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

Progress Report
for
First Quarter FY 2012

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

February 2012

Applied Battery Research for Transportation Program
First Quarter Progress Report for FY 2012

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 U.S. DRIVE 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 U.S. DRIVE Partnership.

The ABR Program is organized into three main technical 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
			Task 1: Battery Cell Materials Development		
ANL	ARRA VT076		Materials Scale-Up Facility	Gregory Krumdick	6
ANL		IV. E.1.1	Process Development and Scale up of Advanced Cathode Materials	Gregory Krumdick	10
ANL		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	15
ANL	ES016	1.1B	New High Energy Gradient Concentration Cathode Material	Khalil Amine	18
ANL	ES017	1.1F	Design and Evaluation of High Capacity Cathode Materials	Christopher Johnson	22
ANL	ES019	1.1G	Development of High-Capacity Cathode Materials with Integrated Structures	Michael Thackeray	25
ANL	ES020	1.1C	Developing High Capacity, Long Life anodes	Ali Abouimrane	28
ARL	ES024		High Voltage Electrolytes for Li-ion Batteries	Richard Jow	31
ANL	ES025	1.1D	Development of Advanced Electrolyte Additives	Zhengcheng Zhang	37
JPL	ES026		Electrolytes for Use in High Energy Li-Ion Batteries with Wide Operating Temperature Range	Marshall Smart	41
INL	ES027		Novel Phosphazene Compounds for Enhancing Electrolyte Stability and Safety of Lithium-ion Cells	Kevin Gering	48
ANL	ES028	1.1E	Streamlining the Optimization of Lithium-Ion Battery Electrodes	Wenquan Lu	54
ANL	ES028	1.3	Screen Electrode Materials, Electrolytes, and Additives	Wenquan Lu	56
LBNL	ES029	1.2.2	Scale-up and Testing of Advanced Materials from the BATT Program	Vincent Battaglia	59

Organization	AMR Project ID	AOP Project ID	Title	PI/Contact Point	Page Number
			Task 1: Battery Cell Materials Development		
ANL	ES112	1.2C	Functionalized Surface Modification Agents to Suppress Gassing Issue of $Li_4Ti_5O_{12}$ Based Lithium Ion Chemistries	Yan Qin	61
ANL	ES113	1.1L	Development of High Voltage Electrolyte for Lithium Ion Battery	Zhengcheng Zhang	64
ANL	ES114	1.2D	High Capacity Composite Carbon Anodes Fabricated by Autogenic Reactions	Vilas Pol	68
ANL	ES115	1.1V	Synthesis and Development of High-Energy and High-Rate Cathode Materials from Ion-Exchange Reactions	Christopher Johnson	71
NAVSEA-Carderock	ES038		High Energy Density Ultracapacitors	Patricia Smith	74
ANL		1.1Y	Transition Metal Precursors for High Capacity Cathode Materials	Ilias Belharouak	78
ORNL			Overcoming Processing Cost Barriers of High Performance Lithium Ion Battery Electrodes	David Wood	84
NREL	ES162		Development of Industrially Viable Battery Electrode Coatings	Robert Tenent	88
			Task 2: Calendar & Cycle Life Studies		
ANL	ES030	2.1B	Fabricate PHEV Cells for Testing and Diagnostics in Cell Fabrication Facility	Andrew Jansen	91
ANL	ES031	2.2B	Model Cell Chemistries	Kevin Gallagher	94
ANL	ES032	2.3A	Diagnostic Evaluations - Electrochemical	Dan Abraham	98
ANL	ES032	2.3B	Diagnostic Evaluations - Physicochemical	Dan Abraham	102
LBNL	ES033	1.1.1 and 2.4	Strategies to Enable the Use of High-Voltage Cathodes and Diagnostic Evaluation of ABRT Program Lithium	Robert Kostecki	106

			Battery Chemistries		
Organization	**AMR Project ID**	**AOP Project ID**	**Title**	**PI/Contact Point**	**Page Number**
			Task 2: Calendar & Cycle Life Studies		
BNL	ES034	2.4 and 3.3	Life and Abuse Tolerance Diagnostic Studies for High Energy Density PHEV Batteries	Xiao-Qing Yang	109
ORNL	ES039		Online and Offline Diagnostics for Electrodes for Advanced Lithium Secondary Batteries	David Wood	112
ANL	ES111	2.2A	Battery Design Modeling	Kevin Gallagher	119
			Task 3: Abuse Tolerance Studies		
ANL	ES035	3.1	Develop & Evaluate Materials & Additives that Enhance Thermal and Overcharge Abuse	Zonghai Chen	122
SNL	ES036	3.2	Abuse Tolerance Improvements	Chris Orendorff	125
LBNL	ES037	1.2.1	Overcharge Protection for PHEV Batteries	Guoying Chen	130

APPENDIX

Individual Project Progress Reports

TASK 1
Battery Cell Materials Development

Project Number: ARRAVT076 **2012 Q1 update**

Project Title: Materials Scale-Up Facility

Project PI, Institution: Gregory Krumdick, Argonne National Laboratory

Collaborators (include industry):
Barton Malow, Design Build Subcontractor

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

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

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

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

The approach to achieve the facility plan is to:

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

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

Milestones:

Materials Engineering Facility Construction

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

Interim Facilities and Equipment

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

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
- Construction deliverable #1 completed – 9/17/2010
- Construction deliverable #2 is on schedule to be completed by 2/1/2012
  - **Beneficial occupancy is on track to be issued on 1/31/2012**
- Construction deliverable #3 is on schedule to be completed by 3/31/2012

Figure 1. Materials Engineering Research Facility Construction Site – December 28, 2011

Progress towards interim facilities and equipment milestones:

- All interim labs are fully operational
- 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 – fully operational
    - 4L reactor system is fully functional
    - 20L reactor system is fully functional
    - Powders hood has been delivered and installed

Capital equipment delivery status

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

TASK 1
Battery Cell Materials Development

Project Number: IV.E.1.1 **2012 Q1 update**

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

Project PI, Institution: Gregory Krumdick, Argonne National Laboratory

Collaborators (include industry):
Young-Ho Shin, Argonne National Laboratory
Kaname Takeya, Argonne National Laboratory

Project Start/End Dates: start: 10/1/2011; end: 9/30/2012

Objectives: 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.

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. 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.

Last quarter, it was reported that process optimization of $Li_{1.14}Mn_{0.57}Ni_{0.29}O_2$ on the 4L system was completed and work had begun on scaling the process to the 20L system. A primary issue identified on the 4L system was the fact that prior to reaching steady state, particles continued to grow past the optimal size forming a mixture of sized particles both larger and smaller than optimal. A technique was identified and tested to overcome this issue to allow for continuous processing.

Approach: A particle growth control technology was installed on the 20L system and tested on the synthesis of $Li_{1.14}Mn_{0.57}Ni_{0.29}O_2$.

Schedule and Deliverables: Deliverables will include scaled materials for independent testing, publications and a topical report.

Financial data:
Total project duration: 12 mo.
Staff and M&S: $500K with an additional $500K to be allocated in Q2.

Progress towards deliverables: A particle growth control technology was installed on the 20L system and the particle size and distribution of precursor growth was tested. Initial results are promising, indicating the ability to reduce particle growth and narrow the particle size distribution, see figures 1&2. However, the run was cut short after 15 hours due to plugging of the lines due to precursor buildup, see figure 3. A method to prevent fouling and plugging needs to be explored and tested. An invention disclosure has been filed on this new particle growth technology.

It is expected that the precursor generated during this initial run will produce approximately 10 kg of cathode materials. It has not been fully processed at this time. Solutions to the plugging issue are currently being tested.

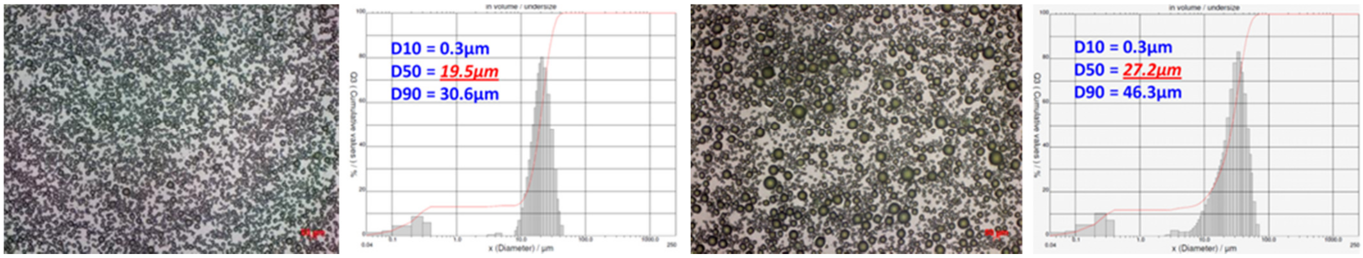


Figure 1. Precursor growth with and without growth control technology installed.

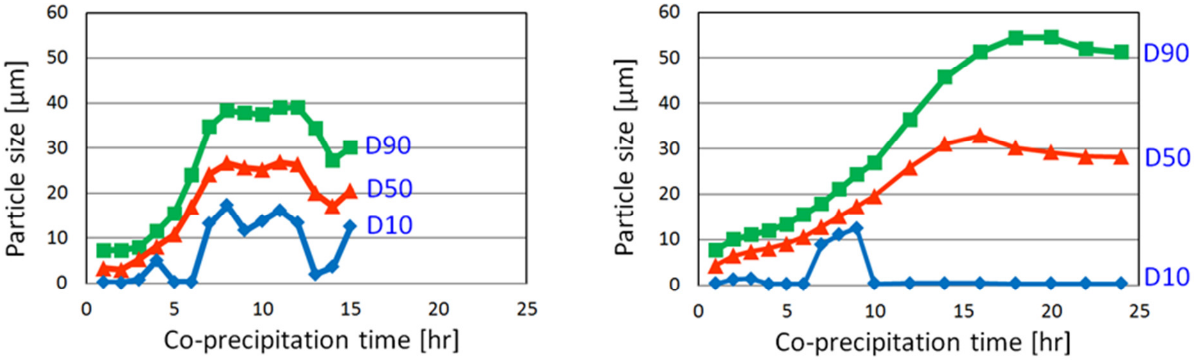


Figure 2. Particle size distribution with and without growth control technology.

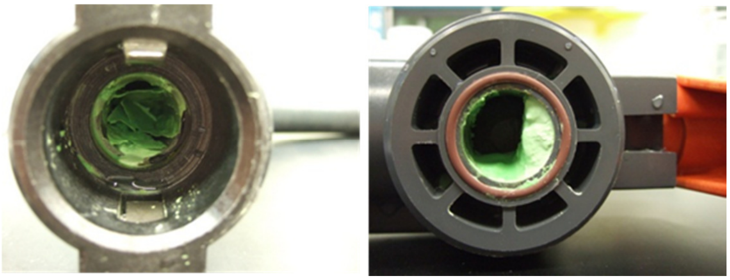


Figure 3. Line fouling and plugging due to precursor particle buildup

TASK 1
Battery Cell Materials Development

Project Number: IV.E.1.2 **2012 Q1 update**

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

Project PI, Institution: Gregory Krumdick, Argonne National Laboratory

Collaborators (include industry):
Krzytof Pupek, Argonne National Laboratory
Trevor Dzwiniel, Argonne National Laboratory

Project Start/End Dates: start: 10/1/2011; end: 9/30/2012

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 lift 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: A formal approach for the scale-up of electrolyte materials has been defined. This approach starts with the initial discovery of a new electrolyte material and an initial electrochemical evaluation. This determines if the material is to be added to the inventory spreadsheet, ranked and prioritized. At this point, the scale-up process begins with the initial feasibility study, proof of concept testing, 1st stage scale-up and 2nd scale scale-up. Go/No go decisions are located after feasibility determination and electrochemical validation testing. See Figure 1 for more details.

Schedule and Deliverables: The schedule of electrolyte materials to scale will be determined once the scale-up spreadsheet has been ranked and prioritized. This will reflected in the project milestones. Deliverables will include scaled materials for independent testing and a technology transfer package of information on each material scaled.

Financial data:
Total project duration: 12 mo.
Staff and M&S: $500K with an additional $500K to be allocated in Q2.

Progress towards deliverables:
Work initially started in FY11 on the passivation additive LiDFOB and the solvent 1S1M3 continues. Work on the passivation additive HFiPP for the Army Research Lab has been completed.

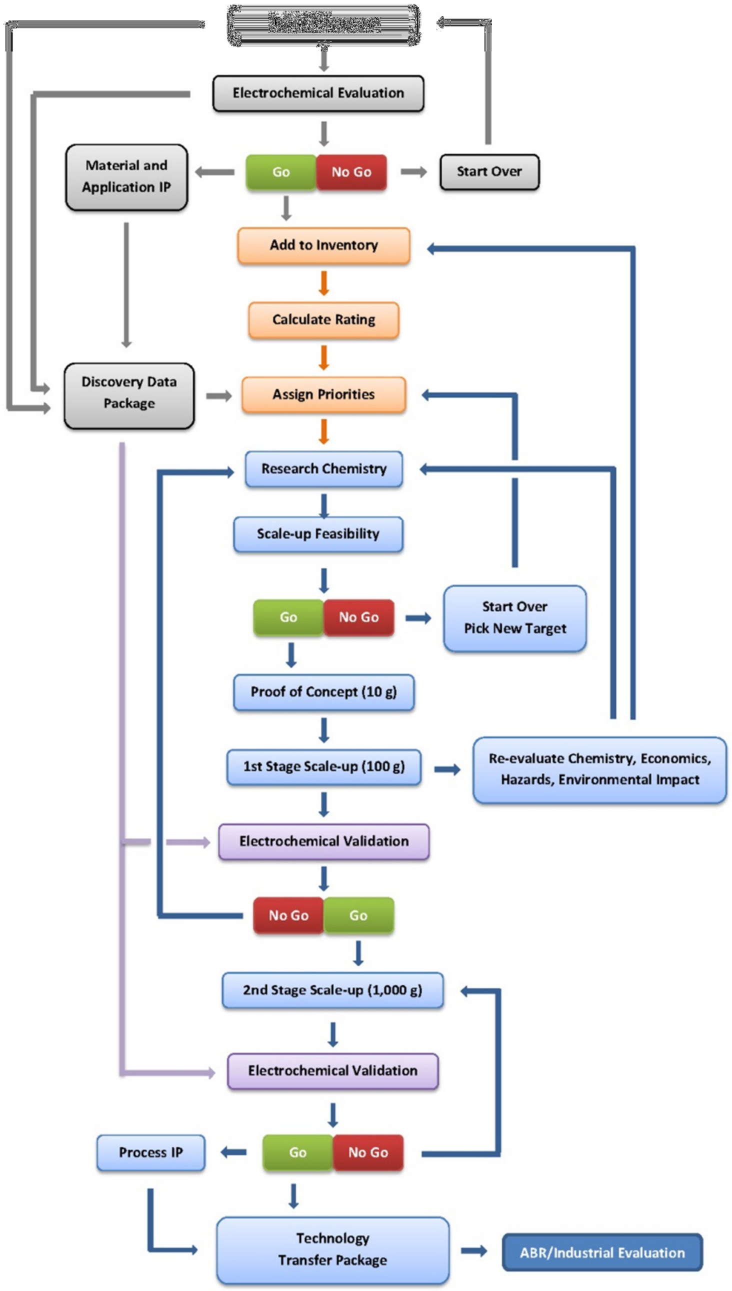


Figure 1. Electrolyte Materials Process R&D Flowchart

Milestones: Note: additional electrolyte materials will be added for FY12 upon prioritization of the current materials to scale spreadsheet.

MILESTONE	DATE	STATUS	COMMENTS
LiDFOB (Continued from FY11)			
Select CSE material to scale	01/07/2011	Completed	
Assess scalability of CSE process	08/12/2011	Completed	
WP&C documentation approved	06/22/2011	Completed	
Develop and validate scalable process chemistry (10g scale)	08/26/2011	Completed	
First process scale-up (100g bench scale)	11/07/2011	Completed	The material (~150 g) was synthetized, purified and analyzed.
Second process scale-up (1000g pilot scale)	TBD	On hold	To further scale we need to solve technical manipulation issues of moisture-sensitive material. Economic feasibility of the process has to be evaluated.
1S1M3 (Continued from FY11)			
Select CSE material to scale	01/04/2011	Completed	
Assess scalability of CSE process	08/03/2011	Completed	
WP&C documentation approved	2/22/2011	Completed	
Develop and validate scalable process chemistry (10g scale)	09/02/2011	Completed	The reaction was successfully run in several 2 g-scale batches
First process scale-up (100g bench scale)	11/04/2011	Completed	The material was synthesized, purified and analyzed (80 g, >99%)
Second process scale-up (1000g pilot scale)	3/08/2012	In Progress	
HFiPP, tris(1,1,1,3,3,3-hexafluoro-2-propyl) phosphate			
Assess scalability of disclosed process	10/07/2011	Complete	
WP&C documentation approved	10/21/2011	Completed	
Develop and validate scalable process chemistry (10g scale)	11/30/2011	Completed	
First process scale-up (100g bench scale)	12/22/2011	Completed	
Second process scale-up (1000g pilot scale)	1/27/2012	Completed	1230g produced in a single batch, purity >99.5%.
MILESTONE	DATE	STATUS	COMMENTS
Relocation to Materials Engineering Research Facility			
Decommission Interim Lab	3/15/2012		Start date 3/08/2012
Transfer Equipment	3/22/2012		Start 3/15/2012
Set up Equipment in MERF	3/30/2012		Start 3/22/2012
Electrolyte Lab Operational	3/30/2012		DOE Milestone

TASK 1
Battery Cell Materials Development

Project Number: 1.1A (ES015)

Project Title: Engineering of high energy cathode material

Project PI, Institution:
Khalil Amine (Argonne National Laboratory)

Collaborators (include industry):
Huiming Wu (ANL); Ilias Belharouak (ANL); Ali Abouimrane (ANL);Y.K. Sun (Hangyang University); Army Research Lab; Toda Corporation, USA & Japan; BASF, USA & Germany

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

Objectives:
Develop high-energy composite layered cathode of $xLi_2MnO_3{\cdot}(1\text{-}x)LiNiO_2$ for use in 40-mile plug-in hybrid vehicle, having following characteristics:

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

Approach:
Argonne's high-energy composite layered cathode $xLi_2MnO_3{\cdot}(1\text{-}x)LiNiO_2$ (M=Ni, Co, Mn) delivers a high capacity of ~250 mAh/g. However, charging the material to a high voltage (4.6 V) is a huge challenge for commercial electrolyte. high-voltage electrolyte additives where then used to stabilize the performance of the electrode since this material shows different charge and discharge behavior from the conventional cathode. It is believed that the high energy composite releases a gas during the first charge which may affect the integrity of the electrode. Therefore, a new binder with high binding strength is neededto hold the electrode together. The packing density of the high-energy composite layered cathode must also be improved, which was described in a previous report. Overall, there are three major tasks:

- Investigate Hfip high-voltage electrolyte additive to improve the performance of the high-energy composite material.
- Investigate carboxymethyl cellulose (CMC) binder to improve the performance of the high-energy composite material.
- Modify the precursor fabrication process to improve the strength of the powder and tap density. In the past, the precursor was prepared by the carbonate process using

the co-precipitation method. Currently, we use the hydroxide process to prepare spherical metal hydroxide precursor.

Milestones:
Kilogram levels of Co-free high-energy cathode material ($Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$) were prepared at Argonne, and cathodes of this material were used in pouch cells to complete the following milestones:

a) Determine the electrochemical performance of a $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$/graphite full cell with Hfip high-voltage electrolyte additive cycled at room temperature and high temperature. Hfip additive could improve the performance at high temperature (ongoing).
b) Determine the stability of the high-energy electrode using CMC and conventional polyvinylidene fluoride (PVDF) binders (ongoing).
c) Usehydroxide process for preparing the metal hydroxide precursor (ongoing).

Financial data:

Total project funding
- DOE share: $300K

PROGRESS TOWARD MILESTONES

(a) Summary of work in the past quarter related to milestone (a).
Our high-energy cathode material was charged to a high voltage (4.6 V), which is extremely demanding for commercial electrolyte. We are testing high-voltage electrolyte additives to stabilize the electrode performance. The additive Hfip, developed in the Army Research Lab, was reported to improve the performance for the 5-V $LiNi_{0.5}Mn_{1.5}O_4$ cathode. This additive is used now for testing high-energy cathode material.

(b) Summary of work in the past quarter related to milestone (b).
During activation of the cathode material on the first charge, the high-energy cathode material releases gas. When the gas is released, not only does the bulk and surface of the active material change, but so do other compounds in the electrode and the physical state of the electrode. We are thus searching for new binders to decrease the electrode damage. During this quarter, we compared the electrode's performance using 8 wt% PVDF and 3 wt% CMC binder. The capacity vs. cycle life at high temperature is shown in Fig. 1. The CMC electrode needed about 10 cycles for the capacity to reach 250 mAh/g and then stabilize. The PVDF electrode reached a very high capacity at the first cycle, but the capacity started to fade with further cycles. After 50 cycles, the capacity of the PVDF electrode is about 240 mAh/g, less than that of the CMC electrode.

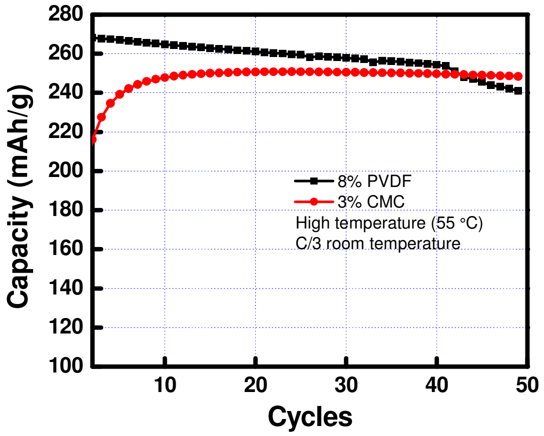


Figure 1. Cycling performance of high-energy cathode with PVDF and CMC binders at high temperature (55 ºC)

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

We prepared metal hydroxide precursor by a co-precipitation process and mixed it with Li_2CO_3 to synthesize $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$. The morphology of the final powders was examined by scanning electron microscopy (SEM). It is evident that the material consists of uniform, spherical secondary particles with sizes varying from 5 to 15 µm (Fig. 2, left). The size of the primary particles is 50 nm, and these particles completely agglomerate to form secondary particles (Fig. 2, right). The electrochemical performance of a cathode fabricated with the metal hydroxide precursor was evaluated in a coin cell. It showed similar performance to material prepared by the carbonate co-precipitation process.

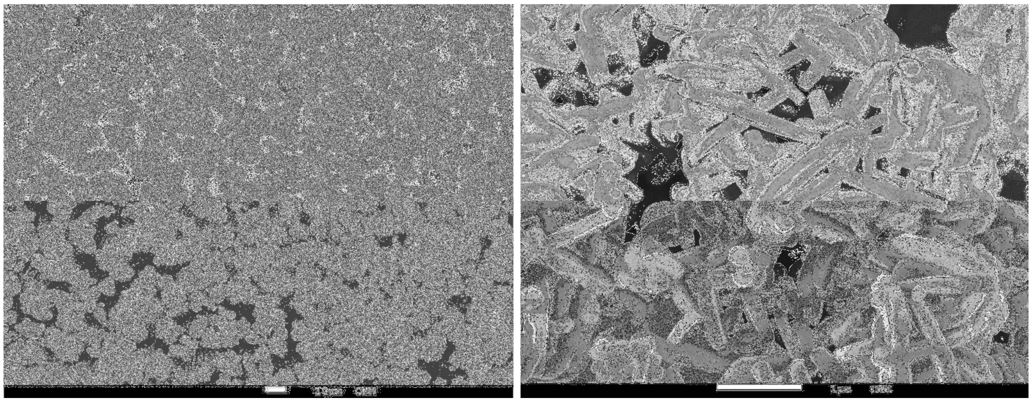


Figure 2. SEM images of the $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$ from hydroxide co-precipitation process

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

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

TASK 1
Battery Cell Materials Development

Project Number: 1.1B (ES016)

Project Title: New High Energy Gradient Concentration Cathode Material

Project PI, Institution: Khalil Amine, Argonne National Laboratory

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

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

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

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

Milestones:

a) Develop a model to predetermine the concentration gradient in particles produced via co-precipitation. This is necessary to have reproducibility of synthesized cathode materials. Complete.

b) Develop a process for precursors with a gradient in transition metal composition that was enriched in manganese. Manganese enriched materials have shown excellent safety and cycle life. Complete.

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

d) Demonstrate high capacity (>200 mAh/g) in final materials produced using the gradient precursors. On schedule

e) Demonstrate that a tailored relative transition metal composition at the surfaces of gradient particles influences safety and cycle life. Complete.

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

Financial data: $300K/year

PROGRESS TOWARD MILESTONES

We have been developing the hydroxide co-precipitation process to add the possibility of increasing Ni compositions in the core. In this case, we targeted an average composition $Li(Ni_{0.75}Co_{0.10}Mn_{0.15})O_2$ with high concentration of nickel in the core**.** To prepare the full concentration gradient cathode material, $NiSO_4·6H_2O$, $CoSO_4·7H_2O$ and $MnSO_4·5H_2O$ (0.90:0.1:0.0 in molar ratio) were used as the starting materials for the co-precipitation process. During the reaction, a manganese-rich aqueous solution (Ni:Co:Mn=0.64:10:26 in molar ratio) was continuously pumped into the stock solution tank containing the starting nickel-rich solution, after which the homogeneously mixed solution was continuously fed into a continuously stirred tank reactor. The obtained particles were filtered, washed with deionized water and dried at 25°C in vacuum to remove the residual water. Finally, a mixture of $LiNO_3$ (Li/(Ni+Co+Mn)=1 in molar ratio) was calcined at 750°C for 20 hours in air before being cooled down to room temperature in the furnace. Several localized characterization techniques, including electron probe X-ray microanalysis (EPMA), hard X-ray nano-tomography and transmission electron microscopy (TEM), were deployed to characterize the expected inhomogeneous features. Figure 1 shows the scanning electron microscopy (SEM) images and element distribution of Ni, Co and Mn in a single particle of both the precursor $[(Ni_{0.75}Co_{0.10}Mn_{0.15})(OH)_2]$ and the final lithiated product $Li(Ni_{0.75}Co_{0.10}Mn_{0.15})O_2$. Figures 1c and 1d represent the atomic ratio between Ni, Co and Mn from the integrated 2D-EPMA data as a function of distance from the center of the interested particle. Figure 1 clearly demonstrates that the atomic percentage of Co remained constant at about 10% in both the precursor and the lithiated particles as originally designed. Figure 1 also shows that the concentration of Ni decreased continuously from the center towards the edge while the concentration of Mn increased accordingly. Worth pointing out is that the slope of concentration gradient of the precursor was bigger than that of the lithiated material because of the directional migration of metal elements during high temperature calcination to increase the entropy or disordering of the system. The long term electrochemical stability of the material was further characterized using constant current at C/5 charge/discharge of half cells using lithium metal as the counter electrode between 2.7 V and 4.5 V vs. Li^+/Li. The inner composition ($LiNi_{0.86}Co_{0.10}Mn_{0.04}O_2$) and the outer composition ($LiNi_{0.72}Co_{0.10}Mn_{0.18}O_2$) were also tested using the same procedure for comparison. Figure 2b shows that the inner composition with the highest nickel content had the highest initial capacity, but the reversible capacity decreased dramatically with the cycling number. The rapid capacity fade of the inner composition was mainly caused by the direct exposure of high content of Ni(IV)-based compound towards non-aqueous electrolyte at high potential that led to the chemical decomposition of both the electrode material and the electrolyte. On the other hand, the outer composition had higher manganese content and lower oxidizing capability towards non-aqueous electrolytes. Therefore, the outer composition had a lower reversible capacity, but much better capacity retention. Figure 2b shows that the reported full concentration material had blended advantages of high capacity from the high nickel-content materials and high electrochemical stability of high manganese-content materials. More detailed investigation by varying the upper cutoff voltage is underway.

Further work on varying the concentration of the gradient by maximizing the Ni in the bulk and maximizing the Mn at the outer layer is underway.

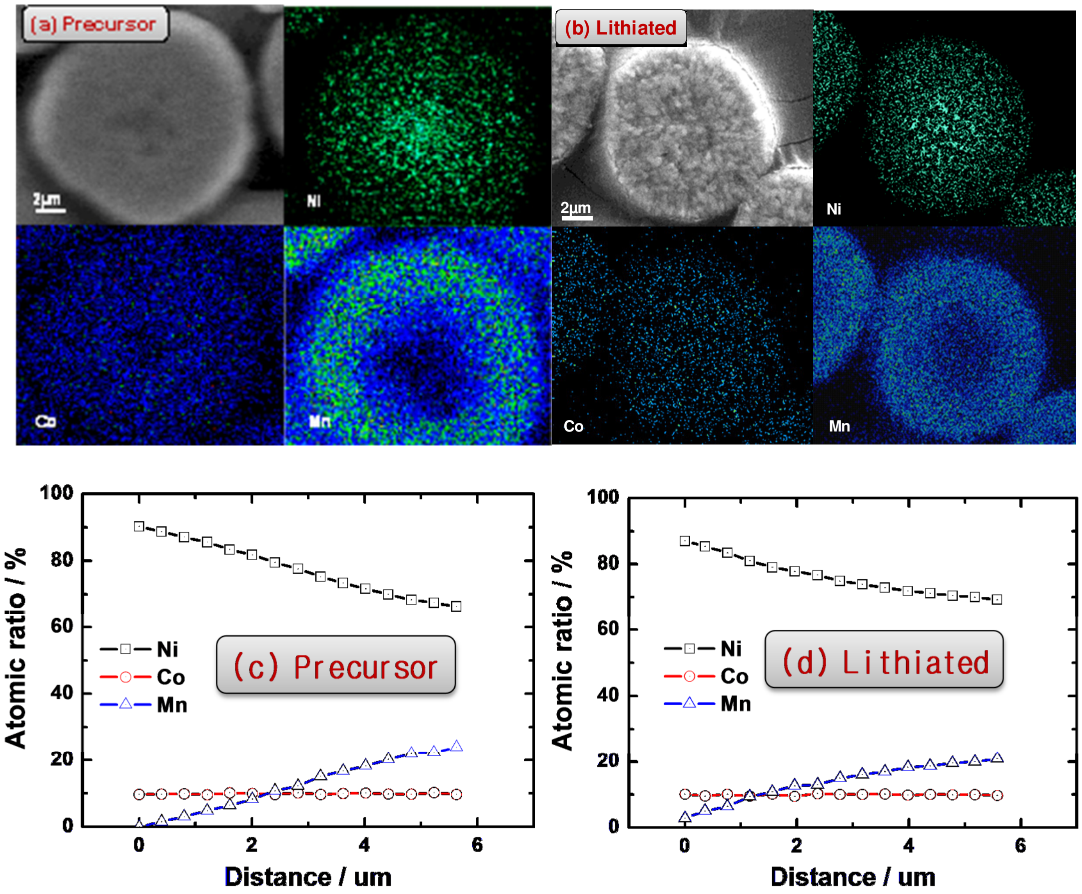


Figure 1 Scanning electron microscopy images and electron-probe X-ray micro-analyzer mapping of (a) a precursor particle and (b) a lithiated particle; and integrated atomic ratio of transition metals as a function of the distance from the center of the particle for (c) the precursor and (d) the lithiated material

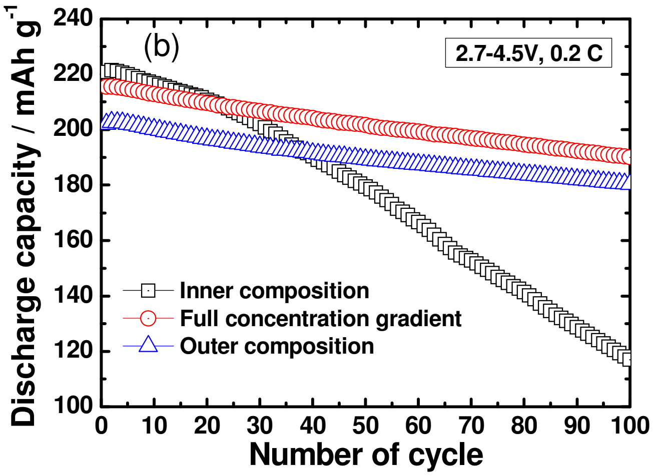


Figure 2 cycling performance of half cells using the full concentration gradient material, inner composition [Li($Ni_{0.86}Co_{0.10}Mn_{0.04}$)$O_2$] and the outer composition [Li($Ni_{0.72}Co_{0.10}Mn_{0.18}$)$O_2$] cycled between 2.7 V and 4.5 V vs. Li^+/Li using a constant current of C/5 (about 44 mA/g).

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

Publication in preparation

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
Tijana Rajh, Argonne National Laboratory, Center for Nanoscale Materials
Sanja Tepavcevic, Argonne National Laboratory, Center for Nanoscale Materials
Wenquan Lu, Argonne National Laboratory
Vic Maroni, Argonne National Laboratory
Dean Bass, 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 MnO_2 (308 mAh/g), $Li_{1.2}V_3O_8$ (LVO; 372 mAh/g), and V_2O_5 (442 mAh/g) charged cathode materials together with a high lithium containing material, Li_5FeO_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 LiV_3O_8 (LVO), V_2O_5, and MnO_2 will be improved. The optimization of the charged LVO and 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, November 2012, (completed)
- Zn-doped LFO synthesized, March 2012, (on-schedule)

(b) Characterize electrochemical properties of synthesized materials, February 2012, (on-schedule)

- Demonstrate high-rate of 200 mAh/g @ C rate for a VOx material, May 2012, (on-schedule)

(c) Characterize structure of materials, March 2012, (on-schedule)

(d) Conduct thermal analysis studies, June 2012, (on-schedule)

(e) Continue pursuit of improved Si-anodes, May 2012, (on-schedule)

Financial data: $100K

PROGRESS TOWARD MILESTONES

(a) $CrVO_4$ which has a theoretical capacity in excess of 400 mAh/g was successfully synthesized. We plan to couple this charged material with the LFO in a full Si-based cell, but will first conduct studies of the electrochemistry of this material in Li half cells.

- In addition we worked on increasing the amount of Li in the LFO material during the synthesis. It is evident from the XRD and Raman results that only 5Li/Fe are incorporated in the anti-flourite structure, although it is important to add extra Li in the synthesis in order to account for any Li evaporation loss.

(b) A nano-type bi-layered V_2O_5 was synthesized by electrodeposition from aqueous vanadyl solution. This material has a layer gap of ~ 13 angstroms which will be capable for Li insertion and removal (Fig. 1). We expect that the material will have high capacity and will show excellent reversibility. This material will also be tested in a full cell with LFO.

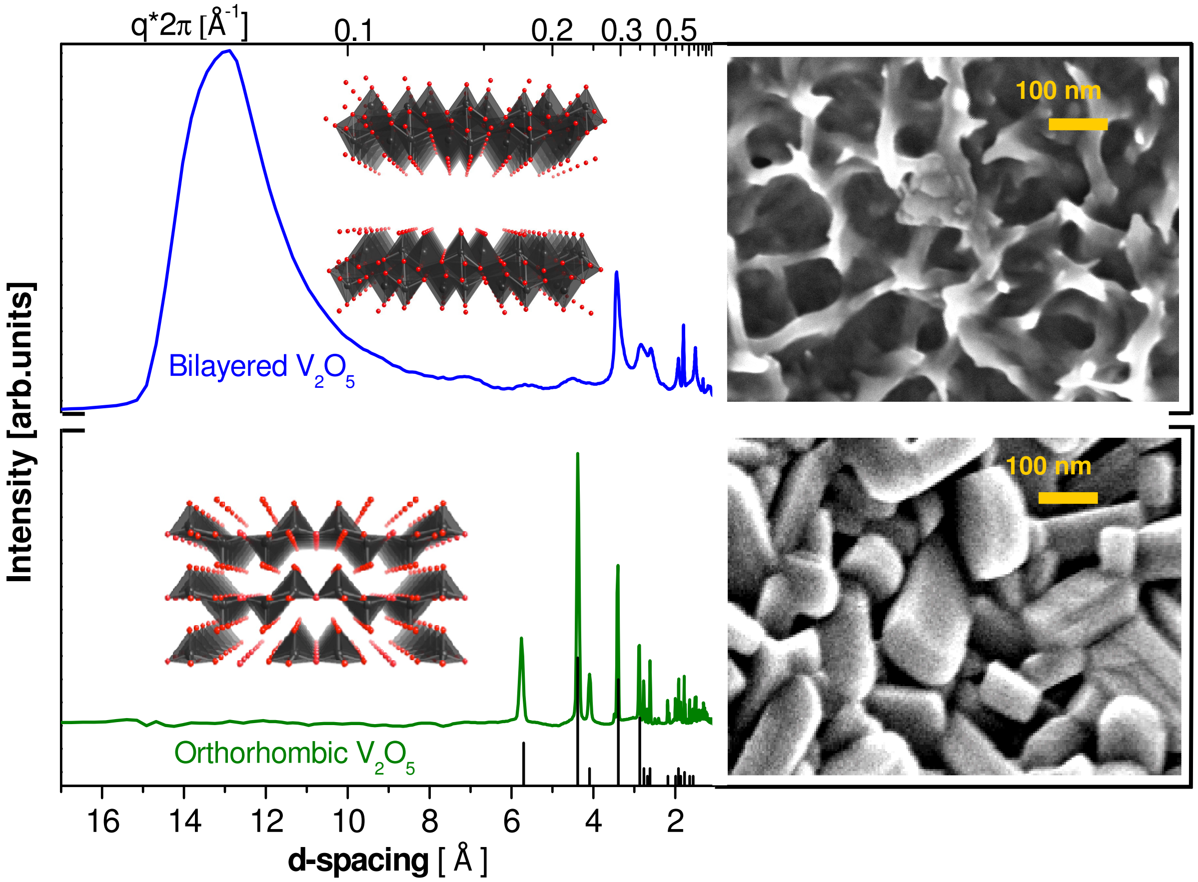


Fig. 1. XRD pattern of bi-layered V_2O_5 and SEM. The traditional orthorhombic V_2O_5 is shown for comparison. The theoretical capacity of V_2O_5 is 440 mAh/g.

(c) Raman spectroscopy of starting materials is completed. Group theory has been performed. The next report will show the results.

(d) Initial cycling with Li/Si anode half-cells was initiated. Samples were provided by Dr. Kumta. The Si –material needs better cyclability, and other samples are being procured and tested.

(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: 1.1G (ES019)

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

Project PI, Institution: Michael Thackeray, Argonne National Laboratory

Collaborators (include industry):
Donghan Kim, Kevin Gallagher, Giselle Sandi-Tapia, Argonne National Laboratory
Peter Chupas, Karena Chapman, Matthew Suchomel, APS, Argonne National Laboratory
Yang Shao-Horn, Chris Carlton, Massachusetts Institute of Technology

Project Start/End Dates: October 2009/September 2014

Objective: The objective of this work is to develop low cost Li- and Mn-rich cathode materials with integrated structures that offer good thermal stability, high capacity (~240 mAh/g), good rate capability (≥200 mAh/g at C/1 rate) and high first-cycle efficiency. The targeted performance values are 240 mAh/g of reversible capacity and a first-cycle efficiency of at least 85%. If successfully developed, the energy density of a cell coupled with graphite would be ~460 Wh/kg (assuming 300 mAh/g graphite, 3.7 V nominal).

Approach: 'Layered-layered' composite cathode materials, $x\mathrm{Li_2MnO_3}\bullet(1\text{-}x)\mathrm{LiMO_2}$ (M=Ni,Co,Mn) can deliver a high capacity of 240-260 mAh/g. However, these materials have drawbacks such as low first-cycle efficiency, voltage fade on cycling, transition metal dissolution and poor power performance. The concept of embedding a spinel component into 'layered-layered' structures is being exploited to improve their electrochemical properties and cycling stability. Studies of blending $x\mathrm{Li_2MnO_3}\bullet(1\text{-}x)\mathrm{LiMO_2}$ with high-power cathode materials, such as $\mathrm{LiFePO_4}$, are being continued to improve impedance at low states of charge.

Milestones:
(a) Optimize the chemical composition of 'layered-layered-spinel' electrodes, including coatings such as $\mathrm{AlF_3}$;
(b) Characterize the structural properties of 'layered-layered-' and 'layered-layered-spinel' electrodes, for example, by X-ray diffraction, X-ray absorption spectroscopy, and transmission electron microscopy to determine, in particular, the causes for the voltage fade phenomenon;
(c) Identify performance degradation mechanisms, particularly voltage fade phenomena in structurally-integrated 'layered-layered-spinel' electrodes;
(d) Blend and evaluate 'layered-layered-spinel' electrodes with high power cathode materials.

Financial data: $300K

PROGRESS TOWARD MILESTONES

Summary of work related to milestone (a): Chemical composition optimization

It was previously reported that cathode materials with composition $Li_{1.25}Mn_{0.65}Ni_{0.33}Mg_{0.02}O_y$ showed good rate capability and high initial capacity with improved first-cycle efficiency (89%). However, capacity fading and voltage decay were still an issue. Although surface modification using AlF_3 showed lower capacity (198 mAh/g) compared to uncoated samples, the coatings enhanced the cycling stability and provided cells with an apparent 'built-in' voltage decay, as shown in Figures 1(a) and 1(b). Electrochemical evaluations of these materials in a full cell, lithium-ion configuration are currently being undertaken.

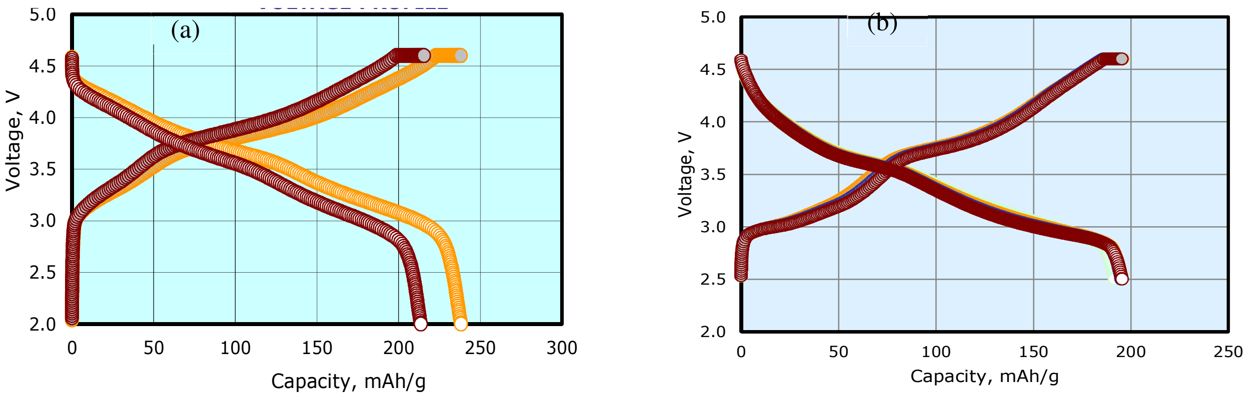
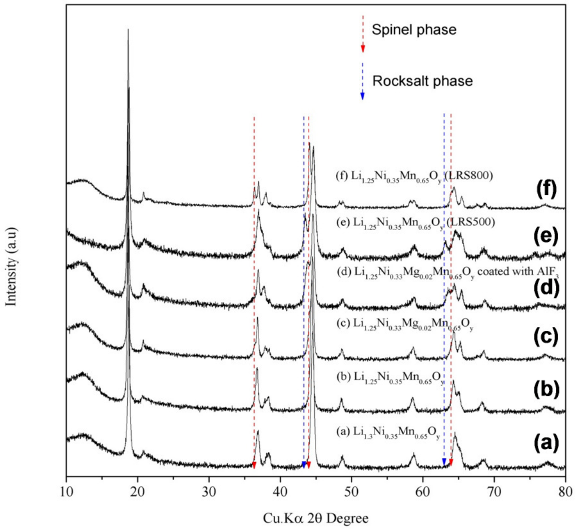


Figure 1: Cycling performance of lithium cells with a) uncoated $Li_{1.25}Ni_{0.33}Mg_{0.02}Mn_{0.65}O_y$, and
b) AlF_3-coated $Li_{1.25}Ni_{0.33}Mg_{0.02}Mn_{0.65}O_y$ cathodes. Cycles 21st and 41st are shown.

Summary of work related to milestone (b).

The X-ray powder diffraction of a $Li_{1.3}Ni_{0.35}Mn_{0.65}O_y$ product (equivalent to $0.3Li_2MnO_3{\bullet}0.7LiNi_{0.5}Mn_{0.5}O_2$) is shown in Figure 2(a), which is typical of a 'layered-layered' structure. For comparison, 'layered-rocksalt-spinel' samples were synthesized by J. Croy using a solution-synthesis approach and annealed at 500 °C and 800 °C, as shown in Figure 2(e) and (f), respectively.



The structural features of coated and uncoated $Li_{1.25}Mn_{0.65}Ni_{0.33}Mg_{0.02}O_y$ as well as Mg-substituted compounds have also been studied, the X-ray diffraction patterns of which are shown in Figure 2(b), (c) and (d). It is clear that the structures are highly complex. It appears that for materials synthesized at the lower temperatures, e.g., Figure 2(e) and for the AlF_3-coated electrode (Figure 2(d)), a rocksalt phase appears to be evident. At higher annealing temperatures, however, the samples have predominantly layered- and spinel character. Electrochemical evaluations of these complex composite electrode materials are in progress and will discussed in a future report.

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

To obtain a deeper understanding of the significant voltage decay exhibited by 'layered-layered' lithium-metal-oxide cathode materials, high-resolution X-ray diffraction (HRXRD) and pair-distribution function measurements (PDF) have been initiated at the Advanced Photon Source. As an example, xLi_2MnO_3•$(1-x)LiCoO_2$ samples with x=0.1, 0.3, 0.7, and 0.9 were prepared and annealed at 850°C. HRXRD and PDF plots are shown in Figures 3a and 3b. These preliminary data suggest the formation of a complex structure, exhibiting solid-solution behavior within a composite "Li_2MnO_3" and "$LiCoO_2$" matrix. Structural refinement and fitting are being conducted that will provide additional insights to the framework connectivity before and after cycling.

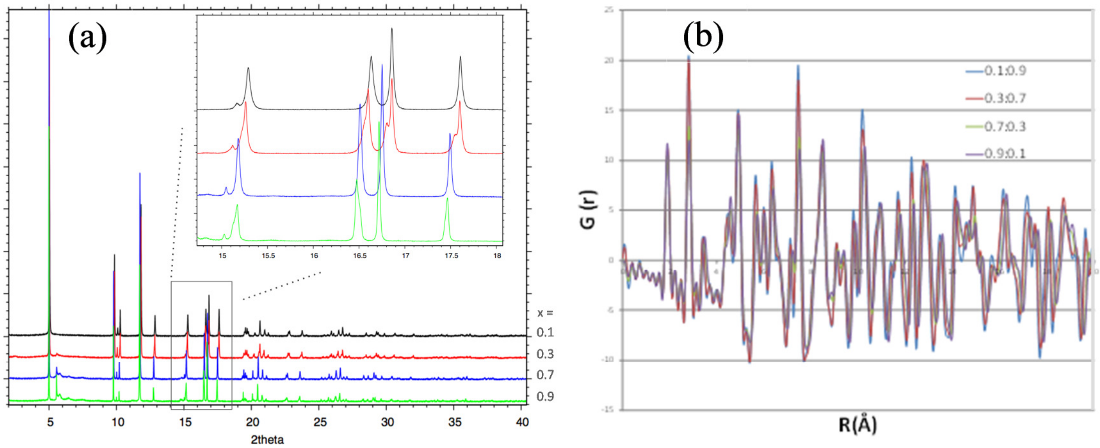


Figure 3: a) X-ray powder diffraction patterns and b) PDF spectra of xLi_2MnO_3•(1-x)$LiCoO_2$, for x=0.1, 0.3, 0.7, and 0.9 annealed at 850°C.

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

No work conducted this quarter

Publications, reports, invention reports or patent applications

K. G. Gallagher, S.-H. Kang, S. U. Park, S. Y. Han, *$xLi_2MnO_3 \cdot (1-x)LiMO_2$ blended with $LiFePO_4$ to achieve high energy density and pulse power capability*, J. Power Sources, **196**, 9702 (2011).

TASK 1
Battery Cell Materials Development

Project Number: 1.1C (ES020)

Project Title: Developing High Capacity, Long Life anodes

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

Collaborators (include industry):
- B. Liu, D. Dambournet (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 1st, 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.

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Approach:
- ☐ MO-$Sn_xCo_yC_z$ (MO=SiO, SiO_2, SnO_2, MoO_2, GeO_2) anode materials were selected for investigation as high energy anode based on the following criteria:
    - SnxCoyCz 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 cyleability.
    - The formation of Sn_xCo_yCz and MO composite could lead to the increase in the capacity, reduce the amount of cobalt in the material and improve the cyleablity as SnxCoyCz 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- Prepare materials with at least 600 mAh/g capacity with cycleability more than hundred cycles (2011-2012);
2- Identify the best material in term of cost, voltage output, cycling performance, and deliverable capacity (2011-2012);

3- Prepare a scalable amount of anode material (~ 200 grams) with 600 mAh/gas capacity for 100 cycles (2012);
4- Deliver a full cell battery (coin cell configuration) with a least 420 Wh/kg energy density (when combined with NMC) (2013-2014);

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

PROGRESS TOWARD MILESTONES

(a) Summary of work in the past quarter related to milestone (1)
We used ultra-high energy ball milling (UHEM) and SPEX milling methods to prepare SiO-$Sn_{30}Co_{30}C_{40}$ anode materials. UHEM, as compared with SPEX milling, showed remarkably more-reversible specific capacity, excellent cycling performance, and good rate capability. The UHEM sample powder had a particle size distribution whose main peak was located at ~2 µm, and the 50% cumulative particle size was less than 2.5 µm. The SPEX sample had 50% particles smaller than ~13 µm, which was much larger than that of the UHEM sample. (On schedule)

(b) Summary of work in the past quarter related to milestone (2)
We have successfully prepared three anodes materials based M_aO_b-$Sn_xCo_yC_z$ (where MO: SiO, MoO_3, GeO_2). Based on the price and the voltage profile and for industrial application our work will focus on the cheapest SiO- $Sn_xCo_yC_z$ system. (On schedule)

(c) Summary of work in the past quarter related to milestone (3)
250 grams of the material was prepared by ultra-high energy ball milling (UHEM).
Galvanostatic charge-discharge experiments with the OAC anode material were carried out at current rates of 100 mA g^{-1}, 300 mA g^{-1}, and 900 mA g^{-1}, respectively, within a voltage window of 0.005-1.5 V. In the first cycle, UHEM anode exhibited charge and discharge capacities of 1030 mA h g^{-1} and 1480 mA h g^{-1} at 300 mA g^{-1} current (~C/3), corresponding to a coulombic efficiency of 69.6% (Fig. 1). The coulombic efficiency in the first cycle of SiO was tested using the same procedure, which was less than 55%. Therefore, the OAC anode material can provide higher first-cycle efficiency than that of SiO alone. All the discharge capacity was delivered below 0.3 V. A small variation was observed in the voltage profile with continued cycling at 300 mA g^{-1} and 900 mA g^{-1} (Fig. 1), indicating excellent capacity retention.
As indicated by Fig. 2, the UHEM anode delivered a specific capacity of 900 mA h g^{-1} at the rate of 300 mA g^{-1}, much higher than that (~600 mA h g-1) of the SPEX anode at the same current. Moreover, at low current of 100 mA g-1 (~C/9), the specific capacity of the UHEM anode increased to 1040 mA h g^{-1}. (On schedule) "The progress to this milestone is achieved at 75%"

FY 2011 Publications/Presentations
1. 2011 DOE Annual Peer Review Meeting Presentation, May 9th-13th 2011, Washington DC.

2. Provisional patent application A. Abouimrane & K. Amine “Anode materials for lithium batteries: ANL-IN-10-013”

3. “A new anode material based on SiO-$Sn_{30}Co_{30}C_{40}$ for lithium batteries” B. Liu, A. Abouimrane, D. Wang, Y. Ren, Z. Fang and K. Amine (submitted paper).

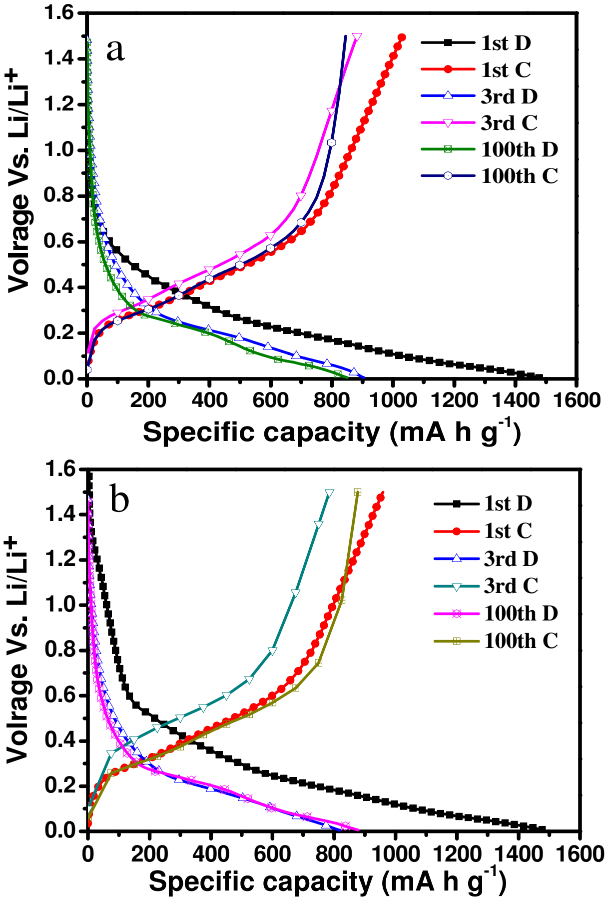


Fig.1 Charge-discharge curves of cells with UHEM anode cycled at rates of (a) 300 mA g^{-1} (~C/3) and (b) 900 mA g^{-1} (~1C).

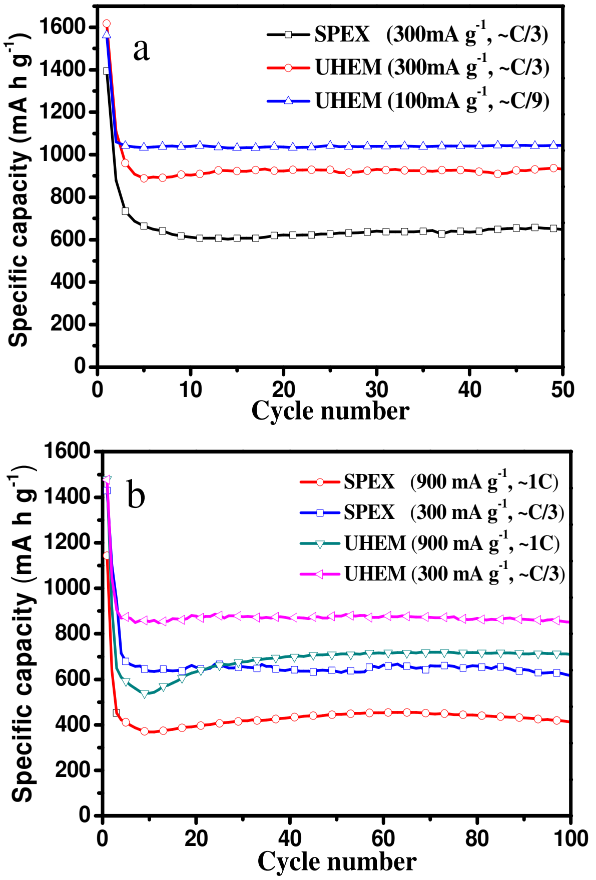


Fig.2 Cycling performance of cells under C/3 current rate (a) and 1C current rate (b).

TASK 1
Battery Cell Materials Development

Project Number: ES024

Project Title: High Voltage Electrolytes for Li-ion Batteries

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

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

Project Start/End Dates: June 2011 / May 2014

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 understand the surface chemistry at the high voltage cathode and electrolyte interface through surface characterization and computational effort. With better understanding, better electrolyte components and cathode materials can be developed.

Approach: Three approaches were taken.

1. **Develop additives for carbonate based solvents for high voltage cathodes**
   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
2. **Characterize interfacial chemistry at the cathode/electrolyte interface**
   a. Use high resolution XPS
   b. Use mass spectroscopy method, NMR, AFM, etc
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

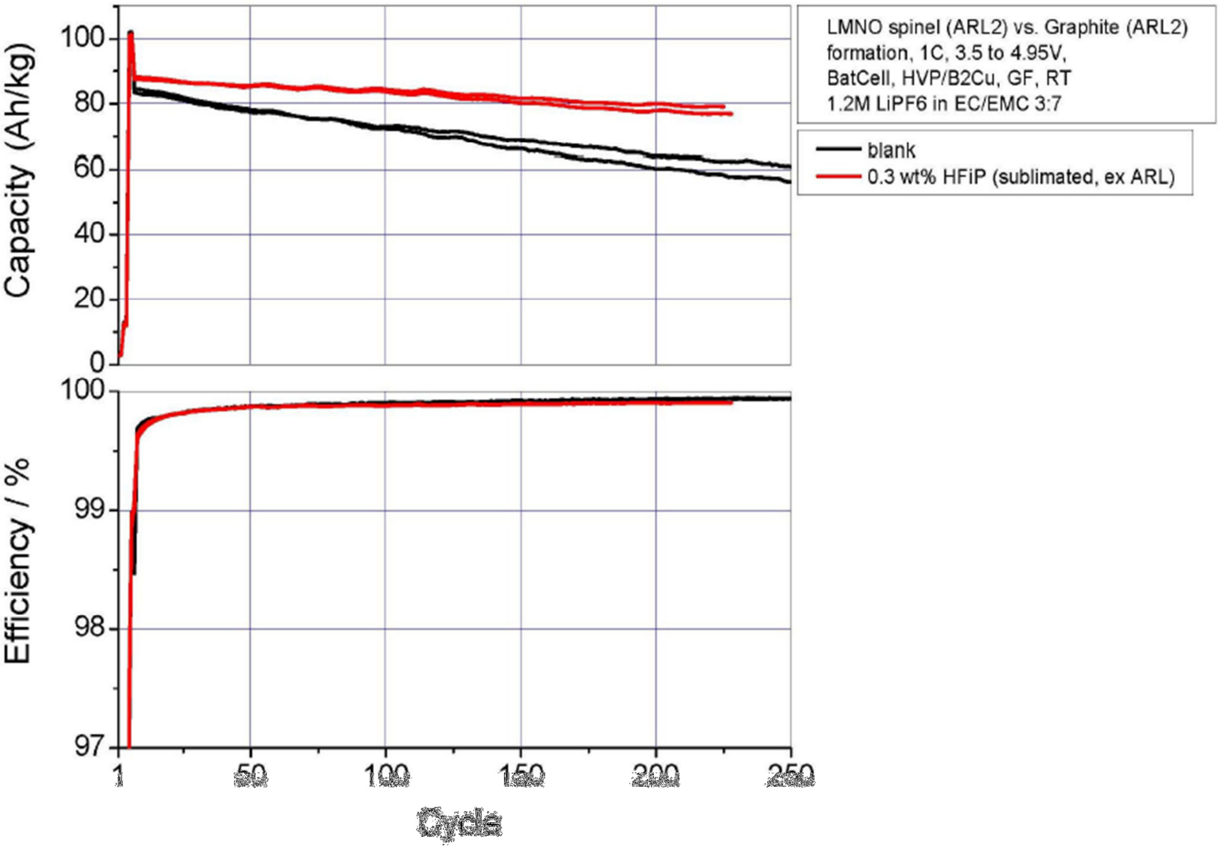
Milestones:

- **(a)** Explored new additives for high voltage cathodes (June 2012)
- **(b)** Evaluate electrolytes with additives in both half cells and full cells (Dec 2012)
- **(c)** Diagnostic studies: surface characterization and SEI chemistry (Dec 2012)
- **(d)** Understand reactive pathways of electrolyte components through computational effort (June 2012)
- **(e)** Develop stable high voltage cathodes and understand their electronic structures (Dec 2012)

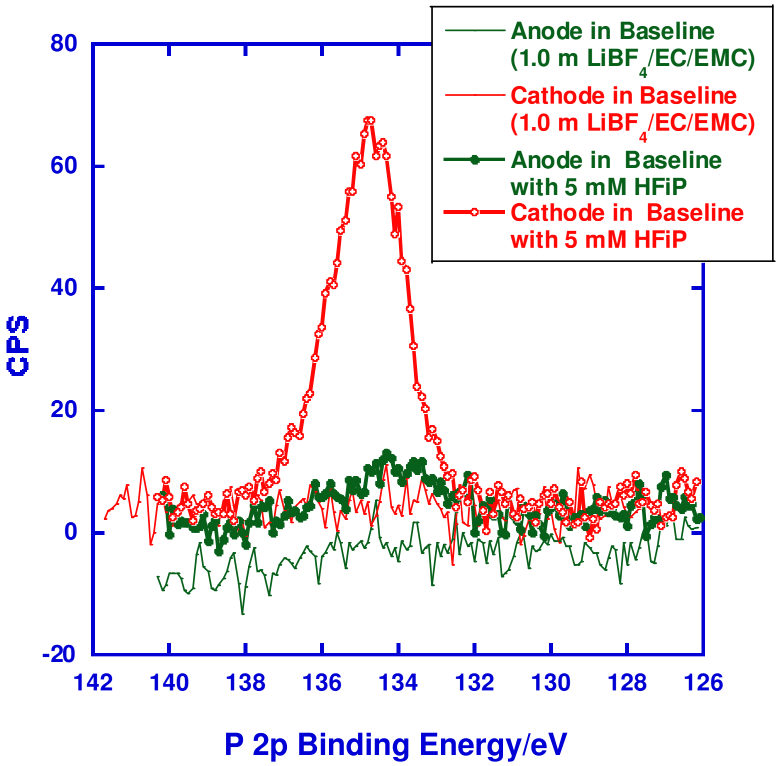
Financial data: $315,000/year

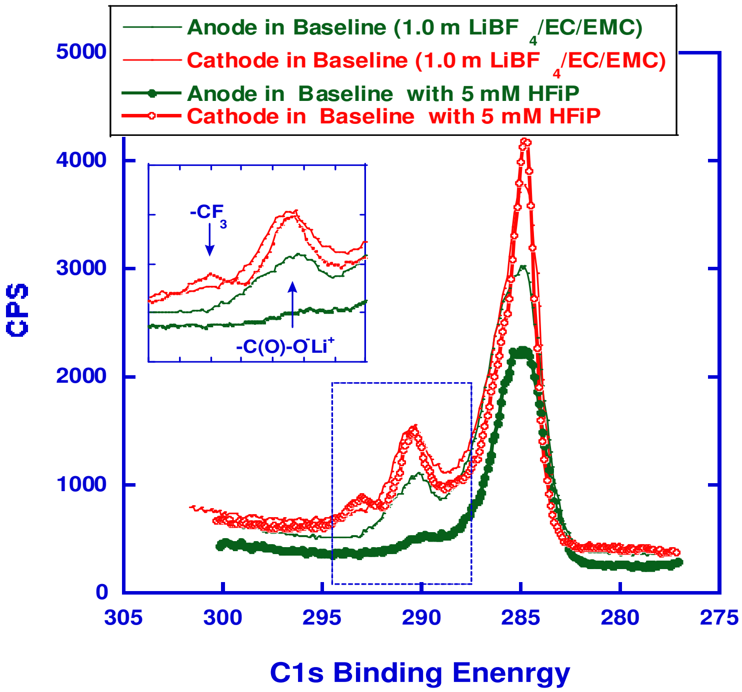
PROGRESS TOWARD MILESTONES

(a) Cycling of high voltage electrolytes in full cells made of high voltage $LiNi_{0.5}Mn_{1.5}O_4$ cathode and graphite anode: The full cells were made of $LiNi_{0.5}Mn_{1.5}O_4$ cathode and graphite anode (A12), both of these electrodes were provided by Argonne National Laboratory. The state-of-the-art electrolyte made of 1.2 m $LiPF_6$ in EC:EMC (3:7 wt. ratio) was used as a baseline electrolytes (or as Gen 2 electrolyte). The high voltage electrolyte was made of the baseline electrolyte with 0.3% HFiP as an additive. The capacity of full cells cycling at room temperature in both the baseline and the high voltage electrolyte are shown as a function of cycle number in the figure below. After initial drop in capacity, the capacity retention for the cell cycled in high voltage electrolyte is 91% versus 70% for that in Gen 2 electrolyte after 200 cycles. The coulombic efficiency of the cycling reaches 99.8 % for the cell cycling in the high voltage electrolyte.



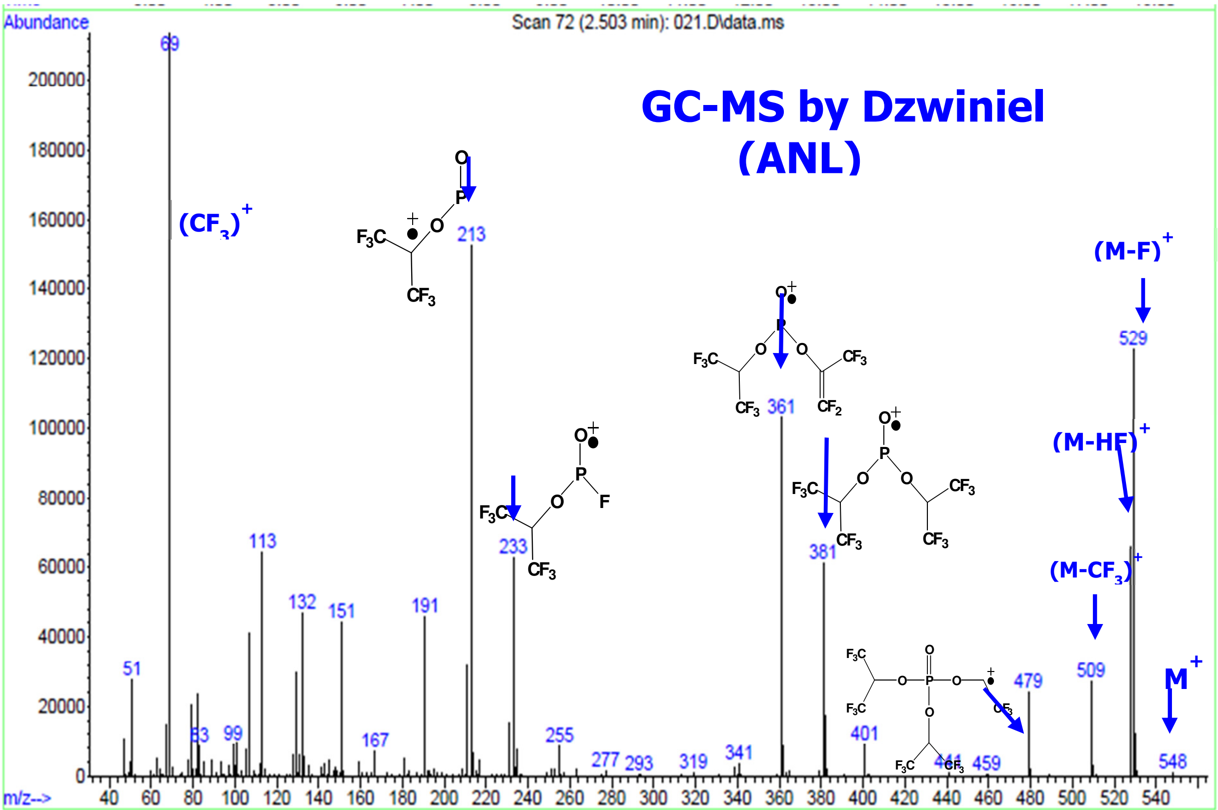
(b) Surface Analysis with HR-XPS: High resolution XPS was conducted on both cathode and anode cycled in the baseline and the HFiP-containing electrolytes. As shown in the two figures below, we found that P 2p absent in control samples but appeared on samples tested in the HFiP-containing electrolyte with a 5 to 10 times more on cathode than on anode and C 1s for CF_3 only found on cathode. These results indicate that the phosphate in the electrolyte ends up on both cathode and anode while the fluorinated alkyls substructure was shown on cathode only. It is highly suspicious that HF released at elevated temperature is responsible for less than perfect electrochemical performance.





(c) MS Analysis

HR-XPS results so far could not pin-point the structure of cathode interphase. Mass Spectroscopy of HFiP in acetonitrile was performed to learn if indirect structure information could be derived from this analysis.

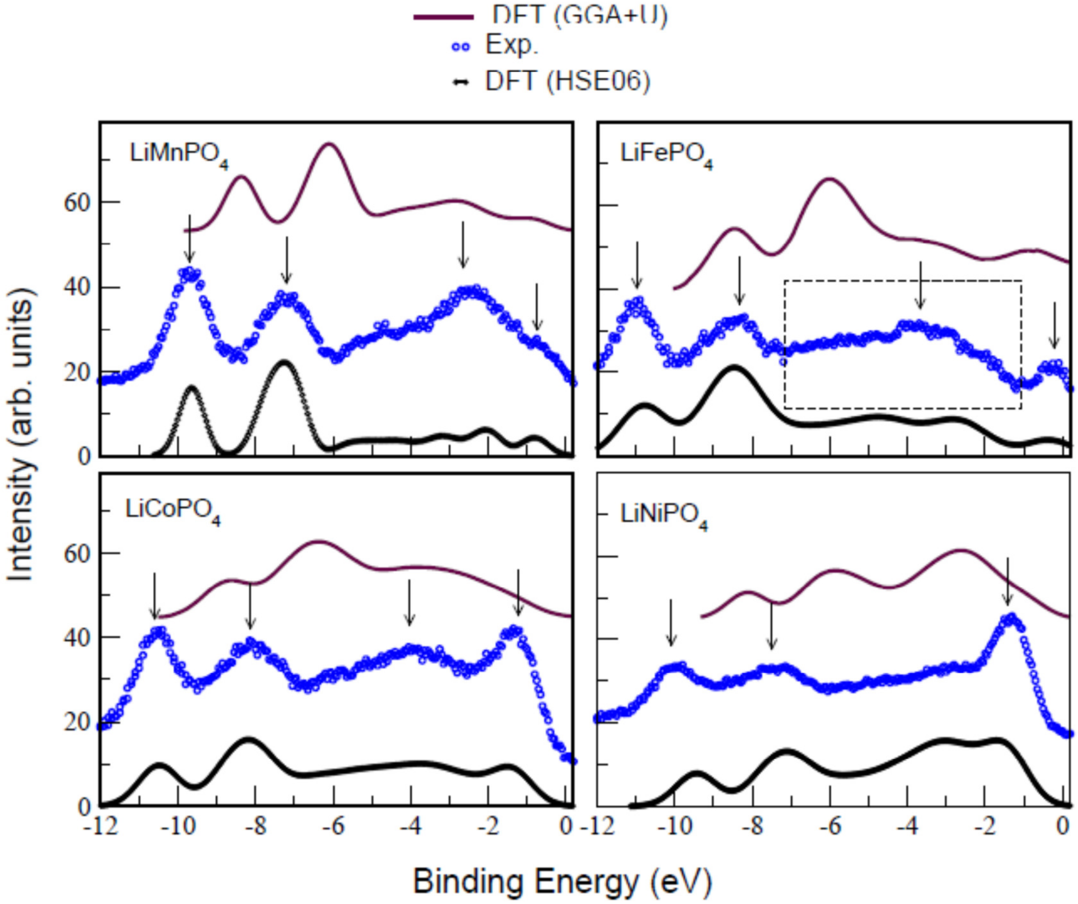


The above spectrum suggests the following: possible participation of the transition metal cores, new bond-formation between the transition metal and O, P, F and C, and de-activation on cathode surface at the transition metal centers similar to catalyst poisoning.

(d) Electronic structure studies of high voltage lithium cobalt phosphate cathodes (Reference 6)

We investigated the electronic structures of lithium olivine phosphate using DFT method. Comparing the calculated XPS spectra using DFT method with two different correlation exchange functional, GGA+U and HSE06, and experimentally measured XPS, we found out that DFT with the HSE06 functional can best capture the the electronic structures of $LiFePO_4$, $LiMnPO_4$, $LiCoPO_4$ and $LiNiPO_4$ determined by the experiments at the same time. This is shown in the figure below. The polaron migration barrier of $LiFePO_4$, $LiMnPO_4$ and $LiCoPO_4$ are also calculated as shown in the table below, which is consistent with the reported conductivity values. The results conclude that $LiCoPO_4$ can sustain polaron and has only a moderately higher polaron migration barrier than $LiFePO_4$.

	Migration barrier, eV	**σ, S/cm**
$LiFePO_4$	0.20	$1.8x10^{-8}$
$LiMnPO_4$	0.33	$<10^{-10}$
$LiCoPO_4$	0.23	$\sim 10^{-9}$



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

1. "Interfacing electrolytes with electrodes in Li-ion batteries." Xu, K., Cresce, A., *J. Mater. Chem.*, 2011, 21, 9849~9864**.**
2. "Preferential Solvation of Li+ Directs Formation of Interphase on Graphitic Anode", *A. v. Crecse,* and K. Xu, *Electrochemical and Solid State Letters*, 2011, 14, A154~156.
3. "Reaction Mechanisms for the Limited Reversibility of Li/O_2 Chemistry in Organic Carbonate Electrolytes", W. Xu, K. Xu, V. V. Viswanathan, S. A. Towne, J. S.

Hardy, J. Xiao, Z. Niea, D. Hu, D. Wang, and J. Zhang, *J. Power Sources*, 2011, 196, 9631~9639.

4. "A non-aqueous electrolyte for the operation of Li/Air battery in ambient environment", S. Zhang, J. Read, and K. Xu, *J. Power Sources* 2011, 196, 3906~3910.
5. "Improved cycle life of Fe-substituted $LiCoPO_4$", Allen J. L.; Jow T. R.; Wolfenstine J., J. Power Sources, 2011, 196(20), 8656-8661.
6. "Hole polaron formation and migration in olivine phosphate materials", Johannes, M.D.; Hoang, K.; Allen, J.L., *2011 ECS Boston Meeting*, Abstract #669, Oct 2011.
7. "Density Functional Theory Study of the Role of Anions on the Oxidative Decomposition Reaction of Propylene Carbonate", Xing, L.; Borodin, O.; Smith, G. D.; Li, W, *J. Phys. Chem. A,* 2011, 115, 13896-13905.
8. "Molecular Dynamics Simulation Studies of the Structure of a Mixed Carbonate/LiPF6 Electrolyte near Graphite Surface as a Function of Electrode Potential", Vatamanu, J.; Borodin, O.; Smith, G. D., *J. Phys. Chem. C*, 2011, 116 (1), 1114-1121.

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, Wei Weng, and Peng Du
Project Start/End Dates: 10/01/2008~09/30/2014

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

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

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

Financial data: $300K/FY2011

PROGRESS TOWARD MILESTONES

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

Based on our previous developed empirical rule of degree of unsaturation of chemical structures, new electrolyte additive is discovered and their performance is evaluated. Chemicals with high degree of unsaturation always have cyclic structure and double bonds, which could be beneficial to the SEI formation process. The screening process consists of formation, impedance measurements, and fast cycle test at elevated temperature. A new heterocyclic compound 1,3,5-triallyl-1,3,5-triazinane-2,4,6-trione, as shown in Fig. 1, have been selected for additive study.

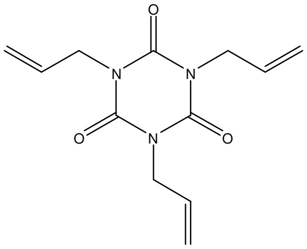


Fig.1. Chemical structure of 1,3,5-triallyl-1,3,5-triazinane-2,4,6-trione.

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

Fig. 2 is the differential capacity vs voltage of MCMB-1028/Li1.1[Ni1/3Co1/3Mn1/3]0.9O2 coin cells in 3E7EMC/PF12 with 1 wt% additive of 1,3,5-triallyl-1,3,5-triazinane-2,4,6-trione. The cell was formed at C/20 rate at room temperature. The cut-off voltage is 3.0~4.0 V. A slightly difference could be observed on the profile in the area of 2.0-2.5V, which is absent in the cell without additive (didn't shown). The additional peak is apparently due to the additive which is reduced within voltage range forming a new SEI film on the anode surface.

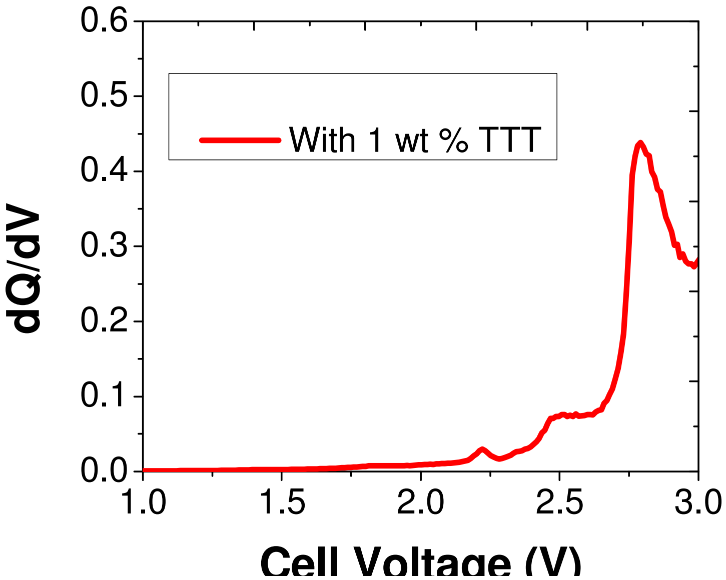


Fig.2. dQ/dV profile of MCMB-1028/$Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O_2$ coin cells in 3E7EMC/PF12 with 1 wt% additive 1,3,5-triallyl-1,3,5-triazinane-2,4,6-trione .The cells were charged to 3.8 V.

In capacity retention profiles shown in **Fig.3**, various concentrations were used to find the optimized condition. With 0.2 wt% additive, the cell showed dramatic improvements in capacity retention. **Fig. 4** is the impedance results of additive 1,3,5-triallyl-1,3,5-

triazinane-2,4,6-trione at various concentrations. With small amount of additive, the impedance increase can be controlled and the power capability will not be affected. Based on our preliminary investigation, this is an excellent electrolyte additive for electrified vehicle application.

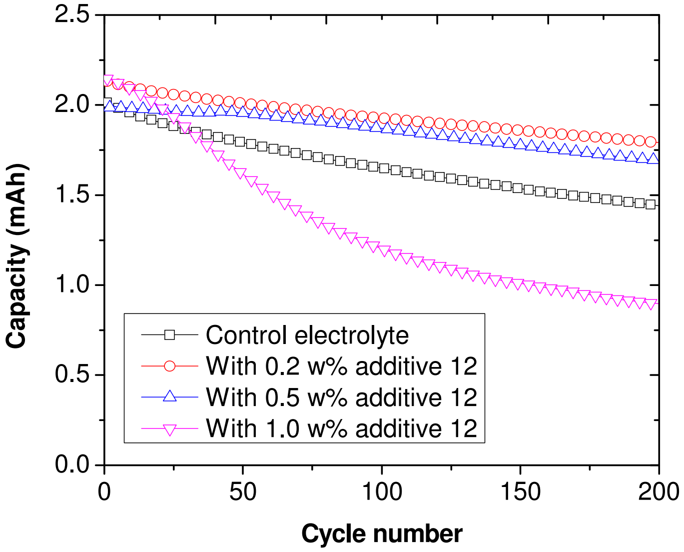


Fig.3. Capacity retention of MCMB/NCM cells cycled between 2.7 and 4.2V at 55 ◦C in electrolyte of 1.2M $LiPF_6$ EC/EMC 3/7 with various additive concentrations.

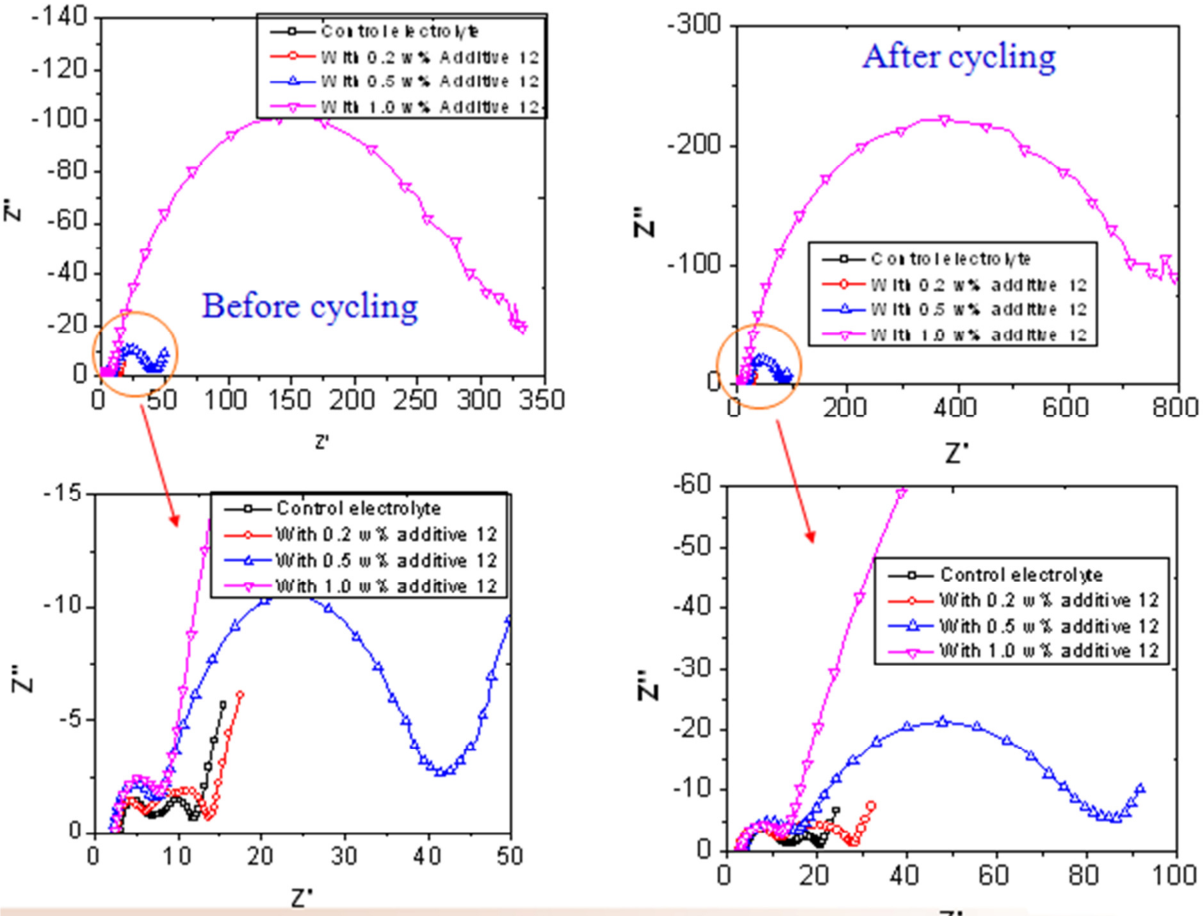


Fig.4. AC impedance profiles of MCMB-1028/Li$_{1.1}$[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]$_{0.9}$O$_2$ coin cells in 3E7EMC/PF12 with none or 0.2 wt% additives. The cells were charged to 3.8 V. The charge rate was 1C.

In the next Quarter, we will explore the identity of the SEI formed by this new additive. SEM, XPS and other analytical techniques will be used.

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

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

TASK 1
Battery Cell Materials Development

Project Number: ES026

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

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

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

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

Objectives:

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

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

The candidate electrolytes are characterized using a number of approaches, including performing ionic conductivity and cyclic voltammetry measurements, and evaluating the performance characteristics in experimental ~ 200-400 mAh three electrode cells. 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. Cells will be fabricated using a number of electrode couples: (a) MCMB /$LiNi_{0.8}Co_{0.2}O_2$, (b) graphite /$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, (c) graphite/$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, (d) $Li_4Ti_5O_{12}$ (LTO)//$LiNi_{0.5}Mn_{1.5}O_2$ (LMNO), and (e) graphite/$LiNiCoMnO_2$. 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) individually and the identification of performance limiting mechanisms for each electrode and for the cell. Electrodes are easily harvested from these test cells and samples will be delivered to collaborators (i.e., URI and LBNL).

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 several battery vendors and also has the capabilities to perform extensive testing. Typical prototype cell designs 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/or obtained through on-going collaborations

Milestones:

Month/Year	**Milestone**
Sept. 2012	Milestone A: Prepare and characterize experimental laboratory cells containing Gen-3 electrolytes, designed to operate over a wide temperature range in high voltage systems (i.e., $Li(NiMnCo)O_2$ and $LiNi_{0.5}Mn_{1.5}O_2$), and identify performance limiting characteristics (Sep. 12)
Sept. 2012	Milestone B: Demonstrate improved performance of second generation electrolytes over a wide temperature range (-30^{o} to $+60^{o}C$) compared with baseline electrolytes, in experimental and prototype cells (Sep. 12).

Financial data:

Total project funding:

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

Funding received:

FY'10 = 175K (Start Date = Oct 1, 2009)
FY'11 = 175K
FY'12 = 170K

Accomplishments and Progress toward Milestones:

In the recent quarter, we have characterized a number of 12 Ah cells (MCMB Carbon/$LiNiCoAlO_2$) obtained from our collaborator, Quallion, LCC, that contain electrolytes previously identified to have excellent wide operating temperature range. One of the electrolyte formulations investigated, namely 1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %) (where MP=methyl propionate) was previously demonstrated to have excellent rate capability at low temperatures in smaller prototype Quallion 0.250Ah cells, which has been reported previously. In an attempt to improve the life characteristics, especially at high temperature, formulations incorporating mono-fluoroethylene carbonate (FEC) were further investigated, based on favorable characteristics ascertained in experimental cells. In particular, the electrolyte 1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %) + 4% FEC was evaluated in the larger 12 Ah cell. As illustrated in Fig. 1, excellent performance was observed down to temperatures as low as -50^{o}C, with over 75% of the room temperature capacity being delivered up to 2C rates with both formulations. These cells have been evaluated over a wide temperature range (-60 to +20^{o}C) and will be subjected to cycle life testing.

In an extension of this work, we are also evaluating a number of smaller 0.25Ah MCMB/$Li(NiCoAl)O_2$ cells (manufactured by Quallion, LCC) that we recently obtained that contain methyl propionate-based electrolytes with varying amounts of mono-fluoroethylene carbonate. Cells possessing 1.20M $LiPF_6$ in EC+EMC+MB (20:20:60 vol %) + 0.10M LiBOB were also fabricated, since the use of LiBOB as an additive has been previously identified to result in improved low temperature performance and improved cathode kinetics. A number of performance tests will be implemented on these cells, including discharge rate characterization as a function of temperature, charge rate characterization, and cycle life performance under various conditions (including cycling at high temperatures).

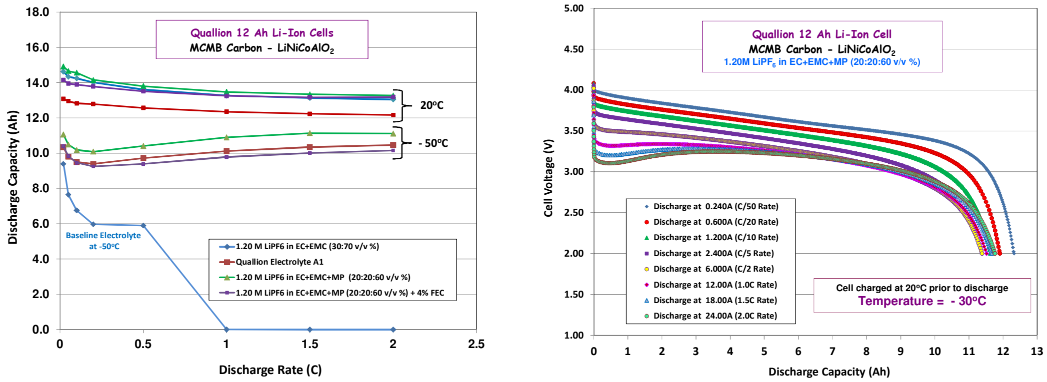


Figure 1: Discharge rate capability of 12 Ah MCMB-LiNiCoAlO$_2$ cells (Quallion, LCC) containing various electrolytes at +20^{o}C and -50^{o}C (Figure 1A) and discharge rate capability of a cell containing 1.20M LiPF$_6$ in EC+EMC+MP (20:20:60 vol %) (Figure 1B).

Recent work has also been devoted to studying these electrolytes in high voltage systems. We have investigated ester-based solutions in conjunction with LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$, LiNi$_{0.5}$Mn$_{1.5}$O$_2$ (LMNO), and the excess lithium layered-layered composite Li(NiCoMn)O$_2$ (NMC) materials (from two sources). In our most recent efforts, we have investigated the effect of electrolyte type upon the performance Conoco graphite anodes and NMC cathodes supplied by Argonne National Labs. As illustrated in Fig. 2, we have generally observed good compatibility of the methyl butyrate-based electrolytes with this high voltage system. The rate capability of cells at room temperature containing 1.20M LiPF$_6$ in EC+EMC+MB (20:20:60 vol %) is very comparable to cells containing the baseline all carbonate blends. Based on previously published work under a NASA-funded project, we have demonstrated that the addition of LiBOB to flame retardant additive-containing electrolytes increases its compatibility with high voltage systems. Utilizing this approach, we have investigated wide operating temperature range electrolytes (i.e., methyl butyrate and methyl propionate-based) that contain LiBOB, with the intent of improving the cathode interface. We have also explored the use of comparable type of compounds as additives, such as the lithium malonate borate-based salt (LiDMMDFB) developed by LBNL and the URI (Li Yang, John Kerr, and Brett Lucht). As illustrated in Fig. 2, a modest improvement in the cycle life performance is obtained with MB-based electrolytes containing LiBOB, whereas the use of LiDMMDBB appears to have a detrimental effect on life. We are currently evaluating other additives and co-solvents, including mono-fluoroethylene carbonate as well as other fluorinated carbonates, with the intent of improving the life characteristics. As a comparison, we have also evaluated the life characteristics of the low flammability electrolyte developed under a NASA funded program, namely 1.0M LiPF$_6$ + 0.15M LiBOB in EC+EMC+TPP (20:70:10 vol %) (where TPP = triphenyl phosphate), with the Argonne developed electrode materials. As shown, good cycle life performance is obtained with this electrolyte formulation, outperforming the baseline all carbonate-based electrolytes (i.e., 1.0M LiPF$_6$ in EC+DEC+DMC (1:1:1). As a result of interest that DOE has expressed, some of the low flammability electrolytes developed at JPL will be subjected to safety testing by collaborators at Sandia National Laboratory.

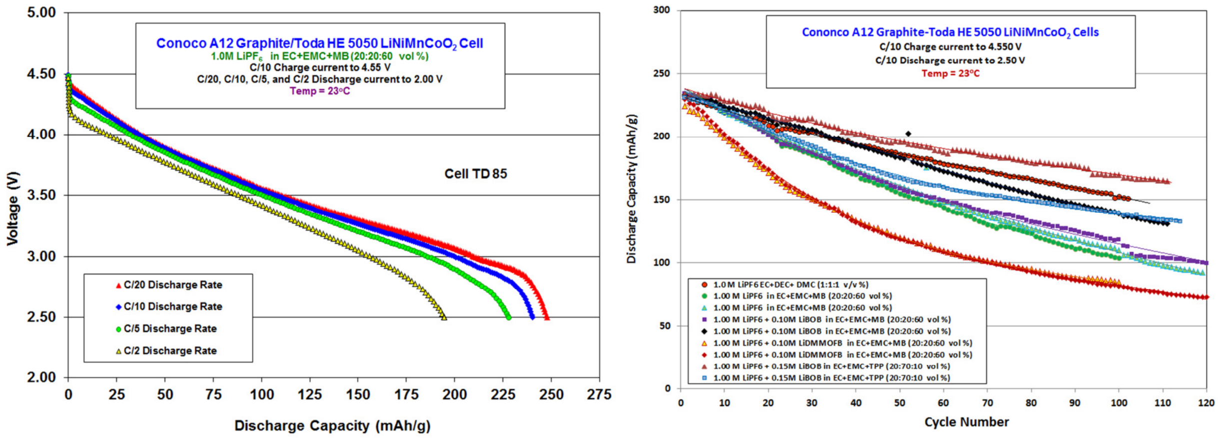


Figure 2: Rate capability at 23°C of a cell containing Cononco A12 graphite and Toda HE 5050 LiNiCoMnO$_2$ (C/20, C/10, C/5, and C/2) (Fig. 2A) and 100% cycle life performance of Cononco A12 graphite and Toda HE 5050 LiNiCoMnO$_2$ cells containing various electrolytes (Fig. 2B).

We also continue to evaluate the life characteristics of a number of A123 cells that possess methyl butyrate-based electrolytes previously investigated under this program (i.e., specifically 1.20M LiPF$_6$ in EC+EMC+MB (20:20:60 vol %) + 4% FEC and 1.20M LiPF$_6$ in EC+EMC+MB (20:20:60 vol %) + 2% VC). As reported previously, these cells have exhibited excellent rate capability over a wide temperature range (-60 to +20°C) being able to support up to 10C rates at temperatures as low as -50°C and C rates at -60°C. As illustrated in Fig. 3A, excellent cycle life has been obtained with the cells exhibiting over 4,500 cycles to-date and displaying comparable performance to the baseline electrolyte. We also continue to evaluate the high temperature resilience of these systems by implementing a number of cycle life tests (i.e., at 40° and 50°C), as shown in Fig 3B. Thus far, the performance is encouraging with over 2,500 cycles being delivered, with the cells containing the 1.20M LiPF$_6$ in EC+EMC+MB (20:20:60 vol %) + 2% VC electrolyte outperforming the baseline system, and the FEC containing variant displaying increased capacity fade. These results are notable given the demonstrated low temperature performance capability of these systems.

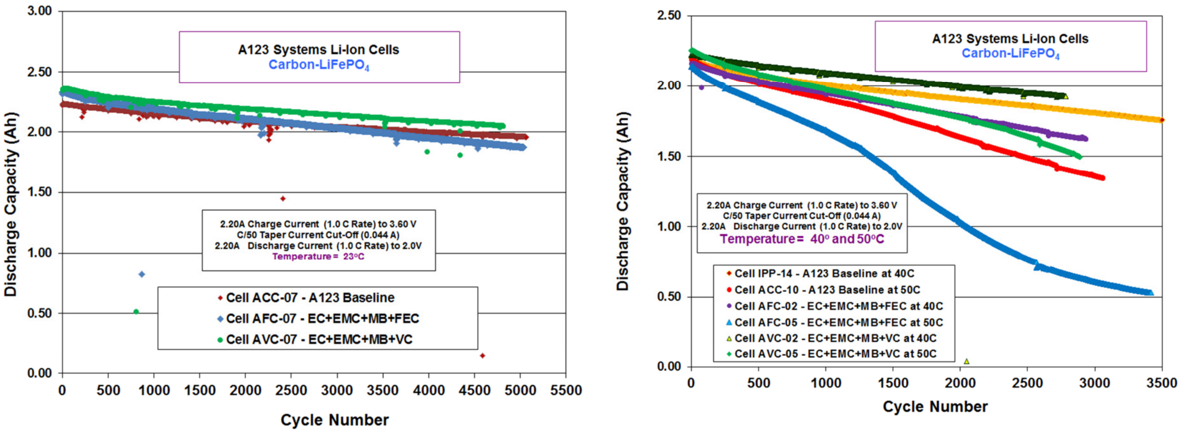


Figure 3: Cycle life performance of LiFePO$_4$-based A123 cells containing various electrolytes at +23°C , +40°C and +50°C.

Future work will involve continuing the investigation of the use of additives in conjunction with ester-based, wide operating temperature range electrolytes evaluated with different electrode chemistries, with a focus upon (i) assessing other candidate additives, (ii) studying the high temperature and cycle life degradation modes, (iii) correlating electrochemical trends with performance, and (iv) identifying performance limiting aspects at extreme temperatures. Future work will also focus upon demonstrating these systems in prototype cells.

Publications:

1. N. Leifer, M. C. Smart, G. K. S. Prakash, L. Gonzalez, L. Sanchez, P. Bhalla, C. P. Grey, and S. G. Greenbaum, "^{13}C Solid State NMR Study of SEI Formation in Carbon Lithium Ion Anodes Cycled in Isotopically Enriched Electrolytes Suggests Unusual Breakdown Products", *J. Electrochem. Soc.*, **158 (5)**, A471-A480 (2011).
2. M. C. Smart and B. V. Ratnakumar, "Effect of Cell Design Parameters on Lithium Plating in Lithium-Ion Cells", *J. Electrochem. Soc.*, **158 (4)**, A379-A389 (2011).
3. M. C. Smart, A. S. Gozdz, L. D. Whitcanack, and B. V. Ratnakumar, "Improved Wide Operating Temperature Range of High Rate Nano-Lithium Iron Phosphate Li-Ion Cells with Methyl Butyrate-Based Electrolytes", 220th Meeting of the Electrochemical Society, Boston, MA, October 11, 2011.
4. M. C. Smart, B. L. Lucht, S. Dalavi, F. C. Krause, and B. V. Ratnakumar, "The Effect of Additives upon the Performance of MCMB/LiNiCoO$_2$ Li-Ion Cells Containing Methyl Butyrate-Based Wide Operating Temperature Range Electrolytes", J. Electrochem. Soc., submitted for publication.
5. S. Dalavi, M. C. Smart, B. L. Lucht, F. C. Krause, and B. V. Ratnakumar, "The Effect of methyl butyrate (MB), a low temperature co-solvent on the solid electrolyte interphase (SEI) formed on the surface of lithium ion battery (LIB) electrodes", 220th Meeting of the Electrochemical Society, Boston, MA, October 10, 2011.

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

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

TASK 1
Battery Cell Materials Development

Project Number: ES027 **Reporting Period:** FY 2012 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: Our focus is to understand stability of our new classes of phosphazene materials and to establish viability for their 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)
- temperature stability
- lithium salt solubility
- transport properties (viscosity, conductivity)
- chemical compatibility with the cell environment
- molecular interactions (solvent-ion)

Coin cell testing covers issues of formation, interfacial impedance, polarization testing, and aging, using our compounds as electrolyte additives (1-10%). In previous quarters we investigated the performance of our electrolytes with two electrode couples (LNMO/LTO and NMC(3M)/Carbon), and in this quarter we report on results with the HE5050/Carbon couple.

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

Milestones (cumulative over FY 2011):

🟩	**= Activity completed in reporting period**

Milestone	Status	Date
a. Synthesis of Fluorinated Phosphazene series (FM1,2,3)	completed	March 2011
b. Synthesis of Gen1 Ionic Liquid Phosphazene (PhIL-1)	completed	Feb. 2011
c. Synthesis of newer SM series (SM 5,6,7)	completed	October 2010
d. Development of improved voltammetry techniques for SEI characterization.	completed	December 2010
e. DFT simulations of selected phosphazenes regarding interaction with lithium ions	completed	Feb./March 2011
f. Thermal stability testing of blends with SM6 and SM7	completed	March 2011
g. Cell testing using LNMO/LTO and NMC/Carbon* couples: characterization of capacity and impedance attributes	completed	March 2011
h. Cell testing using LNMO/LTO and NMC/Carbon* couples: aging studies	completed	October 2011
i. Phase 1 concept validation for alternative anode materials	completed	October 2011
j. Cell testing using HE5050/Carbon couple: characterization of capacity and impedance attributes	completed	December 2011
k. Cell testing using HE5050/Carbon couple: aging studies	In Progress	
l. Synthesis of newer FM series and second-generation Ionic Liquid Phosphazenes	In Progress	
m. Abuse testing of INL Phosphazene electrolyte additives at SNL	In Progress	
n. Collaboration with ANL regarding scale-up of INL electrolyte compounds	In Progress	
Various supporting characterization and cell testing will be ongoing throughout FY 2012.		

* Initial set of NMC/Carbon electrodes received from SNL were not calandared. We repeated the experimental matrix for calendared sets of this electrode material.

Financial data: Funding Received: FY 10: $ 400K; FY 11: $ 400K ; FY 12: $550K (under subcontract, a small portion of this might go Washington State University and Idaho State University for specialized NMR and PALS measurements).

PROGRESS TOWARD MILESTONES

(a, b) Completed 2011 Q2.

(c) Completed 2011 Q1.

(d) Completed 2011Q1.

(e) Completed 2011 Q2.

(f) Completed 2011 Q2.

(g) Completed 2011 Q2.

(h) We concluded our testing with phosphazene-doped electrolytes using the LNMO/LTO couple provided by ANL and the NMC/Carbon electrode couple provided by SNL. Aging data for conditions at elevated temperature and 3C cycling indicates that the phosphazenes act to prolong cell life in some cases. We will substantiate which additives are superior in this regard following post-mortem evaluation of cell groups.

(i) We completed Phase 1 validation testing for highly-engineerable anodes based on alternative intercalation materials. Of the earliest formulations, some showed promising behavior toward cycling up to 5V, as seen in Fig. 1 for 2032-type coin cell cycling. Based on these early encouraging results, a new generation of electrode material was synthesized and will undergo cell testing in FY 2012 Q2. We are targeting high-voltage (≥5V) anode materials that will compete with carbon, exhibiting effective capacities of more than 300 mAh/g (based on total mass of anode laminate). Properties of these alternative materials are highly tunable to meet specific performance requirements regarding energy and power.

(j) Characterization of capacity and impedance attributes was completed for coin cells made with phosphazene-doped electrolytes and the HE5050/Carbon couple provided by ANL. Capacity over cycling rate is shown in Fig. 2, wherein electrolyte formulations contained three percent phosphazenes additives SM-4, SM-6, FM-2, or PhIL-2 in a baseline of EC-EMC (2:8) with 1.2M $LiPF_6$. Electrolyte performance is on par with that seen for earlier testing with LNMO/LTO and NMC/Carbon couples. In some cases the electrolytes with SM-6 and FM-2 performed better than the baseline system. These early results suggest that the INL additives are compatible with the HE5050/carbon couple.

(k) We will continue to test coin cells from (j) at 45 °C and a 3C rate to determine if the phosphazene compounds prolong cell life at these mildly abusive conditions. Initial indications are that the phosphazenes act to prolong cell life at elevated temperature. We will conclude this work in Q2 and report on the efficacy of our INL additives.

(l) Synthesis targets are being used to generate newer generations of FM and phosphazene-based ionic liquid (PhIL) compounds. Additional batches of various members of the FM series of phosphazenes were synthesized and purified. These batches were combined with existing stocks to form the library of the FM series of phosphazenes in sufficient quantities of each FM-1 through FM-4 to begin a comprehensive physical and electrochemical characterization using a standardized array of testing. Synthetic efforts continued to produce a series of related phosphazene-based ionic liquid electrolyte solvents. Work in this area was on the synthesis of PhIL-3 which had initial stability issues and was decomposing during synthesis. An alternate synthetic route was discovered and PhIL-3 was successfully produced.

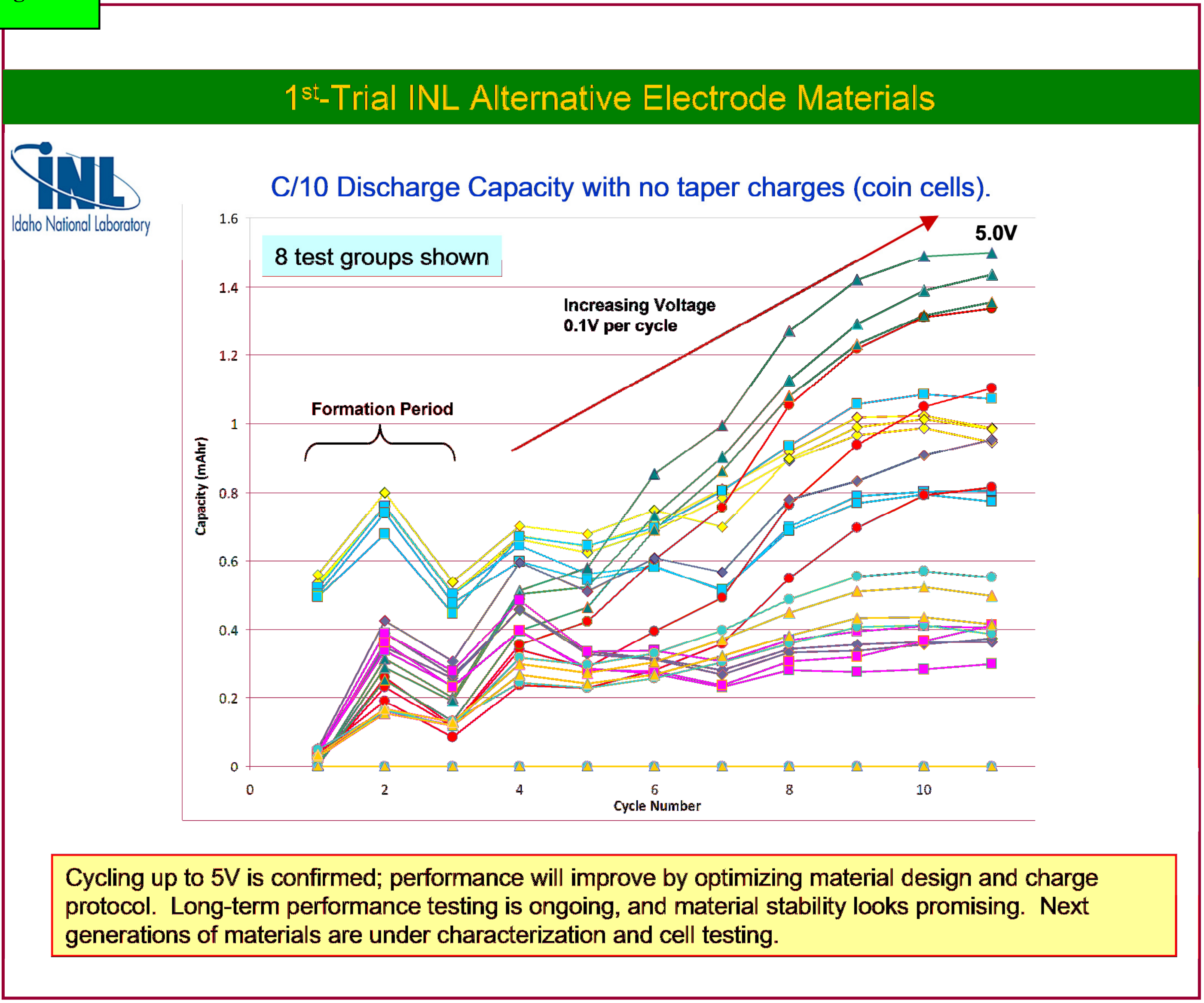
(m) Abuse testing (ARC) of INL Phosphazene compounds at SNL is active as of January 2012, using 18650 cells containing the NMC (3M)/carbon (A10) couple. INL additives include FM-2, SM-6, and PhIL-2 at one and three percent levels. The focus of this work is to determine how INL additives help mitigate (delay) the onset of thermal runaway.

(n) In this quarter efforts started in earnest to collaborate with ANL regarding the synthesis of INL phosphazene electrolyte compounds in the ANL materials scale-up facilities. The top candidate for scale-up will be the best compound that emerges from the SNL abuse testing described in (m).

Publications, Reports, Intellectual property

- Based on a presentation from the Fall 2011 ECS meeting, a paper was submitted to ECS Transactions entitled, “Phosphazene Based Additives for Improvement of Safety and Battery Lifetimes in Lithium-Ion Batteries”, M. Harrup, K. Gering, H. Rollins, and S. Sazhin.
- A full patent application was filed in this quarter: IONIC LIQUIDS, ELECTROLYTE SOLUTIONS INCLUDING THE IONIC LIQUIDS, AND ENERGY STORAGE DEVICES INCLUDING THE IONIC LIQUIDS, inventors K. L. Gering, M. K. Harrup, and H. W. Rollins.
- A draft paper is in final edits that covers DFT modeling of INL FM-series phosphazene compounds: “Lithium Binding in Fluorinated Phosphazene Trimers”, M. Benson, M. Harrup, H. Rollins, and K. Gering.

Fig. 1



1st-Trial INL Alternative Electrode Materials

Idaho National Laboratory

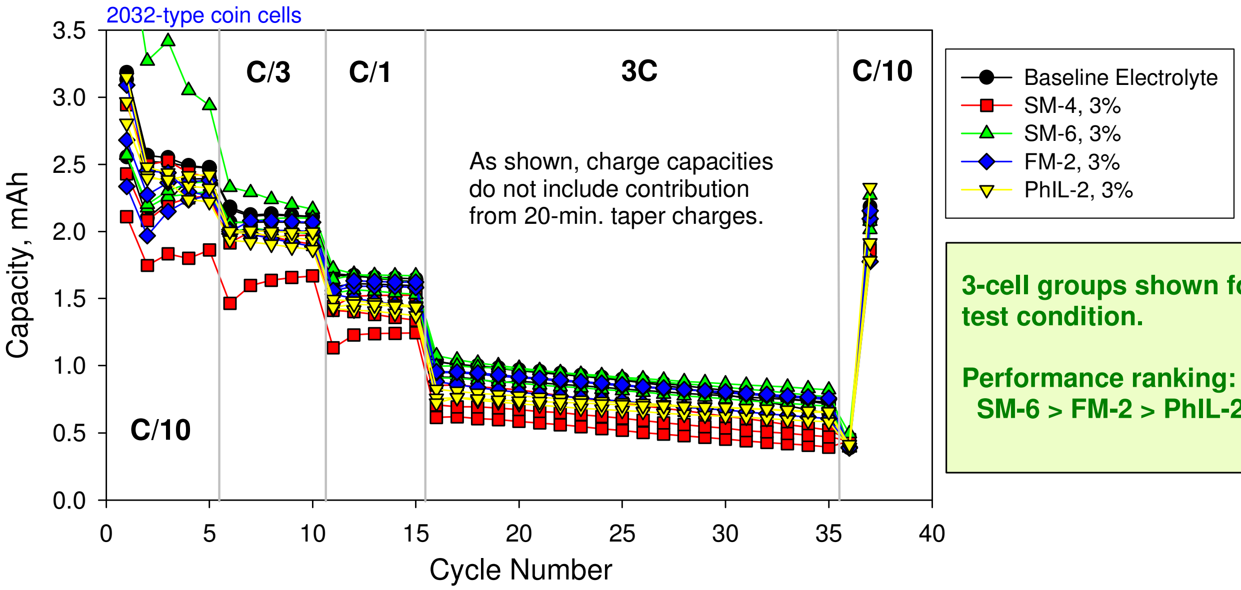
C/10 Discharge Capacity with no taper charges (coin cells).

Cycling up to 5V is confirmed; performance will improve by optimizing material design and charge protocol. Long-term performance testing is ongoing, and material stability looks promising. Next generations of materials are under characterization and cell testing.

Fig. 2

Cell Testing, Capacity Attributes (HE5050/Carbon)

HE5050/Carbon, Charge Capacities

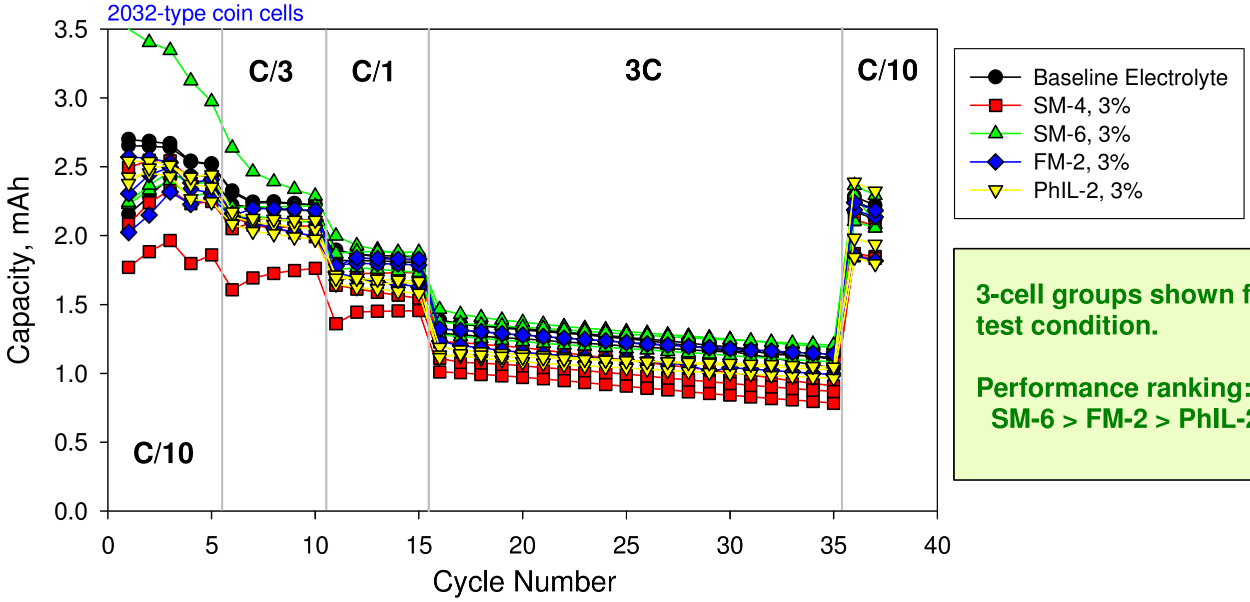


As shown, charge capacities do not include contribution from 20-min. taper charges.

3-cell groups shown for each test condition.

Performance ranking:
SM-6 > FM-2 > PhIL-2 > SM-4

HE5050/Carbon, Discharge Capacities



3-cell groups shown for each test condition.

Performance ranking:
SM-6 > FM-2 > PhIL-2 > SM-4

Improvement over baseline performance is seen in SM-6 and FM-2 in some cases.

TASK 1
Battery Cell Materials Development

1st Quarter Report, Oct. ~ Dec. 2011

Project Number: 1.1E (ES028)

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

Project PI, Institution: Wenquan Lu, Argonne National Laboratory

Collaborators (include industry):
Qingliu Wu, Argonne National Laboratory
Khadija Yassin-Lakhsassi, Argonne National Laboratory
Miguel Miranda, Argonne National Laboratory
Thomas K. Honaker-Schroeder, Argonne National Laboratory
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) Good laminate was made using SBR aqueous binder
(b) Composition effect on electrochemical performance of graphite was carried out.

Financial data: $300K carryover fund

PROGRESS TOWARD MILESTONES

SBR binder has been widely used in industries due to its low content in composite electrode and environmentally friendliness. In this work, aqueous binder SBR (JSR) was investigated comprehensively. The good quality graphite laminate was successfully made by using SBR/CMC binder. The graphite with various SBR and PVDF content was also made into electrodes for adhesion and electrochemical testing.

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

The laminate with SBR binder showed bad adhesion compared to laminate with PVDF binder using same drying process. It was find out that the drying temperature played a significant role to improve the adhesion. For SBR binder, the curing temperature at 120°C is needed to make laminate with good adhesion. The graphite with various SBR contents (2%, 4%, 6%, and 8%) was made into laminates. Simple tape test indicates that the comparable adhesion was obtained for all the laminates regardless of the SBR content in the composite electrodes. In the meanwhile, the adhesion is comparable to the laminate with equivalent amount of PVDF binder in composite electrode.

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

Electrochemical performance of graphite (A12) with various contents of SBR binder (2%, 4%, 6%, and 8%) was carried out using half cells. It was observed that the graphite electrode with 2% SBR (1% CMC) showed lowest resistance and good electrochemical performance. It can be seen from the Fig. 1 shown below that area specific impedance (ASI) increases with increasing SBR binder in the half cells.

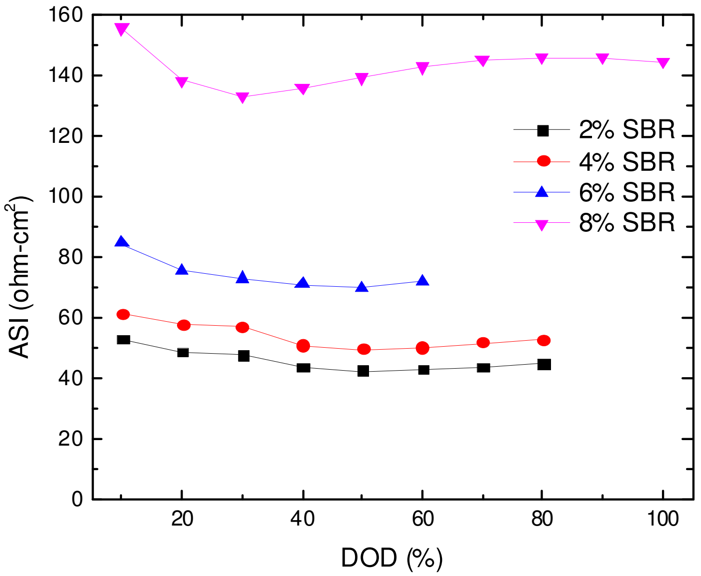


Fig. 1 ASI results of Li/graphite half cells with various SBR

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

TASK 1
Battery Cell Materials Development

1st Quarter Report, Oct. ~ Dec. 2011

Project Number: 1.3 (ES028)

Project Title: Screen Electrode Materials, Electrolytes, and Additives

Project PI, Institution: Wenquan Lu, Argonne National Laboratory

Collaborators (include industry):
Qingliu Wu, Argonne National Laboratory
Khadija Yassin-Lakhsassi, Argonne National Laboratory
Miguel Miranda, Argonne National Laboratory
Thomas K. Honaker-Schroeder, Argonne National Laboratory
Bryant Polzin, Argonne National Laboratory
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:

Based 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 1st Quarter:

- a) Complete screening of NEI high voltage spinel LiNi0.5Mn1.5O4
- b) Complete screening of Samsung Li4Ti5O12
- c) Complete screening of Morgan A&M graphite
- d) Complete evaluation of high voltage redox (RS6) from ES (ANL)

Financial data: $450K

PROGRESS TOWARD MILESTONES

Material screening on a) high voltage spinel LiNi1.5Mn0.5O4 from NEI Corporation, b) Li4Ti5O12 from Samsung, and c) four graphite samples from Morgan A&M were completed in this quarter. For all the materials, both half cell (vs. Li) and full cell (vs. A12 graphite) were fabricated for series of electrochemical testing, including formation, hybrid pulse power characterization, rate performance, and cycling testing. The results were analyzed and the reports delivered to the customers.

In support of battery material scale up activities at ES (ANL), high voltage redox shuttle (RS6) was received and investigated in terms of its electrochemical performance. A12 graphite and LiMn2O4 electrode couples were used investigate RS6's effect on overcharge. The electrochemical performance of A12/LiMn2O4 performance with and without RS6 was carried out. The A12/LiMn2O4 cells with RS6 additive with and without overcharge were also studied.

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

Half cells using LiNi1.5Mn0.5O4, from NEI corporate has been investigated. The cells were cycled between 4.95V and 3.5V at C/10 rate. The 133 mAh/g specific capacity of LiNi1.5Mn0.5O4 was obtained from the formation cycles with about 8% irreversible capacity loss. The high voltage spinel was also coupled with A12 graphite for full cell test. The Area specific impedance (ASI) derived from hybrid pulse power characterization (HPPC) test was determined to be about 60 ohm-cm2. Good rate performance and cycle life were obtained from half cells when cycled between 4.95V and 4.5V.

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

Half cells using Li4Ti5O12 from Samsung Cell has been investigated. The cells were cycled between 1.8V and 1.2V at C/10 rate. The 160 mAh/g specific capacity was obtained from the formation with about only 3% irreversible capacity loss. The Li4Ti5O12 was coupled with LiMn2O4 electrode for full cell test. Excellent rate and cycle performance were obtained.

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

Two artificial and two natural based graphite samples were obtained from Morgan A&M. Half cells vs. lithium were fabricated to investigate their electrochemical properties. When cycled between 1.5V and 0V at C/10 rate, both natural based graphite samples show higher specific capacity (350mAh/g) and lower irreversible capacity loss (5%) compared to artificial based graphite, which show about 295mAh/g specific capacity and about 8% irreversible capacity loss. In the meanwhile, natural based graphite shows better rate performance.

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

A12/graphite cells were used as test vehicle for RS6 high voltage redox shuttle. Three sets of experiments, cells with and without additive, cells with additive with and without overcharge, were carried to investigate the effect of RS6 on cell overcharge. From HPPC test, notable impedance rise was observed from the cells with RS6 without overcharge. The redox potential at about 4.8V vs. Li/Li^+ was obtained during overcharge.

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

NEI high voltage spinel evaluation, internal report, Dec 2011.

Evaluation of $Li_4Ti_5O_{12}$ from Samsung, internal report, Dec 2011.

TASK 1
Battery Cell Materials Development

Project Number: 1.2.2 Electrode Material Development (ES029)

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

Lead PI and Institution: Vince Battaglia, Lawrence Berkeley National Laboratory

Support PI and Institution: None

Barrier: Cost is too high (energy density needs to be increased.)

Specific Objectives: (*i*) Identify materials in the BATT Program that are ready for enhanced screening diagnostics, (*ii*) Procure *ca.* 10 grams of new material to make laminates for coin cell or pouch cell testing, (iii) Work with BATT researchers to improve their materials by identifying shortcomings.

General Approach: Work with BATT PIs in deciding what materials are ready for scale-up and enhanced testing and diagnostic evaluation in full cells. Once materials are identified, decide on the best approach for increasing the quantity of the material to approximately 10 g. Make laminates of the material and test in coin cells against Li. Based on initial test results, decide on best automotive application for material, design the electrodes for the application, and perform long-term cycling tests. Provide a comparison to state-of-the art materials and cells.

Current Status as of October 1, 2010: Eight materials were identified for scale-up and further testing. Three of the materials showed significant problems during preliminary testing: two exhibited large first-cycle irreversible capacity losses, and the other displayed low specific capacity. Four materials continue on long-term cycling, and one material has recently begun preliminary testing. This last material, from MIT, was scaled-up and its claimed high-rate capability has been confirmed.

Expected Improvement by September 30, 2011: Will have identified at least three more BATT Program materials that should undergo further testing. Will have developed some basic principles for the optimal scale-up of the MIT material.

Schedule and Deliverables: Attend review meetings and present interim results on the scale-up of BATT Program materials (November 2010, February 2011, August 2011.)

Deliverable: Battery design, performance, and cycling characteristics of three BATT materials will be reported on at the DOE Merit Review (June 2011.)

Quarter 1 Report

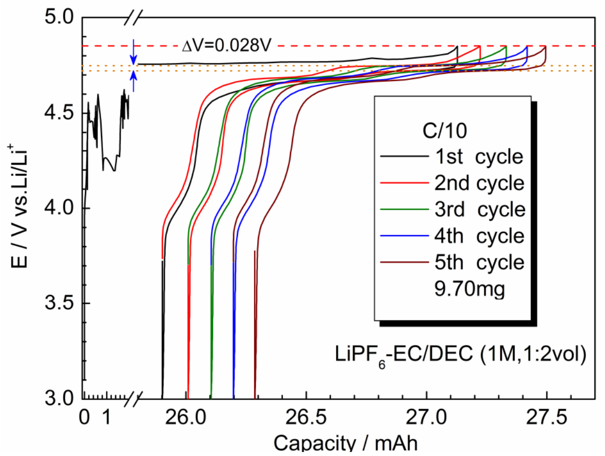
During last year's AMR, a presentation by the Army Research Laboratory indicated that HFiP (hexafluoroisopropanol) works well as an electrolyte additive for high-voltage systems. Dr. Brett Lucht (U. Rhode Island) carried out preliminary investigations of this additive using a $LiNi_{1/2}Mn_{3/2}O_4$ cathode and then sent a sample to LBNL.

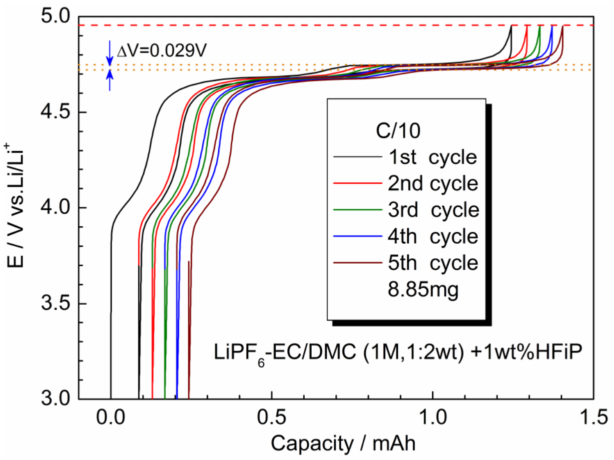
Recently, our group has been evaluating a second batch of NEI material, which is targeted for use in the BATT Program baseline cathode laminate to be prepared by HydroQuebec. This material differed from the first NEI batch in several ways, the most obvious being visible in SEM images. In the SEM images (not shown here) one can see that the secondary particle size in the second batch is five times larger than that in the first batch.

In a FY 2011 quarterly report we showed that a cell using the first batch of NEI material could not be charged above 4.88 V without transitioning to an erratic voltage response for several mAh before reaching the cut-off voltage. In nearly every half-cell tested using the second batch of NEI material, there was again a long first-cycle delay in fully charging the material as a result of a side reaction, as seen in the figure to the left below, although in this case the reaction was initiated at about 4.5 V. After the first charge was completed, the cells cycled normally.

The second batch of NEI cathode material was tested with an electrolyte containing 2% VC. The long first cycle charge was no longer present; however, there was a large impedance rise in the cell, which worsened with each cycle, and an increase in the rate of the side reaction was measured for all subsequent cycles.

The cathode was then tested with the HFiP additive provided by Dr. Lucht at a level of 1%. This additive effectively limited the first-cycle side reaction in the half-cell and provided good cycling with limited impedance rise per cycle. The polarization of this cell is comparable to that without the additive. The next steps will be to test the material in a full cell to determine the extent of first-cycle side reactions with graphite, and evaluate the role of additives in such cells.





TASK 1
Battery Cell Materials Development

Quarter 1 2012

Project Number: 1.2C (ES112)

Project Title: Functionalized Surface Modification Agents to Suppress Gassing Issue of $Li_4Ti_5O_{12}$ Based Lithium Ion Chemistries (Mechanism of LTO Gassing and Potential Solutions)

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

Collaborators (include industry):
EnerDel
University of Colorado

Project Start/End Dates: October 2010 / September 2014

Objectives: The objective of this work is to investigate the gassing mechanism of $Li_4Ti_5O_{12}$ and to develop advanced technologies to solve this problem.

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

Approach: In-situ x-ray adsorption spectroscopy technique (XAS), specifically XANES, has been applied to observe the Ti valence change during aging at various temperatures. Correlated with previous gas chromatograph data, we can link the valence change of Ti to the H2 evolution. Surface coating through Atomic Layer Deposition shows positive effect in reducing the gassing.

Milestones:
(a.) Self-discharge of the $Li_7Ti_5O_{12}$ during high temperature aging has been linked to gassing evolution. (On schedule)
(b.) Surface coating through atomic layer deposition technique shows positive effect in reducing the gassing. (On schedule)

Financial data: $300K

PROGRESS TOWARD MILESTONES

Gassing mechanism has been further understood through in-situ XANES study of the Ti valence state change during aging at elevated temperatures. The first step is the self-discharge of $Li_7Ti_5O_{12}$, which releases lithium ion and electrons and causes the Ti valence change from Ti^{3+} to Ti^{4+}. Evolution of the gas is the sequent reaction involving the electrons released from the self-discharge. Surface passivation of LTO has been proposed in order to cut off the direct electron transfer pathway through which the electron is shuttled to participate the gassing reaction. Besides additives demonstrated previous, surface coating of LTO particles through atomic layer deposition technique also shows positive effect by reducing gassing.

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

Previously, we have quantified the relation between Ti^{3+} and H_2, Now, we directly witnessed the Ti valence state change during aging at various high temperatures by applying in-situ XANES technique. Fig 1 shows the Ti edge spectra before and after aging at 60°C. The Starting material is lithiated LTO, $Li_7Ti_5O_{12}$.

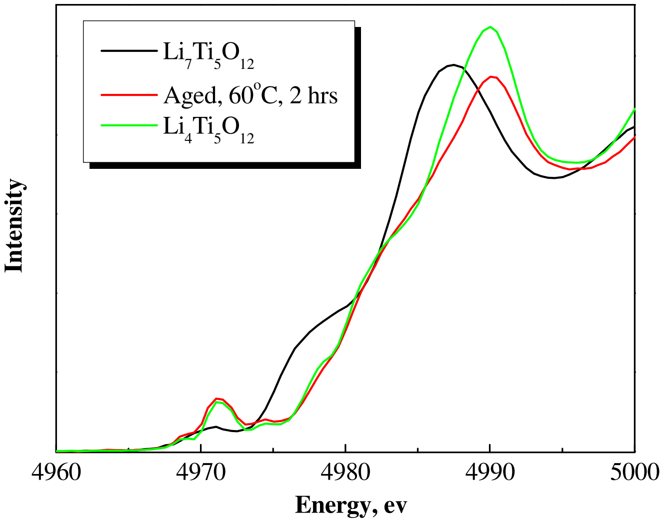
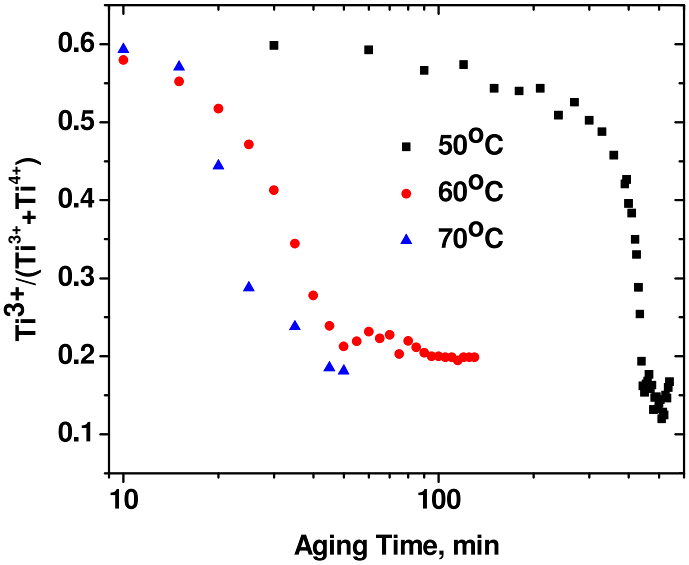


Fig 1 shows the Ti edge shifting when $Li_7Ti_5O_{12}$ was aging at 60°C with electrolyte 1.2M $LiPF_6$ in EC:EMC=3/7. After about 2 hours aging, the valence of Ti is shifted from Ti^{3+} close to Ti^{4+}.

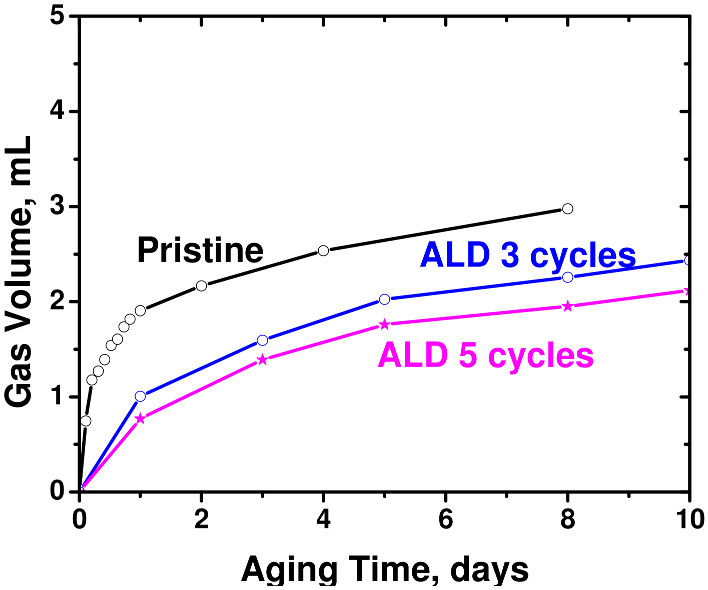
Fig 2 shows the Ti^{3+} concentration change with time at different temperatures. As the temperature increases, the change from Ti^{3+} to Ti^{4+} takes shorter time. Regardless of the temperature, about 15~20% Ti^{3+} remains unchanged at the end of the observation period.



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

Since the charged LTO surface is the place the reaction taking place, passivation of the LTO surface might be able to shut off the reaction pathway. Previously, we demonstrated that certain additives can form effective passivation film on the surface of the LTO electrode, hence to reduce the gas generation.

Fig 3 shows the effect of surface coating through ALD in reducing the gas. With Al_2O_3 coating on the surface of LTO particles, the generated gas volume is reduced. Thicker coating (ALD 5 cycles) shows better improvement than thinner coating (ALD 3 cycles). 100 mAh pouch cells.



Besides that, direct surface coating of the protection film also shows positive effect in reducing gassing. Fig. 3 shows the gas evolution with time. With ALD coated Al_2O_3 on the surface of LTO particles, the generated gas is reduced. Thicker coating (ALD 5 cycles) has better performance in reducing gassing than thinner coating (ALD 3 cycles).

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

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

TASK 1
Battery Cell Materials Development

Project Number: 1.1L (ES113)

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

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

Collaborators (include industry):
Libo Hu, Argonne National Laboratory
Ali Abouimrane, Argonne National Laboratory
Huiming Wu, Argonne National Laboratory
Wei Weng, Argonne National Laboratory
Kevin Gering, Idaho National Laboratory

Project Start/End Dates: October 2010 / September 2014

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

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

Approach: Investigate new none carbonate solvent as high voltage applications. Based on the theoretical calculation, the introduction of electron-withdrawing group will increase the oxidation stability. We will continue the fluorinated carbonate based electrolyte study in the new fiscal year. We will also design and synthesize new solvents to further explore other possibilities for high voltage application. Exploring a hybrid electrolyte made of the mixture of the above solvents is the general approach.

Milestones:
(a.) Material evaluation in the graphite cell system, December, 2012 (Complete)
(b.) New material synthesis and purification, March, 2012 (On schedule)
(c.) Physical properties of the new high voltage electrolyte candidates
(d.) Complete initial evaluation of new candidates using LNMO/LTO and LNMO/Graphite chemistries, September 2012 (On schedule)

Financial data: $300K

PROGRESS TOWARD MILESTONES

(1) Summary of work in the first quarter related to milestone

Fig.1 shows the voltage-specific capacity profiles of the electrode materials used for the testing. To ensure the cell test result consistent, homogeneous LNMO cathode ($LiNi_{0.5}Mn_{1.5}O_4$/Carbon Black/Binder: 84%/8%/8%) and A12 graphite electrode (A12/Carbon Black/Binder: 90%/2%/8%) were provided by a commercial battery company.

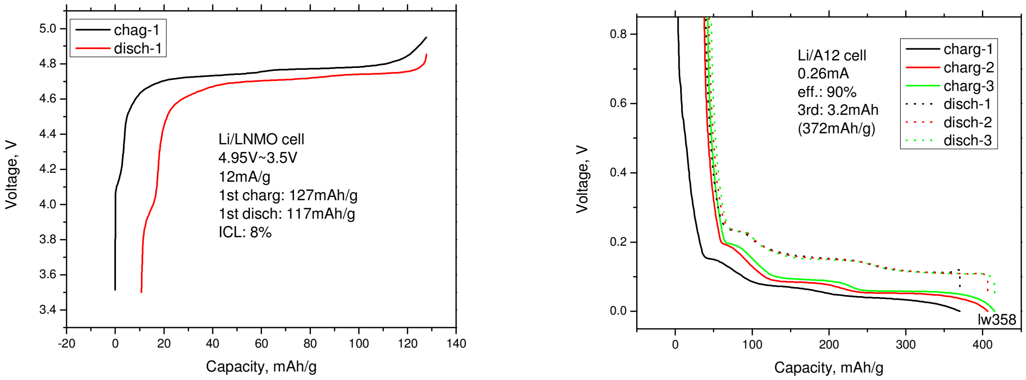
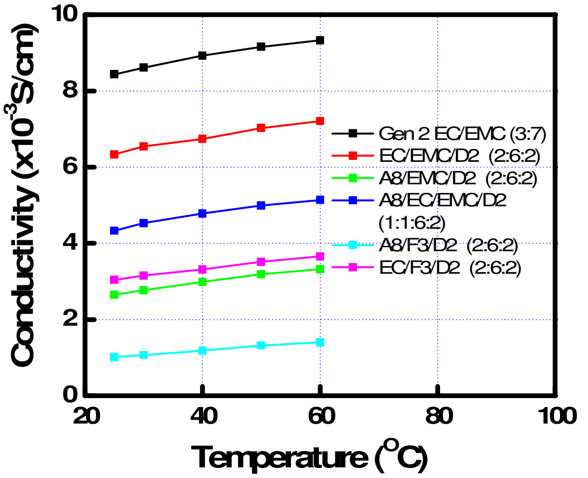


Fig. 1. Voltage profile of the LNMO cathode material (a) and A12 graphite (b).

Five high voltage electrolytes were formulated with Gen 2 EC/EMC (3:7) 1.2 M $LiPF_6$ as baseline for performance comparison. The new electrolyte candidates include EC/EMC/D2 (2:6:2) 1.2 M $LiPF_6$, EC/F3/D2 (2:6:2) 1.2 M $LiPF_6$, A8/EMC/D2 (2:6:2) 1.2 M $LiPF_6$, A8/EC/EMC/D2 (1:1:6:2) 1.2 M $LiPF_6$ and A8/F3/D2 (2:6:2) 1.2 M $LiPF_6$.

Fig.2 shows the ionic conductivity of the new candidates. Compared with Gen2, all the new electrolytes display low conductivities at all the testing temperature indicating the poorer power capability.



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

The fluorinated electrolytes provide excellent compatibility with 5V LNNO and graphite electrode (Fig.3a), which is quite different from the previous studied sulfone-based electrolytes (Q2 report, 2011). It is assumed that EC and A8 (a functionalized EC molecule) is functioning as an effective SEI additive to protect the surface of electrode, especially the graphite anode. The ambient cycling performance (C/10) is shown in Fig.3b. The electrolyte with D2 as part of the formulation showed best performance based on the initial cycles of the test, however all other candidates showed slightly poor performance with all fluorinated electrolyte (the purple line) showing the worst.

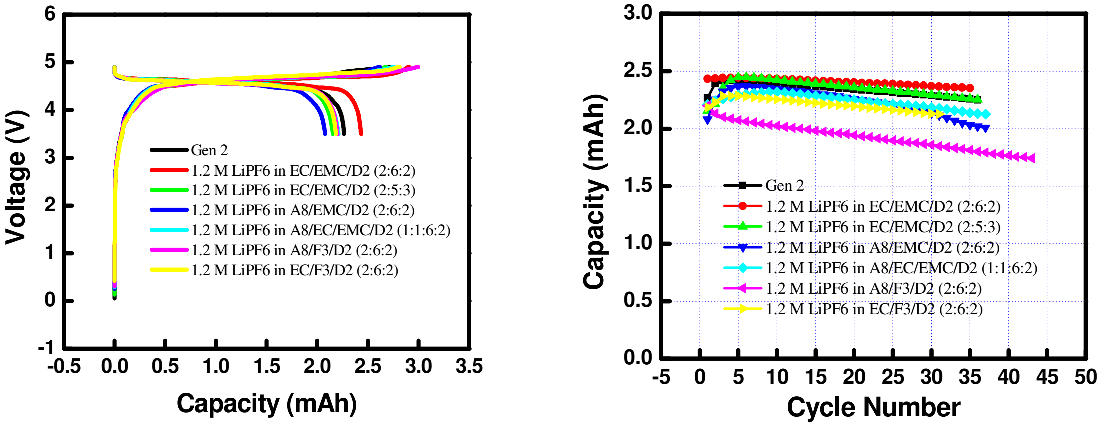


Fig. 3. LNMO/Graphite cell first cycle voltage profiles (a) and the cycling performance using fluorinated electrolytes at room temperature (b) (Room temperature, C/10, cutoff voltage: 3.5-4.9 V).

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

The ambient cycling performance at higher rate (C/3) is shown in Fig.4. As indicated from the conductivity results, all the high voltage electrolyte candidates showed low capacity retention with cycling. The performance is expected to be improved by raising the temperature. We will report the high temperature performance in the next quarter.

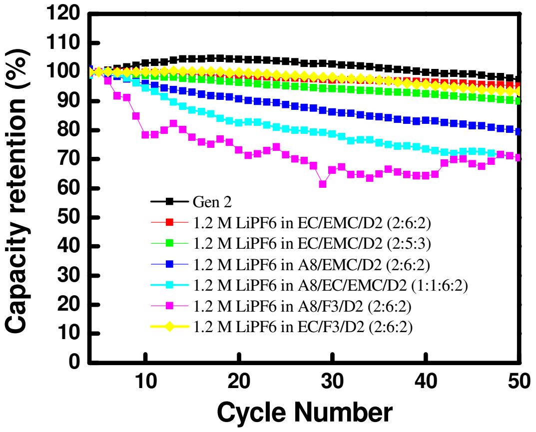


Fig.4. Cycling performance of $LiNi_{0.5}Mn_{1.5}O_4$ /Graphite full cell at room temperature with C/3 rate (Room temperature, C/10, cutoff voltage: 3.5-4.9 V).

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

Hybrid Electrolyte Patent-ANL-IN-09-039
Argonne-Daikin Joint Workshop on High Voltage Electrolyte, Jan. 25, 2011.

TASK 1
Battery Cell Materials Development

Project Number: 1.2D (ES114)

Project Title: High Capacity Composite Carbon Anodes Fabricated by Autogenic Reactions

Project PI, Institution: Vilas G. Pol, Argonne

Collaborators (include industry): Michael M. Thackeray (Co-PI, Argonne), ConocoPhillips, Superior Graphite

Project Start/End Dates: 1 October 2011/30 September 2012

Objectives:
The objectives of this project are to evaluate *high capacity*, spherically-shaped carbon particles, combined with lithium-alloying elements as anode materials for HEVs, PHEVs and EVs and to compare their electrochemical behavior with commercial carbon-composite electrode materials.

Approach:
1) Exploit autogenic reactions to prepare spherical carbon quickly, cost-effectively and reliably;
2) Collaborate with industry to access high-temperature furnaces to increase the graphitic component in spherical carbon;
3) Increase the capacity of the carbon spheres by combining them with lithium alloying elements to form carbon-composite anode materials;
4) Study and compare the electrochemical, chemical, physical and thermal properties of Argonne's carbon-composite products with commercially available carbon-composite materials;
5) Optimize processing conditions and evaluate the electrochemical properties of pristine and carbon-composite materials in collaboration with industry;

Milestones:
(a) Consolidate industrial collaboration for this project (January 2012);
(b) Prepare carbon samples for industrial partner for heat-treatment; prepare carbon-composite samples from Argonne's carbon materials and from industrial products (April 2012);
(c) Evaluate and optimize the electrochemical properties of carbon-composite samples in lithium half cells and full cells (September 2012);
(d) Determine the chemical, physical and thermal properties of Argonne's carbon-composite anodes with commercial carbon-composite materials (September 2012);

Financial data: $300K/year

PROGRESS TOWARD MILESTONES

Milestone (a). Consolidate industrial collaboration for this project

The initial project on autogenically-prepared carbon materials was funded by the EFRC; invention reports and patent applications were filed through this funding. This project was subsequently extended to ABR to explore the feasibility of exploiting these materials in practical lithium-ion cells, which resulted in collaboration with two industrial partners, Superior Graphite and ConocoPhillips. NDA agreements have been signed with both companies. The initial purpose of these interactions was to obtain access to high temperature furnaces in order to heat Argonne's carbon products to extremely high temperatures (2400-2850 °C) under inert conditions to increase the graphitic component in the materials. A preliminary investigation of these pure spherical carbon electrodes is now complete; they typically offer a stable rechargeable capacity of 250 mAh/g. To increase the electrode capacity, Argonne's carbon-sphere products are now being combined with lithium alloying elements to form composite materials that offer a higher theoretical capacity than graphite (372 mAh/g). Based on recent promising results, collaborations with industry are being expanded to include the electrochemical evaluation of Argonne's technology as it pertains to carbon spheres and industry-fabricated carbon products for lithium-ion batteries and other applications.

Milestone (b). Prepare carbon samples for industrial partner for heat-treatment; prepare carbon-composite samples from Argonne's carbon materials and from industrial products

Autogenically-fabricated spherical carbon samples are being made on a regular basis and are being sent to industrial partners for heat-treatment. Without scale-up facilities, spherical carbon samples are restricted to about a one gram batch size. Samples are in the process of being heated to slightly higher temperatures (>2800 °C) and for longer dwell times (>1 hr) than in the past to monitor these parameters against electrochemical performance. The heated-treated samples are subsequently combined by a proprietary process with lithium alloying elements to form carbon-composite materials to increase the reversible capacity of the electrodes above the theoretical value of graphite, with an initial target of 500 mAh/g. Early results indicate that with the addition of approximately 10% of a lithium alloying element to the carbon spheres, a stable rechargeable capacity in excess of 400 mAh/g can be obtained in lithium half-cells. Commercial carbon products are being sent to Argonne for treatment with lithium alloying elements and comparative electrochemical evaluations.

Milestone (c). Evaluate and optimize the electrochemical properties of carbon composite samples in lithium half cells and full cells

The electrochemical properties of carbon sphere electrodes (heat treated by ConocoPhillips at 2800 ^{o}C/1h) were evaluated in lithium-ion full cells against an Argonne high-capacity $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$) counter electrode.

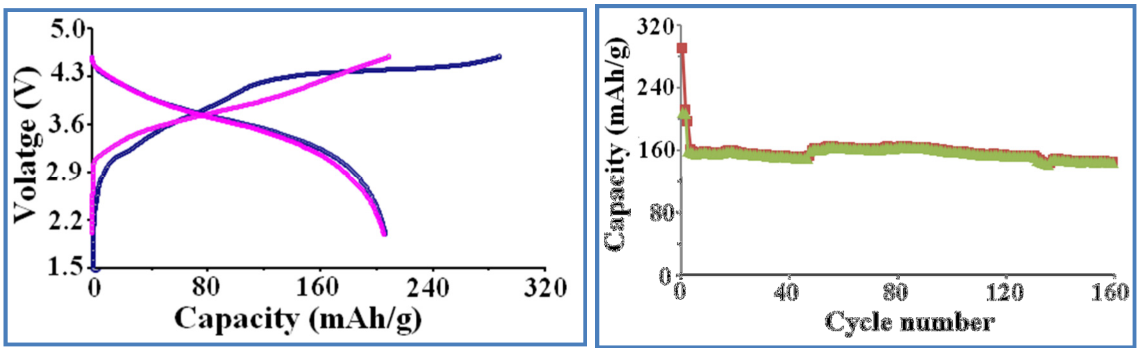


Figure 1. First and second charge-discharge profiles (left) and cathode capacity vs. cycle number plot (right) of a lithium-ion cell with a heat-treated (2800 ºC) carbon sphere anode and a $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$ cathode between 4.6 and 2.0 V at a C/3 rate.

The initial two discharge/charge curves of a cathode-limited lithium-ion cell with a carbon sphere anode and a $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$ cathode, cycled between 4.6 and 2.0 V at a constant current density of 100 mA/g (~C/3 rate), as well as a corresponding capacity vs. cycle number plot, are provided in Figure 1. When charged above 4.6 V, a process that activates the Li_2MnO_3 component by Li_2O extraction and leaves an electrochemically-active MnO_2 component within the cathode structure, very high capacities (>200 mAh/g) can be delivered by the cathode. The electrochemical profile in Figure 1 (left panel) demonstrates that the lithium ions extracted from the $LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$ and Li_2MnO_3 components of the cathode above ~2.9 V and ~4.2 V, respectively, are intercalated into the carbon sphere anode during the initial charge; the large irreversible capacity loss on the first cycle is attributed predominantly to the electrochemical activation of the Li_2MnO_3 component of the cathode**.** Figure 1 (right panel) indicates that approximately 160 mAh/g is delivered reversibly by the cathode for more than 100 cycles, reflecting the excellent cycling stability of the carbon spheres in a full lithium-ion cell configuration. Efforts to optimize electrode thickness and cell balancing are in progress.

Milestone (d). Determine the chemical, physical and thermal properties of Argonne's carbon-composite anodes with commercial carbon-composite materials

The analytical details of the structural, chemical, morphological and thermal properties of Argonne's carbon-composite anodes are currently being used for patent applications, not yet filed; these data will be presented in a subsequent report.

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

None to date. (Note: An invention report and a subsequent patent application on the concept of using autogenically-prepared carbon and carbon-composite materials as an anode for lithium batteries were filed with EFRC funding prior to this ABR project.)

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):
Michael Slater, Argonne National Laboratory
Donghan Kim, Argonne National Laboratory
Shawn Rood, Argonne National Laboratory
Eungje Lee, Argonne National Laboratory
Wenquan Lu, Argonne National Laboratory
Stephen Hackney. Michigan Technological University

Project Start/End Dates: October 2010 / September 2016

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

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

Milestones: Materials will be produced and tested that will show progressively improved properties as the project moves forward.
(a) Synthesize new materials, September 2011, (completed)
- Optimize ion-exchange reaction conditions, February 2012 (on-going)

(b) Characterize electrochemical properties of synthesized materials, March 2012, (on-schedule)
- Demonstrate high-rate of 205 mAh/g @ 2C rate, March 2012, (on-schedule)

(c) Characterize structure of materials, February 2012, (on-going)
- Examine morphology of starting materials, and ion-exchange products, June 2012, (on-schedule)

(d) Continue optimization of Na, Li and transition metal content ratios in materials, September 2012, (on-schedule)
(e) Initiate measurement of thermal properties of charged cathode materials that have been compositionally optimized using DSC, September 2012, (on-schedule)

Financial data: \$500K; \$50K subcontracted to Prof. S. Hackney (Michigan Technological University)

PROGRESS TOWARD MILESTONES

(a) Optimization of Li ion-exchange reaction conditions for a set composition of the precursor ($Na_{1.0}Li_{0.2}(Ni_{0.25}Mn_{0.75})O_y$) material is continuing. Solvents tried were methanol, ethanol, and water. Methanol in combination with a two-fold excess of LiBr appears to be the best solvent/salt composition for maximizing capacity of the resultant product when measured as a cathode in Li cells. In addition, we found that a post-anneal temperature of 550 °C leads to the most favorable electrochemical response. The water route also has advantages of cost, simpler manufacturing scale-up, and is more green synthesis process, but the electrochemical performance is slightly worse and the variability from batch to batch is more significant. Work is ongoing to improve this process. In addition, we are starting to eliminate Li from the pre-ion exchange precursor as a means to create compositions that are Li free prior to exchange. The concern is to avoid spinel formation in the IE products

We believe, however, that ultimately an ion-exchange process from a Na-precursor layered oxide could be superior to the direct Li route high-temperature reaction for large scale manufacturing since the content of Li in the product is critical and must be controlled for desirable electrochemical performance. Even a 5% variation in Li/TM ratio can drastically change the product characteristics. Therefore, using the ion-exchange process with Na allows us to scale-up very easily because the content of Na is easily controlled in a large batch due to negligible Na_2CO_3 evaporation, contrasted to easy Li_2CO_3 loss at high temperatures of 800 °C. The second step in the IE process is a wet step whereby the Li content can be precisely controlled. The anneal step makes favorable products at low temperatures below 550 °C, where Li has a low vapor pressure.

(b) 1C rate of > 205 mAh/g is consistent even with various compositions. We are striving more a material with a 2C of 200 mAh/g. However, the water ion-exchanged sample initially showed high 235 mAh/g at high rate 0.5C – 1C, but with cycling, fade occurs and so the inferior electrochemistry may likely be due to proton for lithium exchange and formation of a product phase that blocks Li diffusion.

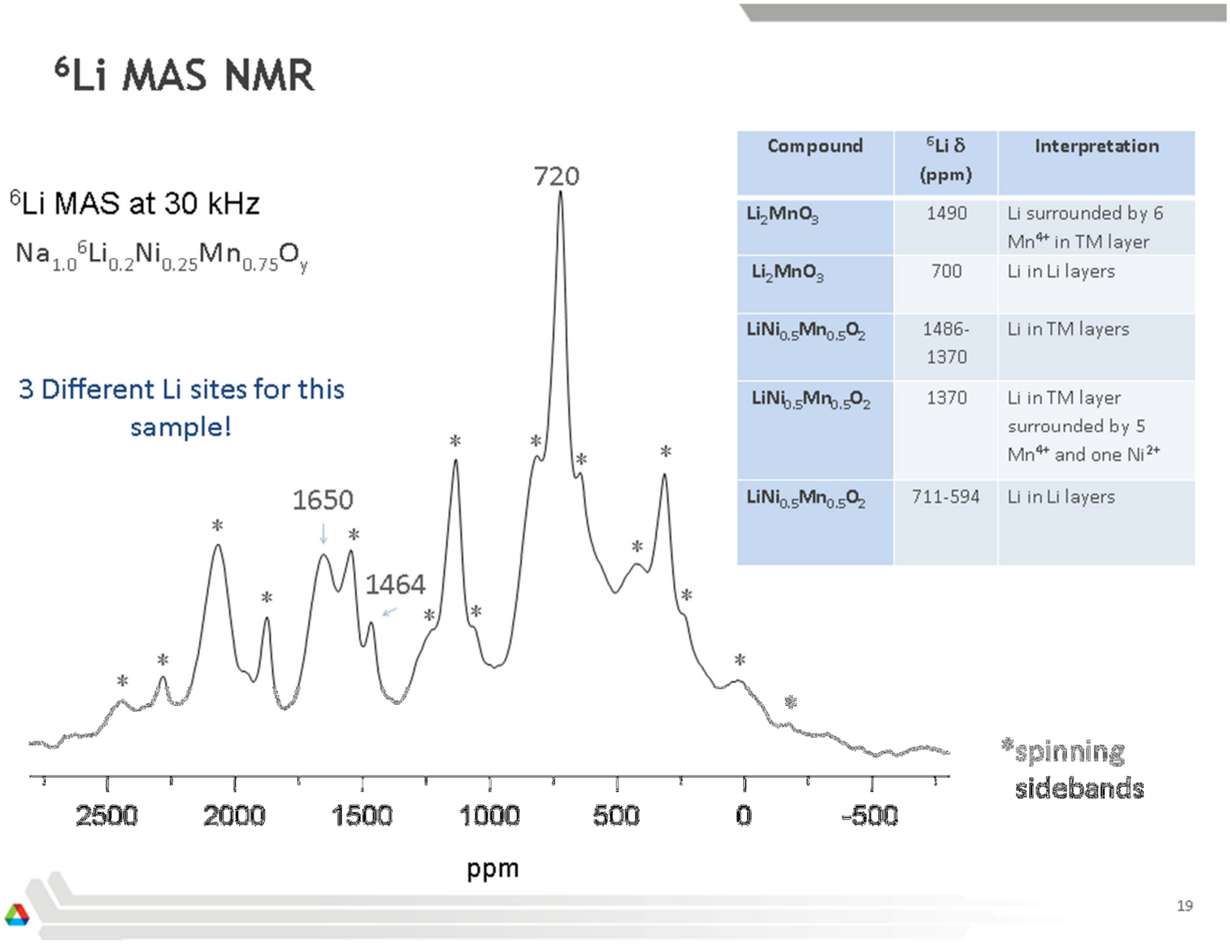
(c) Solid-state ^{6}Li-NMR (Fig. 1) on IE of $Na_{1.0}Li_{0.2}(Ni_{0.25}Mn_{0.75})O_y$ precursors (i.e. $Na_{0.02}Li_{1.17}Ni_{0.24}Mn_{0.75}O_y$) indicates that there are 3 different sites for Li cations in the IE product. We now believe that there is Li in the layered TM layer, Li in a Li_2MnO_3-like environment, and Li in a third environment which has not yet been identified.

(d) The Mn/Ni ratio continues to be varied; we are working on $Na(Ni_{0.5}Mn_{0.5})O_2$ type precursor phase now with and without Li in the material. This will be reported in the next quarter.

(e) Thermal properties of the charged materials in milestone (a) are on-going. Coatings may be evaluated in this task since they are known to belay the heat output.

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

"High Performance Oxide Cathodes for Li-ion Batteries" Oral presentation, Michael Slater, Aaron DeWahl, Donghan Kim[1], Shawn Rood, Sun-Ho Kang, Stephen Hackney, Christopher Johnson, 220th Electrochemical Society Meeting, Boston, MA, October 10-14, 2011.



^{6}Li MAS NMR

Compound	^{6}Li δ (ppm)	Interpretation
Li_2MnO_3	1490	Li surrounded by 6 Mn^{4+} in TM layer
Li_2MnO_3	700	Li in Li layers
$LiNi_{0.5}Mn_{0.5}O_2$	1486-1370	Li in TM layers
$LiNi_{0.5}Mn_{0.5}O_2$	1370	Li in TM layer surrounded by 5 Mn^{4+} and one Ni^{2+}
$LiNi_{0.5}Mn_{0.5}O_2$	711-594	Li in Li layers

Fig. 1. Solid state Li-6 NMR on Li IE material derived from $Na_{1.0}Li_{0.2}Ni_{0.25}Mn_{0.75}O_y$ precursor. Nominal stoichiometry of this material is $Na_{0.02}Li_{1.17}Ni_{0.24}Mn_{0.75}O_y$.

TASK 1
Battery Cell Materials Development

Project Number: ES038

Project Title: High Energy Density Ultracapacitors

Project PI, Institution: Patricia Smith, NAVSEA-Carderock

Collaborators: Thanh Tran and Thomas Jiang (NAVSEA-Carderock), Michael Wartelsky (SAIC), Steven Dallek (Spectrum Technologies), Deyang Qu (University of Mass., Boston), and Jae Sik Chung (PC Test)

Project Start/End Dates: FY09 to FY12

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

Approach:

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

Milestones:

(a) Safety and performance evaluation of 1st generation LIC cell technology (March 2011). Status: Complete
(b) Identification of negative electrode material that exhibits high reversible capacity, high power capability, and good low temperature performance. (September 2012). Status: Initiated
(c) Identification of high-performance, low-temperature electrolyte (July 2011). Status: Complete
(d) Safety and performance evaluation of 2nd generation LIC cell technology (September 2011). Status: Complete

Financial Data: Project budget/year, amount subcontracted if appropriate
Funding Expensed 3Q FY11: $107,527.00

Progress Toward Milestones:

The safety evaluation of second generation LIC capacitor was completed. A manuscript describing the safety and performance characteristics of LIC cells and their comparison to EDLCs and LIBs is being written and will be submitted to the Journal of Power Sources. During this period, ARC experiments were conducted on a 100% state-of-charge 2,000 F EDLC and 2.4 Ah LIB to measure the thermal-runaway characteristics. This compliments our previous study of 2,000 F LICs (last quarter). Figure 1 shows the ARC data from a 2,000 F EDLC cell. In comparison to the LIC experiment, no exothermic reactions were observed with the EDLC cell. At 170°C the cell vented benignly. The thermal behavior of the LIB cell (Figure 2) was similar to the LIC cell; both cells underwent self-heating and vented. The LIB and LIC showed an increase in temperature at 100°C to 120°C which is consistent with the negative electrode SEI decomposition. DSC experiments show that at higher temperatures, the lithiated carbon reacts with the electrolyte. Unlike the LIC however, the LIB contains a faradaic electrode material and exothermic reactions involving the cathode can occur at temperatures greater than 200°C. This difference may contribute to the significant temperature rise observed in the LIB cell (> 1000°C/min) in comparison to the LIC (120 °C/min).

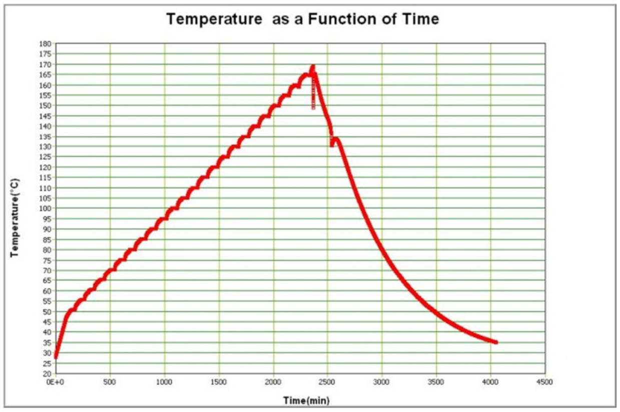


Figure 1. Results of ARC experiment conducted on a 2,000F electrochemical double layer capacitor. Calorimeter/EDLC temperature profile.

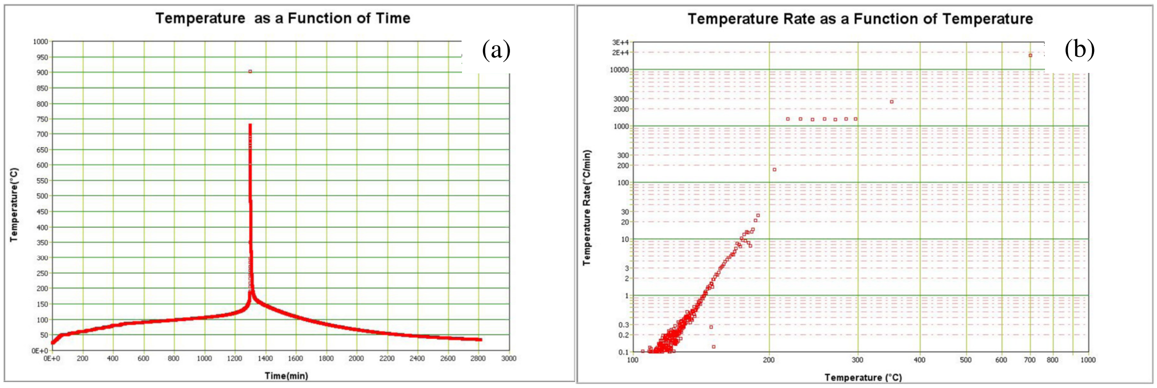


Figure 2. Results of ARC experiment conducted on a 2.4 Ah lithium-ion battery, (a) Calorimeter/LIB temperature profile, (b) LIB self-heating rate profile.

Self-discharge experiments were conducted on experimental 1,000 F LIC cells containing two different electrolytes (JM Energy Gen- 1 and Gen- 2), a 2,000 F EDLC cell (Maxwell Technologies and 2.37 Ah LIB cell (Moli Energy) at various temperatures. Voltage decay is expected to be greater for an EDLC and LIC than for a LIB because they contain high surface-area carbon electrodes that can more effectively oxidize the electrolyte. Table I shows the percentage of the cell voltage drop over 3 days. The cells were charged at a 0.5 C rate to the manufacturer's recommended charge voltage (LIC: 3.8V, LIB: 3.9V, EDLC: 2.4V) at which time the cell was held at OCV for a period of 3 days. The OCVs of EDL and LIC cells stabilized quickly while the LIB cell required approximately 30 minutes to stabilize. The data reported in Table I was calculated after the OCV had stabilized. Voltage decay was lowest for the LIB as expected. When cells were held at open circuit for 7 days at room temperature then discharged at the manufacturer's recommended rate, EDLCs delivered 89% of its initial capacity, LIC Gen-1 and Gen-2 had 90 and 91% capacity remaining, while the LIB had 98% of its initial capacity.

Table I. 3-Day Self Discharge Characteristics of Electrochemical Cells

	% Voltage Drop ($V_{30\,min}$ to V_{72h})			
Temp (^oC)	EDLC	LIC-Gen 1	LIC-Gen 2	LIB
-20	0.4	1	1	0.2
RT	2	2	2	0.4
40	6	1	1	0.1
60	6	2	2	0.2

Investigations continued to identify electrolyte formulations that promote both good low-temperature discharge and cycle-life performance. One carbonate electrolyte was shown to yield higher half-cell capacities than the 1st generation electrolyte as shown in Figure 3. This completes our half-cell low temperature electrolyte experiments. Future efforts will focus on assessing the new electrolyte in full cells.

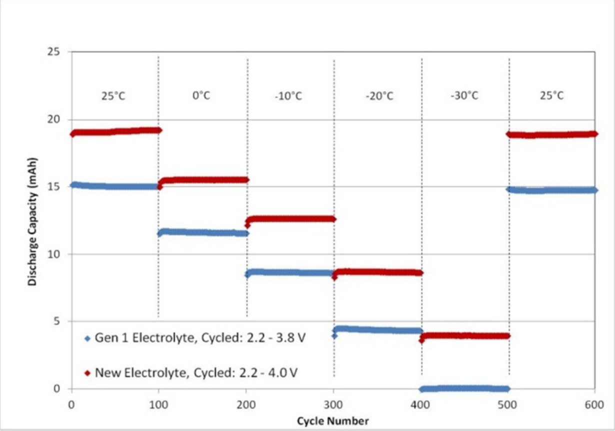


Figure 3. Effect of electrolytes on the discharge capacity of a lithiated, negative electrode.

Investigations were initiated to identify negative electrode materials that exhibit high reversible capacity, high power capability, and good low temperature performance. Two mildly-graphitized, activated-carbons are presently being evaluated. Experiments are also being conducted using stabilized lithium metal powder (SLMP) as a method to pre-dope the negative electrode. The SLMP process is an alternative to the sacrificial, lithium electrode presently used by manufacturers. This process should allow improved manufacturability.

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

P. Smith, T. Tran, and T. Jiang, M. Wartelsky, G. Zoski, “The Effect of Temperature on Capacity and Power in Cycled Lithium Ion Capacitors”, Electrochemical Society Meeting, October 9-14 2011, Boston, Mass.

G. Gourdin, P. Smith, T. Jiang, T. Tran, and D. Qu, “Lithiation of Anode for Lithium Ion Capacitor”, Electrochemical Society Meeting, October 9-14 2011, Boston, Mass.

P. Smith, T. Tran, and T. Jiang, “Lithium Ion Capacitors: Electrochemical Performance and Thermal Behavior” at the 21st International Seminar on Double Layer Capacitors and Hybrid Energy Storage Devices, 5-8 December 2011, Deerfield Beach, FL.

TASK 1
Battery Cell Materials Development

Project Number: 1.1Y

Project Title: Transition Metal Precursors for High Capacity Cathode Materials

Project PI, Institution: Ilias Belharouak, Argonne National Laboratory

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

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

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

Approach: Carbonate is developed to prepare the precursors that will serve to produce high capacity cathode materials $Li_{1+t}(Ni_xCo_yMn_z)_{1-t}O_2$ ($t \geq 0$, $x+y+z=1$). A comparative study using the three routes (carbonate, hydroxide, and oxalate) will be made at the level of the materials morphology, physical characteristics, and electrochemical properties.

Milestones:

a) Synthesis of ($Ni_{0.25}Mn_{0.75}CO_3$) carbonate precursor using a continuous stirred tank reactor (CSTR) continued. (Completed).
b) Structural, physical, and chemical characterizations of ($Ni_{0.25}Mn_{0.75}CO_3$). (Completed).
c) The electrochemical performance of the final lithiated cathode materials is investigated (On schedule).

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

PROGRESS TOWARD MILESTONES

Carbonate co-precipitation by the CSTR method was employed to prepare precursor materials that can be used to produce large quantities of cathode materials for lithium-ion batteries. Because of the continuous stirring in this method, the carbonate precursor particles formed and trapped within the reactor walls can undergo significant growth, as outlined in our previous work.17 In our experimental setup, the precursor Ni0.25Mn0.75CO3 was continuously collected for 7 hours after the solution reached steady state.

The XRD pattern of the collected precursor $Ni_{0.25}Mn_{0.75}CO_3$ is shown in Fig. 1. The material was a single phase and could be indexed based on the space group (R3c) of $MnCO_3$. Despite the broadness of the diffraction peaks, which was previously attributed to the small grain size of the primary particles, the structure of $(Ni_{0.25}Mn_{0.75})CO_3$ is a derivative of the structure of $MnCO_3$, where a part of the manganese is replaced by nickel within the carbonate matrix.

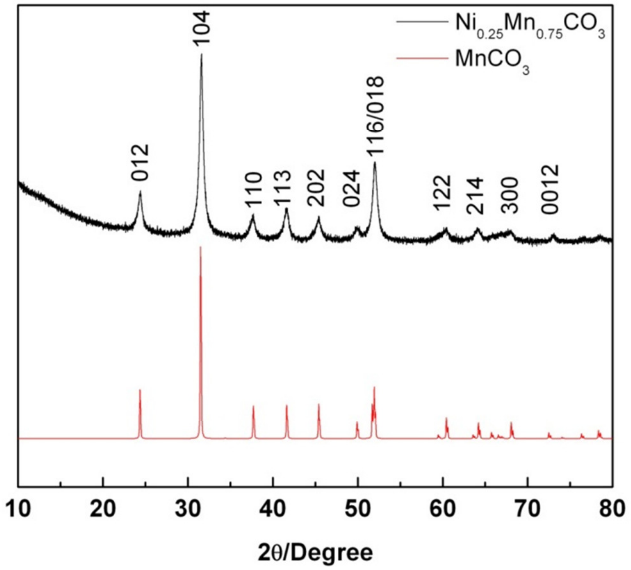


Fig. 1. X-ray diffraction pattern of the synthesized carbonate precursor

The morphology and particle size distribution of $(Ni_{0.25}Mn_{0.75})CO_3$ are shown in Fig. 2. The particles, in general, seemed to be dense and spherical with smooth surfaces. They had sizes however, ranging from 15 to 50 µm. The particle size distribution measured by laser diffraction primarily exhibited a broad and symmetric peak centered at 30 µm (inset in Fig. 2). We anticipate that the particles above 20 µm would neither be suitable for electrode fabrication nor yield high electrochemical performance. However, particle size fluctuation is expected in the synthesis of large quantities of materials. Attaining more consistent size distribution, whether by engineering controls or particle size selection, would be detrimental to promoting the electrochemical properties. The surface area of the particles determined by the BET method was 150 m^2/g, indicating that the particles had a high porosity despite the dense appearance. This finding confirmed that the particles were porous secondary agglomerates made of nanosize primary particles. On the one hand, the high porosity could improve lithium diffusion if cathodes synthesized by these precursors retained their porous character. On the other hand, the high specific surface area renders the precursor particles vulnerable to moisture. For this reason, special care with regard to precursor drying and storage was taken to avoid fluctuation from batch to batch. To be specific, the as-prepared precursor particles were dried at 120°C under vacuum for 12 hours and then were stored in a controlled-environment sealed box.

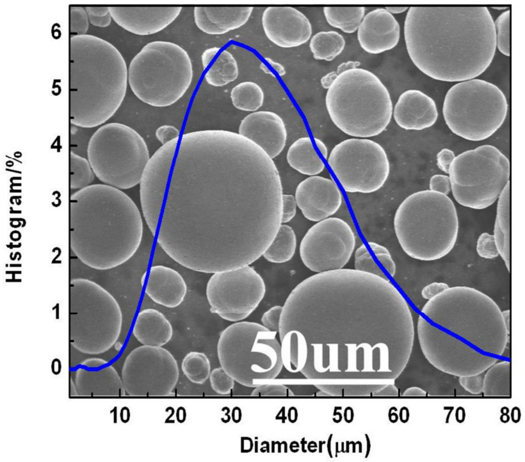


Fig. 2. Particle size distribution superimposed on SEM image of synthesized carbonate precursor

We used a TGA apparatus coupled with MS-FTIR systems to characterize the precursor materials during their thermal decomposition from room temperature to 950°C. Figure 3 assembles the TGA curve (Fig.3a), TGA first-derivative curve (Fig. 3b), CO_2-evolution MS curve (Fig. 3c), and CO_2-evolution FTIR curve collected at a wavenumber of 2350 cm^{-1} (Fig. 3d) for the $Ni_{0.25}Mn_{0.75}CO_3$ precursor. The TGA first derivatives were plotted to study thermal phenomena that may not be easily detectible in the TGA curve. These experiments were conducted under a high-purity dry nitrogen atmosphere. Purchased $MnCO_3$ and $NiCO_3 \cdot xH_2O$ (only nickel carbonate form available) were also subjected to these experiments for the purpose of comparison.

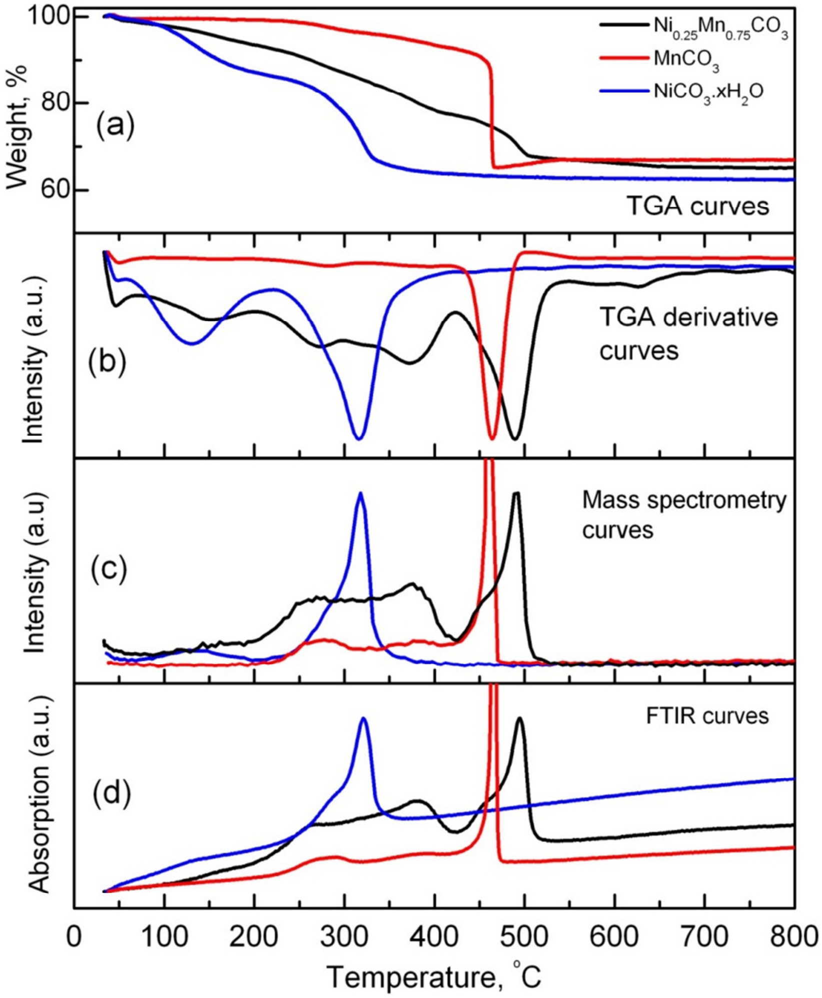


Fig. 3. TGA-MS-FTIR results for precursor materials during thermal decomposition from room temperature to 950 °C.

The TGA curves (Figs. 3a and 3b) indicated that $MnCO_3$ had an abrupt overall weight loss of 35% at 465 ^{0}C, which is associated with the loss of CO_2 to yield MnO and possibly some Mn_2O_3 due to the partial oxidation of MnO. The curves for $NiCO_3{\cdot}xH_2O$ had mainly two thermal events: one that occurred between room temperature and 220°C with a maximum at 130°C, and the other, between 220 and 450°C with a maximum at 315°C (Figs. 3a and 3b). These events were attributed primarily to the loss of water and CO_2, respectively. However, the MS and FTIR curves (Figs. 3c and 3d) of $NiCO_3{\cdot}xH_2O$ revealed a positive CO_2 uptake starting at 100°C. This shift signifies that along with the removal of adsorbed water, some CO_2 species were removed as well. The same observation can be made for $MnCO_3$, whose thermal decomposition started at much lower temperature, 230°C, and resulted in CO_2 evolution, as is evident from Fig. 3c. These results amplify the usefulness of the MS tool because we could clearly observe CO_2 gas produced at very low temperatures, which was not detected with TGA only.

The TGA curve of $Ni_{0.25}Mn_{0.75}CO_3$ has several complex thermal features starting at around 100°C and indicates 34 wt.% weight loss at 630°C (Fig. 3a). Despite the complexity, the TGA features of $Ni_{0.25}Mn_{0.75}CO_3$ include all the TGA features observed for both $NiCO_3 \cdot xH_2O$ and $MnCO_3$ but with some temperature shifts (Figs. 3b, 3c, and 3d). We mainly noted that $Ni_{0.25}Mn_{0.75}CO_3$ had positive MS and FTIR signals for CO_2 starting at around 100°C, as was also observed for $NiCO_3 \cdot xH_2O$. At this low temperature, water removal could be also possible, although the material had been dried for 12 hours in a vacuum oven, and a positive MS signal for H_2O was not obtained. In our previous paper, we demonstrated that the growth of manganese and nickel carbonate precursors begins with nickel hydroxide seed particles. In general, the earlier thermal phenomena noted for $Ni_{0.25}Mn_{0.75}CO_3$ resemble those noted for $NiCO_3 \cdot xH_2O$, and the later phenomena resemble those observed for $MnCO_3$. In a perfect solid solution of $Ni_{0.25}Mn_{0.75}CO_3$, where nickel is randomly distributed within the manganese carbonate structure, the thermal behavior of $Ni_{0.25}Mn_{0.75}CO_3$ would mainly incorporate the thermal behavior of $MnCO_3$. However, the decomposition of $Ni_{0.25}Mn_{0.75}CO_3$ at low temperature was quite similar to that of $NiCO_3 \cdot xH_2O$. Therefore, even though XRD showed that $Ni_{0.25}Mn_{0.75}CO_3$ had a strong analogy with $MnCO_3$, the real structure of this compound could actually contain a structural feature derivative of $NiCO_3 \cdot xH_2O$.

Next, we mixed $Ni_{0.25}Mn_{0.75}CO_3$ with carbonate and calcined the mixture at 900°C to prepare $Li_{1.42}Ni_{0.25}Mn_{0.75}O_{2+\gamma}$. The as-prepared material had a low specific capacity of only 155 mAh/g, which could be due to the wide particle size distribution that the material preserved from the precursor (Figs. 4a and 4e). To investigate this matter, we classified the $Li_{1.42}Ni_{0.25}Mn_{0.75}O_{2+\gamma}$ secondary particles into three size groups by sieving the as-prepared material: below 20 μm, between 20 μm and 38 μm, and above 38 μm. The morphology and particle size distributions of the $Li_{1.42}Ni_{0.25}Mn_{0.75}O_{2+\gamma}$ before and after sieving are shown in Fig. 4. Before sieving, the cathode material had a wide particle size distribution, with a peak centered at 30 μm (Fig. 4e), similar to $Ni_{0.25}Mn_{0.75}CO_3$. Figure 4f plots the three particle size distributions, which are centered at 15 μm (red solid line), 25 μm (blue solid line), and 40 μm (green solid line), respectively.

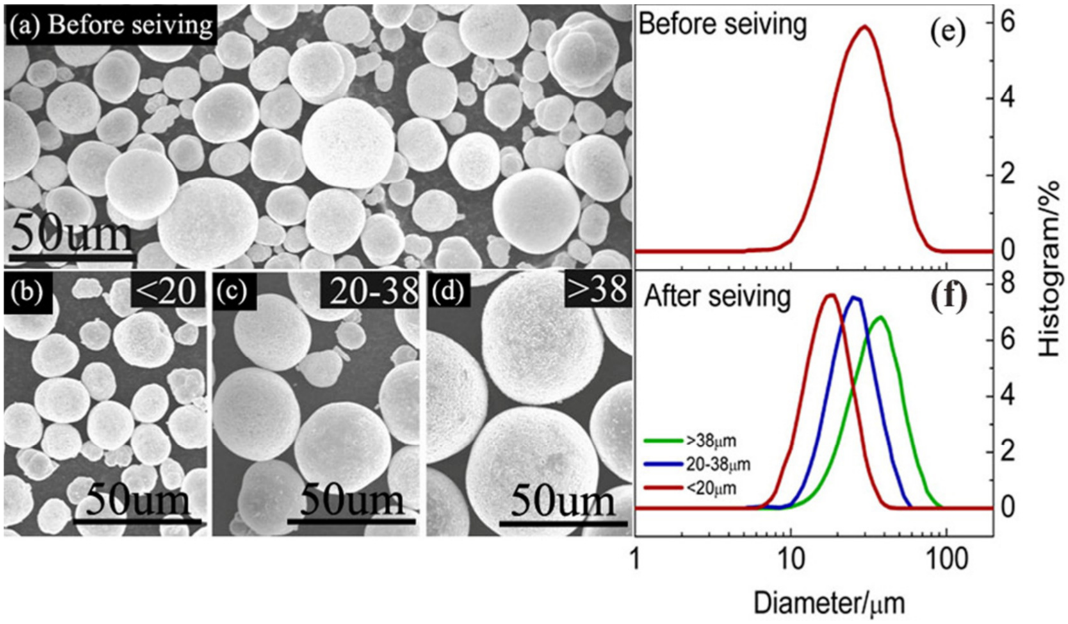


Fig. 4. Cathode morphologies and particle size distributions before and after sieving

In the next report, we will report on the continuation of this study and the electrochemical properties of the lithiated compounds.

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

Chemistry and Electrochemistry of Concentric Ring Cathode Materials for Lithium Batteries
Dapeng Wang, ILias Belharouak, Sabine Gallagher, Guangwen Zhou,
and Khalil Amine
Submitted to Journal of Materials Chemistry

TASK 1
Battery Cell Materials Development

Project Number: FY12 New Start

Project Title: Overcoming Processing Cost Barriers of High Performance Lithium Ion Battery Electrodes

Project PI, Institution: David Wood, Oak Ridge National Laboratory

Collaborators: Argonne National Laboratory, Sandia National Laboratories

Project Start/End Dates: 10/1/11 to 9/30/12

Objectives: Electrode suspensions for lithium ion batteries are currently formulated using expensive polyvinylidine fluoride (PVDF) binder and toxic, flammable n-methylpyrrolidone (NMP) solvent. It is desirable to replace these components with water and water-soluble binders, but methods of mass production of these suspensions are currently underdeveloped. The major problems with aqueous electrode dispersions are: 1) agglomeration of active phase particles and conductive carbon additive; 2) poor wetting of the dispersion to the current collector substrate; and 3) cracking of the electrode coating during drying. NMP based processing also has the inherent disadvantages of high solvent cost and the requirement that the solvent be recovered or recycled. Initial projections of the minimum cost savings associated with changing to water and water-soluble binder are 70-75%, or a reduction from $0.210/Ah to $0.055/Ah. The objective of this project is to transform lithium ion battery electrode manufacturing with the reduction or elimination of costly, toxic organic-solvents.

Approach: Fabrication of composite electrodes via organic (baseline) and aqueous suspensions will be completed. A focus will be placed on the effect of processing parameters and agglomerate size on the aqueous route cell performance and microstructure of the composite electrode. Several active anode graphite and cathode (NMC, $LiFePO_4$, etc.) materials will be selected with various water-soluble binders. The conductive carbon additive will be held constant. Rheological (viscosity) and colloidal (zeta potential) properties of the suspensions with and without dispersant will be measured with a focus on minimization of agglomerate size. These measurements will show the effects of agglomerate size and mixing methodology on suspension rheology and help determine the stability (i.e. ion exchange processes across the surfaces of various crystal structures) of active materials in the presence of water. Composite electrodes will be made by tape casting and slot-die coating, and the drying kinetics of the electrodes will be measured by monitoring the weight loss as a function of time and temperature. Solvent transport during drying will also be monitored as a method to control electrode morphology, porosity, and tortuosity. Electrode microstructure and surface chemistry will be characterized and correlated with cell performance. Electrochemical performance of electrode coatings made from the various suspensions will be supplied to ORNL's strategic industrial partners for external validation in large cell formats.

Improved cell performance with reduced processing and raw material cost will be demonstrated using pilot-scale coatings. At ORNL coin cells will be tested and evaluated for irreversible capacity loss, AC impedance, capacity vs. charge and discharge rates, and long-term behavior through at least 500 charge-discharge cycles. Half cells, coin cells, and pouch cells will be constructed and evaluated. The coin cells will be used for screening and coarse evaluation of different suspension chemistries and coating methodologies. A fine tuning of these research areas will be completed using ORNL pouch cells and large format cells with ORNL's industrial partners. Electrode coatings will be produced on the ORNL slot-die coater and supplied in roll form to the industrial partners for assembly into large format cells.

Electrode morphology will be characterized by scanning electron microscopy (SEM) and TEM. The bulk structure and surface of the active materials will be characterized using XRD and XPS, respectively. In addition, in-situ TEM will be performed to investigate real-time SEI layer formation as a function of the different suspension chemistries.

Milestones:

a) Development of an aqueous formulation for cathodes (March 2012); on schedule.
b) Development of an aqueous formulation for anodes (May 2012); on schedule.
c) Coating technique and drying protocol for anodes and cathodes (July 2012); on schedule.
d) Development of porosity control in thin electrodes (September 2012); on schedule.
e) Match cell performance in terms of initial capacity, irreversible capacity loss, and cyclability through 100 cycles of aqueous suspension and water-soluble binder to NMP/PVDF based suspensions (Sept. 2012); on schedule.

Financial data: $300k/year for FY12

PROGRESS TOWARD MILESTONES

Summary of work in the past quarter related to milestone (a).
The Toda NCM 523 baseline material has not yet been received from ANL/SNL, so wrok has continued to focus on $LiFePO_4$ based electrodes. However, the work performed last quarter is generally applicable to any water based cathode dispersion. Figure 1 shows the surface energy data for a $LiFePO_4$ cathode dispersion with poly(ethyleneimine) (PEI), which is added to reduce agglomeration of the active and conductive additive particles, and for various Al foil surfaces with and without corona treatment. It is seen that the surface energy of the electrode dispersion is well above that of the untreated Al foil (62.9 vs. 47.9 mJ/m^2). This situation results in poor wetting of the dispersion to the current collector foil, but the data in Figure 1 shows that corona treatment conditions of $\geq$0.4 J/cm^2 raise the surface energy of the foil above the surface energy of the dispersion, which is the condition required for good wetting. Corresponding half cell performance

data is shown in Figure 2 for the different surface treatment energy densities. An optimum energy density of 0.4 J/cm^2 was found, and cells with corona treatment (regardless of energy density) significantly outperformed the cell with no corona treatment. It is thought that the optimum value of 0.4 J/cm^2 results from sufficiently cleaning the surface of adsorbed hydrocarbons and subsequent hydroxylating, but falls short of possible restructuring of the surface at much higher energy densities. This restructuring could result in significant roughening and formation of pits and voids, which would lower the adhesion energy and raise the interfacial tension of the electrode coating and result in increased half cell high-frequency impedance.

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

The baseline Conoco Phillips A10/A12 anode material was received in December 2011. It exhibited a negative surface charge at pH > 3, and the isoelectric point was pH = ~3. The natural pH for A12 was around 6.2 with zeta potential of -7.6 mV, which indicated this graphite type is not stable in water. Based on the isoelectric point and zeta potential results, a cationic dispersant would be effective in dispersing and stabilizing A12 graphite in water.

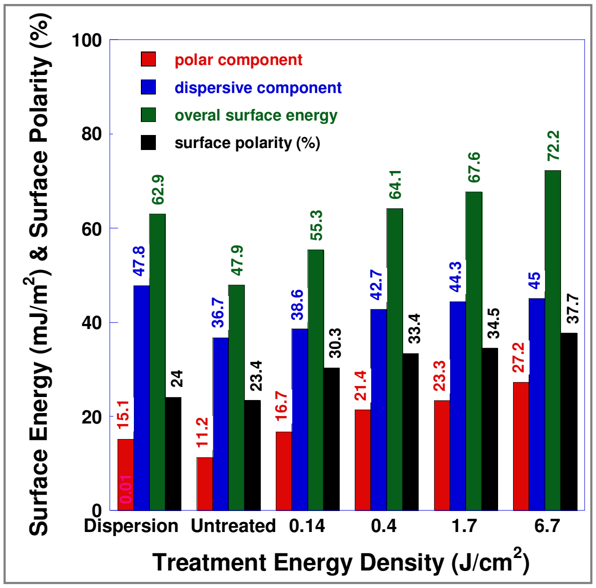


Figure 1. Surface energy of treated and untreated Al foils and LiFePO$_4$ aqueous dispersion. The surface energy and polarity of Al foils increased with increasing corona treatment energy density.

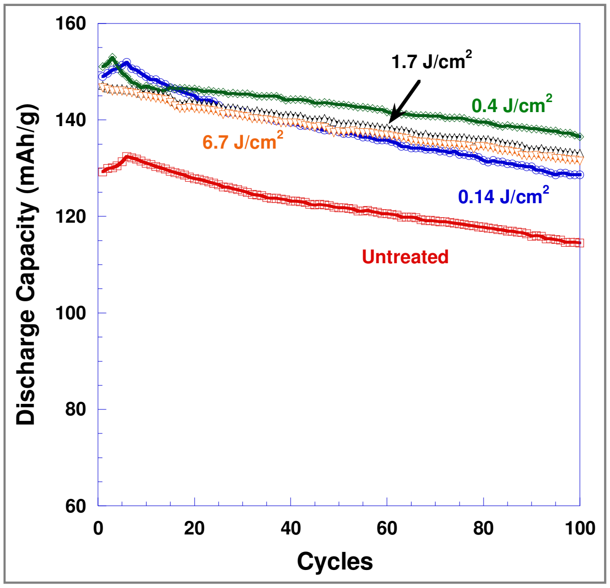


Figure 2. Cycling of LiFePO$_4$ cathodes at 0.5C/0.5C (0.34 mA/cm^2) confirming 0.4 J/cm^2 as the best treatment for long term performance.

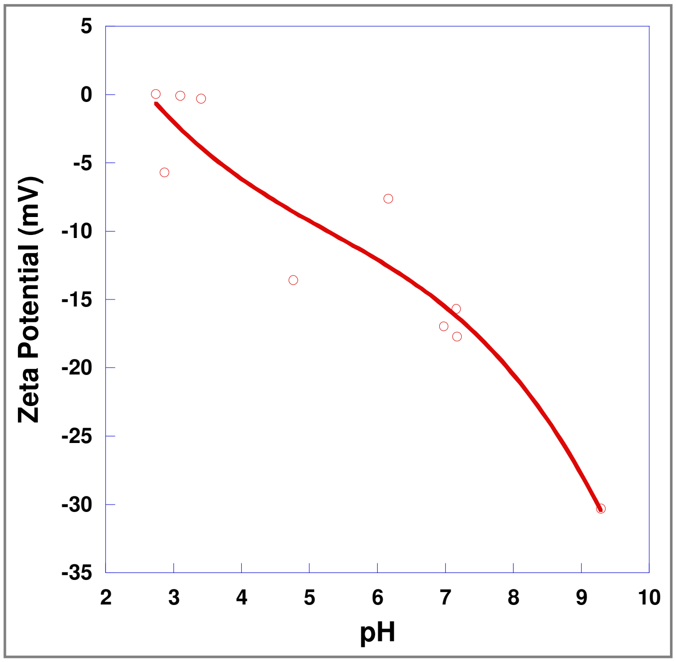


Figure 3. Zeta potential of anode graphite A10 from Conoco Phillips after being dispersed in water for 24 h.

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

1. J. Li, C. Rulison, J. Kiggans, C. Daniel, and D.L. Wood, "Superior Performance of $LiFePO_4$ Cathode Dispersions via Corona Treatment and Surface Energy Optimization," *Energy & Environmental Science*, Submitted, 2012.
2. J. Li, B.L. Armstrong, J. Kiggans, C. Daniel, and D.L. Wood, "Optimization of $LiFePO_4$ Nanoparticle Suspensions with Polyethyleneimine for Aqueous Processing," *Langmuir*, Accepted, 2012.
3. J. Li, B.L. Armstrong, D.L. Wood, and C. Daniel, U.S. Provisional Patent Application No. 61/546,413, "Aqueous Processing of Composite Lithium Ion Electrode Material" (2011).

TASK 1
Battery Cell Materials Development

Project Number: ES162

Project Title: Development of Industrially Viable Battery Electrode Coatings

Project PI, Institution: Robert Tenent and Anne Dillon (co-PI), NREL

Collaborators (include industry): Chunmei Ban (NREL), Steven George (University of Colorado, Boulder)

Project Start/End Dates: December, 2012 – September, 2016

Objectives: (1) Demonstration of Al_2O_3-based Atomic Layer Deposition coatings for improved cycling durability and abuse tolerance using standard electrode materials currently employed within the ABR program. (2) Design of an in-line atmospheric pressure atomic layer deposition (AP-ALD) system to demonstrate a process that may easily and inexpensively be integrated into the existing industrial Li-ion electrode fabrication lines.

Approach: Previously obtained results indicate that atomic layer deposition (ALD) can be used to form thin and conformal coatings on electrode materials that lead to both increased cycling lifetime, especially at high-rate, as well as abuse tolerance (e.g. stable cycling at high temperature and/or high voltage). This project will initially focus on using existing deposition capabilities to demonstrate an Al_2O_3-based ALD protective coating process for materials that are already commercially available at large-scale or are under advanced study within the VTP-EERE programs. This will include both anode and cathode materials in order to facilitate full cell testing and abuse studies. Initially, testing will be performed at the coin cell level to establish a stable baseline for comparison to existing data. In a later phase of the project larger format electrodes will be coated for testing in both pouch and 18650 cells. Coatings will be demonstrated on electrode materials produced at NREL as well as from outside parties. Finally, testing will be conducted both at NREL as well as within collaborating laboratories via a “round robin” process to ensure quality of data and the development of robust and transferrable processes.

In addition to small-scale exploratory research on various possible coating/electrode combinations, design work will be conducted for the development of a deposition system that will allow in-line coating at atmospheric pressure using an ”ALD-like” process. The ultimate goal is to demonstrate a process that can be inexpensively integrated into existing industrial Li-ion battery electrode fabrication lines.

Milestones:

a) Demonstration of an Al_2O_3 ALD coating showing improved durability and abuse tolerance performance for a commercially viable cathode material
Due: May, 2012
Status: On Schedule

b) Design and initiate construction of a deposition system capable of in-line AP-ALD on commercially relevant substrate sizes.
Due: September 2012
Status: On Schedule

Financial data: Current Funding $300K/year

PROGRESS TOWARD MILESTONES

(a) Robert Tenent and Anne Dillon attended the ABR meeting at Sandia National Laboratory in Jan. 2012. Current as well as planned NREL deposition capabilities were presented and discussed among ABR PI's from Argonne, Sandia and Oak Ridge National Laboratories. At the meeting it was decided that NREL will coat various electrodes and/ or active material powders provided from both Sandia and Argonne. NREL has already received materials from Argonne National Laboratory as listed below:

15 sheets of A12 Graphite Electrodes
5 Sheets of Toda HE5050 NCM Electrodes
5 Sheets of Toda NCA Electrodes
2 Sheets of ANL Made LiNiMnO Electrodes
20g ANL Made LiNiMnO powder
20g Toda HE5050 powder
20g A12 Graphite powder

These materials will be coated and initially tested in coin cells at NREL. Once improved performance has been demonstrated at the coin cell level larger format electrodes will then be coated for pouch and/or 18650 cell testing at either Argonne or Sandia. Abuse studies of coated large format full cells will also be performed at Sandia.

(b) Internal general-purpose equipment money totaling $800 K was obtained through NREL to support the equipment required for this project. System design discussions have been initiated with the SierraTherm Corporation. We are currently in process of obtaining the required NDA's to initiate more detailed design discussions. SierraTherm is a world leader in design and construction of in-line atmospheric pressure vapor deposition equipment. Discussions have also been initiated to leverage existing preliminary efforts on in-line atmospheric pressure ALD via collaboration with Prof. Steven George's research group at the University of Colorado, Boulder. We are in the process of outfitting laboratory space for installation of the AP-ALD system. .

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

New award (Dec. 2011)
Project outline was presented to DOE on Dec. 1, 2011

TASK 2
Calendar & Cycle Life Studies

Project Number: 2.1B (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
Steve Trask, Argonne National Laboratory
Wenquan Lu, Argonne National Laboratory
Chris Orendorff, Sandia National Laboratory
Claus Daniel and David Wood, Oak Ridge 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 FY12 is to fabricate in-house pouch and 18650 cells in Argonne's new dry room facility using advanced energy storage materials.

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 battery materials in the capacity range of 0.4 to 2 Ah.

Pouch cells will be used for initial evaluations of long-term exploratory materials. Pouch cells are an efficient method of determining the stability of a cell system during calendar and cycle life aging. If the chemistry is not stable, it is likely that gassing will occur inside the cell. This will result in the pouch cell bulging or rupturing if the gassing is significant. More established materials and chemistries (or those that pass the pouch cell evaluation) will be used in rigid cells (e.g. 18650s).

Milestones:
(a.) Optimize electrode slurry process using new Ross Mixer, March, 2012 (On schedule)
(b.) Evaluate materials from MERF scale-up of Argonne's cathode, May, 2012 (On schedule)
(c.) First cell build using 18650 cell making equipment, June 2012 (On schedule)

Financial data: $1,100K

PROGRESS TOWARD MILESTONES

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

The ability to make cells with long cycle life and good electrochemical performance is dependent on making high quality electrodes. Key to this is the ability to make homogenously dispersed electrode slurries with intimate contact between active particles and conductive additives. To accomplish this step, a high energy/shear planetary mixer was purchased from Ross with a 2 liter chamber capacity. This relatively small capacity size is ideal for the typical electrode builds made with the pilot scale coater, where supply of novel materials is often limited. Installation of this mixer was completed in October, 2011.

Numerous slurry batches were made using ConocoPhillips CGP-A12 high energy graphite to gain experience with the mixer and to optimize the mixing parameters and process steps. It was estimated that the minimum slurry volume is near 300 mL; below that amount resulted in insufficient mixing due to splatter from the high shear blade and not fully engaging the high shear blade. Single-sided and double-sided electrodes were made with the A12 graphite, and mixing trials were begun with Toda' high energy cathode material, HE5050 ($Li_{1.2}Ni_{0.15}Co_{0.10}Mn_{0.55}O_2$).

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

The Materials Engineering Research Facility (MERF) is scaling up the capability to make tens of kilograms of advanced cathode materials in their 20 L reactor – many of these cathode materials were discovered by researchers in the ABR Program. In fact, the first cathode material MERF is scaling up is a high-energy NMC cathode ($Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$) developed by Argonne researchers, and referred to here as ABR1. They had great success in earlier scaling up this cathode to hundreds of grams using their 4 L reactor, and are now in the process of optimizing the process conditions and flow profile using the 20 L reactor. Once this larger batch of ABR1 becomes available, efforts will then center on making electrodes and pouch cells with it. This first MERF cathode material delivery is expected in February 2012.

An Engineering Assistant, Steve Trask, was hired to assist in many of the duties in the Cell Fabrication Facility related to electrode and cell making. Steve joined this effort in December, 2011 and began contributing from the start to the facility's productivity. In addition to training Steve, several members from MERF were trained on making small electrodes and coin cells to aid in their process development efforts.

Until the MERF cathode arrives, effort will continue in the making of xx3450 pouch cells using electrodes made with exploratory materials that are available. One of these is the HE5050 from Toda, and the other is the limited blended supply of ABR1-type cathode

(~0.8 kg left), which is a high-energy NMC cathode ($Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$) made by Argonne researchers in several batches.

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

Effort will be directed toward fabricating 18650 cells with commercially available materials and exploratory materials when they become available. It is anticipated that making 18650 cells will require significantly more material than pouch cell fabrication. For this reason, a commercial source was sought willing to supply openly at least 20 kg of advanced NCM material. Toda Kogyo agreed to supply Argonne with 40 kg of their NCM 5:2:3 cathode ($Li_{1.1}(Ni_{0.5}Co_{0.2}Mn_{0.3})_{0.9}O_2$) . This is expected to arrive in early February of 2012 and will be shared with Sandia and Oak Ridge for their cell builds.

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

None in this quarter.

TASK 2
Calendar & Cycle Life Studies

Project Number: 2.2B (ES031)

Project Title: Model Cell Chemistries (Electrochemistry Cell Model)

Project PI, Institution: Kevin Gallagher, Argonne National Laboratory

Collaborators (include industry):
Dennis Dees, Argonne National Laboratory
Daniel Abraham, Argonne National Laboratory
Andrew Jansen, Argonne National Laboratory
Wenquan Lu, Argonne National Laboratory
Bryant Polzin, 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.) Complete initial parameter estimation of high-energy LMR-NMC/graphite system. September 2012, (On schedule)
(b.) Advance development of PHEV focused electrochemical models in support of programmatic goals. September 2014, (On schedule)
(c.) Complete integration of new differential algebraic equation solver package with enhanced capabilities and complete conversion of existing models to newly adopted package. September 2012, (On schedule)
(d.) Complete implementation and initial testing of full SEI growth model. December 2012, (Delayed)

Financial data: $400K/year

PROGRESS TOWARD MILESTONES

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

Work on this milestone was initiated with the examination of a cross section of the available data on the high energy LMR-NMC/graphite system. Because of its importance and major impact on cell aging, the initial focus of this work is on the positive LMR-NMC electrode. While there are a number of performance and degradation issues that should be addressed by this effort, the cycling hysteresis of the electrode is discussed here because of its impact on cell performance and is an excellent example of the material's complexity.

Very slow cycling data (~C/100 average rate) from a LMR-NMC half-cell is given in Figure 1 for three different cycling limits. The data was obtained from the final open circuit rest potentials of a GITT study (repeating: 10 minute ~C/15 current followed by 50 minute rest) with the half-cell. The relatively large hysteresis between the charge and discharge curves on the full cycling limits (2.0-4.5 V) can be easily seen. Also shown in Figure 1 is the little or no hysteresis for the limited cycling at the top and bottom of charge.

Analysis of the data using an intercalation electrode GITT half-cell electrochemical model allows the lithium diffusion coefficient in the active material to be estimated over the state-of-charge range ($5\text{x}10^{-12}$ – $4\text{x}10^{-13}$ cm^2/s). The diffusion coefficients estimated here are somewhat lower than typically measured for a conventional NMC active material. The GITT modeling studies also indicate the presence of another very slow phenomenon that is obvious during the relaxation of the LMR-NMC material.

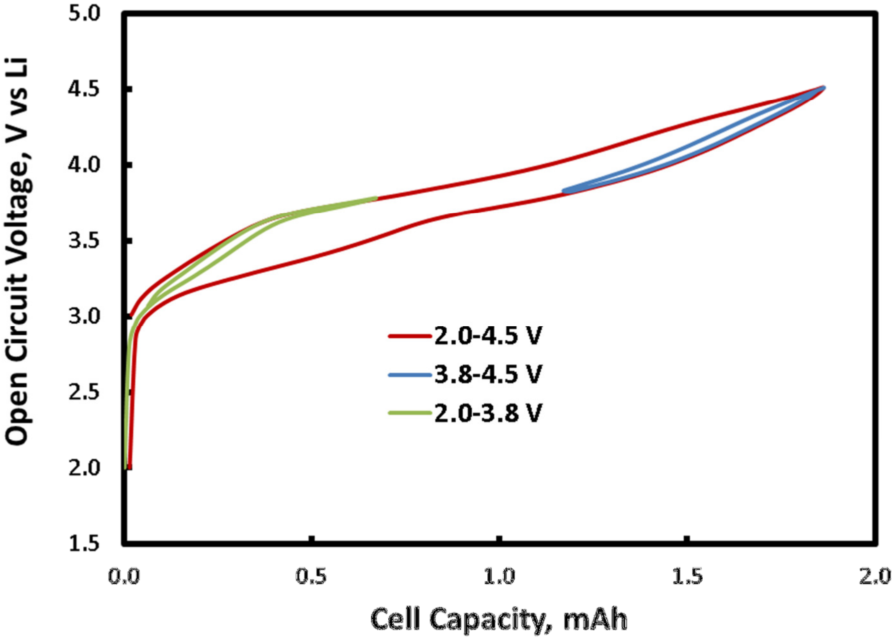


Figure 1 Very slow cycling (~C/100 average rate) data of a LMR-NMC half-cell (1.6 cm^2 area) for the indicated cycling limits. The data was obtained from the final open circuit potentials of a GITT study.

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

It is difficult to envision why a single phase intercalation material would exhibit this sort of hysteresis behavior during cycling, opening the possibility to consider partial multi-phase behavior. A scoping modeling study was conducted, assuming that the LMR-NMC material exhibited one type of single phase behavior at the top of charge, corresponding to one preferred orientation of the cations, and another at the bottom of charge, corresponding to a different preferred orientation of the cations. In between, a slow transition would occur in parallel with the lithium diffusion during cycling. A two phase electrochemical half-cell model was adapted to examine this possibility. Because of the slow average discharge rate, the model was simplified to just include potential effects from the active material (i.e. diffusion and phase change). Adjusting the phase change rate has a direct impact on the amount of voltage hysteresis during cycling. As shown in Figure 2, it is possible to at least qualitatively recreate the observed behavior for the full range cycling. Also shown in Figure 2, if one starts completely in the single phase region and does not cycle too far out of that region one does get the observed behavior without hysteresis. While the electrochemical phase change model does explain much of the observed behavior, a close examination of the results indicate that the phase change rate is so slow that even at the C/100 charge rate only about 80% of the material is converted by the end of charge. Further analysis is being conducted to examine other possible phenomena that can account for the observed voltage hysteresis behavior.

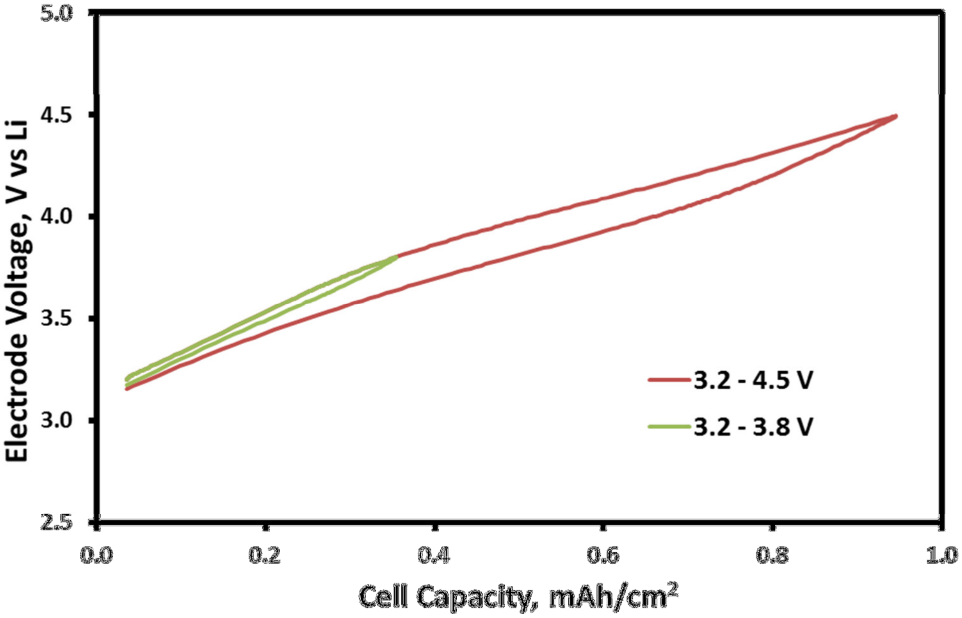


Figure 2 Simulation of very slow cycling (~C/100 average rate) of a LMR-NMC electrode for the indicated cycling limits.

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

This project has been continually challenged by finding efficient ways to solve increasingly complex electrochemical cell models. A new differential algebraic equation solver package (PSE gPROMS) is being adopted to solve a wide variety of cell studies at the required level of complexity. Parameter estimation is always a serious challenge when dealing with the complex phenomenological modeling being used in this project. Previous effort used a "hand-fit" approach where the modeler systematically varied parameters to find a "best-fit" to the eye of the user. The new software package being implemented has parameter estimation algorithms and statistical assessment of the solution. Efforts this period have focused on integrating and improving the phase change model for electrode active materials. The importance of including phase change into the electrochemical model for electrodes like graphite has been well established, and recent work on the LMR-NMC electrode material indicates that more complex models may be needed for that electrode also. Further, the parameter estimation capabilities for the DC model are continuing to be utilized and improved.

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

Implementation of the SEI growth model for the negative graphite electrode has been deemphasized because of the challenges the high energy LMR-NMC positive electrode are presenting.

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 Evaluations - Electrochemical

Project PI, Institution: Daniel Abraham, Argonne National Laboratory

Collaborators (include industry): D. Dees, A. Jansen, M. Bettge, Y. Li, Argonne National Laboratory; Prof. A. Wei, Purdue University; Prof. I. Petrov, University of Illinois

Project Start/End Dates: October 2011/September 2012

Objectives: Electrochemical couples containing various positive and negative electrodes are being examined in the ABR program. The baseline electrolyte in these cells is EC:EMC (3:7, by wt.) + 1.2M $LiPF_6$. The main objective of this study is to use electrochemical diagnostic tools to identify factors that determine cell performance and performance degradation (capacity fade, impedance rise) on long-term storage and on extensive deep-discharge cycling. The electrochemical data obtained from these measurements are used in ABR's phenomenological modeling studies. A secondary objective of this study is to recommend and implement solutions that improve the electrochemical performance of materials and electrodes so that the PHEV cells may meet their 15y life criterion.

Approach: Our electrochemical measurements are conducted in various cell configurations that include coin cells, pouch cells, and reference electrode (RE) cells. Our investigations are conducted both on as-prepared single-sided electrodes, and on double-sided electrodes harvested from pouch- and 18650- cells. Our research includes the following components: (i) Studies in Reference Electrode cells – Data from these cells help identify causes of impedance rise and concomitant capacity fade; this knowledge will help us target the development of solutions to reduce cell performance degradation; (ii) development of electrolyte additives – these form surface films that protect the electrode components from further degradation; (iii) development of electrode coatings – modification of the electrode-electrolyte interfaces by these coatings have been shown to improve cell life.

Milestones:
(a) Determine sources of impedance rise/capacity fade during extensive cycling of cells containing various electrochemical couples; September 2012 (on schedule)
(b) Identify at least one electrolyte additive that improves cell life by 50% at 30°C and 25% at 55°C; September 2012 (on schedule).
(c) Identify at least one electrode coating that improves cell life by 50% at 30°C and 25% at 55°C; September 2012 (on schedule)

Financial data: $450 K (subcontracted $30K to Purdue University)

PROGRESS TOWARD MILESTONES

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

Cells with the ABR-1 baseline chemistry contain $Li_{1.2}Mn_{0.55}Ni_{0.15}Co_{0.1}O_2$ (HE5050) -based positive electrodes, Graphite (A12)–based negative electrodes, Celgard 2325 separator, and EC:EMC (3:7, by wt.) + 1.2M $LiPF_6$ (baseline) electrolyte. The performance of as-prepared "half" and "full" cells was characterized using a series electrochemical charge-discharge cycling and impedance experiments. The discharge capacity of HE5050//Li cells, in the 2-4.1V range, is ~70 mAh/g. In comparison, NCA(+)/Li(-) and NMC_333(+)/Li(-) cells yield a discharge capacity of 150 mAh/g and 140 mAh/g, respectively, in the same voltage window. Cycling over a wider voltage window, beyond the 4.5 (vs. Li) plateau, is needed to obtain higher capacities. However, after oxide "activation", the charge and discharge profiles are no longer symmetric. For example, in the 3.2-4.7V range, the charge capacity of HE5050//Li cells is ~266 mAh/g whereas the discharge capacity is 235 mAh/g, i.e., there is "hysteresis" in the charge-discharge plots.

Fig. 1 shows the effect of partial and full formation cycling on HE5050(+)/A12(-) reference electrode (RE) cells. It is evident that the full cell impedance is higher after cycling in the 2-4.6V range than after cycling in the 3-4.1V range. Almost all the higher impedance arises at the positive electrode; the changes at the negative electrode are relatively small. The higher positive electrode impedance is associated with oxygen evolution from the oxide during the activation cycle that may cause the formation of high impedance species, such as Li2CO3, on the oxide surfaces.

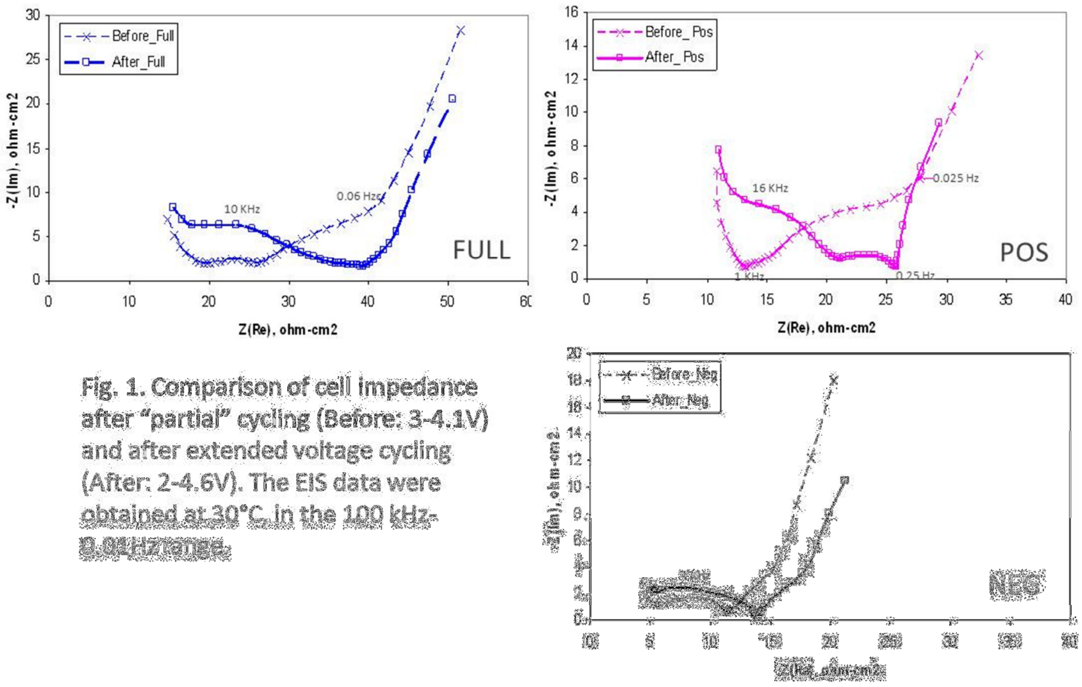


Fig. 1. Comparison of cell impedance after "partial" cycling (Before: 3-4.1V) and after extended voltage cycling (After: 2-4.6V). The EIS data were obtained at 30°C, in the 100 kHz-0.01Hz range.

Elevated voltage tests on the HE5050(+)/A12(-) cells showed that voltage is an important determinant of cell performance degradation. For example, cells held at 4.6V showed performance degradation at a significantly higher rate than those held at 4.4V. Therefore, in order to achieve longer cycles, we decided to limit the upper voltage window to 4.4V.

Fig. 2 shows impedance data on HE5050(+)/A12(-) RE cells after 30°C cycling in the 2.5 – 4.4V voltage window. It's evident that the 30°C cycling creates an impedance increase in both high- and mid- frequency portions of the EIS data. This result is important because capacity data obtained at high rates (C/1, for example) is strongly affected by cell impedance. Fig. 2 also shows that the Full cell impedance increase is dominated by impedance increase at the positive electrode – the changes at the negative electrode are very small. Possible reasons for positive electrode impedance rise include (i) changes at oxide particle surface (surface films/crystal structure changes); (ii) PF_6^- intercalation into cathode carbons; (iii) binder degradation; etc.

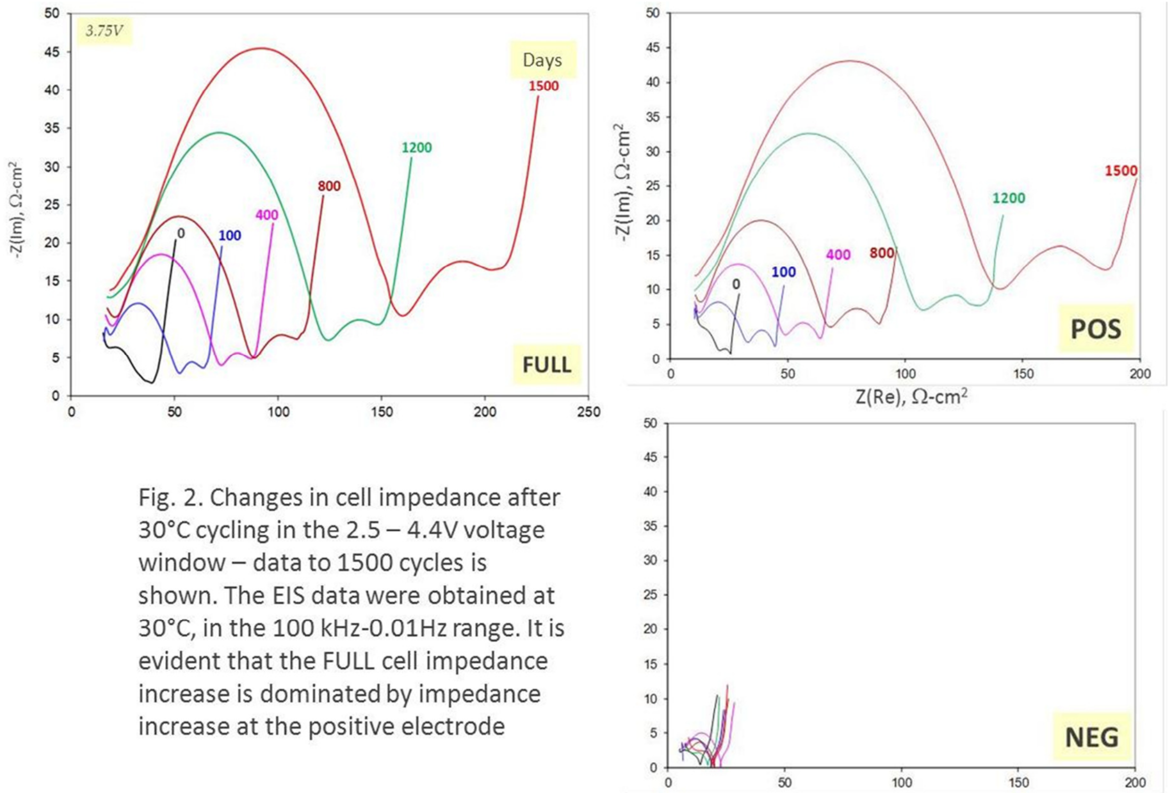


Fig. 2. Changes in cell impedance after 30°C cycling in the 2.5 – 4.4V voltage window – data to 1500 cycles is shown. The EIS data were obtained at 30°C, in the 100 kHz-0.01Hz range. It is evident that the FULL cell impedance increase is dominated by impedance increase at the positive electrode

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

The protective characteristics of electrolyte additives is often specific to electrode couples – data from our Reference Electrode cells, such as that shown in Figs.1 and 2, show that electrolyte additives that target the positive electrode are necessary for the HE5050(+)/A12(-) cells. Therefore, additives that oxidize at the positive electrode, preferably before the oxygen evolution plateau, are being identified and synthesized. We will report on data from these additives at a later time.

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

Our electrochemistry data show that the HE5050(+)/A12(-) cell performance degradation arises at the positive electrode. Furthermore, the data suggest that the impedance arise at both the oxide-carbon and oxide-electrolyte interfaces. Modification of the positive electrode surface by Atomic Layer Deposition (ALD) coatings has been conducted. Initial data show significant improvement in cell performance, i.e., both capacity fade and impedance rise of the full cells decreases significantly. We will report on data from these tests at a later time.

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

None

TASK 2
Calendar & Cycle Life Studies

Project Number: 2.3B (ES032)

Project Title: Diagnostic Evaluations - Physicochemical

Project PI, Institution: Daniel Abraham, Argonne National Laboratory

Collaborators (include industry): M. Bettge, Y. Li, M. Balasubramanian, D. Miller, Argonne National Laboratory; Prof. I. Petrov, University of Illinois; Prof. B. Lucht, University of Rhode Island; Prof. P. Guduru, Brown University

Project Start/End Dates: October 2011/September 2012

Objectives: Various lithium-ion chemistries are being examined for use in cells for PHEV applications. The main objective of this study is to use physicochemical characterization tools and techniques to explain the electrochemical performance and performance degradation mechanisms of ABR cells. The physicochemical data are used to guide development of electrochemical models that relate material and electrode chemistry to observed changes in cell performance during cycling and accelerated aging. Determining degradation mechanisms is an important step towards modifying the cell chemistry to attain the 15y life goal for these cells.

Approach: Our physicochemical examinations employ a combination of spectroscopy, microscopy, diffraction, and chemical analysis techniques. Our investigations are conducted on components harvested from small cells (1 to 50 mAh), and from pouch and 18650 cells subjected to characterization and long-term aging. Our research includes the following three components: (i) studies of the electrode-electrolyte interface using various techniques that include X-ray photoelectron spectroscopy; (ii) electrode studies using techniques that include X-ray diffraction, X-ray absorption spectroscopy (XAS), and Electron Microscopy (AEM); and (iii) stress evolution studies using techniques that include the “wafer curvature method”.

Milestones:

(a) Performance degradation mechanisms in HE5050(+)/A12(-) cells, September 2012 (on schedule)

(b) Initial information on performance degradation mechanisms in $Li_{1.14}Mn_{0.57}Ni_{0.29}O_2$ bearing cells, September 2012 (on schedule)

(c) Stress evolution data on oxide and graphite electrodes during electrochemical cycling, September 2012 (on schedule)

Financial data: $450 K (subcontracted $30K to Brown University; $50K to University of Illinois)

PROGRESS TOWARD MILESTONES

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

X-ray diffraction studies were conducted on positive electrode samples harvested from ABR-1 full cells (see Table 1) to examine the effect of cell aging on electrode degradation; the cells were discharged and held at 2V before electrode extraction. Control experiments were conducted on fresh electrode samples. The positive electrodes contained a coating of 86 wt% $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ (Toda HE5050), 2 wt% SuperP (Timcal), 4 wt% SFG-6 graphite (Timcal) and 8 wt% PVdF (Solvay 5130) binder on a 15-µm thick Al current collector. High resolution synchrotron powder diffraction data were collected using beam line 11-BM at the Advanced Photon Source (APS), Argonne, using an average wavelength of 0.413092 Å. The 2-theta data were converted into values that represent the CuKα wavelength (1.5406) for comparison with previous data – these converted data are shown in this report.

Table 1.

Sample Id.	Details	Estimated Li	Lattice Parameters, nm	
		in oxide	c	a
FRESH	Fresh, no electrolyte exposure	$Li_{1.2}$	1.4247	0.2855
DA383	Few (formation) cycles. discharged to 2V	$Li_{1.02}$	1.4401	0.2863
DA384	300 (2.2-4.4V) cycles. discharged to 2V	$Li_{0.96}$	1.4441	0.286
DA372	1500 (2.2-4.4V) cycles. discharged to 2V	$Li_{0.74}$	1.4463	0.2857

Results

- Representative data over the 10 to 90 2-theta range are shown in Fig. 1. An expanded view of selected ranges are shown in Fig. 2.
- The X-ray diffraction patterns of the fresh sample show "extra" peaks in the 22 to 25 2-Theta range (Fig. 1). These peaks are believed to be from the ordering of "excess" Li-ions in the transition metal planes. The ordering peaks are not evident in the cycled samples.
- A C(002) peak is evident in the fresh sample (Fig. 1); this peak arises from the SFG-6 graphite contained in the electrode coating. This peak becomes very weak and broadens significantly after only a few cycles; however, it does not disappear entirely.
- With increased cell aging, the (003) oxide peak moves to smaller 2-Theta (Fig. 2). This feature is consistent with an expansion of the c-axis parameter that results from extraction of Li-ions from the oxide (see Table 1).
- The separation between (018) and (110) oxide peaks increases with cell age (Fig. 2). The (018) peak is dominated by c-axis expansion and consequently moves to smaller 2-Theta values. The (110) peak arises from changes within the transition metal plane. A closer examination shows that the peak moves to smaller 2-Theta initially (increasing a), and then to larger to 2-Theta values (decreasing a); see Table 2. The reasons for this complex in-plane behavior are not entirely clear.

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

Electrochemical characterization of $Li_{1.14}Mn_{0.57}Ni_{0.29}O_2$-bearing cells is in progress. Physicochemical data will be obtained after completion of the electrochemical tests.

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

Real-time stress evolution in a graphite-based lithium-ion battery negative-electrode during electrolyte wetting and electrochemical cycling was measured through wafer-curvature method. Upon electrolyte addition, the composite electrode rapidly developed compressive stress of the order of 1-2 MPa because of binder swelling; upon continued exposure, the stress continued to evolve towards an apparent plateau. During electrochemical intercalation at a slow rate, the compressive stress increased with the electrode's state-of-charge, reaching a maximum value of 10 – 12 MPa. There appeared to be an approximate correlation between the rate of stress rise and the staging behavior of the lithiated graphite. De-intercalation at a slow rate resulted in a linear decrease in electrode stress. Tensile stress of a few MPa developed at the end of deintercalation in the first few cycles, after which the electrode remains under compressive stress only. More information on this subject is available in the article shown at the end of this report.

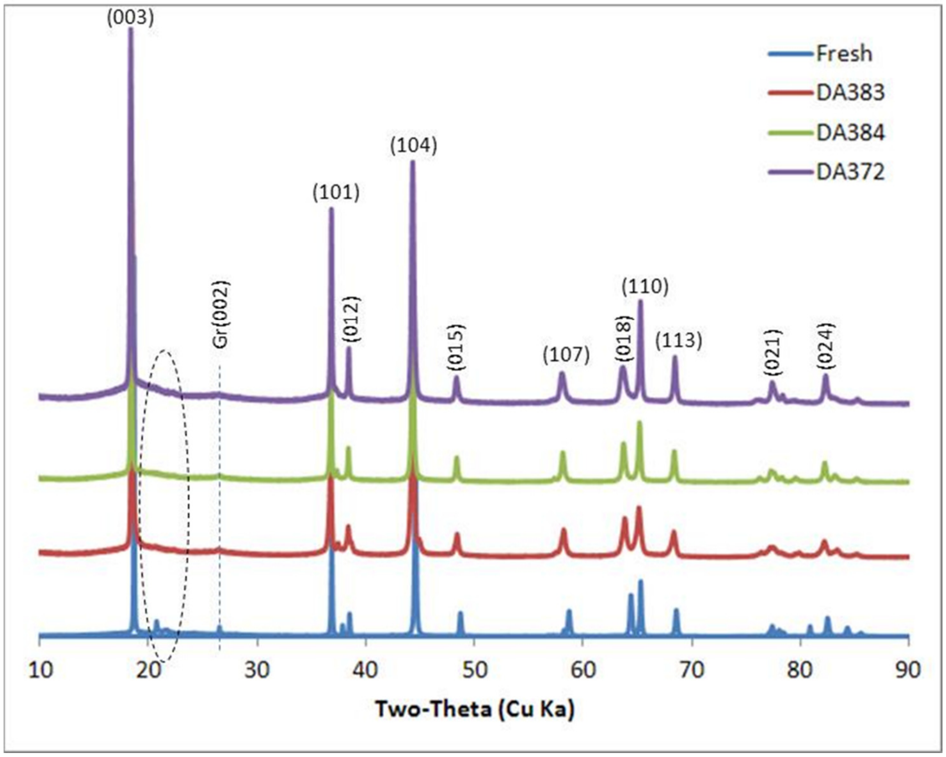


Figure 1. XRD data from positive electrode samples harvested from cells aged under various test conditions. Data from a fresh sample is shown for comparison.

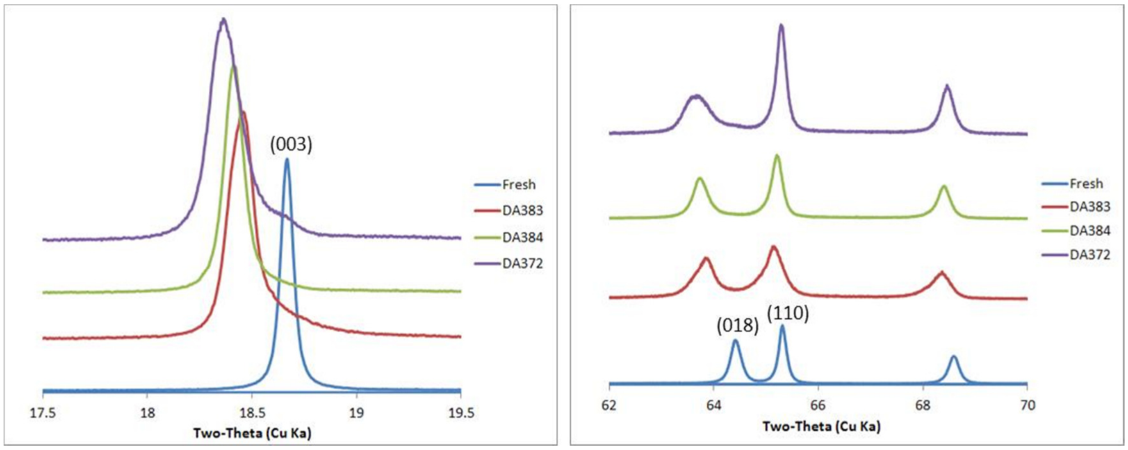


Figure 2. Expanded view of selected data from Figure 1.

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

V.A. Sethuraman, N. Van Winkle, **D.P. Abraham**, A.F. Bower, P.R. Guduru, "Real-Time Stress Measurements in Lithium-ion Battery Negative-electrodes", to appear in: *Journal of Power Sources,* DOI: doi:10.1016/j.jpowsour.2012.01.036

TASK 2
Calendar & Cycle Life Studies

Project Numbers: 1.1.1 and 2.4 (ES033)

Project Title: Strategies to Enable the Use of High-Voltage Cathodes (1.1.1) and Diagnostic Evaluation of ABRT Program Lithium Battery Chemistries (2.4)

Project PI, Institution: Robert Kostecki and Thomas Richardson, Lawrence Berkeley National Laboratory

Collaborators (include industry): None.

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

Objectives: Task 1.1.1: To enable increased energy density by addressing the impact of high-voltage cathodes on the conducting carbon matrix. Task 2.4: (i) Determine the key factors that contribute to the degradation mechanism in the PHEV test cells and individual cell components. (ii) Characterize SEI formation on model electrode surfaces to improve understanding of key interfacial phenomena in PHEV cells.

Approach: **Task 1.1.1:** (i) determine the mechanisms for carbon damage and retreat at high potentials. (ii) Investigate mitigating treatments, additives, and procedures. Task 2.4: Use in situ and ex situ advanced 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.

Milestones: Determine interfacial degradation mechanism CBs in high-voltage cathodes (July 2012). On schedule. Synthesize a new type of CB with improved interfacial properties (September 2012). On schedule. Attend review meetings and present diagnostic results obtained in collaboration with ABRT Program participants. On schedule.

Financial data: FY 2012 funding \$600K

PROGRESS TOWARD MILESTONES

(a) We have previously reported on the electrochemical activity at high potentials of model and commercial carbon samples subjected to different heat treatments. For a model sample (pyrolized polyimide) and commercial samples (Super P, Denka black), heat treatment with N_2 and CO_2 greatly reduced the activity at potentials exceeding 4 V vs. Li/Li^+. To investigate the structural effect this treatment has on the carbon samples, combined TGA-DSC investigations have been carried out. The treatment was the same as for the samples described in previous reports, heating under N_2 up to 900°C (heating rate 5K/min) followed by introduction of CO_2 at 900°C. Fig. 1 compares polyimide (Kapton® HN) samples treated at 900°C, one with CO_2 and one with N_2 only. After a slight onset the sample exposed to CO_2 lost weight rapidly at 900°C, due to reaction with the amorphous carbon formed in N_2, while the sample exposed only to N_2 lost little weight. The shape of the thermogravimetric analysis curve indicates that the CO_2 "cleaning"/modification reaction may initially be surface limited, but later becomes transport limited. This thesis is consistent with the more rapid weight loss in the TGA experiment than during bulk furnace treatment. Further investigations with commercial powder samples will be carried out to investigate this effect, not only to determine the structural effect but also to optimize the procedure in terms of exposure time and setup.

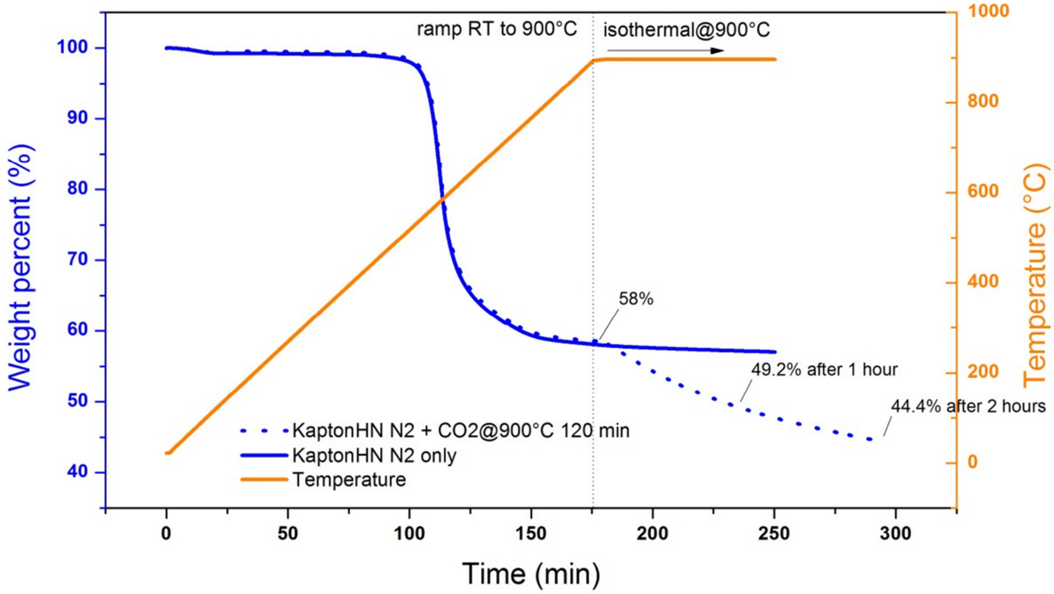


Fig. 1. TGA analysis of Kapton HN with and without CO_2 treatment

(b) We have observed impedance growth on both negative and positive electrodes, using three-electrode impedance spectroscopy of cycled cells. The question was whether this growth is intrinsic to each electrode, or does it result from the fact that both high and low potential electrodes share the same electrolyte, and therefore can exchange soluble decomposition products, causing deterioration of each of them (a phenomenon known as "cross-talk"). Two vacuum-dried baseline graphite electrodes of significantly different areas (20 mm vs. 3 mm diameter) were cycled three times in Gen2 electrolyte (1.2 M $LiPF_6$ in 3:7 EC:EMC) between 0.01 V and 1.2 V vs. Li, and then slowly charged to 0.01 V vs. Li in separate beaker cells. The electrodes were thoroughly washed in EMC and mounted opposite one another in a 2032 coin cell with a Cellgard® separator and 20µl of Gen2 electrolyte. This cell was cycled between -0.01 V and +1.22 V (about 0.01 to 1.24 V vs. Li/) at a C/3 rate, referred to the capacity of the small electrode (dQ/dV plot, Fig. 2). The potential of the larger (overcapacity) electrode was virtually constant. Every ten cycles an impedance spectrum was recorded in the discharged state (-0.01V). No significant changes in the spectra were observed up to 450 cycles (Fig. 3, experiment ongoing). All spectra were exactly same shape, and only a small offset along the ReZ axis was observed (spectra moving back and forth along this axis, without any specific tendency). The origin of that phenomenon will be a subject of further studies. We plan similar experiments with baseline NMC electrodes explain the difference between the full cell and symmetric cell behavior.

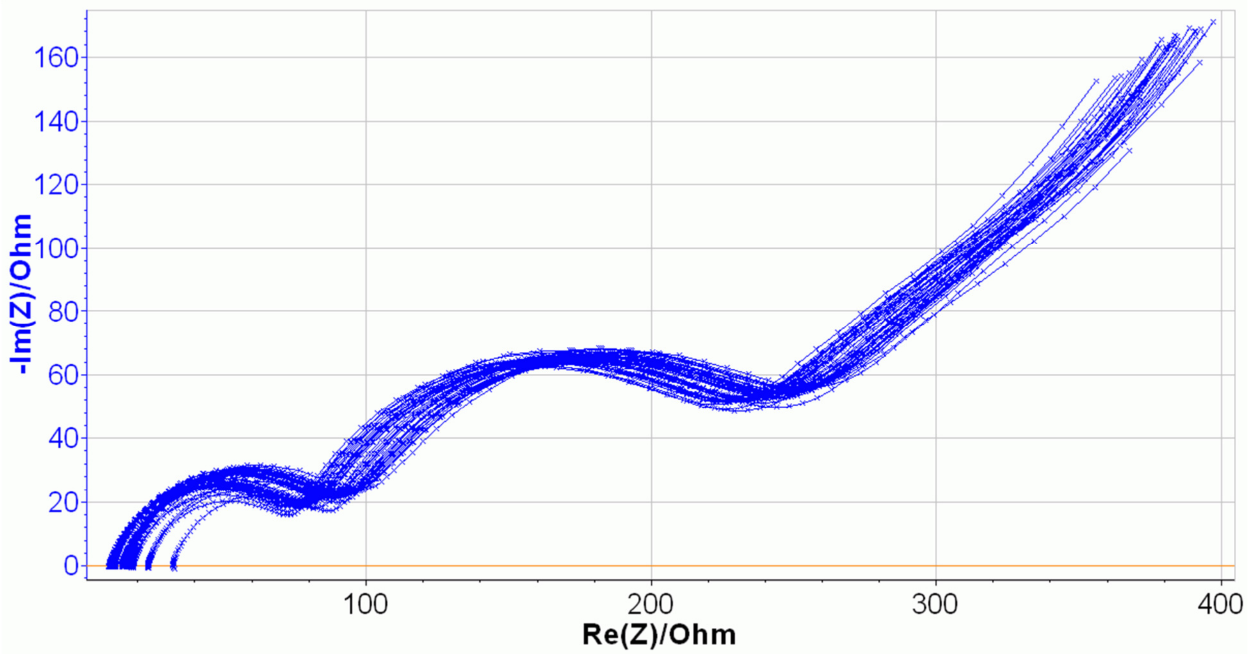


Fig. 3. Impedance spectra of the symmetric graphite-graphite cell obtained every ten cycles between 1 and 450 cycles

TASK 2
Calendar & Cycle Life Studies

Project Number: 2.4 and 3.3 (ES034)

Project Title: Life and abuse tolerance diagnostic studies for high energy density PHEV batteries
Task 2.4: Life Diagnostics, Task 3.3: Abuse Behavior Modeling and Diagnostics

PI, Institution: Kyung-Wan Nam and Xiao-Qing Yang, Brookhaven National Laboratory

Barrier: Calendar and cycling life, Abuse tolerance

Objectives: The primary objectives of the efforts at BNL are: to determine the contributions of electrode materials changes, interfacial phenomena, and electrolyte decomposition to cell capacity power decline, and abuse tolerance; to develop new diagnostic techniques (in situ and ex situ) for lithium-ion batteries; to help other ABR teams and the battery developers to understand the technical barriers by using these new techniques; to explore new techniques to improve the abuse tolerance. The other objective is to design, synthesize and characterize new electrolyte for PHEV oriented lithium-ion and Lithium-air batteries with better performance and safety characteristics. Special attention will be given to the capabilities of electrolytes in improving the high voltage cycling of lithium-ion batteries.

Approach: Our approach is to use a combination of *in situ, ex situ* and time-resolved synchrotron based x-ray techniques to characterize electrode materials and electrodes taken from baseline ABR Program cells. *Ex situ* soft X-ray absorption spectroscopy (XAS) will be used to distinguish the structural differences between surface and bulk of electrodes using both electron yield (EY) and fluorescence yield (FY) detectors. Time-resolved X-ray diffraction technique will also be used to understand the reactions that occur in charged cathodes at elevated temperatures in the presence of electrolyte. In situ x-ray diffraction will be used to monitor the structural changes of the electrode materials during charge-discharge cycling at different conditions. 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 will be applied to study the thermal stability of the electrode materials. The atomic layer deposition (ALD) technique will be used for the surface modification of new cathode materials, which will be studied using time resolved X-ray diffraction (XRD) for the effects of surface modification on the thermal stability. These approaches developed at BNL will be available to other members of ABR projects through extended collaboration. We will continue to develop new synchrotron based x-ray techniques such as combined in situ x-ray diffraction and mass spectroscopy during heating for the thermal stability of cathode material studies. We will continue to develop TEM based in situ diagnostic tools to study the structural changes at both surface and bulk of the electrode particles with high spatial resolution.

Milestones:

(a) By April 2012, complete the study of thermal decomposition of charged $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) cathode materials during heating using combined Time-Resolved XRD and Mass Spectroscopy. **On schedule.** (b) By April 2012, complete the Time resolved r-ray diffraction (TRXRD) studies of ALD coated Al_2O_3 on $Li_{1.2}Ni_{0.17}Co_{0.07}Mn_{0.56}O_2$ new cathode material during heating. **On schedule.** (c) By September 2012, complete the study of charged $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) cathode material. **On schedule.** thermal decomposition during heating using combined Time-Resolved XRD and Mass Spectroscopy. (d) By September 2012, complete the in situ XRD studies of $Li_{1.2}Ni_{0.15}Mno_{0.55}Co_{0.1}O_2$ (Toda HE5050) cathode material during charge-discharge cycling. **On schedule.**

Progress toward milestones for the 1st quarter of FY2012:

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

Progress has been made toward the milestone (a): In order to understand the thermal degradation of the electrodes in Li-ion cells, we have developed techniques using the combination of the *in situ* time resolved X-ray diffraction (TR-XRD) and mass spectroscopy to study the structural changes and gas evolution during the thermal decomposition of charged cathode materials. Our new studies on the structural changes of layered nickel based cathode materials (e.g., $Li_{1-x}NiO_2$, $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ and $Li_{1-x}Ni_{0.33}Co_{0.33}Mn_{0.33}O_2$) during thermal decomposition have made significant progress toward mile stone (a). The combined results from TR-XRD coupled with mass spectroscopy technique provide valuable information for the development of new cathode materials as well as for the improvement of thermal stability of the materials being used currently. The left panel in Figure 1 shows the TR-XRD patterns of $Li_{0.5}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ in the absence of electrolyte as a function of heating temperature together with the mass spectra (MA). A rapid structural change appeared at about 207˚C with oxygen evolution as demonstrated by the MS results shown in the right panel of Fig. 1. In the temperature range from 207 to 238˚C, the coalescence of the original (108) and (110) forms a new peak (marked as (440)), giving clear indication for the formation of the disordered $LiMn_2O_4$-type spinel phase (space group of *Fd3m*). Heating above 238˚C, further decomposition of spinel phase to MO-type with rock-salt structure was formed slowly up to the temperature as high as 500˚C. By introducing mass spectroscopy during TR-XRD experiment, we are able to verify and identify the noticeable oxygen gas evolution with these structural changes.

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

The Time resolved r-ray diffraction (TRXRD) studies of ALD coated Al_2O_3 on $Li_{1.2}Ni_{0.17}Co_{0.07}Mn_{0.56}O_2$ new cathode material during heating are underway.

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

Studies of charged $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) cathode material using TR-XRED and MS are underway.

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

The in situ XRD studies of $Li_{1.2}Ni_{0.15}Mno_{0.55}Co_{0.1}O_2$ (Toda HE5050) cathode material during charge-discharge cycling are underway.

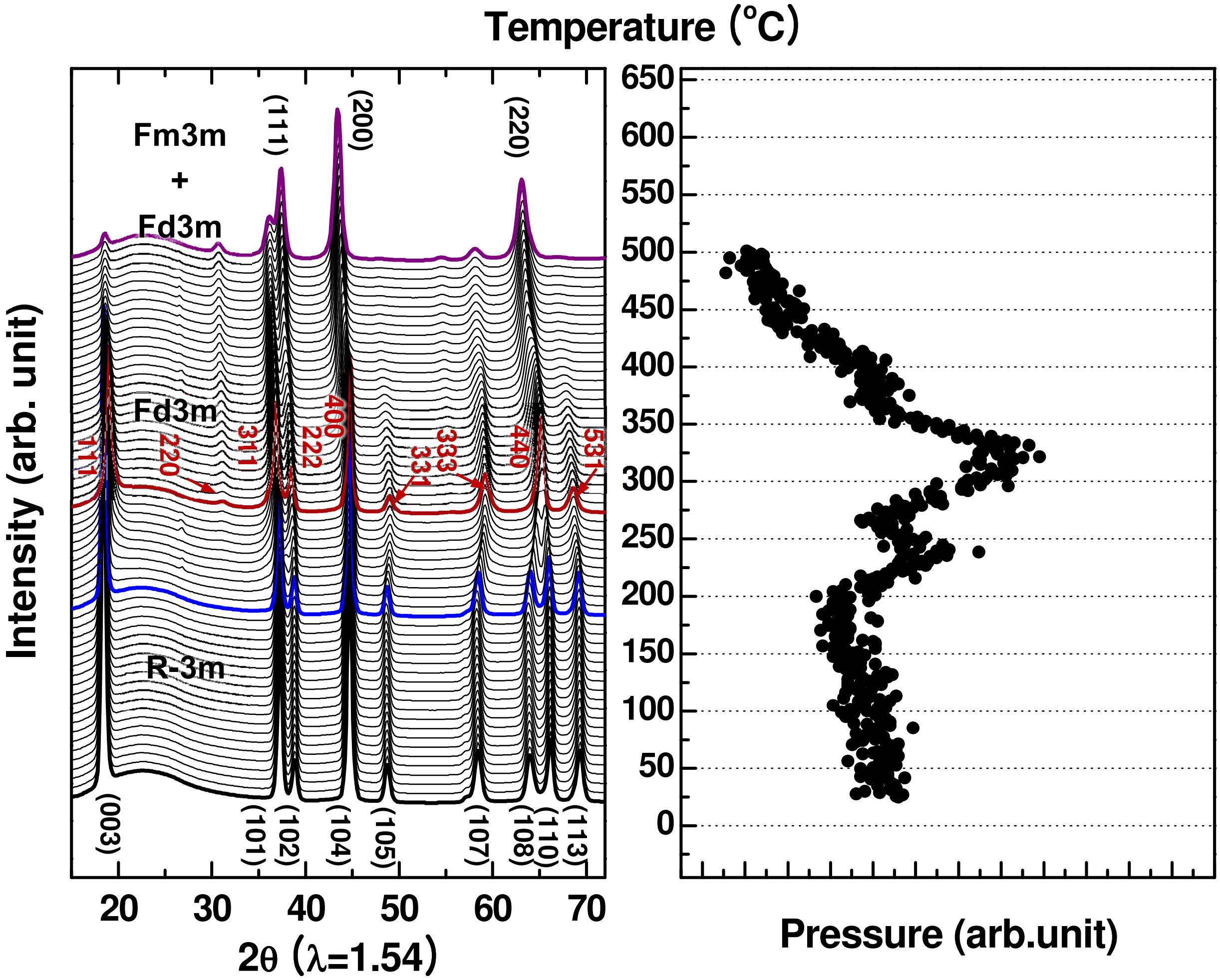


Figure. 1 Thermal behavior of charged cathode material $Li_{0.5}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ studied by TR-XRD with Mass spectroscopy during heating from 25 °C to 500 °C

TASK 2
Calendar & Cycle Life Studies

Project Number: FY12 New task (building on developed technology from ID39)

Project Title: Online and offline diagnostics for electrodes for Advanced Lithium Secondary Batteries

Project PI, Institution: David Wood, Oak Ridge National Laboratory

Collaborators: Argonne National Laboratory, Keyence, Solar Metrology

Project Start/End Dates: 10/1/11 to 9/30/15

Objectives: Due to high scrap rates of 10-20% or more associated with lithium secondary cell production, new methods of quality control (QC), which have been successful in other industries, must be implemented. Often flaws in the electrodes are not detected until the formation cycling when the entire series of manufacturing steps has been completed, and the associated scrap rates drive the costs of lithium secondary cells to an unacceptable level. If electrode flaws and contaminants could be detected in line near the particular processing steps that generate them, then the electrode material could be marked as unusable and the processing equipment could be adjusted to eliminate the defects more quickly. ORNL is considering in line analysis methods such as X-ray fluorescence spectroscopy (XRF) for electrode component uniformity and metal particle detection and laser thickness sensing of the electrode wet thickness measurement. In addition, on-line laser thickness measurement and IR imaging of wet and dry electrode coatings will be implemented for thickness uniformity and coating flaw detection. These methods have been effectively utilized in other industries such as photovoltaic, flexible electronics, and semiconductor manufacturing, but the equipment and measurement methods must still be tailored for lithium secondary cell production. The object of this project is to raise the production yield of lithium secondary battery electrodes from 80-90% to 99% and reduce the associated system cost by implementing in line XRF and laser thickness control. In addition, ORNL is providing its diagnostics capabilities and expertise to address materials issues with ABR cathode materials.

Approach:

Online diagnostics: Solar Metrology has been identified as a top manufacturer of in line XRF instruments for roll-to-roll applications and has a great deal of experience with the photovoltaics industry. ORNL will work closely with them to establish this technology for the lithium secondary battery industry. ORNL will produce tape casted and slot-die coated electrode rolls (anodes and cathodes) with deliberately introduced flaws to test the appropriateness of the method and the equipment modifications to the standard model. All key process parameters, such as line speed, coating thickness range, metal particle density, elemental homogeneity, etc., will be examined. In-line XRF data will also be correlated with ex-situ XCT data to gain a complete chemical and structural picture of the electrode as it is coated and dried.

Keyence has been selected as the partner for developing a laser thickness senor, or set of sensors, for lithium secondary battery electrode production. ORNL has a single-sided slot-die coating system, so only single-sided electrode coatings will be evaluated. ORNL will rent the sensors from Keyence and integrate them directly into ORNL's slot-die coating line for the proof-of-concept experiments.

The output data from the wet layer thickness measurements using the laser sensor(s) will be correlated with the thickness measurement capability by marking the regions that are out of specification during the coating process. The coated electrode rolls with markings will be fed into the in line XRF equipment to determine if wet regions out of specification match with dry regions that are determined to be out of specification. A feedback mechanism will be designed that considers whether the wet or dry thickness is a better input for adjusting the dispersion flow rate into the slot-die coater. The IR imaging QC will be correlated with thickness variation data to determine any further systematic flaw formation mechanisms.

Offline diagnostics:
ORNL characterization capabilities in acoustic emission detection, in-situ and ex-situ X-ray diffraction, neutron scattering, and magnetic property determination will be utilized to investigate cathode materials issues with ABR developed materials.

Milestones:

a) Obtain in-line IR imaging data where different types of electrode coating flaws (pinholes, blisters, etc.) are identified (May 2012); on schedule.
b) A method of correlating wet and dry thickness using laser thickness measurement and in line XRF, respectively (June 2012); on schedule.
c) An in line XRF prototype(s) designed by Solar Metrology that measures electrode component uniformity, metal particle position, and dry electrode thickness (Sept. 2012); on schedule.
d) A new or modified model of Keyence laser thickness sensor(s) specially designed for lithium secondary battery electrode dispersion deposition control (Sept. 2012); on schedule.
e) Provide characterization and analysis for ABR developed HE5050 material provided by ANL

Financial data: $300k/year for FY12

PROGRESS TOWARD MILESTONES

Online diagnostics is currently focusing on acquiring basic diagnostics tools to address processing issues associated with the two mentioned online diagnostics approaches.
In the first quarter of FY12, we have focused on diagnostic studies (XRD, magnetic susceptibility, and half-cell cycling) of the Toda HE5050 cathode provided by Dan Abraham, ANL.

1. *Investigating the structural changes in HE5050 cathode during electrochemical cycling; an in-situ XRD study*

The experiments were performed on cathodes with Toda HE 5050 lithium rich material with composition $0.5Li_2MnO_3 - 0.5LiNi_{0.375}Co_{0.25}Mn_{0.375}O_2$. The electrochemical cycling was performed in a half-cell configuration with lithium metal as a counter electrode. A specially designed cell for in-situ XRD with large (9.8 mm in diameter) Kapton window was used. The coin cell 2032 hardware was utilized in the design. 1.2M $LiPF_6$ in ethylene carbonate / dimethyl carbonate (EC/DMC 3:7 per volume) mixture was used as electrolyte (Purolyte®, Novolyte) and Celgard 2500 separator was placed between the electrodes in the cell. The cathode had the following composition: 86%wt Toda HE5050 – 8%wt PVDF binder – 4%wt Timcal SFG-6 Graphite – 2%wt Timcal Super P. Experiments were controlled by BioLogic VMP3 potentiostat and the cell was positioned inside a cell holder within the XRD (Panalytical Instruments) enclosure for simultaneous collection of diffraction data.

The experiments targeted the following major questions: (a) what are the structural changes in the cathode material upon cycling in large voltage window (2.4 – 4.8V), and (b) what are the changes during the prolonged hold at 4.5V (the plateau voltage).

Figure 1 shows the electrochemical cycling data together with the plots showing the evolution of XRD peaks within the corresponding time intervals. The cell was charged and discharged at 9 mA/g rate. The major observations are: (i) shifting in peak position of (003), (101), (102), (113) planes during cycling; (ii) during the end of first cycle, the (108) and (110) peaks merge with each other (see the white arrow mark in the figure) and then starting to split during discharging; (iii) (101) peak shifts to the lower 2-theta angle during charging and then shifts to the higher 2-theta angle during discharging.

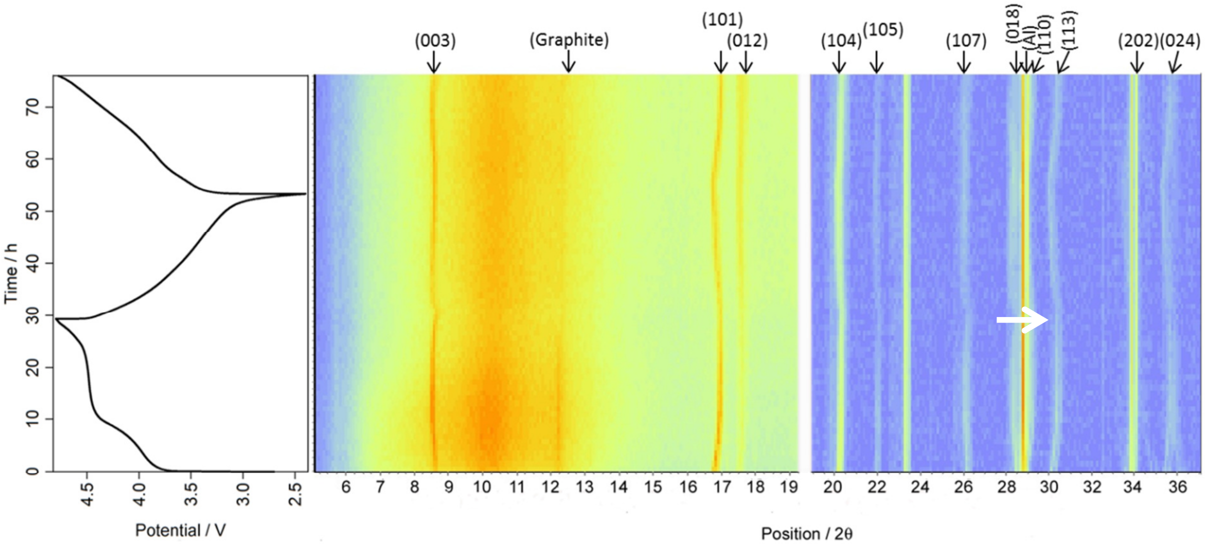


Figure 1 The in-situ XRD plots of HE5050 and the state of electrochemical cycling (left). The color scale represents the intensity of the particular crystallographic plane.

Figure 2 shows the electrochemical response together with the calculated phase percentages corresponding to several points with different state of charge. The experiment targeted observations of structural changes during the prolonged hold at the plateau voltage. The cell made 1.5 cycles at 27 mA/g and then was held at 4.5V for ~ 50 hours. The following observations can be made based on the data in Fig. 2. The percentage of Layered material increases after 2 h of charging within the first cycle. This is possibly due to extraction of Li ions from the transition metal layers instead of lithium layers, which decreases the ordering (C2/m) and increases the fraction of layered material. It can also be seen that with subsequent charging the content of the layered phase is reduced (30% at the end of the second charge as opposed to 39% at the end of the first charge). This is attributed to trapping of lithium ions in the monoclinic phase at higher voltages. The composition does not return to the initial 50:50 ratio at the end of discharge.

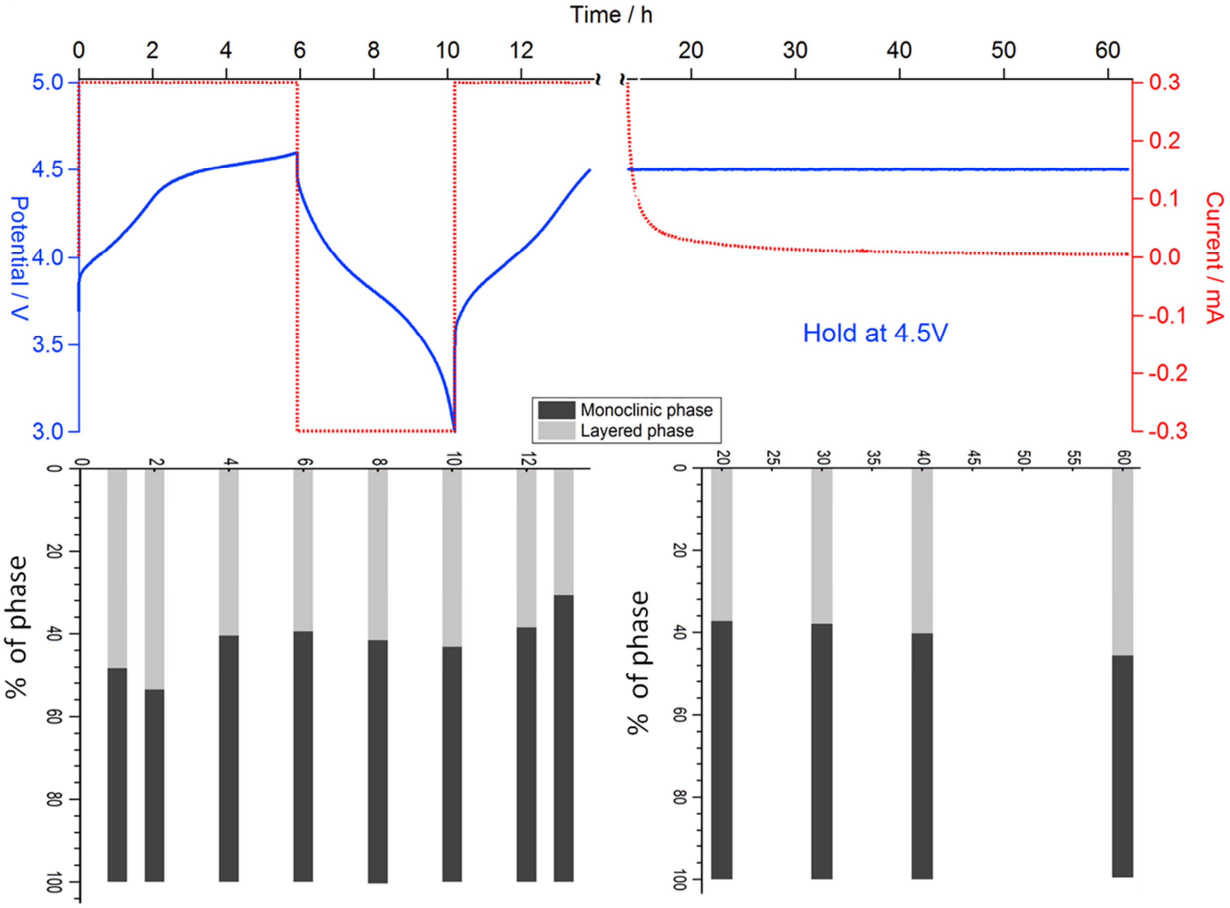


Figure 2 Percentage of monoclinic and layered hexagonal phase as a function of time during electrochemical cycling

Interesting observations can be further made based on the data from the prolonged hold at 4.5 V. Figures 3 and 4 are placed here to aid the discussion. As can be seen (Fig.2) at the end of the hold the composition returns to nearly original 50:50 state. Considering that the current is zero, and thus there is no flux of Li ions to the cathode, this change in composition probably results from the diffusion of ions within the cathode material from the monoclinic to hexagonal layered phase. This behavior can be correlated with the change in c- lattice parameter of the material. The *in-situ* XRD patterns at different time intervals of electrochemical cycling are shown in Fig. 3. To aid observation of changes in the lattice parameter, (003) peak positions are presented as an inset of Fig. 3. During charging, the (003) peak shifts to the lower 2-theta angle raveling the unit cell expansion whereas, during discharging, the (003) shifts towards the higher 2-theta angle showing unit cell contraction. While this result is obvious, the interesting observation was made on the (003) peak positions, during holding the voltage for prolonged period at 4.5V. The (003) peak shifts towards higher 2-theta angle during the voltage holding period indicating the unit cell contraction (similar to discharge process). This can be attributed to the diffusion of lithium ions with in the cathode material, which supports the observation of the distribution of percentage of monoclinic and hexagonal phase during holding period (Fig. 2) and/or self-discharge of battery. The lattice parameters were obtained from the refinement results and plotted as a function of cycling time (Figure 4(a-b)).

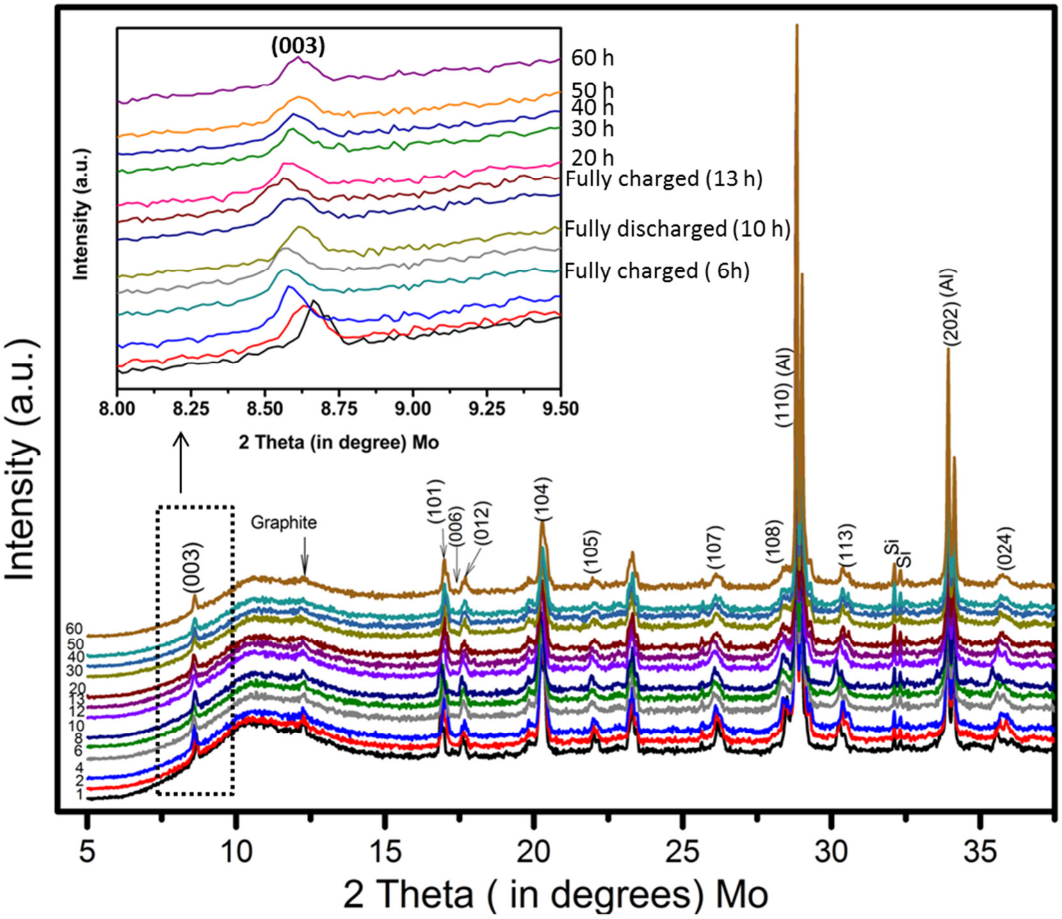


Figure 3: The *in-situ* XRD pattern of HE5050 material. The (003) peaks, highlighted as inset of the figure, show the change in position during charging, discharging, and voltage holding time. The numbers at the beginning of the curves are the time intervals of XRD collection

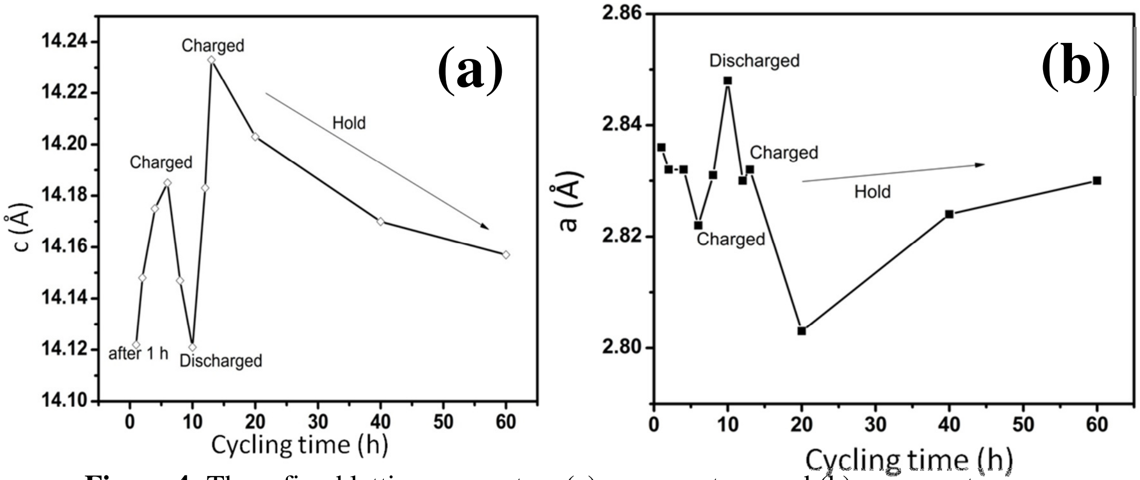


Figure 4: The refined lattice parameters (a) c parameters, and (b) a parameters as a function of cycling time

2. Understanding the local structure of $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.55}O_2$ *(HE5050) cathode via PXRD, magnetic and TEM techniques, in order to predict the capacity decaying pathways.*

Motivation: To investigate the crystal structure and long-range/short-range ordering in HE5050 cathode material and correlate with the electrochemical data in order to propose the capacity fading mechanism. Figure 5 shows the powder XRD of the HE5050 material. All the peaks can be indexed based on the layered phase with hexagonal symmetry (Rhombohedra) of $R\overline{3}m$ space group. The superlattice peaks appear in the 9-10 degree 2-theta region, which could be indexed based on monoclinic phase of *C2/m* symmetry. These superstructures appear due to the ordering of lithium ions in the transition metal layers. Since HE5050 composition has 50% of Li_2MnO_3 phase, that might be the cause of appearance of these superstructures. However, one cannot totally discard the case where Li is ordered with both Ni and Mn ions in the transition metal layers. Investigation of this long-range/ short-range ordering in HE505 material is one of the major aspects of the ongoing study.

In order to investigate this, the magnetic measurement was carried out from the sample. The measurement was performed under field cooling (FC) and zero field cooling (ZFC) using a superconducting quantum interface (SQUID) magnetometer in the temperature range between 2K-320K under the magnetic field H=100Oe. The paramagnetic behavior was observed at the higher temperature region ($T \geq 125$K) which shows that the electron spins are randomly oriented in the structure. At $T \leq 75$, the FC and ZFC bifurcates, the result that is an indication of magnetic ordering in the lattice. This supports the results from XRD (Figure 5) where the ordering was observed.

Detailed analysis and structural refinement are under progress.

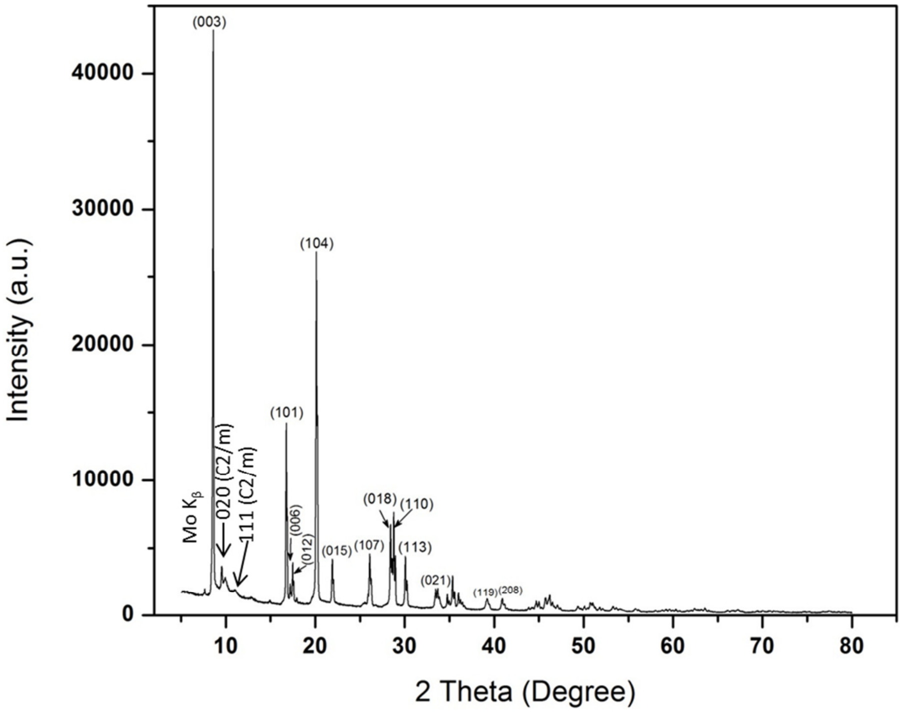


Figure 5: The PXRD pattern of $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.55}O_2$ shows both the layered phase and monoclinic phase (monoclinic phase has been shown as C2/m notation)

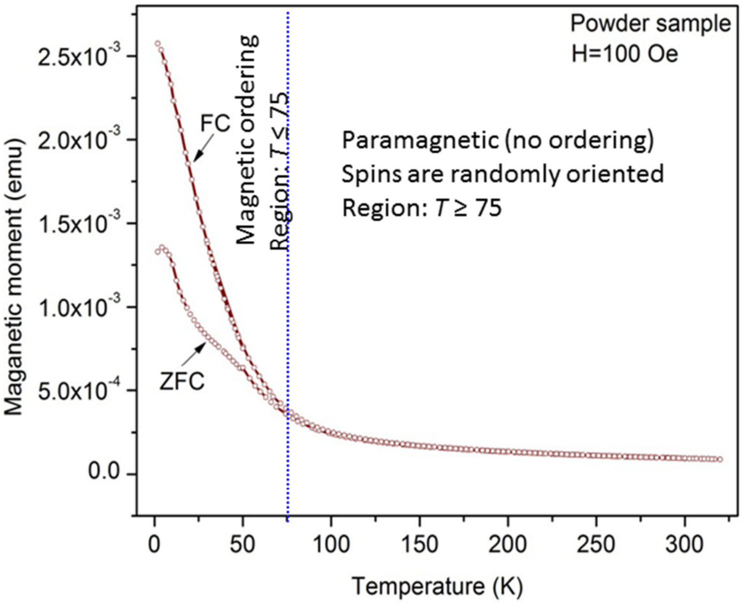


Figure 6: The Change in magnetic moment with the temperature in filed cooling (FC) and zero field cooling (ZFC) shows the magnetic ordering bellow *T*=75K

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

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 2.0 of the Battery Performance and Cost model (BatPaC) with documentation. October 2012 (On schedule)
(b.) Implement liquid and air thermal management and evaluate role in design and cost. May 2012 (On Schedule)
(c.) Support EPA and NHTSA use of BatPaC for 2017-2025 GHG regulation and CAFE standards rule making. March 2012 (On schedule)
(d.) Support the public distribution of the model and report. October 2012 (On schedule)
(e.) Evaluate design and cost modeling of advanced Li-ion electrochemical couples. October 2012 (On schedule)

Financial data: $300K/year

PROGRESS TOWARD MILESTONES

(a) Creation of battery performance and cost model BatPaC v2.0: Modification of the first distribution of BatPaC is already underway. BatPaC v2.0 will include air and liquid thermal management options as well as automatic error bar generation. The 2.0 version is still under development with a targeted public distribution of late summer 2012.

(b) Implement thermal management options: The model initially did not consider thermal management. In response to communication with industry, we are now working to include three options to capture some of those being used in today's hybrid and electric vehicles. The assumed module designs for liquid and air thermal management are shown in Figure 1. Initial calculations are showing a very small difference in cost, with cabin air thermal management being slightly less expensive (~$100 less or 3% for a PHEV20). The use of air requires flow channels between the cells and manifolds above and below the modules. These air flow passage ways significantly increase the pack volume (x4 for a PHEV20). Because of the large volume penalty, we will only use air thermal management for some HEV battery designs.

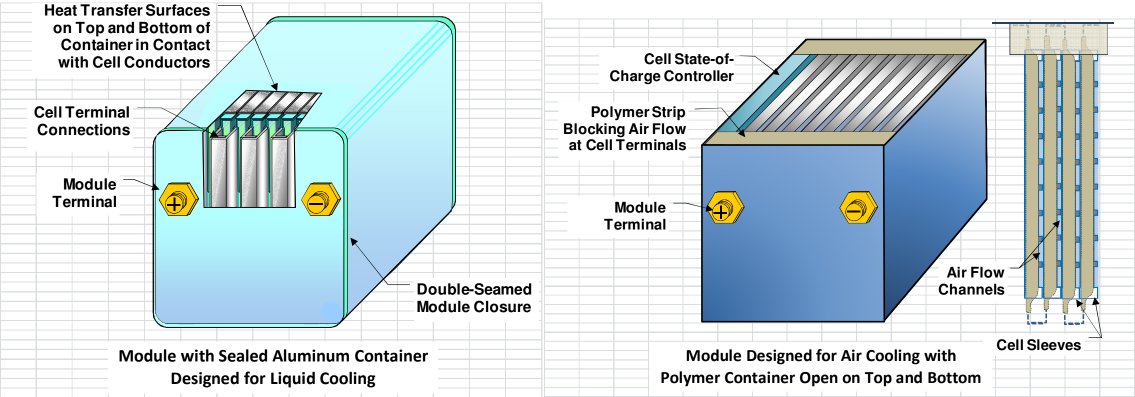


Figure 1: Module designs for liquid thermal management (left) and cabin air thermal management (right). Air designs will result in a larger pack volume with marginally less cost.

(c) Support EPA 2017-2025 rule making: Responding to request to include new aspects into the previously released BatPaC v1.0. We will be implementing passive cabin air, active air, and active liquid thermal management into BatPaC. Additional battery and module arrangement options will also be included (parallel combinations) as requested by the EPA. The necessary documentation will also be included to support the rule making.

(d) Support public distribution: Interacted with multiple small and large companies to discuss BatPaC v1.0 availability, results of the model and some initial tips for use.

(e) Design & cost of advanced Li-ion: Gathering of data regarding graphite/silicon composite anode materials for an analysis of benefits and costs of moving to these advanced anodes. Future work will focus on range of acceptable active material costs and the penalty of lowering cell voltage. Study of cathode materials will focus on defining targets for the developers of the lithium and manganese rich transition metal oxide materials. Previous development efforts have focused solely on a target capacity. Using BatPaC, voltage and capacity targets will be determined to ensure the final developed material will result in a lower cost product than the best “standard” materials coming to production today.

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

Public distribution of BatPaC v1.0 with report on November 1st, 2011 at www.cse.anl.gov/batpac

TASK 3
Abuse Tolerance Studies

Project Number: 3.1 (ES035)

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

Project PI, Institution: Zonghai Chen & Khalil Amine, Argonne National Laboratory

Collaborators (include industry): Yang Ren, Yan Qin, Chi-Kai Lin, Lu Zhang, Superior Graphite

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

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

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

Milestones
(a) Investigating the impact of salt on thermal decomposition of delithiated cathode (finished);
(b) Investigating the thermal decomposition of SEI layer on graphite (on schedule).

Financial data: $500K/FY2012

PROGRESS TOWARD MILESTONES

(a) Summary of work in the past quarter related to milestone (a).
In the past years, we have encountered difficulty in reproduce the difference scanning calorimetry (DSC) profiles of delithiated cathodes with the presence of non-aqueous electrolyte. The poor repeatability greatly hindered the investigation on the safety performance of cathode materials as well as their mitigation technologies. In the previous quarters, we initiated in situ high-energy X-ray diffraction (HEXRD) to

investigate the changes in the solid materials, or delithiated cathodes. With the help of in situ HEXRD, we have investigated the thermal decomposition of delithiated $Li_{1-x}(Ni_{/1/3}Mn_{1/3}Ni_{1/3})O_2$ (@ 4.1 V) with the presence of various liquids; the mixture of delithiated $Li_{1-x}(Ni_{/1/3}Mn_{1/3}Ni_{1/3})O_2$ was housed in a high pressure stainless steel DSC vessel. The liquids investigated include (1) normal Gen2 electrolyte (1.2 M $LiPF_6$ in EC/EMC), (2) dry sample without liquid, (3) solvent EC/EMC only, (4) 1.0 M LiTFSI in EC/EMC, (5) 1.0 M $LiBF_4$ in EC/EMC, and (6) 0.4 M $Li_2B_{12}F_{12}$ in EC/EMC. Figure 1a shows the 2D contour plot of in situ XRD data collected during the thermal decomposition of delithiated NMC (charged to 4.1 V). The characteristic peaks (101) and (012) for layer materials are labeled on Figure 1. It clearly shows that the material decomposed at about 180°C. Figure 1b shows the in situ HEXRD data for delithiated NMC mixed with solvent only, no $LiPF_6$; it shows that the thermal decomposition of delithiated NMC started at about 280°C, about 100°C than that of the sample with $LiPF_6$. In order to confirm the finding, $LiPF_6$ was replaced with LiTFSI, $LiBF_4$ and $Li_2B_{12}F_{12}$, respectively. Figure 1c shows a typical result of that containing LiTFSI instead of $LiPF_6$. It can be seen that the thermal decomposition started at about 240°C. It is clear that lithium salt plays a important role on the thermal stability of delithiated cathodes, and $LiPF_6$ is responsible for a relatively low thermal stability of delithiated cathodes.

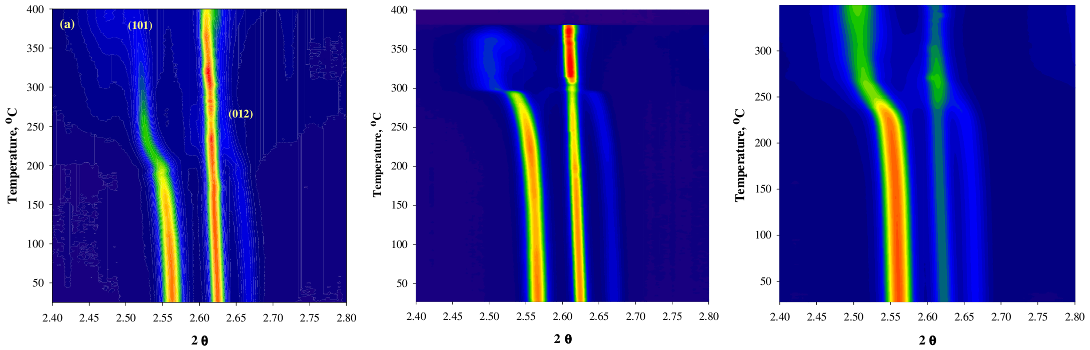


Figure 2 Contour plot of in situ XRD data during thermal decomposition of delithiated NMC with the presence of (a) 1.2 M $LiPF_6$ in EC/EMC (3:7, by weight), (b) EC/EMC (3:7, by weight), and (c) 1.0 M LiTFSI in EC/EMC (3:7, by weight).

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

We have demonstrated previously that the thermal decomposition of SEI layer played a critical in the safety of lithiated graphite. Our previous study showed that natural graphite, a mixture of 2H graphite and 3R graphite, has a better thermal stability than conventional MCMB. In order to validate the impact of surface functional group on the safety of graphite, natural graphite coated with carbon source was acquired from Superior Graphite. Different thermal processing conditions were applied to the precursor, assuming that the content and type of surface functional groups varies with the processing condition. The first batch of experiment was to graphitize the carbon source at different temperatures in inert atmosphere. The treating temperature varies from 700°C to 1100°C. Measuring the activation energy of the thermal decomposition of SEI of this materials using DSC was ongoing. Electrochemical characterization of these materials will be carried out in the following quarter.

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

1. Zonghai Chen, Yang-Kook Sun, and Khalil Amine, Material Perspectives for Safe and High Energy Density Lithium-Ion Batteries, submitted to *Angew. Chem. Int. Ed.*, (**2011**).

TASK 3
Abuse Tolerance Studies

Project Number: 3.2 (ES036)

Project Title: Abuse Tolerance Improvements

Project PI, Institution: Chris Orendorff, Sandia National Laboratories

Collaborators (include industry): ANL, INL, BNL, ORNL, NREL, 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) LiF/ABA electrolyte development (ON GOING, on schedule)
(b) Ionic liquid electrolyte development (ON GOING, on schedule)
(c) Cell prototyping optimization & collaboration with other Labs (ON GOING, on schedule)
(d) Overcharge shuttle evaluation in full cells (DUE 9/30/2012, on schedule)
(e) Support INL phosphazene electrolyte development (DUE 9/30/2012, on schedule)
(f) Evaluation of phosphate coated NMC (DUE 9/30/2012, on schedule)
(g) Evaluation of ALD-coated NMC electrodes (DUE 9/30/2012, on schedule)

Financial data: Total budged \$1.0M; received \$160K (from SNL); \$45K subcontract to Binrad Industries (ABA), \$10K subcontracted to Physical Sciences Inc. (phosphate coated NMC)

PROGRESS TOWARD MILESTONES

(a) LiF/ABA electrolyte development. In FY11, we demonstrated the utility of LiF/ABA electrolytes to passivate cathode runaway reactions on cathode materials by DSC (materials) and ARC (cells) (FY11 ABA will be referred to as lot 1, ABA-1). We also observed some negative attributes of the ABA including instability > 4.3V and some decomposition/diminished performance after ~18 months. FY12 will focus on (1) developing new ABA molecules with improved voltage stability and (2) characterization of the degradation mechanisms of ABAs that lead to cathode passivation during runaway. Contracts were issues to our industrial partners (Binrad Industries) to synthesize greater quantities of ABA-1 (lot-2) and next generation ABA-2 and ABA-3. SNL received lot 2 ABA-1 in December 2011. CVs show improved voltage stability of the lot 2 ABA-1 over lot 1 (Figure 1). NMR also confirms some change in ABA-1 structure (lot 1) compared to the as-received lot 2. Work is ongoing to determine the cause of lot 1 decomposition.

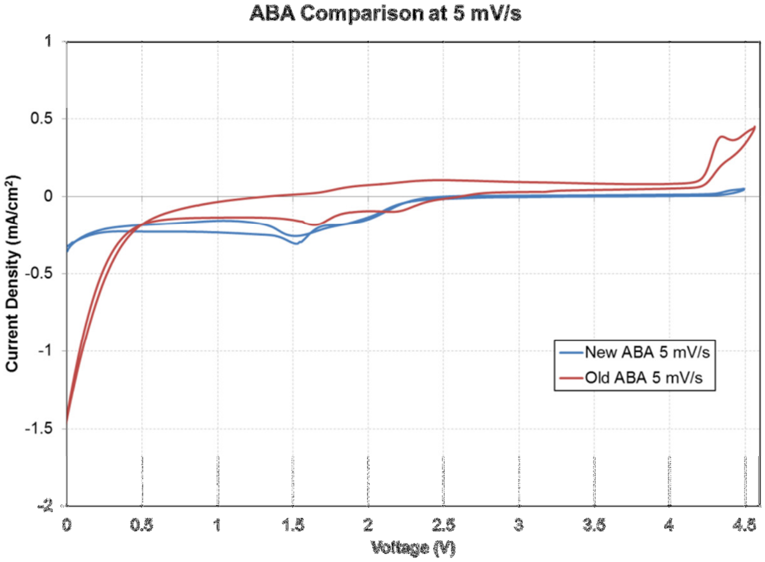


Figure 1. Cyclic voltammetry of ABA-1 lot 1 (old) and lot 2 (new) vs. Li/Li$^+$

(b) Ionic liquid electrolyte development. Two ionic liquids (ILs) have been prepared to date for use as alternative electrolytes with improved high voltage stability and nonflammability. The first IL is an imidazolium bis(trifluoromethane)sulfonimide and the second is an ammonium bis(trifluoromethane)sulfonimide. CVs of the ILs show some significant reduction of the imidazolium approaching the lithium potential, but improved stability of the second IL at low voltage. Both ILs are stable at > 4.5 V vs. Li/Li+. A request has been made to ANL to provide LTO/HV spinel electrodes for evaluation of IL-2 at SNL in coin cells. We will also evaluate it against graphite anodes in Q2. Once baseline performance is determined, Technical Advances will be submitted for these candidates. Q2 will focus on lowering the freezing point of IL-2 by using different substituents (currently -10 C) and continuing to improve the voltage stability of these analogues near the lithium potential.

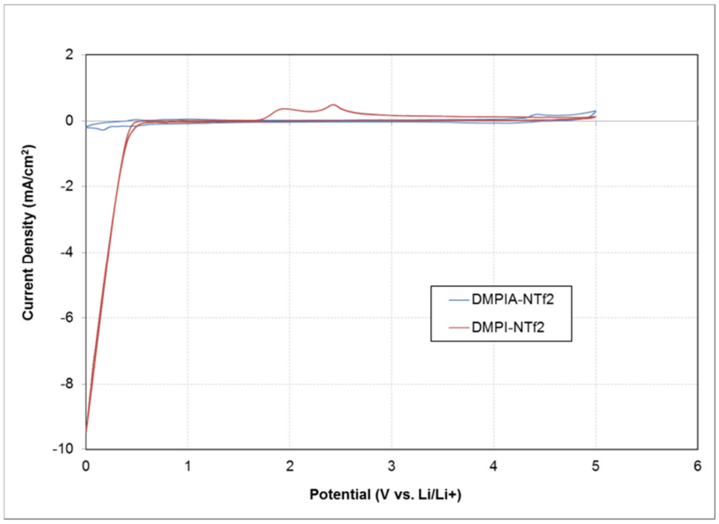


Figure 2. Cyclic voltammetry of IL-1 and IL-2 at 5 mV/s vs. Li/L^{i+}

(c) Cell prototyping optimization & collaboration with other Labs. At the end of FY11, SNL and DOE agreed to use the Toda NMC (111)/Conoco Phillips A10 graphite electrochemical couple for the early FY12 cell builds to support the electrolyte thrust/materials development efforts in ABR. In Q1 FY12, SNL optimized a 1.5 Ah design for this couple in 18650 cells and coated ~150 electrode pairs to support the effort. In addition, SNL has coated the first run of LFP electrodes to support the ANL-RS-2 shuttle development. LFP cells have been built with the shuttle and the first NMC cells have been built with the INL electrolyte. The quantity of cells to support these different programs is 40 (INL Phosphizene), 24 (JPL electrolyte, 24 (ANL-RS-2 shuttle, LFP), ~40 (SNL ABA), and 6-10 (NREL ALD coating).

On January 17, 2012, SNL hosted the first joint cell prototyping meeting to discuss standardization of electrode/cell designs cross ABR. The group decided to prove out this standardization effort using the Toda NMC (523) and A10 graphite couple. This effort is anticipated to take 3-6 months, led by ANL and the materials screening process, followed by electrode evaluation of the other Labs.

(d) Overcharge shuttle evaluation in full cells. Cells with and without the redox shuttle supplied by Argonne National Laboratory, referred to as ANL-RS2, were prepared by both Sandia and A123. Heat generation of the shuttle is determined using isothermal calorimeter by constant current charging cells to 3.8 V at a C/5 rate for cells with and without the shuttle. Figure 3 shows the data for the cells constructed at Sandia. The cell containing the overcharge shuttle behaved similarly to the control cell until ~500 mAh capacity, where the overcharge shuttle becomes electrochemically active, the heat and the voltage increasing until a steady state is reached at ~3.78 volts (left panel). At this point nearly all of the charging current is lost as heat generation. This can be seen in Figure 3 (right panel), where the heat generation is fairly low compared to the input power until nearing the shuttle voltage, where the heat generation from the cell is over 90% of the input power.

The data on the cells provided by A123 shows similar behavior (Figure 4), with the most noticeable difference being a capacity drop between the control cell and the shuttle cell in cells manufactured at Sandia. This may be due differences in the formation process; the Sandia cells were formed to 3.8 volts, causing the shuttle to activate during the forming process, while the A123 cells were formed to 3.6 volts. In addition, the total heat flow from the A123 cell is ~700 mW, compared to ~400 mW from the lower capacity SNL cell. Work will continue to evaluate the rate dependence on heat output of the shuttle, efficacy with cycle number, and ARC measurements to determine the shuttle's effect on the runaway reactions within the cell.

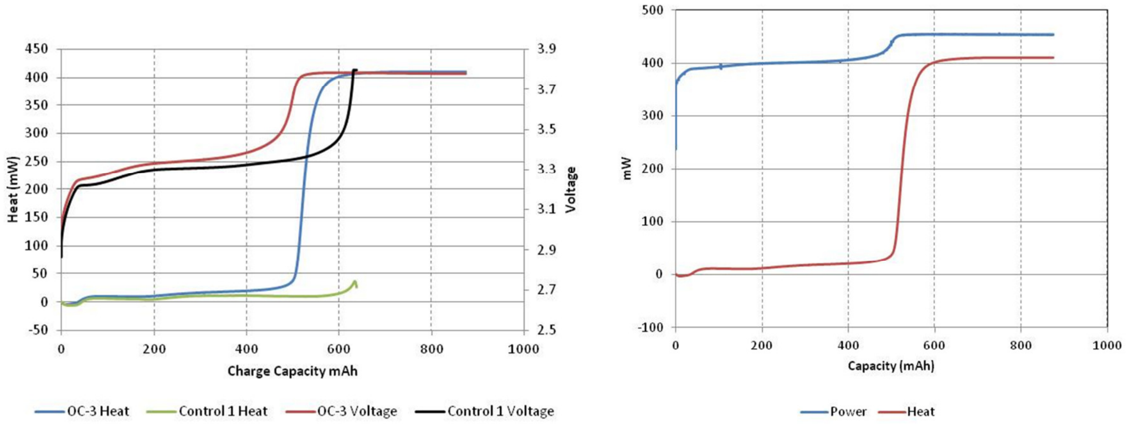


Figure 3. Heat output during charging (right) and heat output and input power during charging (left) for SNL LFP cells

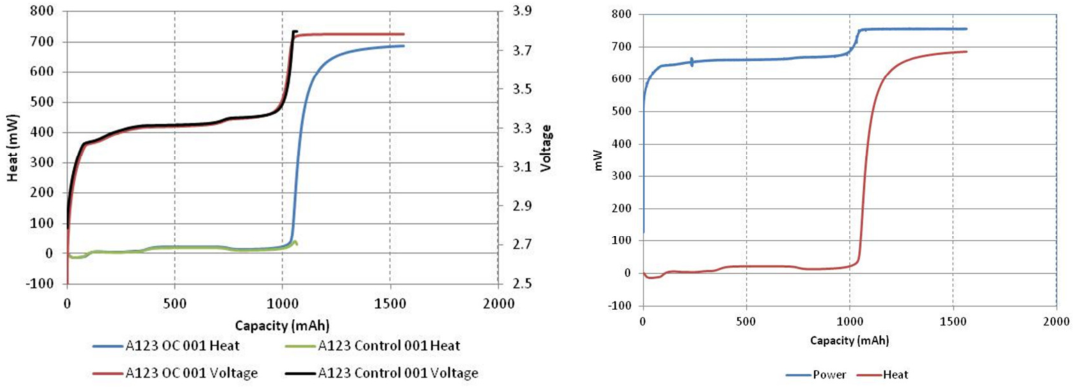


Figure 4. Heat output during charging (right) and heat output and input power during charging (left) for A123 LFP cells

(e) Support INL phosphazene electrolyte development. Electrolytes were received from INL in early Q1 FY12. These include a control (1.2 M $LiPF_6$ in EC:EMC (2:8)) and phosphazene containing electrolytes SM-6, FM-2, and Phil-1 (up to 3% by wt). Control cells were built and formed and have a capacity of 1.4 Ah (Figure 5). ARC measurements have been delayed because of relocation of the calorimeters to a new location (a result of the ARRA project). ARCs have been recalibrated and measurements will begin Q2 FY12. Flammability measurements will be made in Q3 FY12.

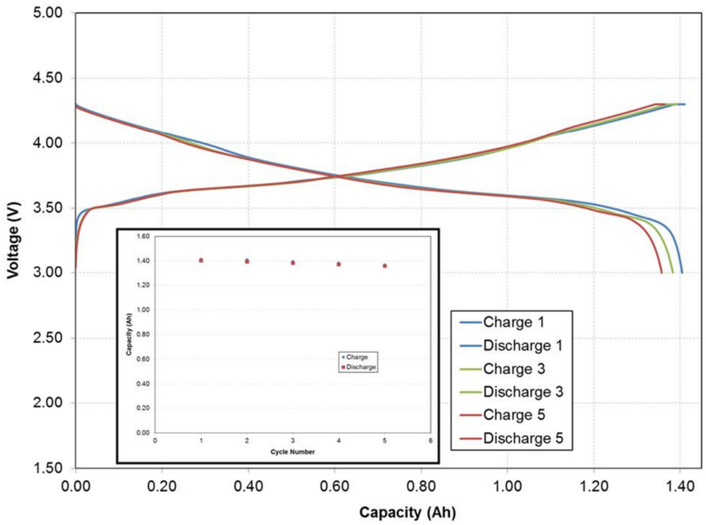


Figure 5. Formation C/D capacity of NMC111/A10 cells with INL baseline electrolyte

(f) Evaluation of phosphate coated NMC. In FY10 and FY11 SNL evaluated the AlF3-coated NMC materials from Prof. Sun and ANL and showed a clear abuse tolerance improvement for the coated materials compared to the uncoated cathodes. As a follow-on to that work, SNL is contracting with Physical Sciences, Inc. (PSI) to evaluate phosphate-coated NMCs using their process developed under a NASA SBIR proposal in FY10/FY11. A PO was issued to PSI in Q1 and SNL delivered 3 kg of Toda NMC 111 to be coated at PSI (500 g for process development, 2 kg final deliverable of coated cathode, 500 g contingency). The 500 g development will be completed February 2012 and PSI will work on the scaled up process. Coated and uncoated electrodes will be prepared at SNL and cell built for ARC evaluation of this coated cathode.

(g) Evaluation of ALD-coated NMC electrodes. Analogous to the coated powder work at ANL and with PSI, NREL and SNL are working on possibly ALD coating some of the SNL electrode inventory for abuse evaluation and ARC measurements. This project is in its infancy with discussions underway and logistics being assessed. However, this seems to be a relatively easy set of experiments to do in order to generate high value data for the NREL project with minimal effort.

Publications, presentations, reports, IP, etc.

C. J. Orendorff, USDrive meeting, October 6, 2011
C. J. Orendorff, "Increasing the Scale of Lithium-Ion Batteries and the Importance of Inherent Cell Safety," ECS Boston, October 11, 2011
C. J. Orendorff, "Abuse Tolerant Lithium-ion Cells for Transportation Applications," Lithium Mobile Power/Safety Meeting, November 9, 2012
C. J. Orendorff, "A Materials Approach to Abuse Tolerant Lithium-ion Batteries" IBA/PPSS meeting, January 9, 2012
C. J. Orendorff, "Safety Performance Advancements for Large Scale Lithium-ion Batteries
Through Materials Development" SAE Government/Industry Meeting, January 26, 2012

TASK 3
Abuse Tolerance Studies

Project Number: 1.2.1 (ES037)

Project Title: Overcharge Protection for PHEV Batteries

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

Collaborators: Robert Kostecki, John Kerr, Vince Battaglia, Marca Doeff, Gao Liu, Yuegang 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) Investigate overcharge protection performance of polymer fiber incorporated composite separators (Jun. 2012). **On Schedule**

b) Evaluate the property and performance of new high-voltage electroactive polymer candidates (Jul. 2012). **On Schedule**

c) Report overcharge protection for pouch and other large-scale battery cells (Sep. 2012). **On Schedule**

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

PROGRESS TOWARD MILESTONES

In this quarter, we investigated the cycleability of lithium battery cells that were overcharge-protected by electroactive polymers. Composite separators were prepared by solution impregnating poly[(9,9-dioctylfluorenyl-2,7-diyl)] (PFO) and poly(3-butylthiophene) (P3BT) into a glass fiber membrane (GF/D grade by Whatman). The typical polymer loadings were 1.3 and 0.67 mg/cm^2 for PFO and P3BT composites, respectively. Compared to the Celgard membranes used in our previous studies, the glass fiber membrane has a higher porosity and a more open pore structure. Both of these features promote uniform polymer distribution in the composite, which leads to better polymer utilization during overcharge protection. A bilayer configuration with the PFO composite adjacent to the cathode and the P3BT composite adjacent to the anode was used. Fig. 1 shows the room-temperature cycling performance of the protected $LiFePO_4$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Gen2) and $Li_{1.05}Mn_{1.95}O_4$ half cells with lithium metal counter and reference electrodes. The $LiFePO_4$ cell was cycled at a 0.5C rate and 80% overcharge. A steady state potential at 4.4V was reached and maintained, indicating that a soft short was established and that overcharge current passed through the conducting polymers. Reversible protection was achieved, and the cell maintained its discharge capacity for well over 150 cycles (Fig. 1a). The $Li_{1.05}Mn_{1.95}O_4$ cell was cycled at a 0.2C rate and 60% overcharge. The upper potential limit increased to 4.5V due to the increased current density, and the cell maintained its discharge capacity for more than 120 cycles (Fig. 1b). Fig. 1c shows the testing results of the Gen2 cell with 90 cycles at 0.2C and 50% overcharge, followed by 60 cycles at 0.5C and 40% overcharge. Although steady state potentials at 4.4 and 4.5V were maintained for 0.2C and 0.5C, respectively, the discharge capacity gradually decreased. The cathode's structural and chemical instabilities at low Li content and side reactions at high voltages may be the causes for the capacity fade.

Our results clearly demonstrate that electroactive polymers are capable of prolonged overcharge protection for lithium-ion batteries.

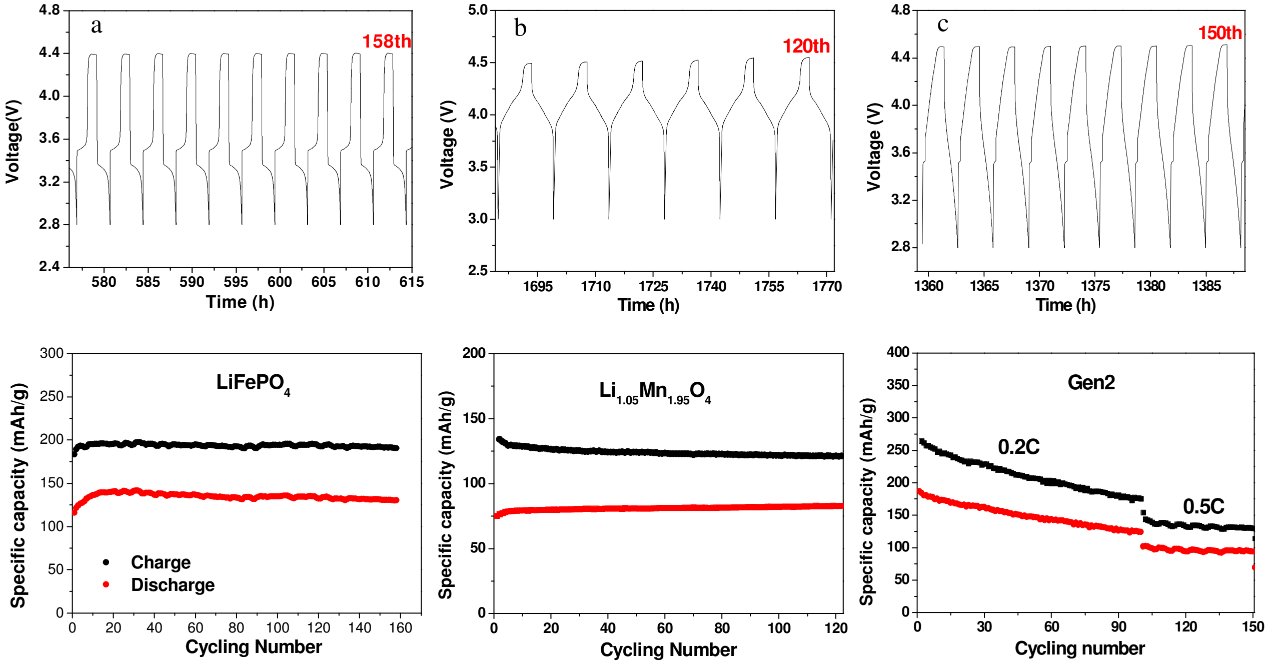


Figure 1. Voltage profiles and cycling capacities of polymer-protected cells with a) $LiFePO_4$, b) $Li_{1.05}Mn_{1.95}O_4$ and c) $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Gen2) cathodes.