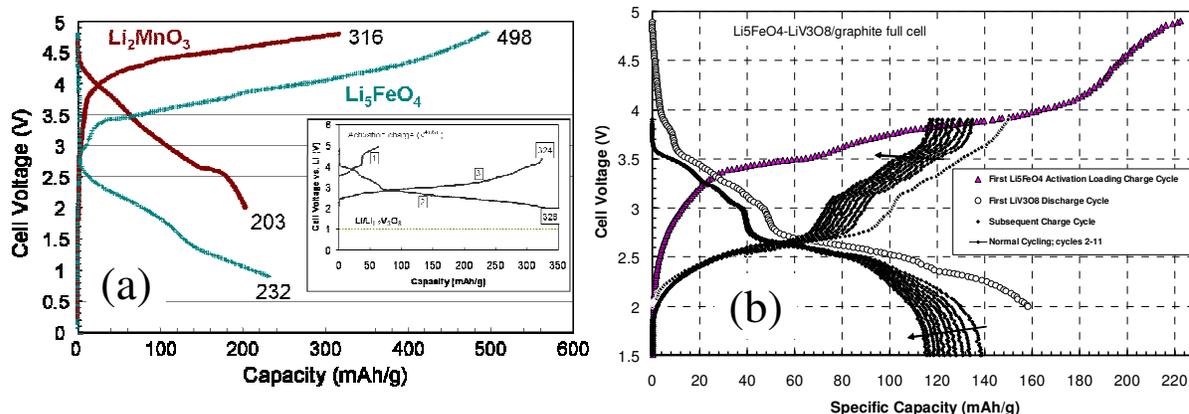


Fig. 1. (a) Voltage profile of C/LFO and C/Li<sub>2</sub>MnO<sub>3</sub> full-cell (with C (graphite)). Inset is the electrochemical voltage profile of Li/LVO, and (b) C/LFO-LVO cell demonstrating the milestone of 120 mAh/g.

In addition, the coated LVO showed a capacity of an average of 290 mAh/g and 140 mAh/g at 1.3C rate. This coated LVO will be used in full cells.

(c) The XRD patterns of the materials discussed in milestone (a) were completed. Lattice parameter calculations indicate an anti-fluorite material was synthesized. The coated LVO showed the correct structure. Raman spectra of LFO were also completed. There is a vibration mode at 656 cm<sup>-1</sup> characteristic of LFO. No Li<sub>2</sub>CO<sub>3</sub> or LiOH was observed in the sample.

(d) Si anode work is ongoing with the assistance of Dr. Kumta.

(e) Thermal properties of the charged materials synthesized in milestone (a) are planned.

**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:** 1.1K (ES018)

**Project Title:** Evaluation of  $\text{Li}_2\text{MnSiO}_4$  Cathode

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

**Collaborators (include industry):** D. Dambournet, A. Abouimrane, K. Amine, K.W. Chapman, P.J. Chupas, Argonne National Laboratory.

**Project Start/End Dates:** October 1, 2008-December 30, 2010

**Objectives:** Understand the capacity fading of  $\text{Li}_2\text{MnSiO}_4$  upon cycling and achieve an overall structural and electrochemical evaluations of  $\text{Li}_2\text{MnSiO}_4$  material with regard to its possible use in high-energy density Li-ion batteries.

**Approach:** Possible reasons for the degradation of performance of  $\text{Li}_2\text{MnSiO}_4$  are (1) Jahn-Teller distortion associated with  $\text{Mn}^{3+}$  and Mn dissolution and (2) Loss of crystallinity of  $\text{Li}_2\text{MnSiO}_4$  at the end of the first charge. Our measurements show that the charged  $\text{Li}_2\text{MnSiO}_4$  becomes amorphous according to conventional x-ray diffraction using Cu-K $\alpha$  radiation. Therefore, no long range structural information can be extracted for charged  $\text{Li}_2\text{MnSiO}_4$ . To distinguish between possible mechanisms we needed to conduct high resolution x-ray on  $\text{Li}_2\text{MnSiO}_4$  upon charge.

#### **Milestones:**

- a) Perform high-energy x-ray diffraction experiments on charged and discharged  $\text{Li}_2\text{MnSiO}_4$  cathode (completed).
- b) Pair distribution analysis of  $\text{Li}_2\text{MnSiO}_4$  electrode upon lithium removal and uptake (completed).
- c) Understand the discrepancy between the results of conventional and high-energy x-ray experiments carried out on  $\text{Li}_2\text{MnSiO}_4$  electrode (completed).

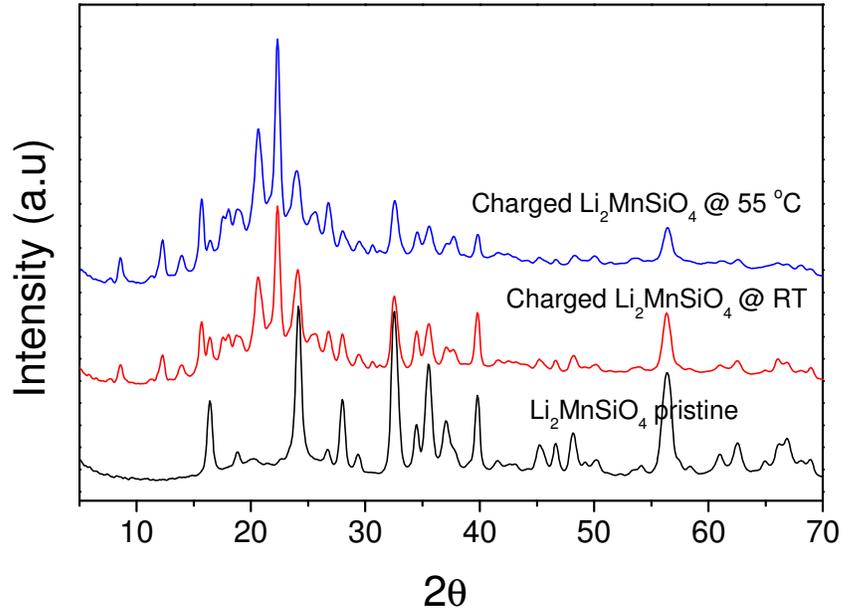
**Financial data:** \$300K/year in FY09, \$300K in FY10, &50K in FY11.

#### **PROGRESS TOWARD MILESTONES**

Figure 1 shows the high-energy x-ray measurements performed on  $\text{Li}_2\text{MnSiO}_4$  pristine, charged material to 4.8V at RT, and charged material at 55 °C, using 0.21028 Å wavelength. The x-ray experiments were carried out at the Advanced Photon Source. Charged electrodes were sealed in capillary kapton prior to measurements. The results showed that  $\text{Li}_2\text{MnSiO}_4$  was still crystalline after delithiation which is in disagreement with the results of conventional x-ray. We mainly observed the following:

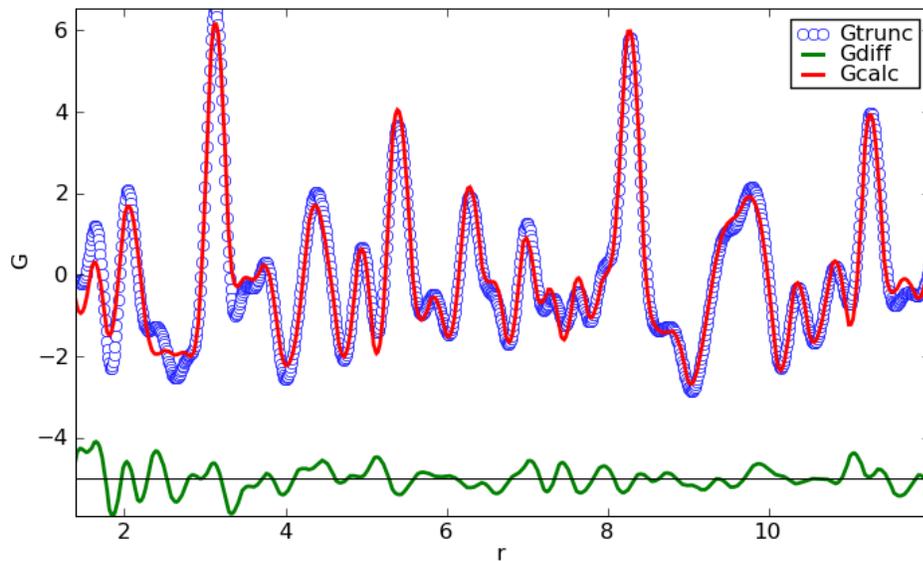
- Decrease of the intensity of the main diffraction lines for the charged  $\text{Li}_2\text{MnSiO}_4$  samples.
- Appearance of new diffractions lines for the charged samples.
- Indexation of the new peaks was not possible based on the structural model of  $\text{Li}_2\text{MnSiO}_4$  available in the literature.

In view of these results, we needed to use Pair Distribution Function (PDF) to help us understand the structure of  $\text{Li}_2\text{MnSiO}_4$  and the additional x-ray features observed upon charge.



**Figure 1.** High-energy x-ray measurements using 0.21028 Å wavelength.

Figure 2 shows the atomic pair distribution function analysis of pristine  $\text{Li}_2\text{MnSiO}_4$ . PDF data were obtained by Fourier Transform of the total scattering function  $S(Q)$  which contains both Bragg and diffuse intensities. PDF refinement revealed the presence of 10%  $\text{Li}_2\text{SiO}_3$  and 5% and  $\text{MnO}$  in  $\text{Li}_2\text{MnSiO}_4$ . Overall, the refinement of  $\text{Li}_2\text{MnSiO}_4$  structure is consistent with the structural model of  $\text{Li}_3\text{PO}_4$  with cationic disorder.



**Figure 2.** Atomic pair distribution function analysis of pristine  $\text{Li}_2\text{MnSiO}_4$ .

High-energy x-ray results revealed for the first time that  $\text{Li}_2\text{MnSiO}_4$  does not become amorphous upon charge. The discrepancy between conventional and high energy x-ray results can be explained by the strong absorption coefficient of the manganese. Using conventional x-ray source, most of the intensity is absorbed by the near-surface region of the sample due to the low penetration ability of  $\text{Cu-K}\alpha$  radiation. It was therefore suggested that the charged  $\text{Li}_2\text{MnSiO}_4$  is amorphous. However, high energy x-ray allows to probe the surface and bulk of the sample so that the crystalline character of the charged  $\text{Li}_2\text{MnSiO}_4$  could be revealed.

New x-ray features observed for the charged  $\text{Li}_2\text{MnSiO}_4$  suggest that the pristine material undergoes a structural change upon delithiation due the strong Yahn-Teller distortion at the Mn-crystallographic site. This structural change is likely the primary cause for the degradation of the electrochemical performance of  $\text{Li}_2\text{MnSiO}_4$ .

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

Paper in preparation

## 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  
Christopher Carlton, Massachusetts Institute of Technology  
Yang Shao-Horn, 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 230 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. To address those issues, we will continue to exploit the concept of embedding spinel component into the layer-layer structure. We will also exploit physical blending of the layer-layer composite materials with other high-power materials to enhance the power performance, especially at low SOC.

**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)

**Financial data:** \$400K

## PROGRESS TOWARD MILESTONES

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

We continued to explore  $\text{Li}_x\text{Mn}_{0.75}\text{Ni}_{0.25}\text{O}_y$  chemistries by varying lithium content ( $x$ ). In this Mn/Ni ratio (3:1),  $\text{Li}_{1.5}\text{Mn}_{0.75}\text{Ni}_{0.25}\text{O}_y$  ( $y \sim 2.5$ ) is the composition for layer-layer (spinel-free) material, which is equivalent to  $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ . The lithium content was varied between  $x=1.2$  and  $1.5$ . Figure 1 shows the first-cycle efficiency (a), rate capability (b), and cycling performance (c) of lithium cells containing  $\text{Li}_x\text{Mn}_{0.75}\text{Ni}_{0.25}\text{O}_y$  ( $1.2 \leq x \leq 1.5$ ) cathodes. Improvement in the first-cycle efficiency was achieved by incorporating spinel component in the layer-layer matrix.  $\text{Li}_{1.2}\text{Mn}_{0.75}\text{Ni}_{0.25}\text{O}_y$  exhibits good rate capability ( $\sim 200$  mAh/g at C/1 rate); however, initial break-in cycles are needed to reach high capacity as shown in Figure 1c.

### (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 TEM and XRD, shown in Figures 2. Significant portion of the material was converted to spinel, which is supposed to be related with significant voltage shape changes during the cycle (reported in previous year). The TEM image also reveals dislocations and disordered structure in the cycled material.

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

Mildly fluorinated  $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.44}\text{Mn}_{0.31}\text{Co}_{0.25}\text{O}_2$ , which has layer-layer structure and delivers high discharge capacity ( $\sim 250$  mAh/g), suffers from poor power performance (or high impedance) especially at low SOC. To improve the impedance characteristics at low SOC, we started to investigate blending of  $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.44}\text{Mn}_{0.31}\text{Co}_{0.25}\text{O}_2$  with  $\text{LiFePO}_4$ .

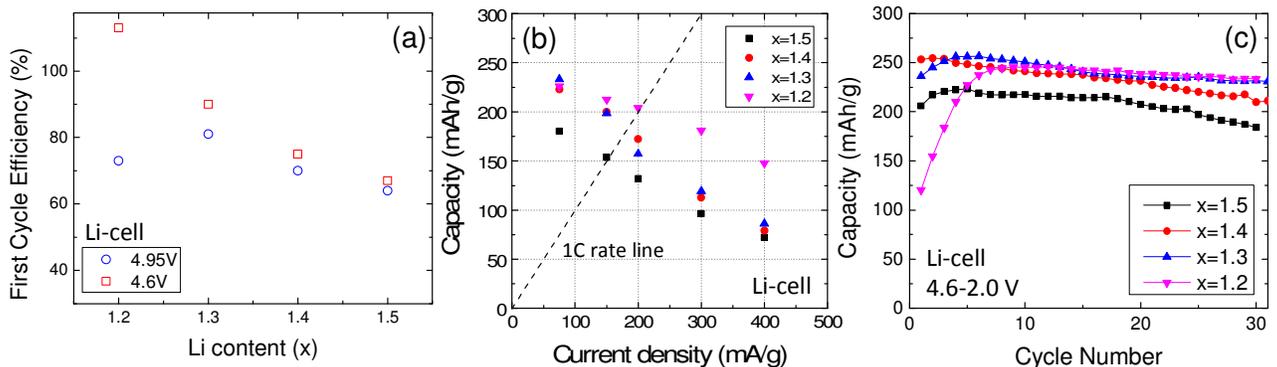


Figure 1. The first-cycle efficiency (a), rate capability (b), and cycling performance (c) of lithium cells containing  $\text{Li}_x\text{Mn}_{0.75}\text{Ni}_{0.25}\text{O}_y$  cathode materials.

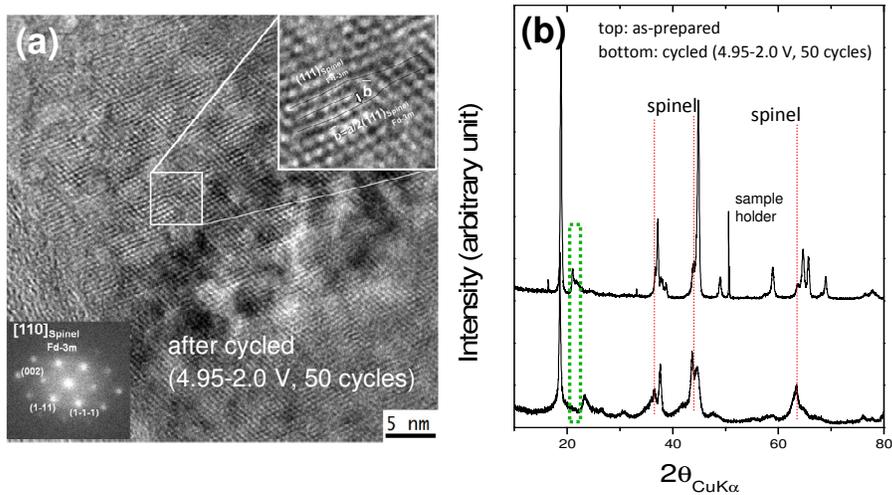


Figure 2. (a) HRTEM image, and (b) XRD pattern of  $\text{Li}_{1.2}\text{Mn}_{0.75}\text{Ni}_{0.25}\text{O}_y$  after cycling at 4.95-2.0 V, 50 times.

**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: 1.1C (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:**

- MO-Sn<sub>x</sub>Co<sub>y</sub>C<sub>z</sub> (MO=SiO, SiO<sub>2</sub>, SnO<sub>2</sub>, MoO<sub>2</sub>, GeO<sub>2</sub>) anode materials were selected for investigation as high energy anode based on the following criteria:
  - Sn<sub>x</sub>Co<sub>y</sub>C<sub>z</sub> 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 Sn<sub>x</sub>Co<sub>y</sub>C<sub>z</sub> and MO composite could lead to the increase in the capacity, reduce the amount of cobalt in the material and improve the cycleability as Sn<sub>x</sub>Co<sub>y</sub>C<sub>z</sub> 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:**

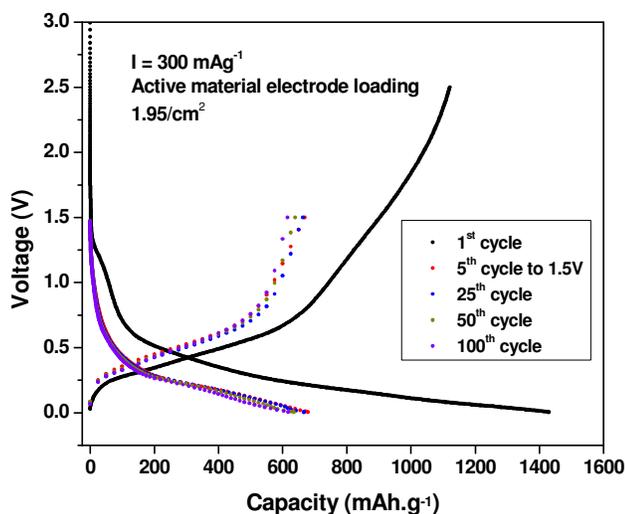
- 1- Explore the M<sub>a</sub>O<sub>b</sub>-Sn<sub>x</sub>Co<sub>y</sub>C<sub>z</sub> system where M= Si, Sn, Mo, Ge (in term of electrochemistry, material structure investigation, binders effect); (2011-2012)
- 2- Prepare materials with at least 600 mAh/g capacity with cycleability more than hundred cycles (2011-2012);

- 3- Study the rate capability of these materials and the effect of the electrode loading on the cell performance (2011-2012);
- 4- Identify the best material in term of cost, voltage output, cycling performance, and deliverable capacity (2011-2012);

## PROGRESS TOWARD MILESTONES

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

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. 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 ethylene oxide- based oligomers, LiF,  $Li_2CO_3$ , and lithium alkyl carbonate ( $ROCO_2Li$ ). As the anode material contains both an oxide and alloys. The electrochemical process involves two major reaction ( $MO + 2Li \rightarrow M + Li_2O$ ) and ( $M + xLi \rightarrow MLi_x$ ). 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 reaction is reversible.



**Figure 1: Voltage profile of Li/50wt% SiO-50wt%  $Sn_{30}Co_{30}C_{40}$  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.**

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

## **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  $\text{MCu}_5\text{Sn}_5$  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, (On schedule)

**Financial data:** \$300K

#### **PROGRESS TOWARD MILESTONES**

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

The mechanical properties of a lithiated copper tin alloy were measured using cast bars of the alloy. Strength and elastic modulus were determined from the four-point bend test, and fracture toughness was determined from notched samples in a 3-point bend test.

Alloy	Strength (MPa)	Biaxial Modulus (GPa)	Fracture Toughness (MPa m <sup>0.5</sup> )
Cu <sub>6</sub> Sn <sub>5</sub>	71±18	54±12	2.19±0.54
NiCu <sub>5</sub> Sn <sub>5</sub>	44.4±2.7	79.1±4.1	1.32±0.13
ZnCu <sub>5</sub> Sn <sub>5</sub>	104.2±3.1	55.3±4.4	2.56±0.23
FeCu <sub>5</sub> Sn <sub>5</sub>	88.0±6.5	74.3±2.8	2.38±0.15
Cu <sub>5</sub> Sn <sub>6</sub>	73.9±2.7	54.0±7.8	2.56±0.40
Li <sub>5</sub> Cu <sub>6</sub> Sn <sub>5</sub>	23.7±9.3	54±19	0.95±0.39

These results are tabulated here with comparison to unlithiated alloys.

From this table it can be seen that lithiation lowers the fracture toughness and strength, but does not affect the modulus. The critical particle size can now be estimated based on Huggins' decrepitation model (Ionics **6** (2000) p.57). This result is compared against unlithiated alloys in the table below. If the results of these data and the model are correct, it predicts an unfortunate response of the particle to

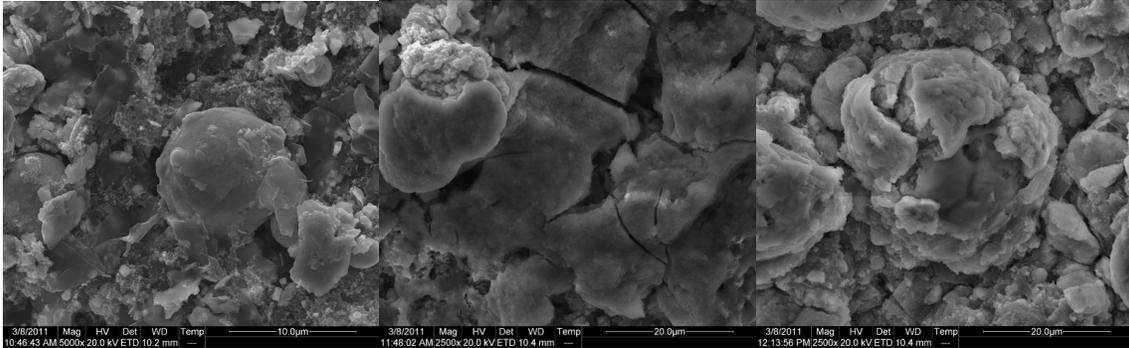
lithiation. Namely, as the alloy becomes lithiated, it becomes more brittle. This indicates that even smaller particle sizes are required to prevent particle cracking upon lithiation.

Intermetallic Alloy	10Li + MCu <sub>5</sub> Sn <sub>5</sub> ↔ 5Li <sub>2</sub> CuSn + M		85Li + 4MCu <sub>5</sub> Sn <sub>5</sub> ↔ 5Li <sub>17</sub> Sn <sub>4</sub> + 20Cu + 4M	
	Critical Particle Size, μm (eT = 0.63)	Theoretical Capacity, mAh/g	Critical Particle Size, μm (eT = 1.8)	Theoretical Capacity, mAh/g
Cu <sub>6</sub> Sn <sub>5</sub>	0.27	257	0.033	507
NiCu <sub>5</sub> Sn <sub>5</sub>	0.046	258	0.0057	510
ZnCu <sub>5</sub> Sn <sub>5</sub>	0.36	256	0.044	507
FeCu <sub>5</sub> Sn <sub>5</sub>	0.17	259	0.021	511
Cu <sub>5</sub> Sn <sub>6</sub>	0.37	~244	0.046	566
Li <sub>5</sub> Cu <sub>6</sub> Sn <sub>5</sub>	0.051	-	0.0063	-

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

Fabrication began on electrodes based on the new smaller alloys from Wildcat Discovery Technologies.

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



*Left: Fresh electrode of  $\text{Cu}_6\text{Sn}_5$  with AB carbon and SFG-6 graphite. Harvested baseline electrode (middle) and FEC-electrode (right) after washing with DMC/DEC.*

Cells were made with large (10 micron) particles of  $\text{Cu}_6\text{Sn}_5$  and cycled with baseline electrolyte and electrolyte with 10% FEC. At the end of life the cells were opened and the electrodes washed with DMC/DEC. A relatively large film was observed covering the electrode particles and large cracks were observed on its surface and the particles underneath. These film sheets are over twice as large as the original particle. FEC had a strong influence on surface morphology but did not appear to prevent particle/film cracking. Copper color was also observed on both electrodes after cycling, which indicates that copper displacement is a problem. The copper foil underneath appeared to be unaffected. It remains to be seen if similar problems exist for smaller particle sizes.

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

One publication submitted:

A. N. Jansen, J. A. Clevenger, A. M. Baebler, J. T. Vaughey “Variable temperature performance of intermetallic lithium-ion battery anode materials”, to *J. Alloys and Compounds*.

## **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:**

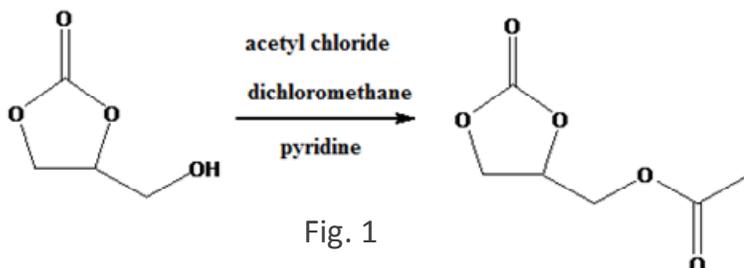
- (a.) Synthesize the methyl ester, methyl carbonate, and other derivatives of glycerol carbonate, September 2011, (on schedule)
- (b.) Examine/evaluate the performance/cycling behavior of the GC-derivative compounds, both as co-solvents and as electrolyte additives, September 2011, (on schedule)

(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

The methyl ester derivative of GC was synthesized as shown in Figure 1.



The methyl carbonate derivative of GC (aka GCMC) was synthesized as shown in Figure 2; the compound was provided by Dr. Kang Xu, ARL.

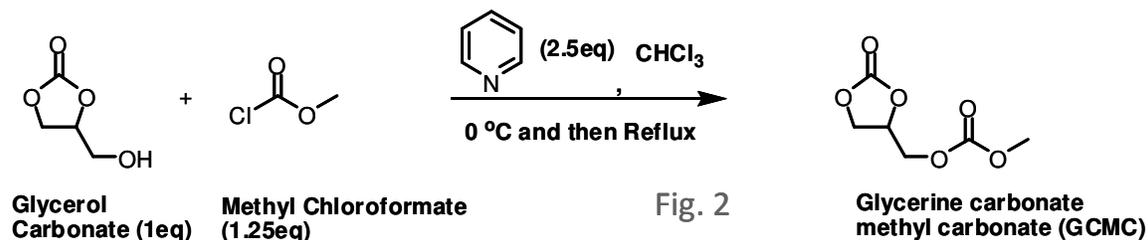


Figure 3 shows cycling and AC impedance data from NCA//Graphite cells comparing the effects of 5wt% GCMC additive in the baseline electrolyte. It is evident that GCMC addition can improve cycling performance of Gen2 electrolyte; 5wt% addition of GCMC to Gen2 electrolyte provides better capacity retention (98%) than that of 2wt% addition (94%). EIS data reveal that the impedance of coin cells containing 5wt% GCMC additive is almost identical to that of the Gen2 electrolyte.

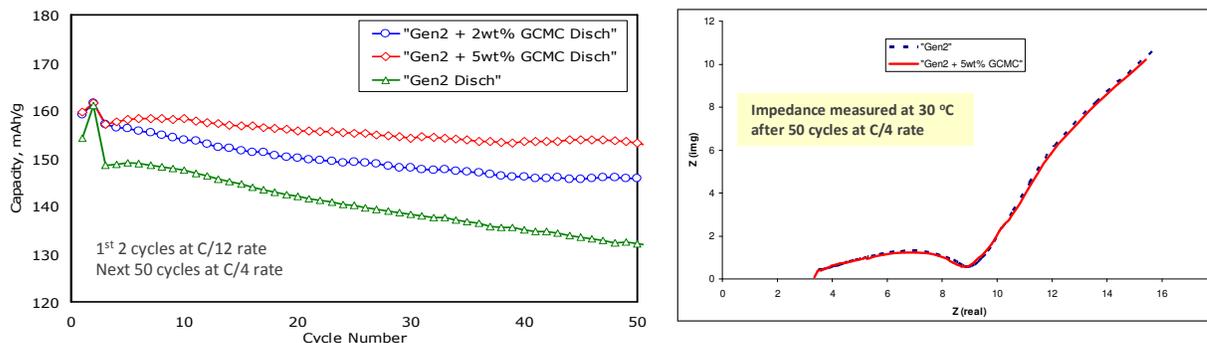


Fig. 3. Cycling and EIS data from NCA//Graphite cells comparing the effects of 5wt% GCMC additive in the baseline electrolyte.

We also evaluated GCMC as an electrolyte co-solvent in place of EC. Cells containing 1.2M LiPF<sub>6</sub> in GCMC:EMC=1:6 wt% showed cycling performance comparable to that EC-bearing cells.

**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:** ES024

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

**Project PI, Institution:** T. Richard Jow/Kang Xu, 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, 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:**

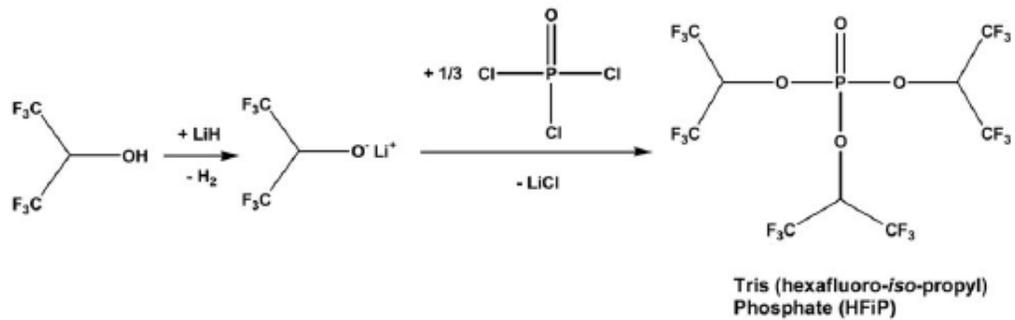
- (a) Explored additives that passivates cathode surfaces at high voltages, (Dec 2010)
- (b) Diagnostic studies: surface characterization and SEI chemistry (Dec 2010)
- (c) Evaluate electrolytes with additives in both half cells and full cells (May 2011)
- (d) Understand reactive pathways of electrolyte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

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

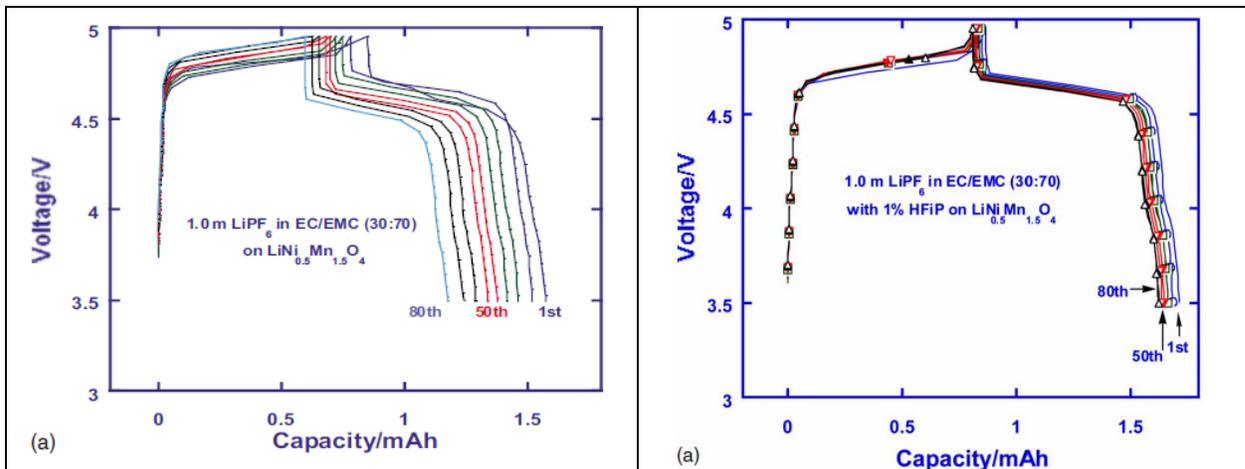
## PROGRESS TOWARD MILESTONES

### (a) Synthesis of tris (hexafluoro-iso-propyl) phosphate (HFiP):

- a. We have looked for molecules that have the propensity to be polymerized under oxidative reactions such fluorinated phosphate esters. Synthesis of HFiP: The starting material is 1,1,1,3,3,3-hexafluoro-2-propanol ( $C_3H_2F_6O$ , Fluka) reacting with LiH in diethyl ether ( $Et_2O$ ) solution until generation of  $H_2$  stopped. Adding phosphorus oxychloride ( $POCl_3$ , Aldrich) and reflux for 5 hours until the phosphorylation of alkoxides was completed.



- (b) Evaluation of HFiP additive:** The HFiP additive was evaluated using high voltage  $LiNi_{0.5}Mn_{1.5}O_4$  spinel as a cathode in half cells (with Li as a counter electrode) with a button cell configuration. The capacity fading of  $Li/LiNi_{0.5}Mn_{1.5}O_4$  cells were significantly lower when the cells were cycled in the baseline electrolyte, 1.0 m  $LiPF_6$  in EC:EMC (3:7 wt. ratio), with 1wt.% HFiP. The cells cycled in the baseline electrolyte without additive is included for comparison. After 200 cycles, the capacity retention for cells in the electrolyte with additive is 88% versus 60% for cells in the baseline electrolyte.



**(c) Synthesis of high voltage cathode LiCoPO<sub>4</sub> for the evaluation of high voltage electrolytes:** The difficulty of cycling LiCoPO<sub>4</sub> was often attributed to the lack of high voltage electrolytes. To evaluate our high voltage electrolytes, we also synthesized LiCoPO<sub>4</sub> as a test cathode for identifying the problems. LiCoPO<sub>4</sub> was synthesized using citrate complexation route. An aqueous mixture is prepared with citrate complexation to prevent heterogeneous precipitation, ensuring intimate mixing and allowing for short sintering time (Pechini-like) because of the short diffusion distances required during the solid-state synthesis.

**(d) Oxidation stability limits of solvents:** The calculation of oxidation stability potential limits of solvents using DTF M05-2X/cc-pvTz indicates that oxidation potential limits are about 1 V too high compared with the experimental values obtained using linear voltammetric scan method using glass carbon electrode. However, the calculated values agree with the experimental values when the anion of the salt is included in the calculation as shown in the table below.

DTF M05-2X/cc-pvTz, <i>oxidation potential, V</i> , and experimental data on non-active electrodes			
	without anion <i>e=20.5</i>	with anion <i>e=20.5</i>	Published experimental
DMC/BF <sub>4</sub> <sup>-</sup>	7.6	6.21	6.7 (GC, 0.65 M Bu <sub>4</sub> NBF <sub>4</sub> )
EC/BF <sub>4</sub> <sup>-</sup>	7.6	6.28	6.2 (GC, 0.65 M Et <sub>4</sub> NBF <sub>4</sub> )
PC/BF <sub>4</sub> <sup>-</sup>	7.3	6.25	6.6 (GC, 0.65 M Et <sub>4</sub> NBF <sub>4</sub> )
TMS/BF <sub>4</sub> <sup>-</sup>	6.7	5.68	5.8 (Pt, 1 M LiBF <sub>4</sub> )
DMC/PF <sub>6</sub> <sup>-</sup>	7.6	6.51	6.3 (GC, 1 M LiPF <sub>6</sub> )
EC/PF <sub>6</sub> <sup>-</sup>	7.6	6.57	
TMS/PF <sub>6</sub> <sup>-</sup>	6.7	5.59	5.8 (Pt, 1 M LiPF <sub>6</sub> )
EMS/PF <sub>6</sub> <sup>-</sup>	6.9	5.93	

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

1. K. Xu, A. v. Cresce, and U. Lee, “Differentiating contributions to “ion transfer” barrier at electrolyte/graphite interphase from Li<sup>+</sup>- desolvation and interphasial resistance”, *Langmuir*, 2010, 26, 11538~11543

2. A. v. Cresce, K. Xu, "High Voltage Electrolytes for Li Ion Batteries", *Proceedings 44th Power Sources Conference*, Las Vegas, NV (June 14~17, 2010)
3. J. L. Allen, J. Wolfenstine, T. R. Jow, "New Cathode Materials for Lithium Ion Batteries", *Proceedings 44th Power Sources Conference*, Las Vegas, NV, June 14-17, 2010.
4. T. R. Jow, J. L. Allen, M. Marx, K. Nechev, B. Deveney, S. Rickman, "Electrolytes, SEI and Charge Discharge Kinetics of Li-ion Batteries", *ECS Trans.*, 2010, 25 (36), 3.

## **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 stabilize the interface of the state-of-the-art lithium-ion battery electrolyte to meet the requirements of EV and PHEV applications.

**Approach:** The approach is to develop additives that polymerizes or either oxidizes or reduces at the surface of the cathode and anode and form a stable passivation film that act as a barrier against surface reactivity between the charged electrodes ( cathode or anode) and the electrolyte..

#### **Milestones**

- (a) Generate screening list based on the semiempirical rule 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**

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

Degree of unsaturation of chemical structures is regarded as one criterion for screening potential additives. Chemicals with high degree of unsaturation always have cyclic structure, double bonds, or both, which could be beneficial to the SEI formation process. The screening process consists of formation process, impedance measurements, and fast cycle test at elevated temperature. The current screening list includes succinic anhydride derivatives shown in Fig. 1.

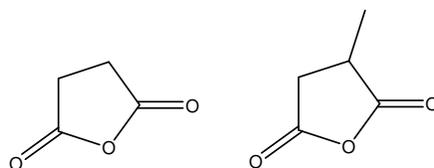


Fig.1, Structures of succinic anhydride derivatives.

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

Fig. 2a shows clear change of the  $dQ/dV$  profiles when additives were added, indicating the formation of SEI layer on the surface of the electrode. Fig. 2b shows obvious improvement in the capacity retention for cells with additives when compared to cells without additives. The comparison of the impedance results showed that when additives were used, the impedance was increased.

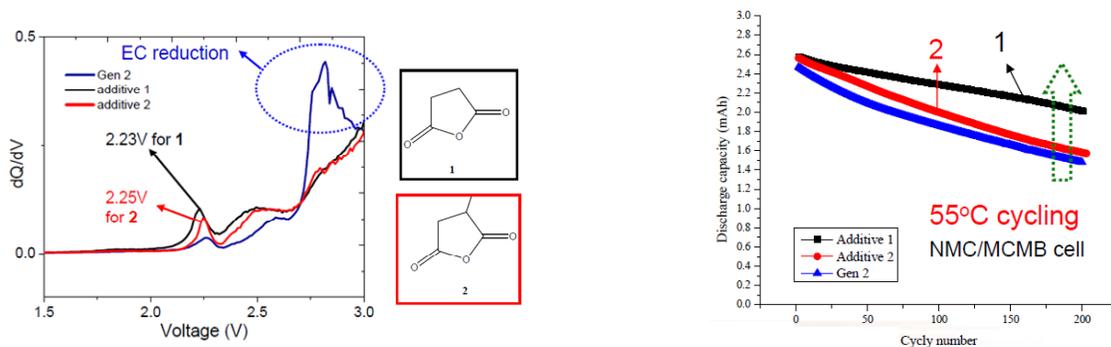


Fig 2. (a) Differential capacity profiles of MCMB/NCM cells with electrolyte of 1.2M LiPF<sub>6</sub> EC/EMC 3/7+1% additive; (b) Capacity retention of MCMB/NCM cells cycled between 2.7 and 4.2V at 55 °C in electrolyte of 1.2M LiPF<sub>6</sub> EC/EMC 3/7 with and without additive.

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

Succinic anhydride additives (1, 2) show clearly a significant improvement in the capacity retention due to the formation of a stable passivation film on the surface of the electrode.

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

No publication in this quarter.

## **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 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

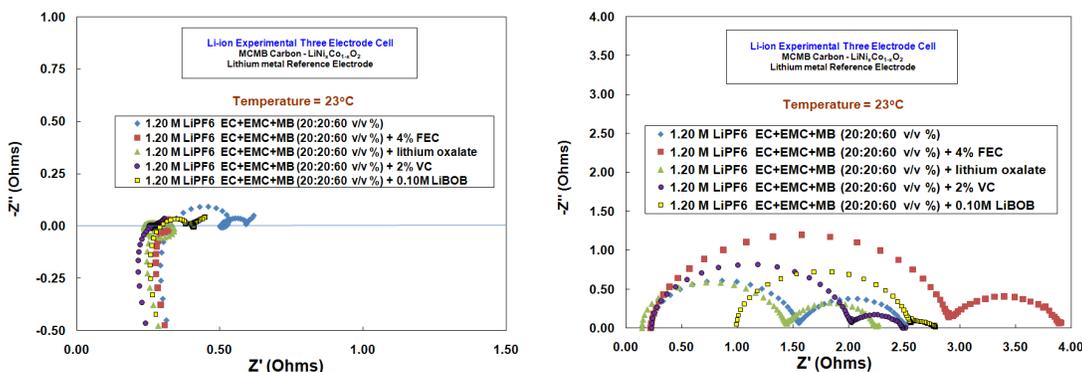
FY'11 = 175K

### **Accomplishments and Progress toward Milestones:**

We have investigated a number of ester containing electrolytes, namely methyl propionate and methyl butyrate-based electrolytes, in conjunction with electrolyte additives, with the intent of providing improved low temperature performance while still delivering acceptable high temperature resilience. More specifically, 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- $\text{LiNiCoO}_2$  and  $\text{LiNiCoAlO}_2$  systems.

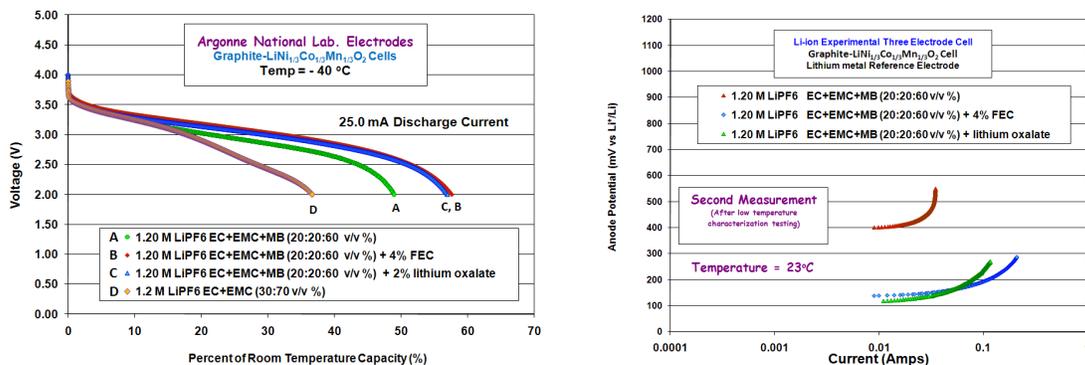
Based upon these approaches, a number of methyl butyrate-based electrolytes were investigated with the anticipation that the high temperature resilience will be improved. Specifically we investigated a number of electrolytes, including: (1) 1.20M  $\text{LiPF}_6$  in EC+EMC+MB (20:20:60 v/v %), (2) 1.20M  $\text{LiPF}_6$  in EC+EMC+MB (20:20:60 v/v %) + 2% FEC, (3) 1.20M  $\text{LiPF}_6$  in EC+EMC+MB (20:20:60 v/v %) + 4% FEC, (4) 1.20M  $\text{LiPF}_6$  in EC+EMC+MB (20:20:60 v/v %) + lithium oxalate, (5) 1.20M  $\text{LiPF}_6$  in EC+EMC+MB (20:20:60 v/v %) + 2% VC, and (6) 1.20M  $\text{LiPF}_6$  in EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB. These electrolytes have been shown to have improved performance in MCMB- $\text{LiNiCoO}_2$  and graphite- $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  experimental Li-ion cells, as described below. It should be noted that the use of these additives, in some cases, improved the low temperature rate capability (reported in FY'11).

After fully characterizing the low temperature performance and electrochemical characteristics at low temperature, the MCMB- $\text{LiNiCoO}_2$  cells were subjected to high temperature cycling (60° and 80°C) and subsequent electrochemical characterization. A number of the electrolyte additives were observed to improve the stability of the methyl butyrate system, especially FEC and VC, when exposed to high temperature cycling, especially on the MCMB anodes as determined using EIS measurements (shown in Figure 1).



**Figure 1:** EIS characteristics of MCMB-LiNi<sub>X</sub>Co<sub>1-X</sub>O<sub>2</sub> cells containing 1.0M LiPF<sub>6</sub> EC+EMC+MB (20:20:60 vol %) electrolytes with and without additives after high temperature cycling: (a) MCMB anodes and (b) LiNi<sub>X</sub>Co<sub>1-X</sub>O<sub>2</sub> cathodes.

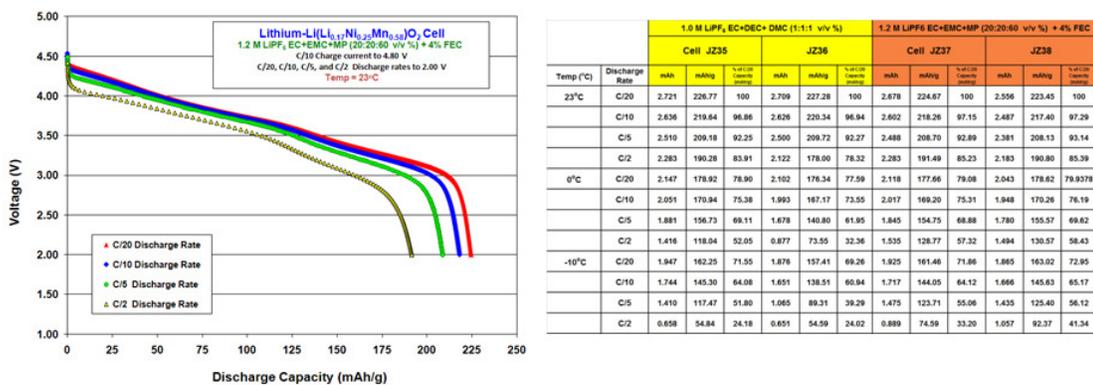
As mentioned, methyl butyrate-based electrolytes (with and without additives) have also been evaluated over a wide temperature with graphite-LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> cells. In a similar fashion, the use of additives was observed to improve the low temperature rate capability as well as the high temperature resilience of the cells. As shown in Fig. 2 (A), the use of FEC and lithium oxalate were observed to improve the low temperature discharge rate capability at -40°C compared to the methyl butyrate system without any additive, as well as the all carbonate-based baseline electrolyte (i.e., 1.2M LiPF<sub>6</sub> in EC+EMC (30:70 vol%). The use of the electrolyte additives were also noticeably observed to preserve the lithium kinetics at the anode after being subjected to cycling, as displayed by the dramatic difference in limiting current densities determined using Tafel polarization measurements on the graphite electrodes, displayed in Fig 2 (B). This finding suggests that either the electrolyte additives are resulting in a more desirable, protective SEI layer on the graphite anodes, or they are participating in a filming process at the LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> electrodes which results in decreased electrolyte degradation and subsequent deposition of byproducts on the anode.



**Figure 2:** (A) Discharge performance at -40°C of graphite-LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> cells containing 1.0M LiPF<sub>6</sub> EC+EMC+MB (20:20:60 vol %) electrolytes with and without

additives (approximately a C/5 discharge rate). (B) Tafel polarization measurements performed at 23°C on graphite electrodes in contact with different electrolytes.

Some of ester based formulations have also been investigated in the context of high voltages systems, namely in Li metal-Li(Li<sub>0.17</sub>Ni<sub>0.25</sub>Mn<sub>0.58</sub>)O<sub>2</sub> cells and graphite-LiNiCoMnO<sub>2</sub> (Toda) experimental coin cells. As shown in Fig. 3, very comparable reversible capacity was obtained when a methyl butyrate-based formulation with FEC was evaluated in Li-Li(Li<sub>0.17</sub>Ni<sub>0.25</sub>Mn<sub>0.58</sub>)O<sub>2</sub> cells compared to an all carbonate-based baseline (i.e., 1.0M LiPF<sub>6</sub> in EC+DEC+DMC (1:1:1 vol%). Improved discharge rate performance with the MB-based solution was also observed at low temperatures (Fig. 3B). Since there is some concern that particular systems may be stable with high voltage cathodes and lithium metal anode but are not compatible with carbon-based anodes, effort is on-going to evaluate promising electrolytes with the graphite-LiNiCoMnO<sub>2</sub> (Toda) system. Furthermore, future work will be devoted to evaluating these electrolyte systems in conjunction with the lithium titanate-spinel electrochemical couple (i.e., LTO-LMO), which is being provided by Argonne National Laboratory under the ABR program.



**Figure 3:** (A) Discharge rate performance at 23°C of Li-Li(Li<sub>0.17</sub>Ni<sub>0.25</sub>Mn<sub>0.58</sub>)O<sub>2</sub> cells containing 1.0M LiPF<sub>6</sub> EC+EMC+MB (20:20:60 vol %) + 4% FEC and a baseline all carbonate blend. (B) Discharge rate performance at various temperatures (cells charged at room temperature prior to discharge).

In collaboration with A123 Systems, two of the promising methyl butyrate-based electrolytes identified have been incorporated into 26650 LiFePO<sub>4</sub>-based Li-ion cells (2.20 Ah size) for evaluation (i.e., namely 1.20M LiPF<sub>6</sub> in EC+EMC+MB (20:20:60 v/v %) + 4% FEC and 1.20M LiPF<sub>6</sub> in EC+EMC+MB (20:20:60 v/v %) + 2% VC). A number of performance tests are on-going to assess the performance under various conditions, including: (a) discharge rate performance at various temperatures (-60 to +25°C), (b) cycle life performance at various temperatures (i.e., 23, 40, and 50°C), (c) variable temperature cycling, and (d) current interrupt impedance measurements at various temperatures.

Future work will involve continuing the investigation of the use of additives in conjunction with ester-based wide operating temperature range electrolytes, 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. These electrolytes will be investigated using a number of different chemistries, including high voltage systems. Effort will also be devoted to demonstrating these systems in prototype cells, such as in LiFePO<sub>4</sub>-based cells (A123), LiNiCoO<sub>2</sub> cells (Yardney), and LiNiCoAlO<sub>2</sub> cells (Quallion).

### Publications:

1. M. C. Smart, B. V. Ratnakumar, L. D. Whitcanack, K. A. Smith, S. Santee, F. J. Puglia, and R. Gitzendanner, "Performance Demonstration of MCMB-LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> Cells Containing Electrolytes Designed for Wide Operating Temperature Range", *ECS Transactions*, **25** (36), 273 (2010).
2. M. C. Smart, B. V. Ratnakumar, A. S. Gozdz, and S. Mani, "The Effect of Electrolyte Additives upon the Lithium Kinetics of Li-Ion Cells Containing MCMB and LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> Electrodes and Exposed to High Temperatures", *ECS Transactions*, **25** (36), 37 (2010)
3. M. C. Smart, B. V. Ratnakumar, F. C. Krause, W. C. West, and L. W. Whitcanack, "The Development of Li-Ion Electrolytes with Improved Operating Temperature Range and Safety Characteristics", 2010 Space Power Workshop, Manhattan Beach, CA, April 22, 2010.
4. M. Tomcsi, M. Nagata, H. Tsukamoto, M. C. Smart, and B. V. Ratnakumar, "Li-Ion Battery with Wide (-42°C to +71°C) Operational Temperature Range", 2010 Space Power Workshop, Manhattan Beach, CA, April 22, 2010.
5. M. C. Smart, B. V. Ratnakumar, M. R. Tomcsi, M. Nagata, V. Visco, and H. Tsukamoto, "Performance of Wide Operating Temperature Range Electrolytes in Quallion Prototype Li-Ion Cells", 2010 Power Sources Conference, Las Vegas, NV, June 16, 2010.
6. M. C. Smart, B. V. Ratankumar, and K. Amine, "Improved wide operating temperature range of MCMB-Li<sub>1+x</sub>(Co<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>)<sub>1-x</sub>O<sub>2</sub> cells with methyl butyrate-based electrolytes", 218<sup>th</sup> Meeting of the Electrochemical Society, Las Vegas, Nevada, Oct. 13, 2010.
7. B. V. Ratnakumar, V. P. Reddy, M. C. Smart, M. Homer, and W. C. West, "Cyclic Voltammetric Studies of Li-ion Battery Electrolytes", 218<sup>th</sup> Meeting of the Electrochemical Society, Las Vegas, Nevada, Oct. 13, 2010.
8. M. C. Smart, B. V. Ratnakumar, K. B. Chin, and L. D. Whitcanack, "Lithium-Ion Electrolytes Containing Ester Cosolvents for Improved Low Temperature Performance", *J. Electrochem. Soc.*, **157** (12), A1361-A1374 (2010).

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 Q1

**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%). In coming months, we will investigate the performance of our electrolytes with at least two electrode couples: LNMO/LTO and NMC/Carbon. Our cell testing schedule will be dependent on availability of the prepared electrode laminate from ANL and elsewhere. To date (end of 2011 Q1) we have not yet received LNMO/LTO from ANL, but we have received a small amount of NMC/Carbon electrode material from SNL (the NMC (3M commercial 1/3 variety) is coated on carbon coated aluminum, and the graphite is from Conoco Phillips (G8)).

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

  = Activity completed in reporting period

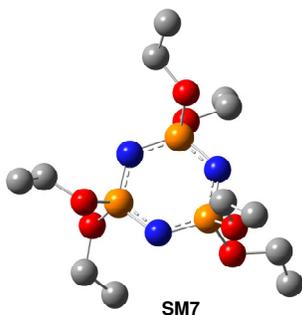
Milestone	Status	Date
a. Synthesis of newer SM series (SM 5,6,7)	completed	October 2010
b. Development of improved voltammetry techniques for SEI characterization.	completed	December 2010
c. Optimize synthesis routes for first-generation ionic liquid phosphazenes	completed	November 2010
d. Cell testing using ABR-relevant electrode couples (LNMO/LTO and NMC/Carbon)	In preparation	
e. Synthesis of newer FM series Phosphazenes	In preparation	

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

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

**PROGRESS TOWARD MILESTONES**

(a) Three new compounds have been synthesized and characterized over the last quarter, including the SM series SM5, SM6, and SM7. Electrolytes were blended by adding as much as 30% phosphazene additives to the baseline electrolyte EC-EMC-LiPF<sub>6</sub>, then subjected to a number of characterization tests. Initial results are shown in Fig. 1.



Protons removed for clarity.  
**Red** = oxygen,  
**Blue** = nitrogen  
**Orange** = phosphorus,  
**Grey** = carbon  
**Purple** = lithium (when present)

(b) CV work has shown that INL additives such as the SM series can more than double the effective electrochemical window that is achievable with the standard baseline electrolyte. A complementary technique based on a combination of potentiostatic and potentiodynamic measurements has been developed and applied toward investigation of INL phosphazene materials, using Ni and Al metal substrates. Metrics that emerge from this highly accurate method involve rates of SEI formation, degradation, and maintenance, as well as overall SEI electrochemical stability (Fig. 2).

(c) We have significantly improved our synthesis route for our first-generation ionic liquid phosphazenes. Parallel to this is the expansion of our production capacity, wherein a second full synthetic setup has been designed and constructed (Fig. 3). This effectively doubles the technical capability for the synthesis of novel electrolyte compounds at the INL.

(d) Coin cell testing will commence once we receive viable ABR electrode materials from ANL and other possible sources. Late in 2011 Q1 we recently received a small batch of NMC/Carbon electrodes from SNL, and are preparing to test our electrolyte systems with these materials, using phosphazenes at additive levels (up to 10%).

(e) Synthesis targets have been chosen for newer generations of FM compounds, loosely based on the prototype FM1 that was synthesized in FY 2010.

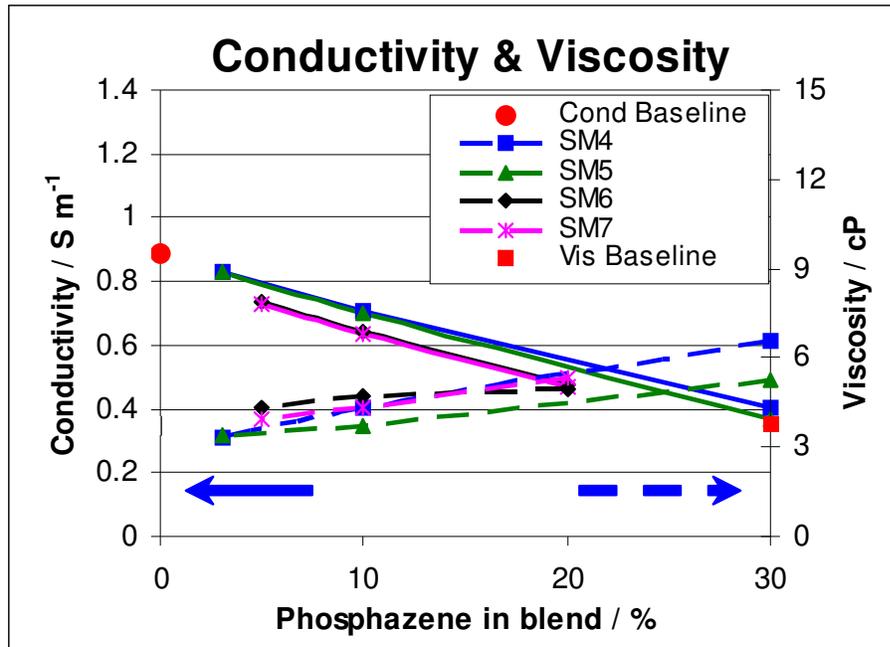
Supporting our overall project is the acquisition of new equipment. A new vapor pressure analyzer was set up and brought to specifications, which will allow us to see how electrolyte additives are able to depress the vapor pressure of more volatile (and flammable) electrolyte solvents. A new 600 MHz NMR spectrometer was installed (via INL internal funds). This high field instrument will allow for more detailed studies of electrolyte formulations, particularly as the blends are either thermally degraded intentionally, or aged in cells.

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

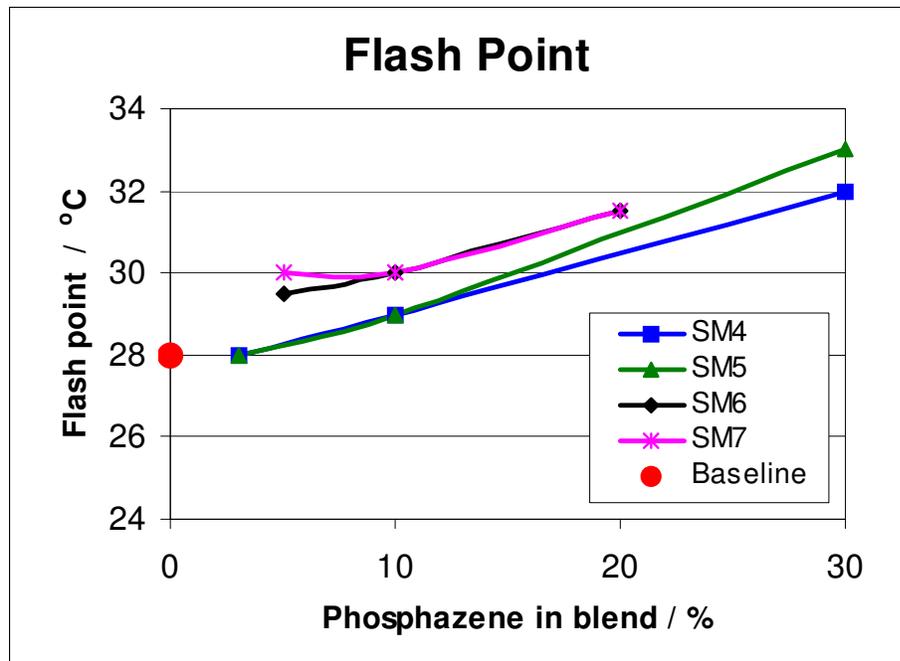
- S. V. Sazhin, M. K. Harrup, K. L. Gering, “Characterization of low-flammability electrolytes for lithium-ion batteries”. Submitted to J. Power Sources.
- Sergiy V. Sazhin, Mason K. Harrup, Harry W. Rollins, Kevin L. Gering, “Investigation of Phosphazene-based Low Flammability Electrolytes for PHEV Batteries”, to be presented at Pacific Power Source Symposium, January 10-14, 2011. (Waikoloa, HI).

Intellectual property documentation of newer phosphazene compounds will be pursued commensurate with the documentation of their performance in lithium-ion cell environments.

Fig. 1



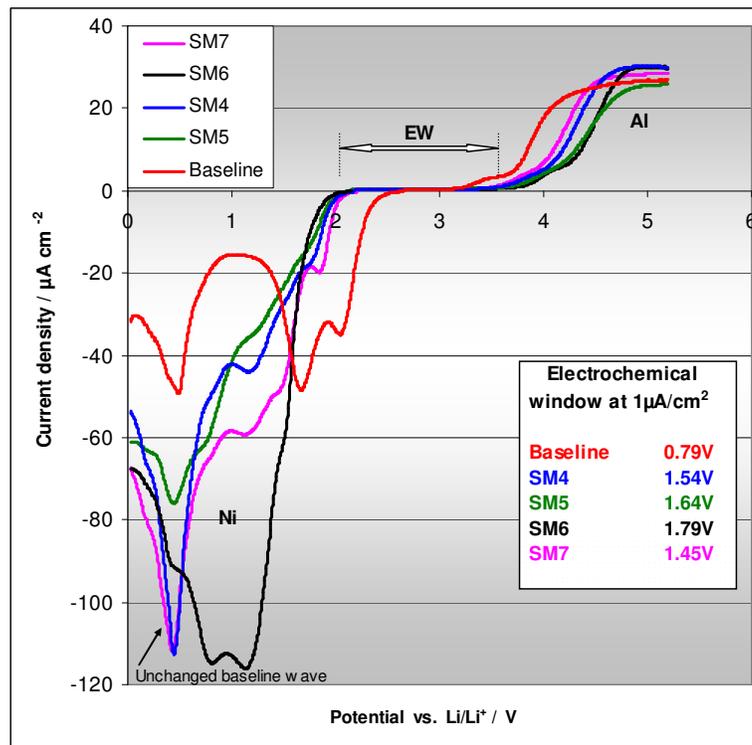
- Moderate changes in transport properties are seen for SM compounds kept at additive levels ( $\leq 10\%$ ).



- Flash point of electrolyte increases with the addition of the SM additives.

Fig. 2

## Voltammetry of Phosphazene-based Electrolytes



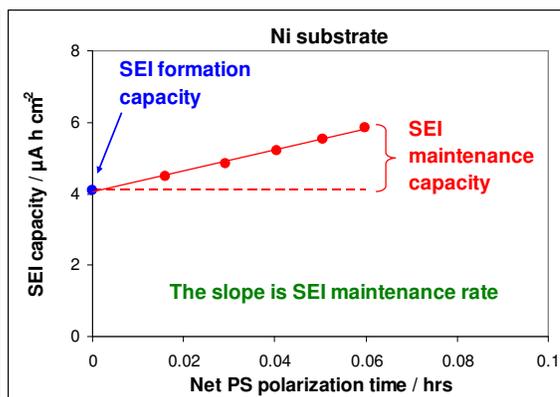
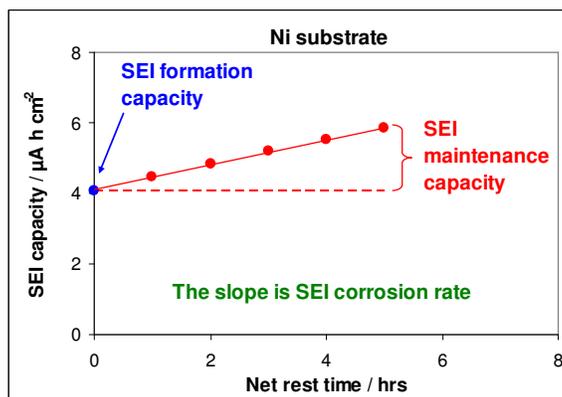
- Phosphazenes do increase electrochemical window at negative and positive ends.
- All the windows are less than operating voltage of Li-ion cells.
- At potentials beyond the electrochemical window, passivation does occur forming SEI films.
- Properties of passivating films need to be measured quantitatively.
- Last year a new method and new criteria were developed for this topic. This year we presented an improved version of the method which is more logical and informative.

Electrolytes: baseline (1.2M LiPF<sub>6</sub> EC:MEC (2:8)) and the blends of 20% of each phosphazene with 80% baseline.

## Electrochemical Characterization of Electrolytes and SEI

**Method:** Potentiodynamic (PD) and potentiostatic (PS) coulometry ("bulk electrolysis" of passivation processes).

**Electrodes:** Ni (from OCV to 20 mV vs. Li/Li<sup>+</sup>)  
Al (from OCV to 5.2 V vs. Li/Li<sup>+</sup>)



Red points in the graphs represent capacities at subsequent PS polarization series received with rest time between the series

**Capacity of SEI formation:** relates to irreversible capacity at cell formation. Lower values are better.

**Rate of SEI corrosion (degradation)** = f (electron transport + physical defects + solubility of SEI). Relates to cell self-discharge. Lower values are better.

**Rate of SEI maintenance** = f (mostly Li<sup>+</sup> mobility in SEI). Relates to cell power capability (higher is better).

**SEI kinetical stability** = [(maintenance rate / (maintenance+corrosion rates)] x 100%. Higher values are better.

Fig. 3



Synthetic efforts have found efficient routes to several different phosphazene-based ionic liquid electrolyte solvents. Most significantly, a second full synthetic setup has been designed and constructed. This effectively doubles the technical capability for the synthesis of novel electrolyte compounds at the INL, allowing us to generate sufficient amounts of purified and dried materials for our ABR testing.

# TASK 1

## Battery Cell Materials Development

1<sup>st</sup> Quarter Report, Oct. ~ Dec. 2010

**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) Morphology characterization of carbon coated NCM powder.
- (b) Electronic conductivity measurement of electrodes made of carbon coated NCM.

**Financial data:** \$300K

**PROGRESS TOWARD MILESTONES**

- (a) The NCM powder with various carbon coating by Hosokawa was prepared for SEM. The morphology of the NCM particles before and after carbon coating was characterized.
- (b) The carbon coated NCM powder was made into electrodes with various carbon black additives to look at its impacts on the conductivity of the whole electrode.

The electronic conductivity was measured using 4 probe methods. In the work, two substrates were used for the laminates, including aluminum foil and polyester film, which will be used to elucidate the interfacial resistance of the electrode.

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

Three different NCM powders with 0%, 1% and 3% carbon coating were characterized using SEM. The carbon coating on the surface of NCM particles was observed. The coated carbon was found to stay in the dents or cavities on the surface of NCM.

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

The carbon coated NCM powder was made into electrodes with various carbon black additives to look at its impacts on the conductivity of the whole electrode. The electronic conductivity was measured using 4 probe method. Much higher resistance was obtained for the composite electrodes with Polyester substrate. For aluminum substrate, the 4 probe measurement includes resistance from the composite electrode in depth. For polyester substrate, the 4 probe measurement is attributed by the sheet resistance of the composite electrode.

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

1. Olivine electrode engineering impact on the electrochemical performance of lithium-ion batteries, Wenquan Lu, Andrew Jansen, Dennis Dees, and Gary Henriksen, J. Material Research, 25 (8) Focus Issue on Materials for Electrical Energy Storage, August 2010, 1656-1660.

# TASK 1

## Battery Cell Materials Development

1<sup>st</sup> Quarter Report, Oct. ~ Dec. 2010

**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 1<sup>st</sup> Quarter:

- a) 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)
- b) Fluorinated solvents, FEC, Fluorinated ether, from Daikin (Japan)

c) Surface modified graphite from ConocoPhillips (USA)

**Financial data:** \$350K

### **PROGRESS TOWARD MILESTONES**

The composite cathode as high energy density material from ANL (H. Wu) was evaluated. This composite material has 1/3  $\text{Li}_2\text{MnO}_3$  but no cobalt, which means less cost for lithium ion batteries. The energy density and irreversible capacity during 1<sup>st</sup> cycle have been tested. Its power and rate capability were also studied using half cells.

The effects on electrochemical and thermal effect of fluorinated solvents (Daikin, Japan) on lithium ion batteries have been completed and summarized.

Surface modified natural graphite as high energy density anode material from ConocoPhillips has been investigated. Its electrochemical performances, such as energy density, irreversible capacity loss, and rate capability, have been tested.

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

The reversible specific capacity of composite cathode,  $1/3\text{Li}_2\text{MnO}_3 \cdot 2/3\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ , was determined to be 240 mAh/g between 4.6V and 2.0V at C/10 rate, which is equivalent to 878 Wh/kg. The irreversible capacity loss was about 15% during first cycle.

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

Compared to 1.2M  $\text{LiPF}_6$  in EC/EMC electrolyte, 1.2M  $\text{LiPF}_6$  in FEC/EMC electrolyte showed higher on-set temperature and less total heat generation at various state of charge using NCA electrodes. However, relatively high conductive resistance was observed for fluorinated electrolyte, leading to less capacity at higher cycling rate (above 1C).

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

Surface modified natural graphite from ConocoPhillips was studied due to its high energy density and lower cost. Reversible capacity of A12 was determined to be about 350mAh/g. However, the Li/Graphite half cells needed few formation cycles to get its full capacity.

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

2. Electrolyte additive to improve performance of MCMB/LiNi1/3Co1/3Mn1/3O2 Li-ion cell, Y. Qin, Z. Chen, W. Lu, and K. Amine, J. Power sources, 195, 2010, 6888-6892.

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number:** 1.2.2 Electrode Material Development (AMR No. 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)

**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 can 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

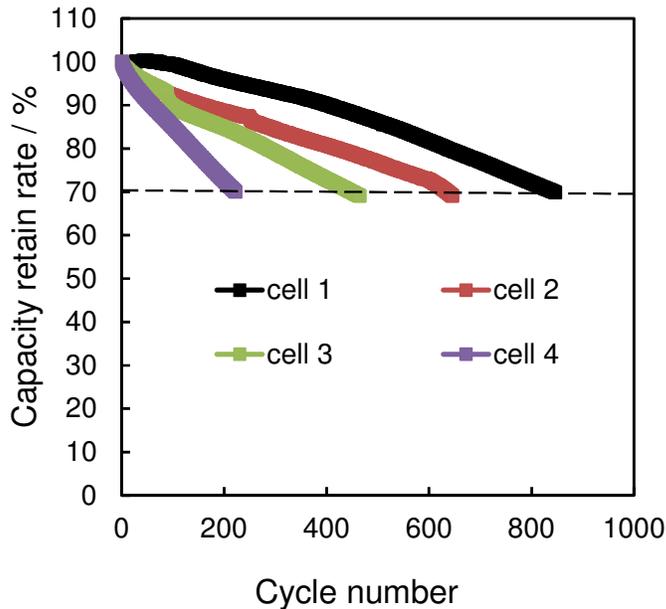
**(a) Summary of work in the past quarter related to milestone (a).**

A visiting scholar from China arrived in the first quarter of FY 2011, and he will be working on this project. During this reporting period, he learned our electrode fabrication methods and equipment.

Another researcher working on this project, visited MIT to learn how to prepare G. Ceder's  $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$  material. Prof. Ceder's Group had not yet perfected their synthesis procedures, and the cognizant MIT post-doctoral scientist had taken paternity leave when our researcher arrived. Our researcher learned as much as possible, and he is not only scaling up the MIT process but also optimizing it. This effort is on-going.

Work from the previous fiscal year on a water-based binder for both the anode and the cathode was completed. This work involved the use of polyacrylic acid (PAA) and its salt derivatives PAALi, PAANa, and PAAK. Both the cathode and anode materials were developed by HydroQuebec under the BATT Program. The anode is known to fail due to

higher-than-typical rates of the side reactions on SNG. For reasons that are unclear, the SNG material (which appears very similar to the BATT baseline graphite CGP-G8) does not form a protective SEI as effective as that formed on CPG-G8.



- Cell 1: anode: 9% PAALi/1% SBR/2% VGCF/88% SNG12  
cathode: 9% PAALi/1% SBR/8% AB/82% LiFePO<sub>4</sub>
- Cell 2: anode: 9% PAALi/1% SBR/90% SNG12  
cathode: 10% PVDF/8% AB/82% LiFePO<sub>4</sub>
- Cell 3: anode: 10% PAALi/90% SNG12  
cathode: 10% PVDF/ 8% AB/82% LiFePO<sub>4</sub>
- Cell 4: anode: 10% PVDF/2% AB/2% VGCF/86% SNG12  
cathode: 10% PVDF/8% AB/82% LiFePO<sub>4</sub>

It was determined that the use of PAAX alone in electrodes showed cracks after drying. This problem was alleviated by adding SBR binder; however, more than 2% SBR binder greatly reduced the rate performance of the electrode. Electrodes based on PAALi were constructed with different levels of PAALi, SBR, vapor-grown carbon fibers (VGCF), and acetylene black (AB). The cycling results are presented in the figure to the left. This plot shows that electrodes with PAALi cycled better than the

traditional PVDF-based system cast from NMP solutions (Cell 4). We believe this is a result of the formation of a more-protective SEI on the anode using PAALi instead of PVDF.

## **TASK 1**

### **Battery Cell Materials Development**

**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:** Khalil Amine, Argonne National Laboratory

**Collaborators (include industry):**

Yan Qin, Zonghai Chen (ANL)

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 solution to solve this problem.

- Identify gassing mechanism.
- Develop solutions to eliminate the gassing issue.

**Approach:** Identify condition that lead to gassing and quantify the nature of gassing investigate component with the cell that catalyze the generation of gases . propose gassing mechanism and possible solutions to mitigate the gassing

**Milestones:**

- (a.) The condition that leads to severe gassing was identified, (On schedule)
- (b.) The major component of the gas was identified. (On schedule)

**Financial data:** \$300K

#### **PROGRESS TOWARD MILESTONES**

In order to identify the source of the gassing, the whole battery, the LTO anode and  $\text{LiMnO}_4$  cathode have been investigated separately at different charge state with different salt and solvent. The results showed that only the LTO at charged state ( $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ ) will release gas at elevated temperature when coexisting with electrolyte ( $\text{LiPF}_6$  and carbonate solvents). No gassing was observed at fully discharged state, or at room temperature ( $25^\circ\text{C}$ ). Similar phenomena was not observed for cells using carbon anodes. GC gas analysis indicated that the major component of the gas is hydrogen.

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

Charged LTO coexisting with electrolyte stored at elevated temperature ( $\geq 55^{\circ}\text{C}$ ) is responsible for the gassing.

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

The major component of the gas is identified as hydrogen.

**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.

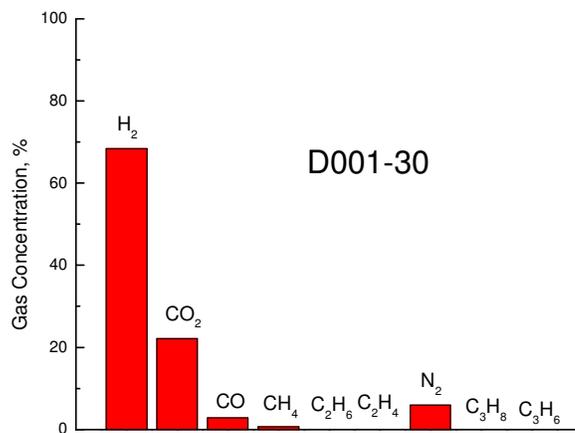


Figure1. The GC-MS analysis shows that the major component of the gas is hydrogen.

## **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 solvents 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. Explore 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, (On schedule)

(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).**

Based on our previous study, sulfone based electrolytes such as ethyl methyl sulfone (EMS) and tetramethylene sulfone (TMS) can dissolve most of the lithium salts. The sulfone/lithium salt complex has advantages over other electrolyte systems such as good conductivity, high voltage stability and non-flammability. However, their high viscosity of this electrolyte causes issues of electrode and separator wetting. We try to utilize the sulfone by hybridizing with silane solvent to mitigate the issue associated with sulfone. Sulfone solvents are commercial available and can be purified by a short pass vacuum distillation and we need to synthesize the silane compounds. An alcoholysis reaction was performed by reacting trimethylchlorosilane with oligo(ethylene glycol) methyl ether using triethyl amine as acid scavenger. The excess of the oligoether was removed by a water washing procedure. The pure silane compounds were obtained by vacuum distillation and their structures were identified by multi NMR technique ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$ -NMR) and FT-IR. 100g of tri(ethylene glycol) methyl trimethylsilane (1NM3) was prepared in high purity for battery evaluation study.

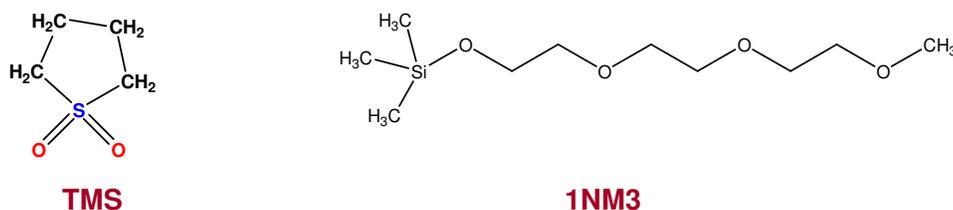


Figure 1.  $^1\text{H}$ -NMR of the purified 1NM3.

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

TMS has low melting point ( $27.5^\circ\text{C}$ ) among the sulfone compounds and is a colorless crystal at ambient temperature. However, it liquefies easily when mixed with 1NM3 at a wide temperature range. Fig.1 shows the conductivity at different temperatures of

TMS/1NM3 mixed electrolyte in 1.0M LiPF<sub>6</sub> salt. Interestingly, the mixed electrolyte exhibited higher conductivity than the either silane or sulfone based electrolyte. This result indicates a certain extent of molecular level of 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 (Fig. 2). It is known that high polar and low viscosity molecules will facilitate the ion dissociation and transfer. 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  $2.0 \times 10^{-3}$  S/cm, which is slightly lower than the conventional carbonate based electrolytes.

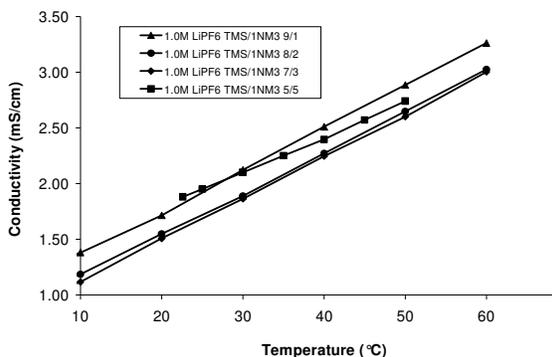


Fig.2. Ionic conductivities versus temperature for 1.0M LiPF<sub>6</sub> TMS/1NM3 hybrid electrolyte.

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

Hybrid Electrolyte, invention report with internal number of 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:** Michael Thackeray, Argonne

**Collaborators (include industry):** Vilas Pol (Co-PI), 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 achieve a spherical carbon anode with comparable capacity (300mAh/g) and enhanced safety relative to graphite. A second later objective is 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 Superior Graphite and General Motors to gain access to high temperature (>2000 °C) furnaces – *Collaborations established*
- (b) Prepare carbon samples for Superior Graphite and General Motors – *First batches completed 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 Superior Graphite and GM:** Collaborative interactions with Superior Graphite (Chicago) and General Motors have been established to heat-treat autogenically-prepared carbon products, such as carbon spheres and prolate spheroids, to temperatures in excess of 2000 °C under inert conditions to increase the amount of the graphitic component in the carbon product, typically a hard carbon.

**Milestone (b). Prepare carbon samples for Superior Graphite and GM:** Samples of carbon spheres were sent to Superior Graphite and GM for heat-treatment between 2000 and 3000 °C. At present, GM is experiencing problems with its high-temperature furnaces; we are therefore looking for alternative industrial partners to overcome this delay.

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

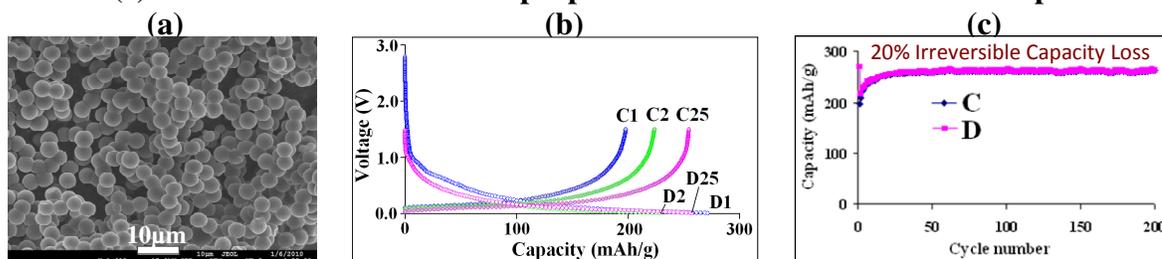


Fig. 1. (a) Spherical carbon particles after heat-treatment at 2400 °C for 1 h (SCP-HT); (b) charge (C) and discharge (D) profiles of a Li/SCP-HT cell; and (c) capacity vs. cycle no. plot of the cell shown in (b).

Heating autogenically-prepared carbon spheres to 2400 °C for 1 hour does not alter their overall morphology (Fig. 1a). SCP-HT electrodes were evaluated in lithium/SCP-HT half cells and compared to the performance unheated SCP electrodes. Both SCP and SCP-HT electrodes give a voltage response to a lithium counter/reference electrode that is typical of a hard carbon. Heat-treated SCP-HT electrodes provide a marginally superior capacity on cycling (~255 mAh/g) (Fig. 1b) compared to unheated SCP electrodes (~235 mAh/g), but show a significantly reduced first-cycle irreversible capacity loss (~20% vs. 60%) (Fig. 1c). The superior capacity of the SCP-HT electrodes is attributed to the increased graphitic character of the spheres, as observed by Raman spectroscopy. A remarkable feature of the heated spheres is that they remain intact on cycling, unlike the unheated spheres that break up during the electrochemical reaction with lithium. The retention of spherical morphology is noteworthy because a uniform current distribution around spherical particles during charge is likely to suppress the early formation of lithium dendrites that can occur more readily at localized, sharp edges of

plate-like graphite particles, particularly as the electrode approaches the lithium potential at high rates. The carbon spheres will be heated to higher temperatures in an attempt to increase their capacity further.

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

Not yet started.

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

Not yet started

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

None to date

## 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 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)
  - Baseline materials synthesized, December 2010 (completed)
- (b) Characterize electrochemical properties of synthesized materials, September 2011, (on-schedule)
  - Demonstrate capacity of 200 mAh/g, December 2010, (completed)
  - Demonstrate high-rate of 200 mAh/g @ C rate, December 2010, (completed)
- (c) Characterize structure of materials, March 2011, (on-schedule)
- (d) Initiate optimization of Na, Li and transition metal content ratios in materials, March 2011, (on-schedule)
- (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)  $\text{Na}_x\text{Li}_y(\text{Ni}_{0.25}\text{Mn}_{0.75})\text{O}_z$  cathode precursors synthesized;  $x=1.0, 1.1, \text{ and } 1.2, y=0.2, 0.1, \text{ and } 0$ . Li ion-exchange reactions of the above Na-Li materials successfully conducted. The typical content of the product material is  $\text{Li}_{1.06}\text{Na}_{0.02}\text{Ni}_{0.21}\text{Mn}_{0.63}\text{O}_2$ . Compositions measured by ICP-AES. Ni and Mn ratio is maintained and most Na was removed in this specific reaction.

(b) The capacity measured at a C/15 rate was 230 mAh/g between 4.8 to 2.0 V in Li-half cells. Over 40 cycles were completed with no loss in capacity. The C rate capacity is above 200 mAh/g.

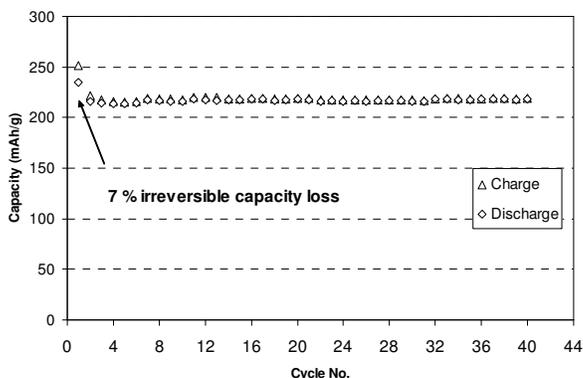


Fig. 1. Li/  $\text{Li}_{1.06}\text{Na}_{0.02}\text{Ni}_{0.21}\text{Mn}_{0.63}\text{O}_2$  half-cell capacity versus cycle number at C/15 rate (0.05 mA/g). First cycle capacity irreversible loss is less than 10% (7%).

(c) The XRD patterns of the materials discussed in milestone (a) were completed. Lattice parameter calculations and d-spacing measurements indicate a layered material was synthesized.

(d) Other  $x$  and  $y$  values in the material from milestone (a) were initiated. The Mn/Ni ratio is still fixed at three, but will be changed during the course of this project.

(e) Thermal properties of the charged materials in milestone (a) were initiated.

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

### Presentations

- C. S. Johnson et al., “*Synthesis of a Series of High Energy Cathodes via an Ion-Exchange Method*”, The 218th Electrochemical Society Meeting, Las Vegas, Nevada, October 2010 (Oral).
- C. S. Johnson et al., “*High-Energy and High-Power Composite Li-Battery Cathodes Synthesized from Ion-exchange Reaction*”, Materials Research Society Spring Meeting, San Francisco, April/May 2010 (Invited).
- C. S. Johnson et al., “*High-Energy and High-Power Li-rich Nickel Manganese Oxide Electrode Materials*”, 1st Argonne-PNNL Battery Workshop, Argonne, November 2010 (Invited).
- C. S. Johnson et al., “*High-Power and High-Energy Li-Ni-Mn Oxides for Lithium Batteries*”, 1st NEDO (Japan)-Argonne Battery Workshop, Argonne, October 2010 (Invited).

### Peer-reviewed Publications

- D. Kim, S.-H. Kang, M. Balasubramanian, C. S. Johnson, “*High-Energy and High-Power Li-rich Nickel Manganese Oxide Electrode Materials*”, *Electrochem. Commun.*, 12 (2010) 1618.

### Patents & Invention Disclosures

- C.S. Johnson, D. Kim, S.-H. Kang, ANL-IN-10-031, U.S. Patent Application Filed, 12/2010, “*Electrode Materials for Rechargeable Battery*”

## **TASK 1**

### **Battery Cell Materials Development**

**Project Number:** ES038

**Project Title:** High Energy Density Ultracapacitors

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

**Collaborators (include industry):** Thanh, N. Tran and Thomas L. Jiang (NAVSEA-Carderock), Michael Wartelsky (SAIC), Steven Dallek (Spectrum Technologies), Deyang Qu (University of Massachusetts, 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 capacity of lithium ion capacitor (LIC) by 25% (in comparison to 1<sup>st</sup> generation LIC cells). Assess safety of present technology.

**Approach:** Identify candidate high-performance electrolyte compositions via discussions with battery manufacturers, other DOE investigators and literature reports. Evaluate most promising systems by fabricating and cycling pouch cells (25 and -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) Identification of high-performance, low-temperature electrolyte (July 2011). In progress
- (b) Safety evaluation of 1<sup>st</sup> generation LIC cell technology (March 2011). Complete
- (c) Safety evaluation of 2<sup>nd</sup> generation LIC cell technology (Sep 2011). In progress
- (d) Initiation of negative carbon electrode graphitization study (June 2011). Delayed

**Financial data:** Project budget/year, amount subcontracted if appropriate  
FY10: \$350K, Funding Expensed 1Q FY11: \$68K (This was from FY10 funding).

**Progress Toward Milestones:**

- (a) Collaboration was initiated with JM Energy to evaluate their 2<sup>nd</sup> generation lithium ion capacitor technology. The 2<sup>nd</sup> generation cells contain an electrolyte that is reported to be more conductive than that of the 1<sup>st</sup> generation at low temperature. We have requested cells and the individual electrodes and electrolyte. Experiments are planned to investigate the behavior of the individual electrodes when cells, containing lithium references, are cycled at low temperatures. Results will be compared to JM Energy's 1<sup>st</sup> generation technology. Efforts were initiated to identify a capacitor cycler that has

sufficient power and sensitivity required to complete this investigation in a timely and more accurate manner.

(b) Differential scanning calorimetry experiments (DSC) were performed to study the reactions between capacitor electrode materials and the electrolyte. Test samples were prepared from components of conventional ultracapacitor cells (Maxwell Technologies) and were hermetically sealed in high-pressure DSC capsules inside an inert atmosphere glove box. Samples were run at a heating rate of 10°C/min from 25°C to 400°C. The exothermicity ( $\Delta H$ ) was determined from the area under the curve. It is seen that the only reaction that generates a significant amount of heat is the LIC negative electrode/electrolyte reaction (2210 J/g). The exothermicity of the LIC positive electrode/electrolyte reaction is an order of magnitude lower (296 J/g). In contrast, the ultracapacitor negative and positive electrodes are virtually nonreactive with the electrolyte (Figure 1).

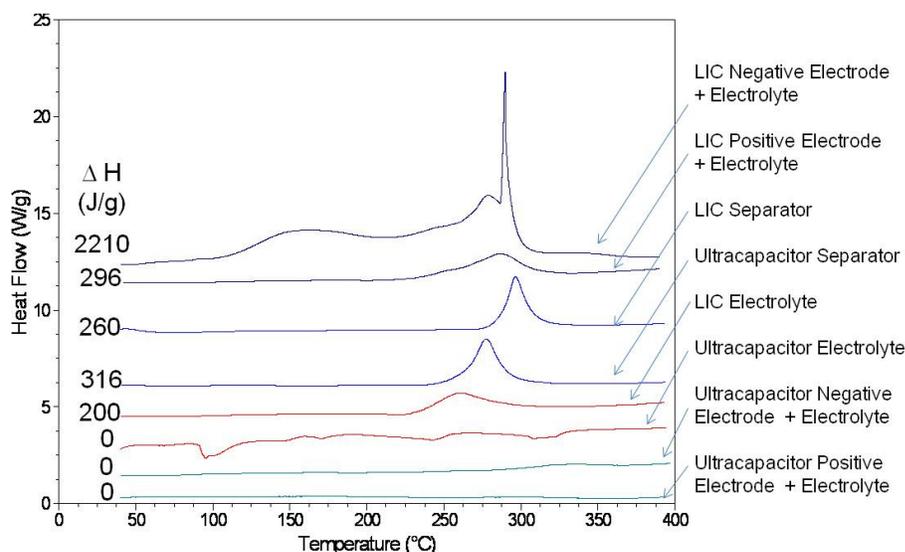


Figure 1. DSC curves comparing the electrode materials, electrolyte, and separator of the 1<sup>st</sup> generation lithium ion capacitor with that of a conventional ultracapacitor. Electrodes were fully charged prior to experiment.

(c) This task cannot be completed until cells are received from JM Energy. JM Energy is expected to produce their 2<sup>nd</sup> generation cells by June 2011.

(d) The initiation of this task has been delayed until June 2011. This study requires a large amount of high surface area activated carbon from Japan. Quantities on hand are limited and efforts are underway to obtain additional supplies.

**Publications, Reports, Intellectual property or patent application filed this quarter.**  
None.

# TASK 1

## Battery Cell Materials Development

**Project Number: 1.1.X**

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

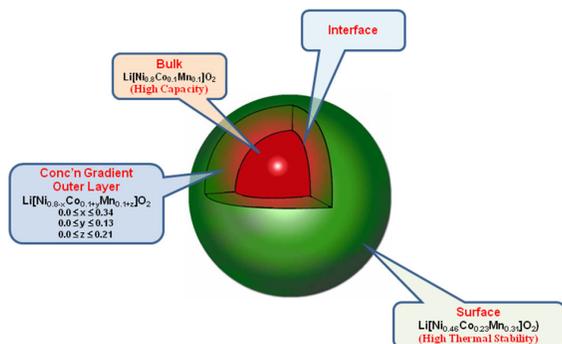
**Project PI, Institution: Gregory Krumdick/Argonne National Laboratory**

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

**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. Upon starting employment at Argonne, Dr. Shin will be assigned this project as his initial responsibility.

## **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, (Delayed)

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

### **PROGRESS TOWARD MILESTONES**

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

This milestone was effectively completed in FY2010, with orders placed for all major pieces of equipment that represented approximately 97% of the total funding. An equipment order for the remaining funds was placed on hold to insure that adequate funds would be available to cover the existing orders. A list of equipment ordered in FY2010 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

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

Under this project, the X-ray diffraction unit and impedance characterization equipment, representing approximately 35% of the total funding, arrived in FY 2010 and were installed. All remaining pieces of ordered equipment (e.g. testing and formation equipment, environmental chambers and ovens, the ARC, and glove box) for this facility, representing another approximately 62% of total funding, have arrived and are being installed. An ancillary piece of equipment (i.e. an Instron materials testing instrument) to be purchased with the remaining funds has also been identified.

**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 due to late start
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 (see Figs. 2 and 3) is being modified to accommodate the new facility. The laboratory was used to house two nuclear magnetic resonance units. The existing equipment has to be removed; new services installed (electrical and inert gas); and the laboratory painted. Additionally, the existing laboratory has to be brought up to current building codes.

The laboratory renovation part of the project is in full-swing. Argonne personnel were used to demolish and remove the existing laboratory equipment. A contractor was hired to perform the remodeling work. The remodeling work consists of removing existing services (water and power), which are not up-to-code. Then new services will be installed along with an inert gas manifold and delivery system. The contractor will repair the walls and floor and paint them. The expected completion time is early-to-mid January.

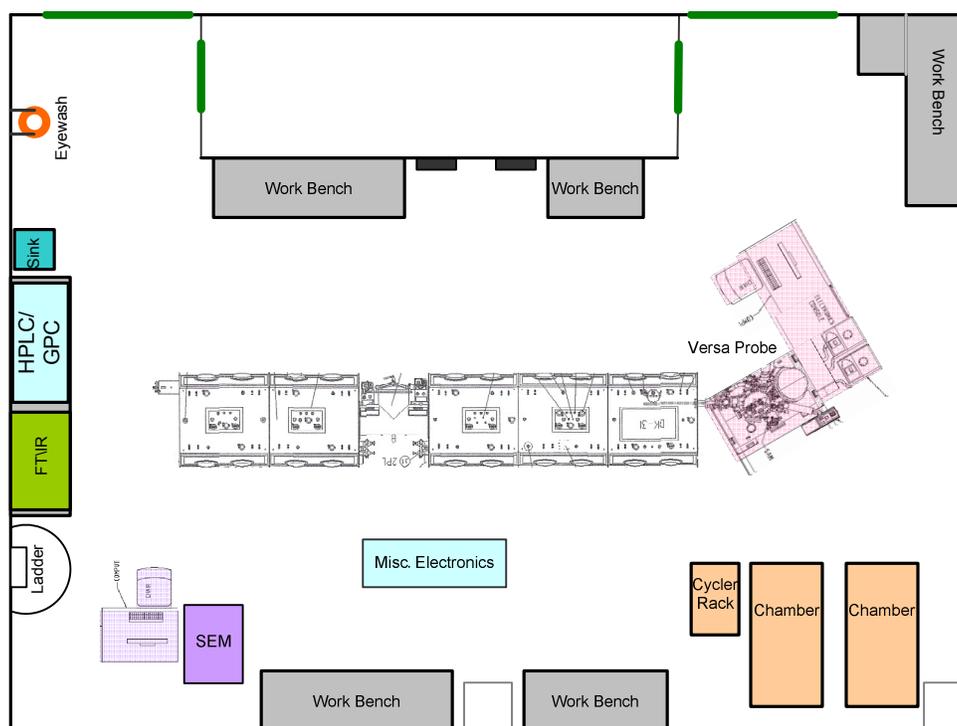


Fig. 1. Overall design of the post-test facility. The large, open area at the top of the figure is not part of the post-test facility. The VersaProbe X-ray photoelectron spectrometer (XPS) was purchased with funds from other sources.

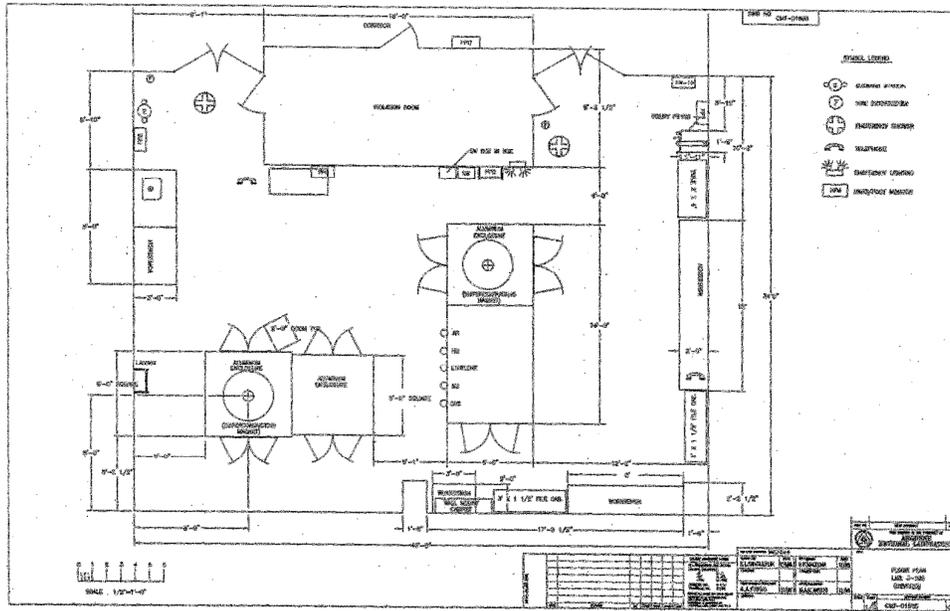


Fig. 2. Schematic of existing NMR laboratory which will be demolished and then used for the post-test facility.



Fig. 3. Photograph showing the existing laboratory space.

Establishing the post-test facility will require procuring many pieces of equipment. Major pieces of equipment have been ordered or have arrived. The glovebox, which is the centerpiece of the facility, has been ordered and is expected in mid-to-late January 2011. The FT-IR and Raman spectrophotometers arrived in December 2010. The environmental chambers (for cell component characterization) are expected in February 2011. A low-vacuum scanning electron microscope has been ordered. The Electrochemical Impedance Spectrometry and metallography equipment have arrived.

## **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:**

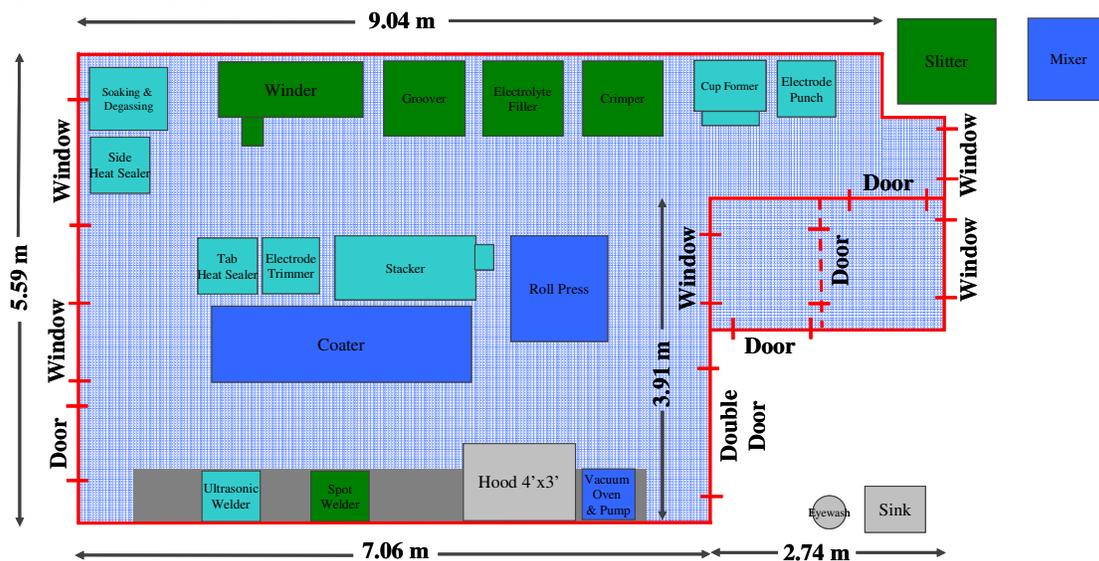
- (a.) All electrode and cell making equipment installed and approved for operation, December, 2011 (Delayed)
- (b.) First cell build using advanced materials in pouch cell, March, 2011 (On Schedule)
- (c.) Second cell build using Argonne's advanced materials in pouch cell, May, 2011 (On Schedule)
-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

The electrode coater and hot roll press were received in September and October of 2010, respectively. Installation and training was provided by the vendor's engineers in December. Modifications are being made to the coater and press to enhance its operation and safety in the dry room. The final layout of the electrode and cell making equipment in the dry room is shown below. A safety review process was begun for approval to operate the equipment.



**Argonne's Dry Room Cell Fabrication Facility**  
(Interior Dimensions)

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

Toda' high energy cathode material, HE5050 ( $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.10}\text{Mn}_{0.55}\text{O}_2$ ), was selected for the first positive electrode build based on its screening results. ConocoPhillips CGP-A12 high energy graphite was selected for the first negative electrode build based on its screening results.

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

Based on favorable results from the Screening Task, one of Argonne's advanced cathode materials under development was selected for the second cell build. This material is a high-energy NMC cathode ( $\text{Li}_{1.2}\text{Ni}_{0.3}\text{Mn}_{0.6}\text{O}_{2.1}$ ) made by Huiming Wu of Argonne. He is now in the process of making 2kg of this powder.

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

Additional 18650 cell parts were ordered. Electrodes were customized for the resistance-welding unit for welding the electrode tabs to the can and cap hardware.

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

One paper was submitted to the J. Power Sources.

## 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 was developed to examine primary-secondary active particle microstructure and properties affecting impedance (e.g. porosity, surface area, electronic conductivity, electronic contacts, and electrolyte wetting). Microscopy and other analytical studies on many positive active materials indicate that their secondary particle microstructure has some degree of porosity, such that electrochemical reactions can penetrate into the secondary particles. A previously developed electrochemical model with a simplified SEI relation was applied on the particle scale. A secondary particle was assumed to be made of primary particles with independent core and outer layer characteristics. The particle porosity allows access of electrolyte and ionic current to reach into the particle core.

A wealth of diagnostic studies and associated model development for NCA active material with Gen 2 electrolyte was utilized to create a baseline parameter set and particle characteristics. Simple relations were also developed for the active material surface area and tap density based on changes in particle porosity. Two specific impedance terms were used to describe particle performance: area specific impedance (ASI), based on particle active area (i.e. not the electrode area), and particle mass specific impedance (MSI). In general, when the ratio of active area to mass is fixed then both impedance effects behave similarly, as is the case for the change in particle impedance with applied voltage.

The impact of electronic conductivity on particle performance is shown in Figure 1. At effective electronic conductivities less than about  $10^{-5} \Omega^{-1} \text{cm}^{-1}$  the particle impedance is a strong function of conductivity, while the impedance is governed by other phenomena at greater conductivities. Similarly, the particle impedance is relatively independent of the number of contacts and the diameter of the particle contacts for effective electronic conductivities greater than  $10^{-4} \Omega^{-1} \text{cm}^{-1}$ .

Varying the diameter of the particle contacts can have a similar impact on impedance.

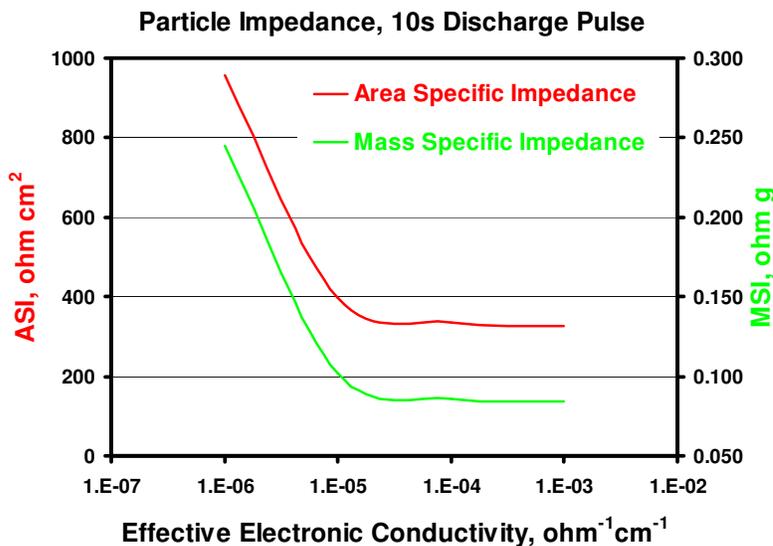


Figure 1 Impact of electronic conductivity on particle performance.

It is much easier for Li ions to diffuse through the liquid electrolyte than the solid-state oxide active material by a factor of about  $10^4$ . Therefore, even a small amount of electrolyte in the oxide particle pores can enhance the overall electrochemical reaction in the core of the particle and reduce its impedance. As the particle porosity increases, its active surface area rises dramatically reducing the particle impedance on a gravimetric basis. However, for a fixed applied polarization, the particle impedance on an active area basis rises significantly with increasing porosity. As the porosity increases, there is less active material available for the lithium to diffuse into, resulting in increasingly higher concentration polarization and ASI.

**(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 that are typically comprised of dynamic coupled one-dimensional multi-scale subsystems. A search for a new solver program was initiated. As a result, a new differential equation solver package (PSE gPROMS) was identified. This package should be able to address several long term issues limiting model advancement. These challenges include: integrating complex dynamic interfaces into full cell Li-ion models to examine factors limiting performance and life; streamlining parameter estimation for new cell chemistries; implementing the AC impedance models with increasingly more intricate interfacial and bulk active particle phenomena.

**(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. A single layer SEI growth model has been completed and implemented into the porous electrode model. The SEI model includes coupled Li interstitial and electron transport through an insulating film.

**(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:**

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:**

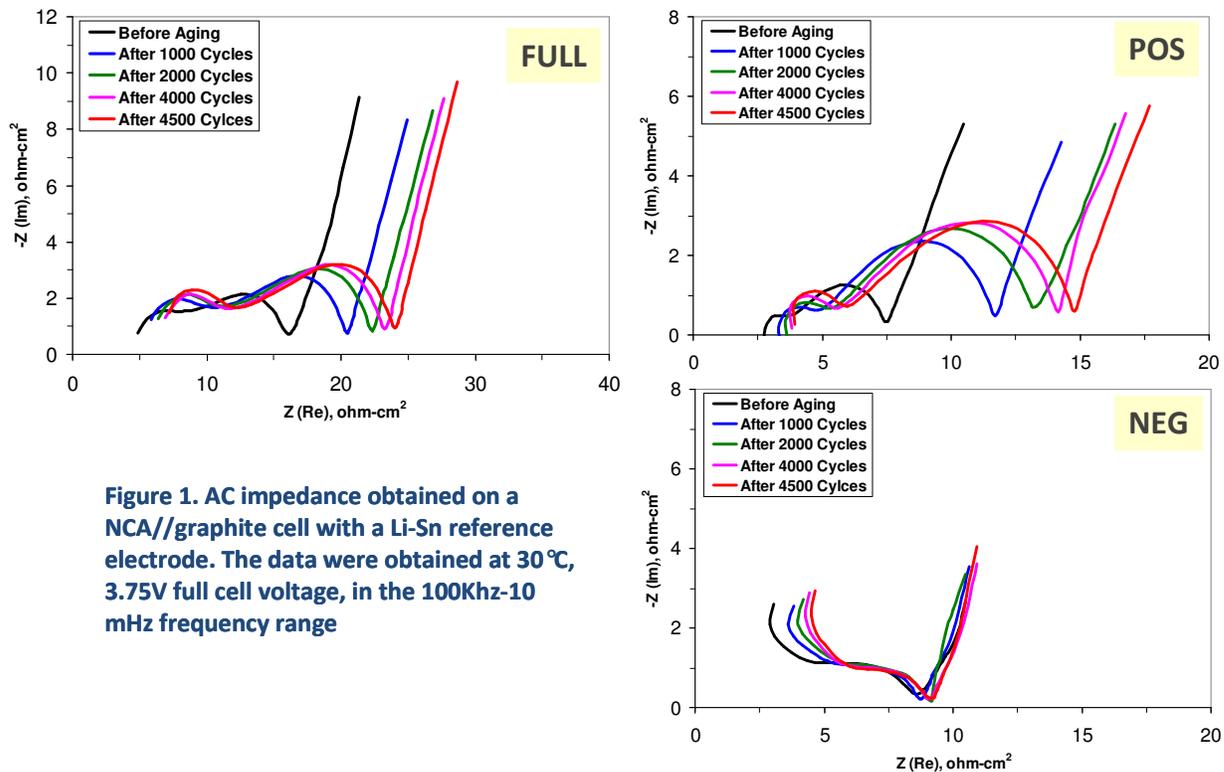
- (a.) Complete accelerated aging of PHEV baseline cells, March 2011, (on schedule)
- (b.) Conduct diagnostic examination of PHEV baseline cells and cell constituents, September 2011, (on schedule)
- (c.) Initiate characterization and aging experiments on electrodes and electrode constituents identified for the next set of ABR PHEV cells, September 2011, (not yet begun)

**Financial data:** \$300K

### **PROGRESS TOWARD MILESTONES**

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  $\text{LiPF}_6$  electrolyte. The performance of as-prepared cells was characterized using a series electrochemical charge-discharge cycling and impedance experiments. The cells are being cycle-life aged at 45C; capacity and impedance data are obtained periodically to characterize performance degradation.

Figure 1 shows AC impedance data obtained on a cell containing a reference electrode that underwent 4000 cycles between 3.6 and 4.0V, then 500 cycles between 3.3 and 4.0V at a C/1 rate. The data show that the full cell impedance increases on aging. Furthermore, all of the impedance rise can be attributed to the positive electrode; the negative electrode contribution is minimal. The positive electrode impedance rise can be attributed to processes (i) at the electrode-electrolyte interface, which is seen from growth of the mid-frequency arc (ii) within oxide bulk, which is observed in the Warburg diffusion tail obtained to low-frequencies (data not shown). This impedance result is very similar to that previously reported for other NCA//graphite cells that were aged under testing conditions relevant to HEV (high-power) cells.



**Figure 1. AC impedance obtained on a NCA//graphite cell with a Li-Sn reference electrode. The data were obtained at 30 °C, 3.75V full cell voltage, in the 100Khz-10 mHz frequency range**

Electrodes and electrode constituents for the next set of ABR PHEV cells were not available for characterization during this quarter.

**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:**

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 show 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, (on schedule)
- (b.) Complete structural study of cycled  $\text{Li}(\text{Li}_{0.2}\text{Mn}_{0.4}\text{Co}_{0.4})\text{O}_2$ , September 2011, (on schedule)
- (c.) Initiate structural characterization of other  $\text{Li}_{1+a}(\text{Mn}_x\text{M}'_z)\text{O}_2$  materials, September 2011, (not yet begun)

**Financial data:** \$300K

## PROGRESS TOWARD MILESTONES

$\text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2$  was synthesized from stoichiometric amounts of  $\text{Li}_2\text{CO}_3$  and  $(\text{Co}_{0.5}\text{Mn}_{0.5})\text{CO}_3$  precursors that were thoroughly mixed and calcined at  $900^\circ\text{C}$  for 12 h in air.

To elucidate the atomic structure of  $\text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2$  ( $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiCoO}_2$  in the two-component notation) we obtained detailed crystallographic data, both in direct and reciprocal space, on as-prepared samples by analytical electron microscopy (AEM). The studies were conducted using a combination of techniques that included high-resolution electron microscopy (HREM), high-angle annular dark-field imaging in scanning transmission electron microscopy (HAADF-STEM), and selected-area electron diffraction (SAED). Elemental compositions were determined using X-ray energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS).

The  $\text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2$  sample was found to possess a rhombohedral ( $R\bar{3}m$ )  $\text{LiCoO}_2$ -like overall structure, with excess Li at TM planes forming ordered areas with local monoclinic ( $C2/m$ )  $\text{Li}_2\text{MnO}_3$ -like structure (see Fig. 1).

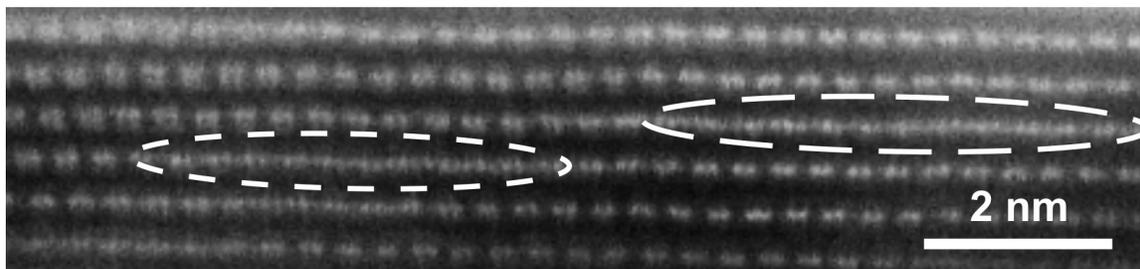


Fig. 1. HAADF-STEM image of  $\text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2$ , revealing the coexistence of  $\text{Li}_2\text{MnO}_3$ -like (dot contrast) and  $\text{LiCoO}_2$ -like (continuous contrast) areas within (0001) transition metal planes.

EELS data showed the presence of Co and Mn in all areas of the sample. The compositional variations across dotted and continuous contrast areas of STEM images was about 10 %, which is too small to be compatible with perfect, or close to perfect, segregation into pure  $\text{LiCoO}_2$  and  $\text{Li}_2\text{MnO}_3$  over length scales longer than the sample thickness. Therefore, from AEM data alone, we cannot be entirely certain of the oxide structure.

Coin cells containing  $\text{Li}(\text{Li}_{0.2}\text{Mn}_{0.4}\text{Co}_{0.4})\text{O}_2$ -bearing positive electrode, Li metal counter electrode and the baseline electrolyte are being cycled in the 3–4.6V voltage range; Electrodes from these cells will be harvested for structural examination of the oxide particles.

Work on milestone (c) is yet to begin.

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

1. J.-G. Wen, J. Bareño, C. Lei, S.-H. Kang, M. Balasubramanian, I. Petrov, D.P Abraham, Solid State Ionics 182 (2011) 98-107.  
Title: Analytical Electron Microscopy of  $\text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2$  for Lithium-ion Batteries

## 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).

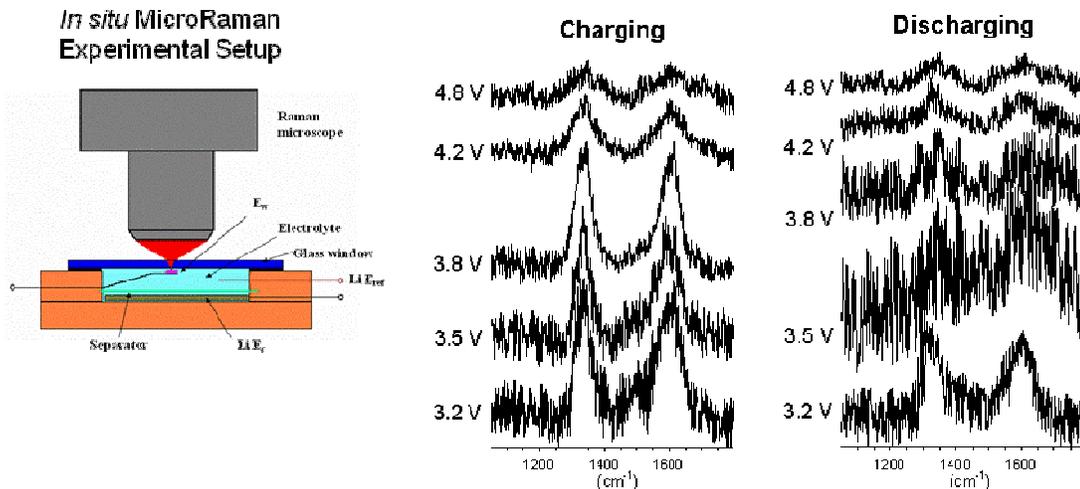
**Financial data:** FY 2011 diagnostics/materials funding \$600K

**Progress toward milestones:** The electrochemical properties of standard carbon additives and possible implications for the performance of high-voltage cathodes were investigated. During the first quarter of FY11, we rigorously examined different types of carbon black (Super P, Shawinigan and Denka), which constitute common conductive additives in Li-ion composite cathodes. Various characterization techniques, such as BET

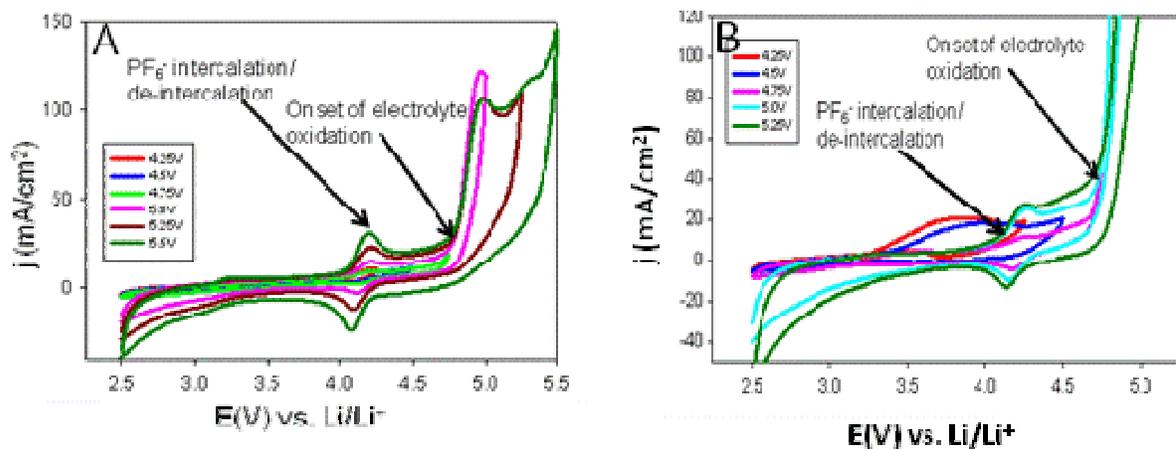
surface area measurements, Raman spectroscopy, SEM, and cyclic voltammetry (CV) were used to assess the structure, stability, and electrocatalytic response of carbon blacks in organic carbonate electrolytes at potentials that correspond to the operating conditions of high-voltage cathodes such as LMNO. CVs of pure carbon black electrodes revealed side effects that could interfere with the main charge-discharge process in composite high-voltage cathodes, namely,  $\text{PF}_6^-$  intercalation into carbon and electrolyte oxidation.

This anion intercalation into carbon black was monitored *in situ* using Raman microscopy (Figure 1). The intercalation of  $\text{PF}_6^-$  ions in amorphous carbons has been found to occur at potentials ca. 4.1 V vs.  $\text{Li}/\text{Li}^+$ , which is significantly lower than in graphite (4.45 V). Larger spacing between short and disordered graphene planes in amorphous carbons is mainly responsible for this effect. The potentials at which  $\text{PF}_6^-$  intercalation in carbonaceous materials occurs is directly related to the distance between the graphene sheets and the degree of structural disorder in the carbonaceous material.

The electrocatalytic properties of carbon toward the organic electrolytes depend on the carbon atom coordination at the surface, the presence of surface functional groups, and the possible presence of contaminants. Prolonged carbon drying and surface-treatment processes such as heat treatment under  $\text{Ar}/\text{H}_2$  atmosphere can be used to remove volatile contaminants and oxygen-containing surface groups from the carbon material. CVs of the pristine and heat-treated carbon black electrodes are shown in Figure 2. No change in electrochemical response can be observed after HT treatment. Thus electrolyte oxidation at the surface of the carbon additive is not related to the presence of volatile contaminants, e.g. residual water, or oxygen-containing surface groups.



**Figure 1: *In situ* Raman of  $\text{PF}_6^-$  intercalation in carbon black**



**Figure 2.** CVs of carbon black electrodes before (A) and after (B) surface treatment with Ar/H<sub>2</sub> at 900°C

### Publications

1. Vijay A. Sethuraman, Laurence J. Hardwick, Venkat Srinivasan, Robert Kostecki, "Surface structural disordering in graphite upon lithium intercalation/deintercalation", *Journal of Power Sources* **195** (2010) 3655–3660
2. Robert Kostecki, "In situ SPM of Local Interfacial Phenomena in Li-ion Batteries", International Workshop on SPM for Energy Applications, Oak Ridge National Laboratory, September 16, 2010
3. Robert Kostecki, "Batteries for Automotive Applications", 2<sup>nd</sup> Annual Workshop on Energy Research Energy Research Institute @ NTU, Singapore, June 16, 2010, (invited talk)

## **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, **on schedule**. (b) Complete 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 by April 2011, **on schedule**. (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).**

Progress has been made toward the milestone (a): The Cr and F co-substituted and Cr substituted spinel samples provided by Tronox LLC (Okalahoma City, OK 73134) have been studied by *in-situ* XRD measurements at beamline X18A of the National Synchrotron Light Source (NSLS). Fig 1 shows *in-situ* XRD patterns of Cr doped  $\text{LiMn}_2\text{O}_4$ , which are different than the pristine  $\text{LiMn}_2\text{O}_4$  reported in the literature. Peak splitting indicates the new crystal structure formed during charge. The split peaks re-converged into single peaks during discharge. This different phase transition behavior than the pristine  $\text{LiMn}_2\text{O}_4$  spinel is originated from the  $\text{Cr}^{3+}$  substitution, and causes negative effects on electrochemical performance with lower capacity. After the co-substitution of both  $\text{Cr}^{3+}$  and F, both the phase transition behavior and the capacity recovered to those for the pristine  $\text{LiMn}_2\text{O}_4$  spinel, but with great improvement in capacity retention.

#### **(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.

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

Progress has been made toward milestone (c). In situ XRD spectra during charge-discharge cycling have been collected on  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  samples synthesized at 800 °C and 700 °C at Duracell (P&G). The results are being analyzed.

#### **(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.

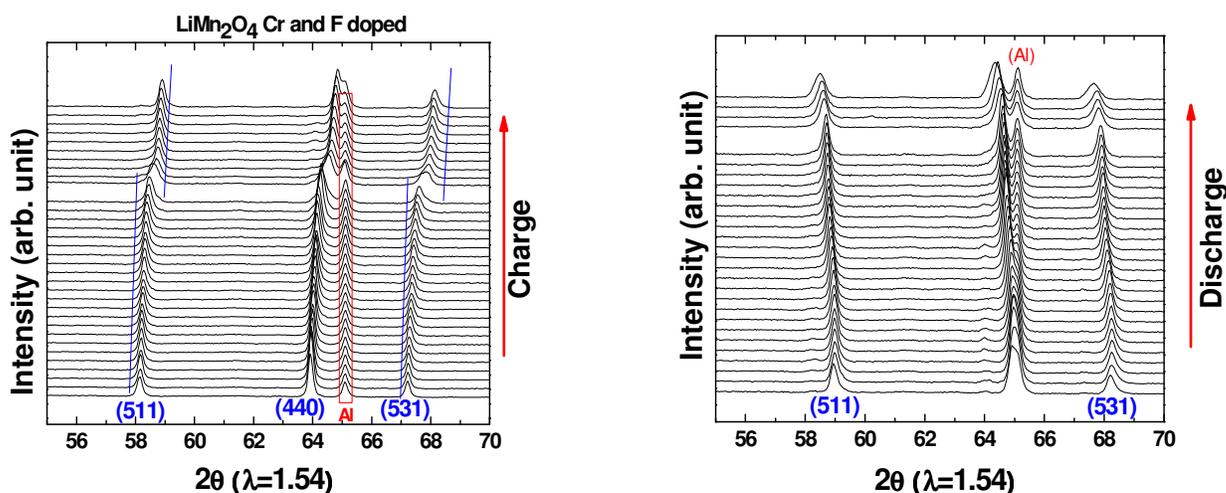


Figure 1: Selected regions in the *in situ* x-ray diffraction patterns for Cr and F doped  $\text{LiMn}_2\text{O}_4$ .

After the co-substitution of both  $\text{Cr}^{3+}$  and  $\text{F}^-$ , the peak-splitting behavior can not be observed and the phase transition recovered, which can be used to explain great improvement in capacity retention.

#### Publications and presentations in this quarter:

1. X. Q. Yang, K. W. Nam, H. S. Lee, X.J. Wang, Y. N. Zhou, X.Yu, L.J. Wu, Y. Zhu, L. F. Li, H. Li, and X. Huang, "The Development of New Electrolytes and *In situ* XRD XAS and TEM Studies of Cathode Materials for Lithium Batteries", the 2010 ( 5th ) International Forum on Li-ion Battery Technology & Industrial Development, November, 5-7, 2010, Beijing, China, **Invited**
2. I. T. Bae, J. Nelson, K-W. Nam, X-Q. Yang, J. Wang, "*In Situ* XAS and XRD Studies of High Voltage Spinel Oxides for Li-ion Batteries", presented at the 218<sup>th</sup> Meeting of the Electrochemical Society, October 10-15, 2010, Las Vegas, Nevada, USA.
3. X.J. Wang, B. Zhang, K. W. Nam, Y. N. Zhou, J. Bai, H. Chen, H. Li, X. Huang, and X-Q. Yang "Phase transition behavior of mesoporous  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ", presented at the 218<sup>th</sup> Meeting of the Electrochemical Society, October 10-15, 2010, Las Vegas, Nevada, USA.
4. X.J. Wang, H. S. Lee, X. Q. Yang, K. W. Nam, Y. N. Zhou, X.Yu, L. F. Li, H. Li, and X. Huang, "The Studies of the Capability to Form Stable SEI on Graphite Anode of New Solvents and Additives for Lithium Battery Electrolytes", presented at the 218<sup>th</sup> Meeting of the Electrochemical Society, October 10-15, 2010, Las Vegas, Nevada, USA. **Invited**
5. K-W. Nam, X-J. Wang, N. Pereira, G. G. Amatucci, and X-Q. Yang, "*In situ* X-ray absorption spectroscopy (XAS) study of nanocomposite C- $\text{FeF}_2$ , C- $\text{FeOF}$  and C- $\text{FeF}_3$  conversion materials during charge-discharge cycling", presented at the 218<sup>th</sup> Meeting of the Electrochemical Society, October 10-15, 2010, Las Vegas, Nevada, USA.

## **TASK 2**

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

**Quarterly report FY2011/01 – Performance period Oct. 1 – Dec. 31, 2010**

**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.
- Si anodes (to be finalized) and NMC cathodes / 1.2M LiPF<sub>6</sub> in EC:EMC (3:7 by wt) / Li
- Application of technique to be utilized by other ABR PIs and their materials.

**Approach:**

Electrode materials for lithium ion batteries (LIB) undergo 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, progress of work in this area 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 purchased experimental anode and cathode materials from General Motors and Argonne National Laboratory.

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. 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.

Measured diffraction patterns include the copper or aluminum current collector signals as internal standards which allow for mathematical correction of z-position and deformation. After this correction, every identified phase is fitted with a detailed Rietveld refinement which then allows for quantitative phase analysis and lattice strain calculations.

#### Milestones:

- Correlate AE with crack events in the active material of cycling cells – **Complete, FY10**
- Identify trends in AE data to improve the understanding of degradation mechanisms – **Complete, FY10**
- Perform true in situ AE-XRD on silicon electrodes over multiple cycles – **Complete, FY10**
- Compare the differences in AE behavior of different Si samples – **Complete, FY10**
- Attempt AE-XRD experiments using different cycling parameters – **Complete, FY10**
- Adapt the AE-XRD technique to cathode materials and test – **In Progress**
- 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

Previous work using combined AE-XRD on silicon anodes showed a complex relationship between state of charge and emission rate. To better understand the source of this complexity the internal structure of the silicon particle was characterized using electron back scattering diffraction EBSD and tunneling electron microscopy (TEM). Particles were dissected and polished using a focused ion beam (FIB).

A study to better understand structural changes undergone by Li(NiMnCo)O<sub>2</sub> (NMC) materials when

cycled to high potentials was performed using the combined AE-XRD technique. No AE was detected likely due to the small size of the NMC particles and no phase transformation. In future studies manganese spinel and NCA materials will be utilized. Figure 1 shows the change in lattice parameters that occurs when NMC is brought to high potentials. Figure 2 shows that these structural changes are retained even when subsequent cycling is performed at a lower potential range. Results similar to those seen during the charge stage have been reported from synchrotron experiments. However, this

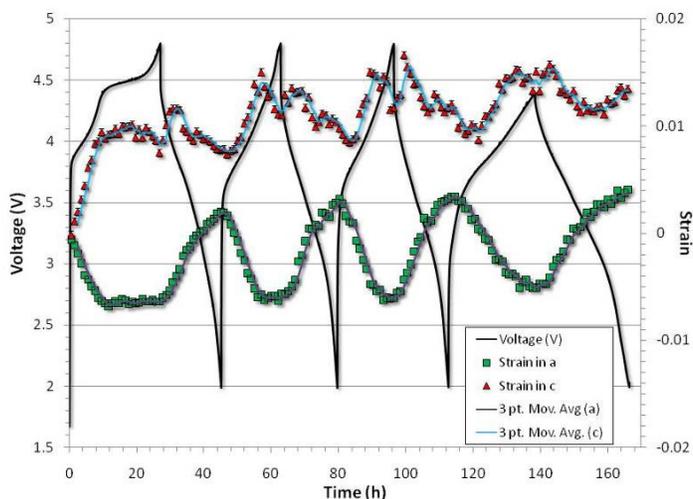
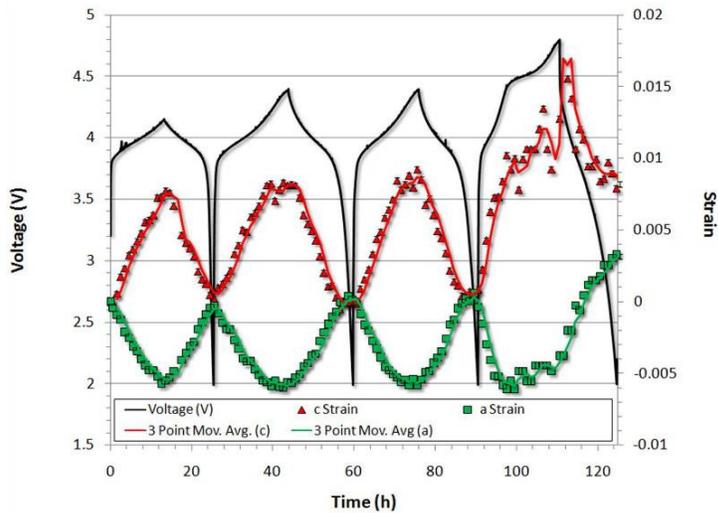


Figure 1



**Figure 2**

is the first time that a standard laboratory X-ray diffractometer has successfully measured them allowing for a low cost alternative with time availability at hand. Additionally, this is the first attempt to look at lattice changes past the first charge stage. Collaborations to better understand and model the observed structural changes are currently underway.

### Publications

- "Understanding the Degradation of Silicon Electrodes for Lithium Ion Batteries Using Acoustic Emission", K. Rhodes, N. Dudney, E. Lara-Curzio, C. Daniel, J. Electrochem. Soc., Volume 157, Issue 12 (Dec. 2010), pp. A1354-A1360 (2010)
- A study of lithium ion intercalation induced fracture of silicon particles used as anode material in Li-ion battery. S. Kalnaus, K. Rhodes, and C. Daniel. *Engineering Fracture Mechanics*, in review

### Presentations

- "Combined In Situ Acoustic Emission and XRD Analysis of Lithium Ion Battery Materials", K. Rhodes, C. Daniel, E. Lara-Curzio, N. Dudney, 218th ECS - Las Vegas, NV, Oct. 10-15, 2010
- S. Kalnaus, K. Rhodes, C. Daniel, Lithium ion intercalation induced stress and fracture of active electrode material, 2010 MRS Fall Meeting, Boston, MA, Nov. 30-Dec. 3, 2010
- K. Rhodes, E. Lara-Curzio, N. Dudney, C. Daniel, In Situ AE and XRD from Cycling Lithium Ion Batteries, 2010 MRS Fall Meeting, Boston, MA, Nov. 30-Dec. 3, 2010

## **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 (On schedule)
- (c.) Support EPA sponsored peer-review of model and modify model inputs or calculations in response to review. May 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:** Version 1.0 of the 2020 model has been completed with the ability to project the mass, volume, and cost of HEVs, PHEVs and EVs. The bottom-up approach allows for a richer understanding of the design requirements and material components that compose the end cost of the battery pack.

A key advance was finalized this quarter in how the model calculates the area specific impedance (ASI). The ASI is an important property as it sets the electrode thickness and thus electrode area for a specific power-to-energy ratio. Previous versions of the battery design model assumed a constant ASI based on cell chemistry regardless of current density, C-rate, and/or electrode thickness.

The new approach is a simple and thus efficient means of capturing the physical limitations within the electrochemical processes.<sup>1</sup> The interfacial ASI equation is found in [1] and includes kinetic, concentration, and thermodynamic contributions. The interfacial contributions of the negative and positive electrodes are added to a lumped constant to capture the entire impedance. The fit of the ASI to experimentally measured values for a NCA-graphite cell couple is shown in Figure 1. Also shown in the figure is the effect of this ASI behavior on the design of a 25 kW HEV battery pack. The smaller electrochemical active area does not increase the voltage losses of a battery when a constant C-rate is maintained. However, the higher ASI values from low electrode loadings require a larger separator and current collector area resulting in a greater battery volume and weight to achieve similar energy and power requirements when compared to a system with a lower ASI.

$$ASI_{intf}^{pos} = \frac{1}{L} \left[ \frac{RT}{ai_o F} \left\{ \left( 1 - \frac{I}{I_{lim}^{ionic}} \right) \left[ 1 - \left( \frac{r_c}{r_{c,lim}} \right)^2 \right] \right\}^{-0.5} - \frac{dU}{dy} \frac{t_{pulse}}{3600 Q \rho \epsilon_{act}} \right] \quad [1]$$

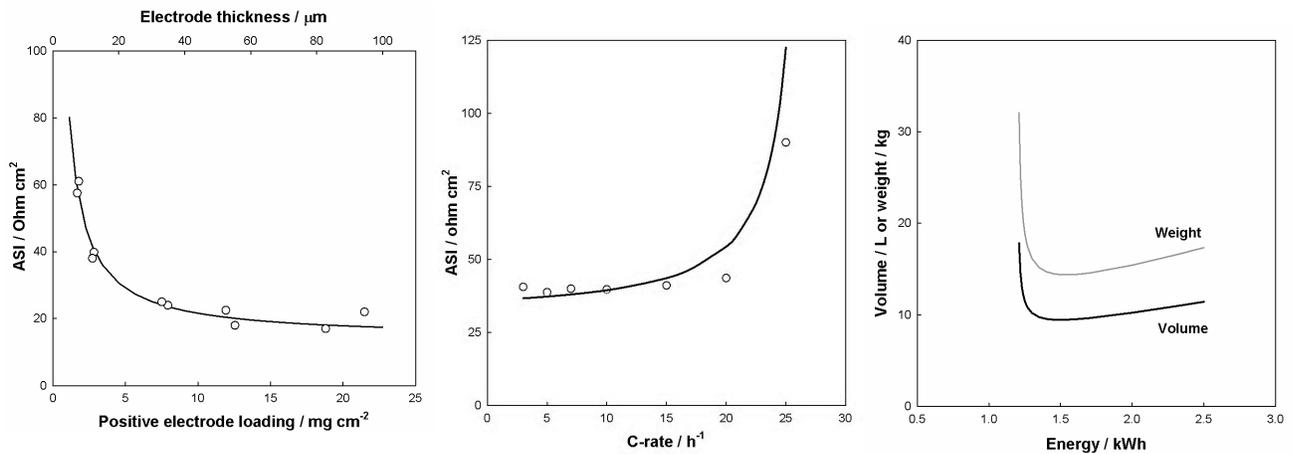


Figure 1: a) NCA-graphite coin cell at 1.8C b) NCA-graphite 32 cm<sup>2</sup> cell c) 25 kW HEV battery

**(b) Documentation of assumptions and methodology:** Documentation is progressing with a focus on the governing equations, methodology and assumptions that drive the calculation. The finished documentation will also include a tutorial for use and

demonstrated results. First completed drafts are being reviewed by colleagues inside and outside of Argonne National Laboratory.

**(c) EPA peer-review:** Working to finish model and documentation on schedule for EPA peer-review process. EPA plans to use the model in support of their development of rules for the 2017-2025 greenhouse gas standards for light-duty vehicles.

**(d) Public distribution:** Collaborating with Ira Bloom to develop stand-alone software for battery design and cost model.

**(e) Design & cost of advanced Li-ion:** Produced internal report on the projected energy densities and costs of lithium metal based batteries.<sup>2</sup>

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

1. K.G. Gallagher, P.A. Nelson, and D.W. Dees, "Simplified Calculation of the Area Specific Impedance for Battery Design," *Journal of Power Sources*, 196, 2289 (2011).
2. K.G. Gallagher and P.A. Nelson, "Estimation of the Cost of Lithium-Sulfur and Lithium-Oxygen Battery Packs for Transportation Applications," Draft report internal to Argonne and DOE.
3. D.J. Santini, K.G. Gallagher, P.A. Nelson, "Modeling the Manufacturing Costs of Lithium-Ion Batteries for HEVs, PHEVs, and EVs," *International Electric Vehicles Symposium EVS-25*, Shenzhen, China, (2010).

## 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):** Lu Zhang, Zonghai Chen, John (Zhengcheng) Zhang, Wenquan Lu, Sandia National Laboratory, EnerDel, Hitachi Chemicals, ECPRO

**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 a) securing additives and stabilized electrodes and investigating their effect on the thermal mitigation of the cell, b) developing in-house additives and shuttles that can mitigate the thermal run away and prevent *overcharge* abuse and 3) validate the effect of chemistry improvement in a full 18650 cells in collaboration with SNL synthesis.

### **Milestones**

- (a) Design and synthesis of novel redox shuttle towards improved compatibility to lithium-ion cell system, Sep. 2011, (on schedule);
- (b) Purification and chemical characterization of the synthesized redox shuttles, Sep. 2011, (on schedule);
- (c) Evaluation and understanding of redox shuttle additive's potential and electrochemical stability, Sep. 2011, (on schedule);

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

### **PROGRESS TOWARD MILESTONES**

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

A new ANL-1 redox shuttle ( Fig. 1) has been successfully synthesized, purified, and scaled up. This redox shuttle additive shows good solubility in conventional EC based electrolyte and excellent overcharge performance.

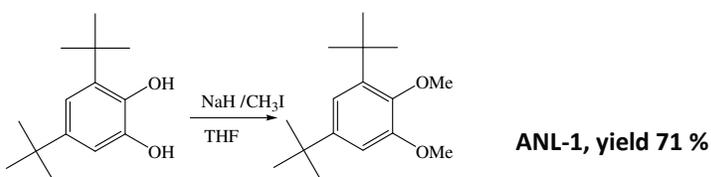


Fig.1, Synthesis route of ANL-1 redox shuttle with improved solubility in Gen 2 electrolyte.

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

The ANL-1 redox shuttle has been fully characterized using  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR (Fig. 2).

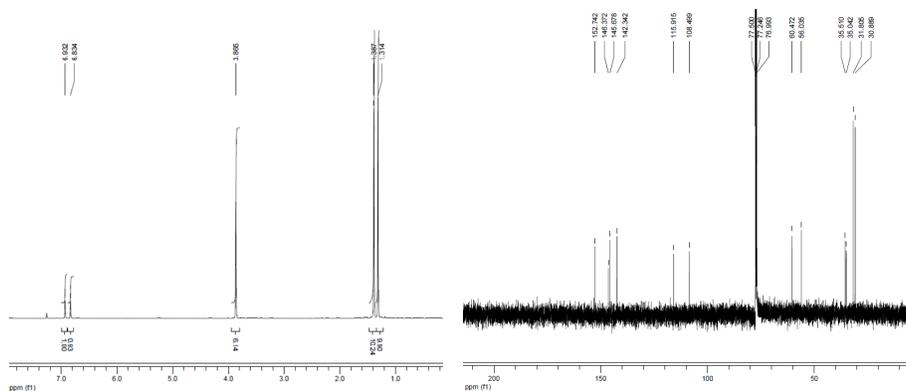


Fig 2.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of ANL-1 redox shuttle.

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

Cyclic voltammetry and coin cells evaluation have been conducted to test out the ANL-1 redox shuttle. ANL-1 showed reversible CV curves (Fig. 3a) but less longevity during overcharge abuse compared 3M's DDB (Fig 3b).

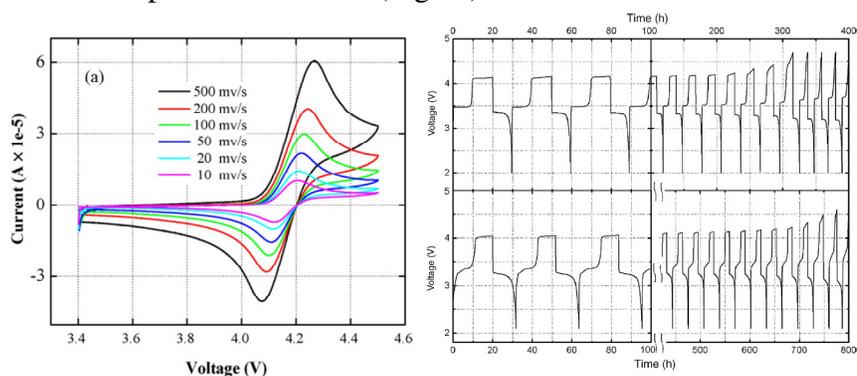


Fig 3. (a) Cyclic voltammograms of ANL-1 (10 mM) in 1.2 M  $\text{LiPF}_6$  in EC/EMC (3:7 by weight) 100mV/s. (b) Voltage profiles of Li/LiFePO<sub>4</sub> and MCMB/LiFePO<sub>4</sub> cells containing 0.1 M ANL-1 in 1.2M  $\text{LiPF}_6$  in EC/EMC (3:7 by weight) during the course of 0-400 and 0-800 h. Charging rate is C/10 and overcharge rate is 100%.

The crystal structures of ANL-1 was determined and was compared to DDB one ( Fig.4). The difference in chemical bonds implied the possible reason of the difference in overcharge protection performance.

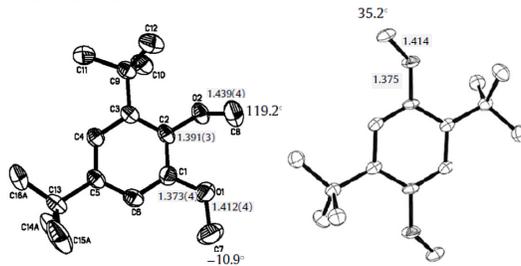


Fig. 4, Single crystal structures of ANL-1 and DDB

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

Zhang, Zhengcheng; Zhang, Lu; Schlueter, John A.; Amine, Khalil; “3,5-Di-tert-butyl-1,2-dimethoxybenzene as a redox shuttle for overcharge protection of lithium-ion cells”, *Journal Power Source*, 195 (2010) 4957–4962.

Zhang, Lu; Zhang, Zhengcheng; Amine, Khalil; “A Comparative Study of 3,5-di-tert-butyl-1,2-dimethoxybenzene and 2,5-di-tert-butyl-1,4-dimethoxybenzene for Overcharge Protection of Lithium-ion Batteries”, *Proceedings of Power Source Conference* 2010.

## **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) ARC upgrade (DUE 1/1/2011, Complete)
- (b) Al<sub>2</sub>O<sub>3</sub>-coated NCA cells (DUE 5/30/2011, Terminated)
- (c) ARC measurements of NMC cells (ON GOING, on schedule)

**Financial data:** Total budgeted \$1.35M; received \$223K (from SNL)

#### PROGRESS TOWARD MILESTONES

(a) **ARC upgrade:** The two CSI ARCs were upgraded with new hardware and software by Thermal Hazard Technology (THT). Both systems are fully operational and verified using K2 cells (comparing data before and after the upgrade). Results show comparable heating rates, runaway profiles, and gas volume profiles before and after the upgrade. The THT ES ARC has also been repaired and is fully operational. The SNL calorimetry lab now has three 18650 cell/materials-scale ARCs and a large volume EV ARC (with an additional ES and EV ARC on the way with the ARRA facility upgrade).

(b) **Al<sub>2</sub>O<sub>3</sub>-coated NCA cells:** Initial ARC work on the coated and uncoated NCA cells (from Argonne) resulting in two cells shorting at ~195 °C and destroying ARC hardware

(including one calorimeter housing) in FY10 Q4. Preliminary x-ray imaging shows no obvious defects in cell construction (built by Ecopro), however, the tab to the headers appear unusually long. Thermal ramp testing of a coated and an uncoated cell show similar behavior: hard short circuit at ~195 °C followed by catastrophic, violent failure. Results suggest some inherent flaw in either the cell construction or materials.

**(c) ARC measurements of NMC cells:** ARC measurements were performed on NMC cathode cells with 40% Ni NMC ( $\text{LiNi}_{0.4}\text{Mn}_{0.3}\text{Co}_{0.3}\text{O}_2$ ), 1/3 NMC ( $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ ), and lithium stabilized NMC ( $\text{Li}_{1.1}(\text{Ni}_{0.4}\text{Mn}_{0.3}\text{Co}_{0.3})_{0.9}\text{O}_2$ ). Results show the lithium stabilized NMC to be the most stable (180 C/min normalized peak heating rate) of the three materials. One would expect the reaction enthalpy for the 40% Ni NMC to be significantly greater than for the 33% Ni NMC, however, results for these two particular materials are quite comparable; 26.7 kJ/Ah and 25.1 kJ/Ah, respectively.

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

**C. J. Orendorff**, “Mitigating Catastrophic Failure in Lithium-ion Batteries” Lithium Mobile Power/Battery Safety Conference, Boston, MA 11/3/2010

## TASK 3 Abuse Tolerance Studies

**Project Number:** 1.2.1 (AMR No. 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:**

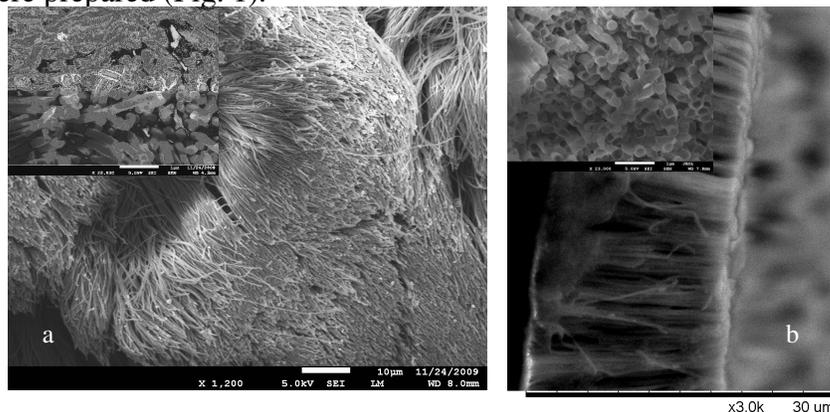
- (a) Report the properties of alternative high-voltage electroactive polymer candidates (July 2011). **On schedule**
- (b) Report overcharge protection performance of modified polymer composite separators and cell configurations (September 2011). **On schedule**

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

### PROGRESS TOWARD MILESTONES

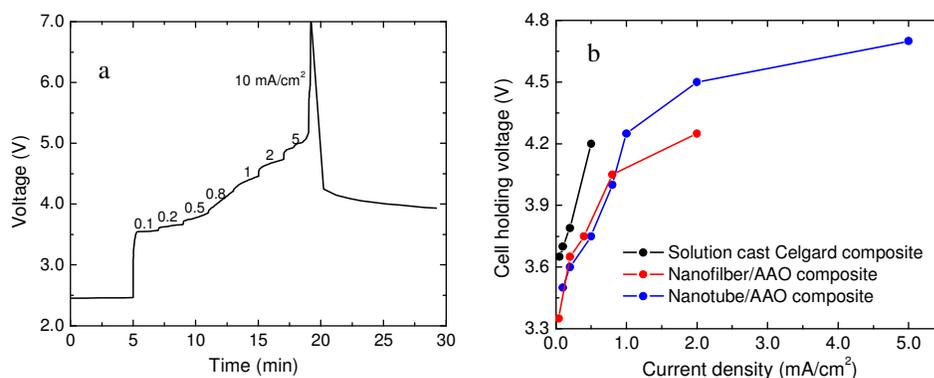
Electroactive polymers protect Li-ion battery cells from overcharging by forming a reversible resistive shunt between the current collectors. The polymer reverts to its non-conducting state and the cell operates normally when overcharging ceases, thus maintaining cell voltage and the full discharge capacity. Unlike redox shuttles, electroactive polymers conduct overcharge current electronically, and are therefore capable of carrying a large amount of current, as well as providing overcharge protection at low temperature. To achieve good rate capability and cycle life in protected Li-ion batteries, however, further optimization of cell design, polymer morphology, and improved polymer utilization are needed.

To this end, approaches were explored to prepare nanofibers of electroactive polymers that are capable of providing direct individual high-current paths between the electrodes. Poly(3-butylthiophene) (P3BT) was electrodeposited into the regular nanosized channels of a porous alumina membrane (AAO template). By adjusting the deposition conditions, arrays of oriented polymer nanorods or nanotubes extending the full thickness of the AAO template were prepared (Fig. 1).



**Figure 1.** (a) P3BT nanorods and (b) P3BT nanotubes prepared by electro-templating. Images were recorded after the removal of AAO templates.

Fig. 2a shows the performance of the P3BT nanotube/AAO composite at different current densities, evaluated in a “Swagelok - type” cell with the composite membrane as the cathode and Li foil as the anode and reference electrode. The cell was able to hold a constant potential by shorting through the conductive polymer for current densities up to  $5 \text{ mA/cm}^2$ , which was ten times higher compared to the maximum current density achieved on a solution-cast P3BT composite with a similar loading (Fig. 2b). The increased sustainable current densities on both nanofiber composites clearly suggests improvement in polymer utilization.



**Figure 2.** (a) Voltage profile of the P3BT nanotube/AAO composite at the indicated current densities and (b) comparison of the sustainable current densities of the various P3BT composites.