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

Progress Report
for
Second Quarter FY 2011

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

April 2011

Applied Battery Research for Transportation Program
Second Quarter Progress Report for FY 2011

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

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

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

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

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

Organization	AMR Project ID	AOP Project ID	Title	PI/Contact Point	Page Number
			Task 1: Battery Cell Materials Development		
ANL	ARRA VT076		Materials Scale-Up Facility	Gregory Krumdick	6
ANL	ARRA VT076	IV. E.1.1	Process Development and Scale up of Advanced Cathode Materials	Gregory Krumdick	10
ANL	ARRA VT076	IV. E.1.2	Process Development and Scale up of Advanced Electrolyte Materials	Gregory Krumdick	12
ANL	ES015	1.1A	Engineering the High Energy Cathode Material	Khalil Amine	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	21
ANL	ES019	1.1G	Development of High-Capacity Cathode Materials with Integrated Structures	Sun-Ho Kang	23
ANL	ES020	1.1C	Developing High Capacity, Long Life anodes	Khalil Amine	27
ANL	ES022	1.1I	Develop Improved Methods of Making Intermetallic Anodes	Andrew Jansen	30
ANL	ES023	1.1H	Development of Novel Electrolytes & Additives for PHEV Applications	Dan Abraham	33
ARL	ES024		High Voltage Electrolytes for Li-ion Batteries	Richard Jow	36
ANL	ES025	1.1D	Development of Advanced Electrolyte Additives	Zhengcheng Zhang	39
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	47
ANL	ES028	1.1E	Streamlining the Optimization of Lithium-Ion Battery Electrodes	Wenquan Lu	54

Organization	AMR Project ID	AOP Project ID	Title	PI/Contact Point	Page Number
			Task 1: Battery Cell Materials Development		
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
ANL	ES112	1.2C	Functionalized Surface Modification Agents to Suppress Gassing Issue of $Li_4Ti_5O_{12}$ Based Lithium Ion Chemistries	Khalil Amine	61
ANL	ES113	1.1L	Development of High Voltage Electrolyte for Lithium Ion Battery	Zhengcheng Zhang	63
ANL	ES114	1.2D	Spherical Carbon Anodes Fabricated by Autogenic Reactions	Michael Thackeray	66
ANL	ES115	1.1V	Synthesis and Development of High-Energy and High-Rate Cathode Materials from Ion-Exchange Reactions	Christopher Johnson	69
NAVSEA-Carderock	ES038		High Energy Density Ultracapacitors	Patricia Smith	72
ANL		1.1X	Paper Study on Continuous Process for Making Gradient Concentration Cathode Material	Gregory Krumdick	75
ANL		1.1K’	Transition Metal Precursors for High Capacity Cathode Materials	Ilias Belharouak	77
			Task 2: Calendar & Cycle Life Studies		
ANL	ARRA VT075		Prototype Cell Fabrication Facility	Andrew Jansen	80
ANL	ARRA VT077		Post-Test Facility	Ira Bloom	82
ANL	ES030	2.1	Fabricate PHEV Cells for Testing and Diagnostics in Cell Fabrication Facility	Andrew Jansen	85
ANL	ES031	2.2B	Model Cell Chemistries	Dennis Dees	88

Organization	AMR Project ID	AOP Project ID	Title	PI/Contact Point	Page Number
			Task 2: Calendar & Cycle Life Studies		
ANL	ES032	2.3A	Diagnostic Evaluation of Lithium Battery Cells and Cell Components	Dan Abraham	91
ANL	ES032	2.3B	Structural Investigations of Layered Oxides for PHEV Applications	Dan Abraham	94
LBNL	ES033	1.1.1 and 2.4.1	Electrochemistry Diagnostics of Baseline and New Materials	Robert Kostecki	97
BNL	ES034		Diagnostic Studies to Improve Abuse Tolerance and life of Li-ion batteries	Xiao-Qing Yang	100
ORNL	ES039		In-situ characterization and diagnostics of mechanical degradation in electrodes	Claus Daniel	103
ANL	ES111	2.2A	Battery Design Modeling	Kevin Gallagher	106
			Task 3: Abuse Tolerance Studies		
ANL	ES035	3.1	Develop & Evaluate Materials & Additives that Enhance Thermal and Overcharge Abuse	Khalil Amine	109
SNL	ES036	3.2	Abuse Tolerance Improvements	Chris Orendorff	112
LBNL	ES037	1.2.1	Overcharge Protection for PHEV Batteries	Guoying Chen	114

APPENDIX

Individual Project Progress Reports

TASK 1
Battery Cell Materials Development

Project Number: ARRAVT076

Project Title: Materials Scale-Up Facility

Project PI, Institution: Gregory Krumdick/Argonne National Laboratory

Collaborators (include industry): < none >

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

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

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

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

The approach to achieve the facility plan is to:

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

- Prepare the environmental and safety plans and NEPA for the facility construction and interim labs.
- Begin work in interim labs to demonstrate that scaling is possible.

Milestones:

Materials Engineering Facility Construction

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

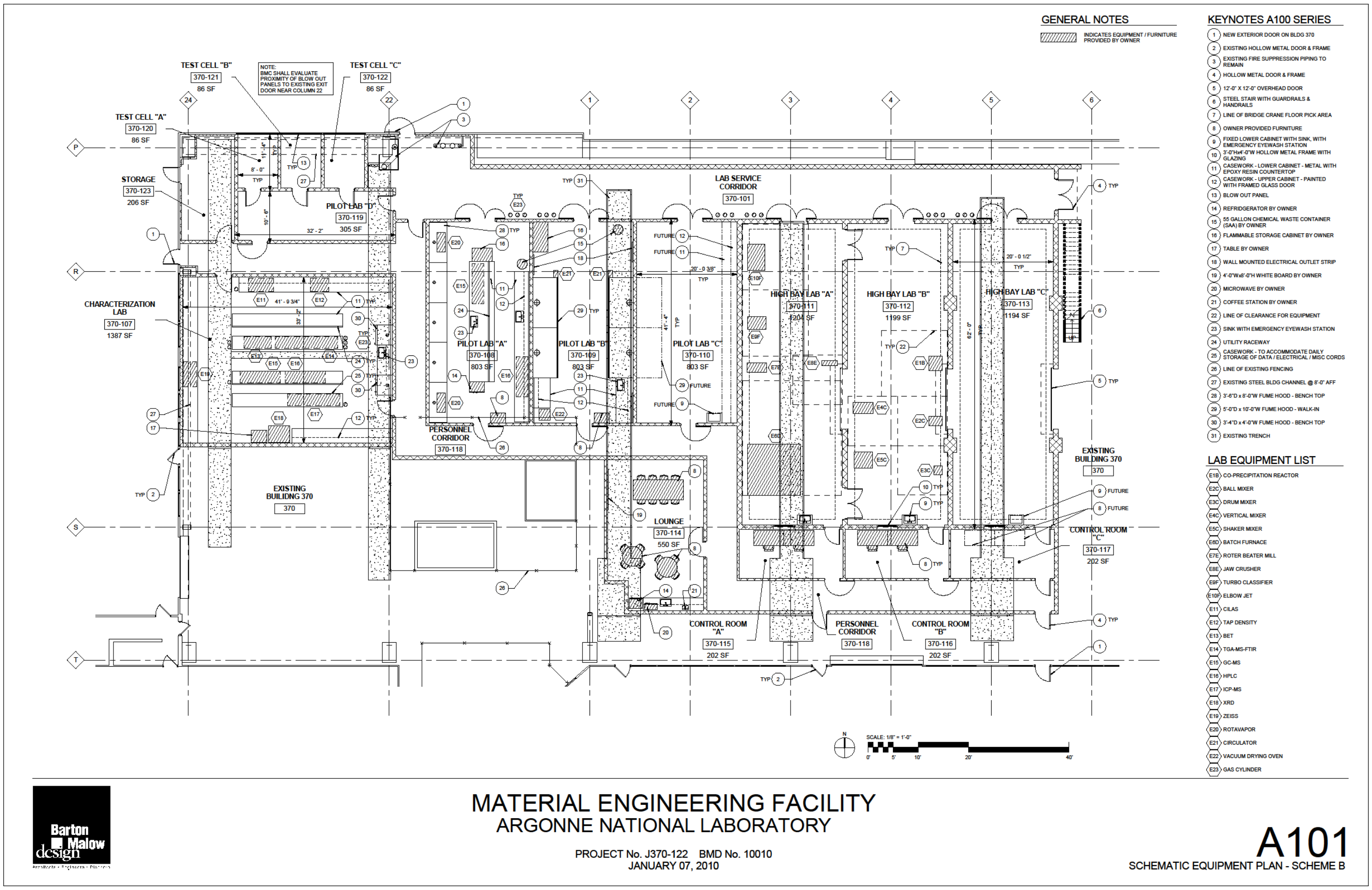
Interim Facilities and Equipment

Milestone / Deliverable	Description	Date	Status
Milestone 1	Interim facility equipment purchased & installed (3 facilities)	12/31/2010	2 COMPLETED 9/17/2010
Milestone 2	Production scale-up facility equipment purchased & accepted	12/31/2011	FUNDING INADEQUATE
Deliverable 1	Interim facility open (3 facilities)	9/30/2010	2 COMPLETED 9/17/2010
Deliverable 2	Full facility open	3/31/2012	

Financial data:
Total project duration: 24 mo.
Construction funds for facility: $3.3M
Capital equipment for process and analytical equipment: $2.5M

Progress towards construction milestones:

- The environmental and safety plans and NEPA for the facility construction and interim labs have been approved.
- First Construction milestone completed – 8/19/2010
  - Jacobs Engineering drafted the Conceptual Design Report and Fire Protection Assessment
- Second Construction milestone completed – 11/22/2010
  - Design Build contract was awarded to Barton Malow
  - Preliminary design has been submitted
  - Contractor is on schedule for final design



Progress towards interim facilities and equipment milestones:

- Electrolyte materials scale up lab – fully operational
  - Equipment has been delivered and installed
- Battery materials analytical lab – fully operational
  - Equipment has been delivered and installed
- Cathode materials scale up – under construction
  - Equipment has been delivered and in the process of being 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	Expected Delivery 7/1/2011

TASK 1
Battery Cell Materials Development

Project Number: IV.E.1.1 (ARRAVT076)

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

Project PI, Institution: Gregory Krumdick/Argonne National Laboratory

Collaborators (include industry): < none >

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

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

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

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

Financial data:
Total project duration: 12 mo.
Staff and M&S: $700K

Progress towards deliverables: A flexible processing system for the production of 10 kg batches of cathode materials was designed and all primary equipment for the processing unit operations has been ordered. Equipment has been delivered and is in the process of being installed. Young Ho Shin from Korea was selected to lead the scale up efforts. It is expected that Young Ho will receive his H1 visa in early April, relocate to the US near the end of April and start work in the beginning of May.

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

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

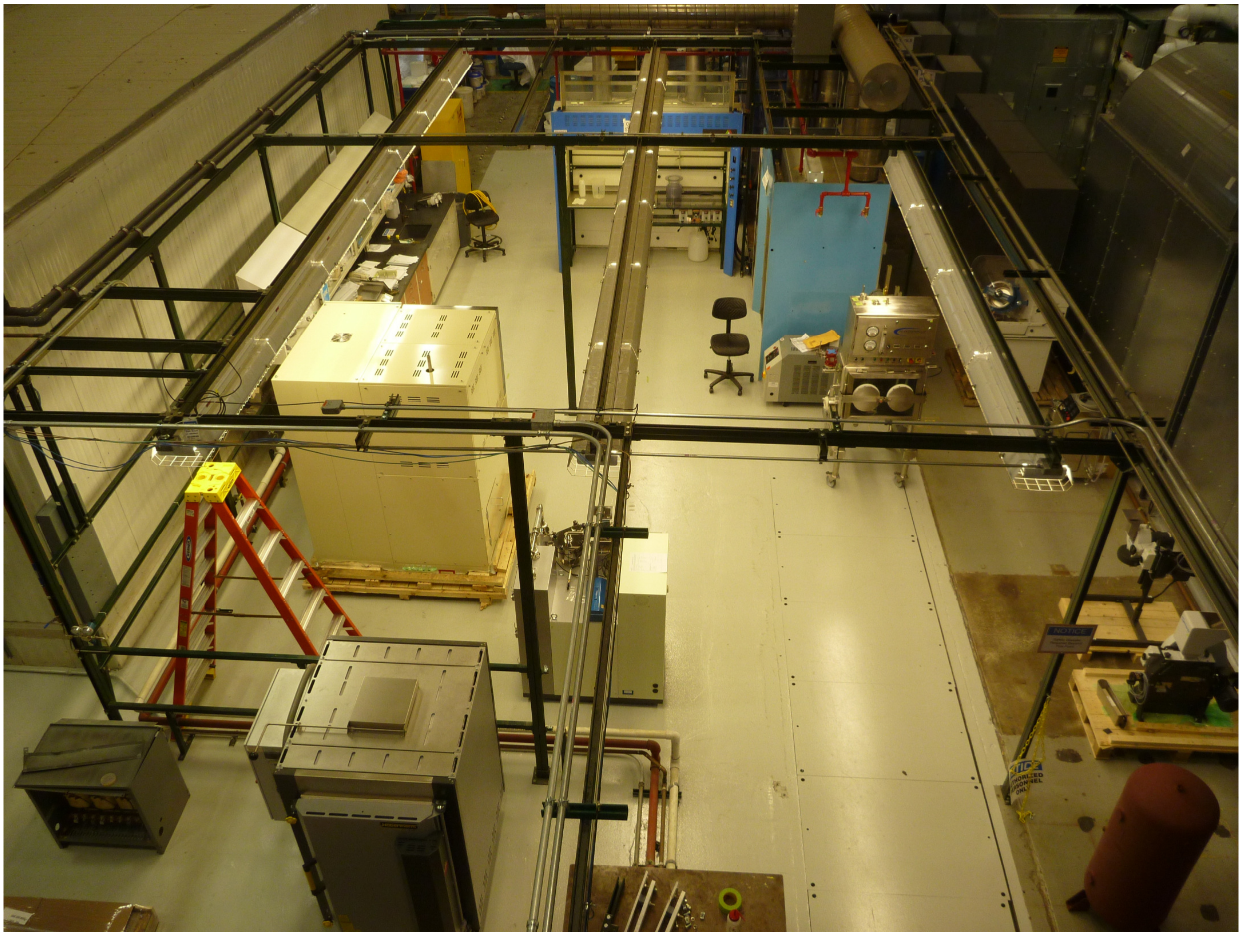


Figure 1. Interim Cathode Materials Lab (under construction)

TASK 1
Battery Cell Materials Development

Project Number: IV.E.1.2 (ARRAVT076)

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

Project PI, Institution: Gregory Krumdick/Argonne National Laboratory

Collaborators (include industry): < none >

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

Objectives: The objective of this task is to conduct process engineering research for scale-up of Argonne's new electrolyte and additive materials. Advanced electrolytes and additives are being developed to stabilize the interface of lithium ion batteries by forming a very stable passivation film at the carbon anode. Stabilizing the interface has proven to be key in significantly improving the cycle and calendar 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: Scaling up of the electrolyte process for semi-continuous mini-pilot-scale production involves modification of the bench-scale process chemistry, development of a process engineering flow diagram, design of a mini-scale system layout, construction of the experimental system and experimental validation of the optimized process. Process engineers will work with these scientists to gain an understanding of the materials and bench-scale processes used to make these materials and then scale–up and optimize the processes. Standard chemical synthesis unit operations will then be utilized to develop flexible systems that will be enable scaling of a wide range of electrolyte/electrolyte additives. The system will be assembled utilizing an existing synthesis reactor system. Electrolyte/electrolyte additives materials produced will be analyzed to confirm material properties and for quality assurance

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

Financial data:
Total project duration: 12 mo.
Staff and M&S: $300K

Progress towards deliverables:

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

ANL-RS2		
Select CSE material to scale	10/1/2010	Completed
Assess scalability of CSE process	10/18/2010	Completed
WP&C safety documentation approved	11/1/2010	Completed
Develop and validate scalable process chemistry (10g bench scale)	12/1/2010	Completed
First process scale-up (100g bench scale)	12/23/2010	Completed
Second process scale-up (1000g pilot scale)	02/21/2011	Completed

Table 1: Redox shuttle ANL-RS2 schedule

Details on ANL-RS2 scale-up:

- The redox shuttle ANL-RS2 was made on the bench scale using a complex process
    - Reaction time was 17h
    - Product yield was 60% (unknown purity)
    - Hazardous feed materials were used
    - Large volumes of waste generated
    - Largest batch size was less than 1g
- A modified, scalable process was developed
    - Reaction time was 5h
    - Product yield was 79% at 99.94% purity
    - Far less hazardous feed materials were used
    - Waste generated was approximately 40 times less than the bench scale process
    - Material was produced in 158g and 1,562g batches
    - The yield and purity of material are highly reproducible from batch to batch
    - ANL-RS2 synthesized by the new process was chemically analyzed and its electrochemical performance characterized and was found to be consistent to the bench scale material synthesized

Figure 1 ANL-RS2 material synthesized

1NM3		
Select CSE material to scale	11/01/2010	Completed
Assess scalability of CSE process	11/15/2010	Completed
WP&C safety documentation approved	12/23/2010	Completed
Develop and validate scalable process chemistry (10g bench scale)	02/18/2011	Completed
First process scale-up (100g bench scale)		In Progress
Second process scale-up (1000g pilot scale)		

Table 2: Electrolyte solvent 1NM3 schedule

TASK 1
Battery Cell Materials Development

Project Number: 1.1A (ES015)

Project Title: Engineering of high energy cathode material

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

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

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

Objectives:
Enable the Argonne high energy composite layered cathode $xLi_2MnO_3 \cdot (1-x)LiNiO_2$ for 40 miles PHEV

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

Approach:

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

Milestones:

- Scale up Co-free high energy cathode material with reproducibility.
- Scale up materials to Kg batch for initial cell build (ongoing)

- **Financial data:**
  Total project funding
  - DOE share: $ 300K

PROGRESS TOWARD MILESTONES

After optimizing the ratio of Ni/Mn, our focus was on developing high-energy cathodes based on the layered lithium-rich nickel manganese oxide composite with a composition of $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$ (Ni/Mn ratio = 1:2). This material shows high capacity of over 200 mAh/g at 1 C rate with good reproducibility.

The next step was to scale up this material to Kg levels to provide enough material for potential cell build.

For scale up, the metal carbonate precursor ($Ni_{1/3}Mn_{2/3}CO_3$) was prepared by a co-precipitation method using a continuous stirred-tank reactor (Fig. 1 left). In this case, 100 gram/hour of precursor can be obtained from a 4 liter continuous stirred-tank reactor. The amount of precursor is determined by the running time. The obtained precursor has uniform and spherical shape (Fig 1 right) which could be favorable for nano-surface coating in the future.

We then optimized the calcinations process for the cathode material as follow:

A stoichiometric metals carbonate and lithium carbonate were well mixed before calcination in air. In this case, the amount of the product was scaled up to 2Kg level from gram level.

The scaled material was then characterized and evaluated in half cells. The material showed excellent electrochemical performance similar to the one obtained in as small batch.

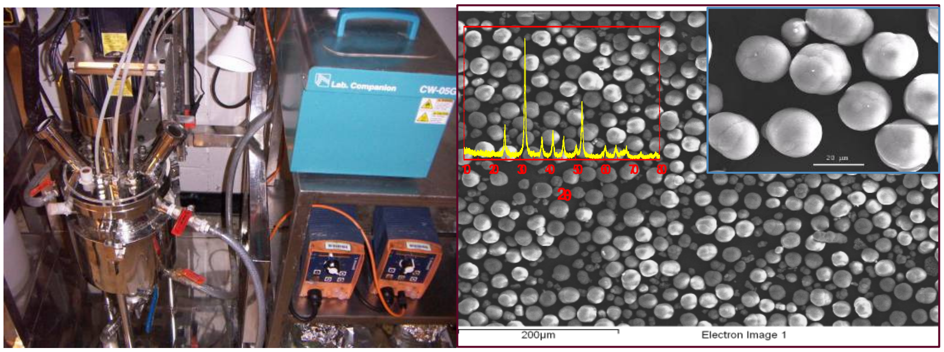


Fig. 1 Precursor scale up process

Fig.2 Cathode material scale-up

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

1. B. -R. Lee, H.-J. Noh, S. -T. Myung, K. Amine, Y.K. Sun, High-Voltage Performance of $Li[Ni_{0.55}Co_{0.15}Mn_{0.30}]O_2$ Positive Electrode Material for Rechargeable Li-Ion Batteries, Journal of the Electrochemical Society, 158(2): p. A180 (2011).

TASK 1
Battery Cell Materials Development

Project Number: 1.1B (ES016)

Project Title: New High Energy Gradient Concentration Cathode Material

Project PI, Institution: Khalil Amine, Argonne National Laboratory

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

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

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

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

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

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

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

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

Financial data: $300K/year

PROGRESS TOWARD MILESTONES (1 page)

a) Model was completed in Q1.

b) Initial synthesis was completed in Q1.

c) Gradual deposition of a relative transition metal gradient was confirmed using SEM and EDXS on both particle surfaces and particle interiors. Figure 1 shows predicted and measured relative Mn compositions (balance Ni) using EDXS on particle surfaces in synthesized gradient precursors. The offset between the predicted and measured concentration at early times is in part due to the interaction volume of EDXS measurements. Figure 2 shows interior cross-sections and relative Mn compositions at selected points within particle interiors. The results in Figure 1 and Figure 2, when combined, are consistent with the synthesis of a material with a gradient in transition metal composition, with a Ni-enriched core and a gradually deposited Mn-enriched surface. Surprisingly, there is also a gradient in internal surface morphology which we are currently investigating. In summary, we have confirmed the synthesis of particles with gradients in internal relative transition metal composition. These particles also have Mn-enrichment (>50% relative transition metal compositions) at their surfaces.

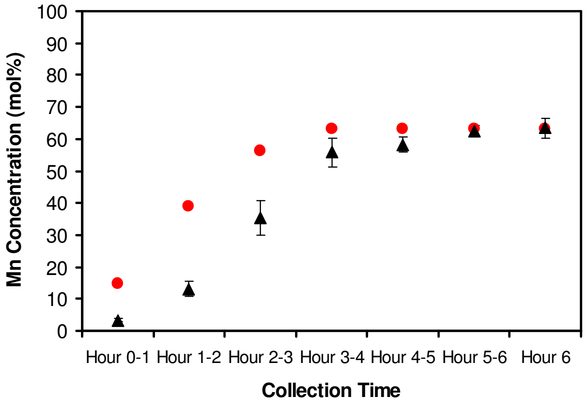
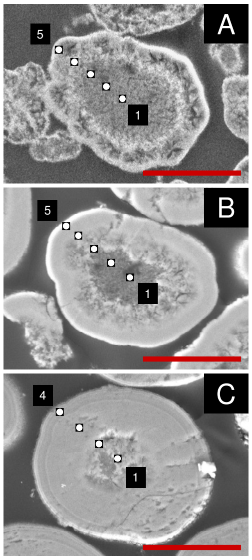


Figure 1. Calculated (red circles) and measured (black triangles, using EDXS) relative molar Mn composition at the surfaces of particles collected from the reactor as a function of time.



Point	%Mn
1	19.1
2	24.2
3	22.5
4	26.3
5	48.4

Point	%Mn
1	21.2
2	25.7
3	34.5
4	56.6
5	54.7

Point	%Mn
1	27.1
2	52.5
3	64.1
4	62.1

Figure 2. SEMs and relative Mn composition (using EDXS) of internal cross-sections from particles collected from A) hour 2-3, B) hour 4-5, and C) hour 6 from the reactor.

d) Detailed electrochemical cycling to determine material capacities is still in progress. Initial data has reversible discharge capacities of up to ~190-200 mAh/g at a rate of 20 mA/g between 2.0 V and 4.6 V.

e) Safety and cycle life experiments are ongoing. Initial data is consistent with an increase in safety and cycle life for precursor materials collected at later times (with increasing Mn enrichment).

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

G. M. Koenig, I. Belharouak, H. Deng, and K. Amine, *Chemistry of Materials*, Accepted. (2011)

TASK 1
Battery Cell Materials Development

Project Number: 1.1F (ES017)

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

Project PI, Institution: Christopher Johnson, Argonne National Laboratory

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

Project Start/End Dates: October 2008 / September 2014

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

Approach: In this approach we utilize the high capacity 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, September 2011, (on-schedule)
    - Doped LFO synthesized, March 2011, (completed)
(b) Characterize electrochemical properties of synthesized materials, September 2011, (on-schedule)
    - Demonstrate capacity of 140 mAh/g with MnO_2, March 2011, (completed)

- Demonstrate high-rate of 200 mAh/g @ C rate, September 2011, (on-schedule)

(c) Characterize structure of materials, March 2011, (completed)

(d) Evaluate Si anodes to pair with blended LFO, June 2011, (on-schedule)

(e) Initiate measurement of thermal properties of charged material in DSC, June 2011, (on-schedule)

Financial data: $300K

PROGRESS TOWARD MILESTONES

(a) Co-doped LFO was successfully synthesized; $Li_5Fe_xCo_{1-x}O_4$, $0 \leq x \leq 1$. The concept is to activate the material releasing lithium. On discharge the Co should be electrochemically active, and tests are being undergone to evaluate the electroactivity of Co.

(b) The AC impedance of LFO, fresh, and charged is shown in Fig. 1 (a). The charged LFO shows very little impedance which indicates that it will not affect the high-rate cycling of blended electrodes. Panel (b) shows the result of a C/MnO_2-LVO full cell.

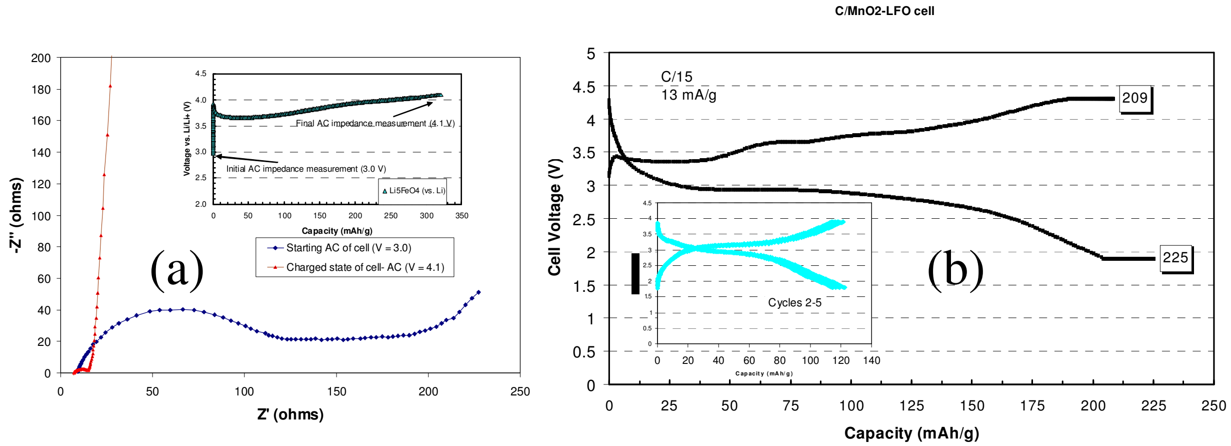


Fig. 1. (a) AC impedance of Li/LFO cell; red – charged, blue- fresh cell, and (b) C/MnO_2-LFO cell indicating over 200 mAh/g. The cycling decreases to about 120 mAh/g.

(c) The XRD patterns of the $Li_5Fe_xCo_{1-x}O_4$, $0 \leq x \leq 1$ series of doped materials discussed in milestone (a) were completed. The samples are phase pure.

(d) Initial cycling with Li/Si anode half-cells was initiated. Samples were provided by Dr. Kumta. Cycling results of a Si/LFO-LVO cell will be reported in the next quarterly.

(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: Sun-Ho Kang, Argonne National Laboratory

Collaborators (include industry):
Donghan Kim, Argonne National Laboratory
Keving Gallagher, Argonne National Laboratory
Michael Thackeray, Argonne National Laboratory
Mahalingam Balasubramanian, Argonne National Laboratory
Hanwha Chemical

Project Start/End Dates: October 2009/September 2014

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

Approach: Layer-layer composite cathode materials, $x\mathrm{Li_2MnO_3}\bullet(1-x)\mathrm{LiMO_2}$ (M=Ni,Co,Mn) deliver high capacity of ~240 mAh/g. However, the materials have drawbacks such as low first-cycle efficiency and poor power performance. We will continue to exploit the concept of embedding spinel component into the layer-layer structure to improve the first-cycle efficiency and rate performance. We will also continue to explore the blending of $x\mathrm{Li_2MnO_3}\bullet(1-x)\mathrm{LiMO_2}$ with high-power cathode to improve the impedance characteristics at low SOC. We have chosen $\mathrm{LiFePO_4}$ as the high-power cathode. We have extended our research to studying of voltage decaying and Mn dissolution issues of $x\mathrm{Li_2MnO_3}\bullet(1-x)\mathrm{LiMO_2}$.

Milestones: Project deliverables and decision points. Milestones should clearly show progress towards your project objectives, including overcoming issues, and should clearly support achieving a significant improvement in cell energy density, safety, and/or cost. If your material or couple has known issues, please address some or all of them in your milestones.
(a) Chemical composition optimization (on schedule)
(b) Characterization of integrated structural feature using analytic techniques (on schedule)
(c) Blending of $x\mathrm{Li_2MnO_3}\bullet(1-x)\mathrm{LiMO_2}$ with high power cathode materials (on schedule)

(d) Identification of performance degradation mechanism of xLi_2MnO_3•(1-x)$LiMO_2$ materials (on schedule)

Financial data: $400K

PROGRESS TOWARD MILESTONES

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

$Li_xMn_{0.75}Ni_{0.25}O_y$ chemistry nicely demonstrated the concept of embedding spinel component in the layer-layer matrix. However, it was observed that $Li_xMn_{0.75}Ni_{0.25}O_y$ suffers from too severe voltage profile changes during cycling. To enhance the structural stability during cycling, higher Ni content (Mn:Ni=65:35) was examined; $Li_xMn_{0.65}Ni_{0.35}O_y$ has been synthesized and evaluated in lithium cells. When the lithium content is in the range of 0.20-0.25, the materials show significantly improved first-cycle efficiency (~90%) while the high initial capacity is maintained (Figure 1a). Those cathode materials also exhibit good rate capability (Figure 1b). Further electrochemical characterization is being carried out. (Note: For this Mn/Ni ratio, x=1.3 is the lithium content for spinel-free, layer-layer structure.)

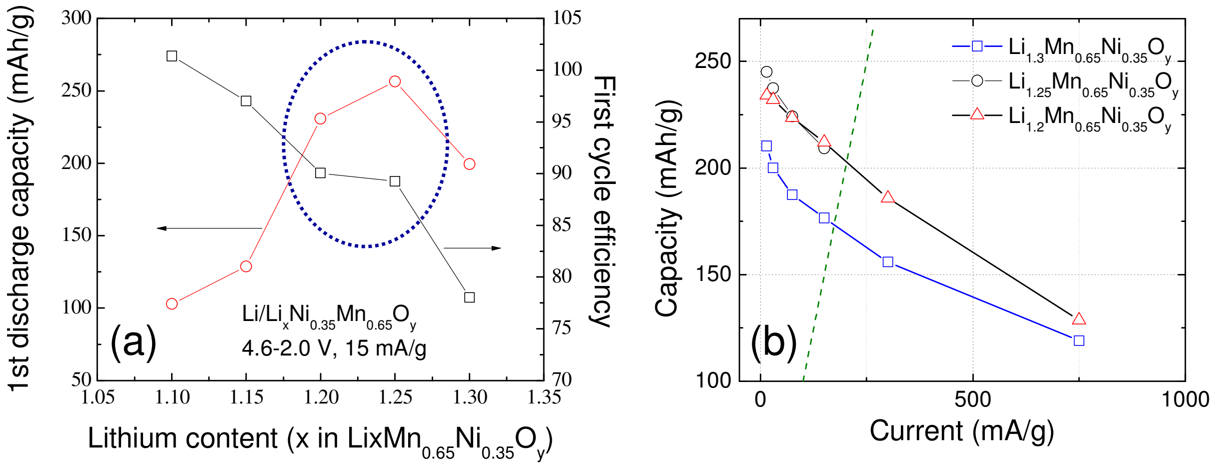


Figure 1. (a) 1st discharge capacity and cycle efficiency, and (b) rate capabilities of $Li/Li_xMn_{0.75}Ni_{0.35}O_y$ cells.

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

Structural changes in $Li_{1.2}Mn_{0.75}Ni_{0.25}O_y$ after extensive cycling (50 cycles) between 4.95 and 2.0 V in a lithium cell have been studied using X-ray absorption. Mn spectra shows large reduction (close Mn^{3+}) after 50 cycles in the fully discharged state, similar to discharged spinel. However, Ni environment shows little change with cycling; Ni is predominantly Ni^{2+}.

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

Mildly fluorinated $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Mn_{0.31}Co_{0.25}O_2$ (ANL-NMC) was blended with 20 wt% $LiFePO_4$. In spite of the low specific capacity of olivine, the blended electrode shows higher capacity at moderate-to-high current (Figure 2a). The blended electrode also shows significantly improved impedance characteristics (Figure 2b). Further evaluations including cycle life in full cell configurations are being performed.

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

Study of performance degradation of layer-layer cathode materials has been initiated and the degradation mechanism is being explored. Of many issues, voltage decay with cycle and Mn dissolution issues of $xLi_2MnO_3 \bullet (1-x)LiMO_2$ have been focused on. At current stage, phenomenological study is being carried out and analytic technique will be employed to study those issues.

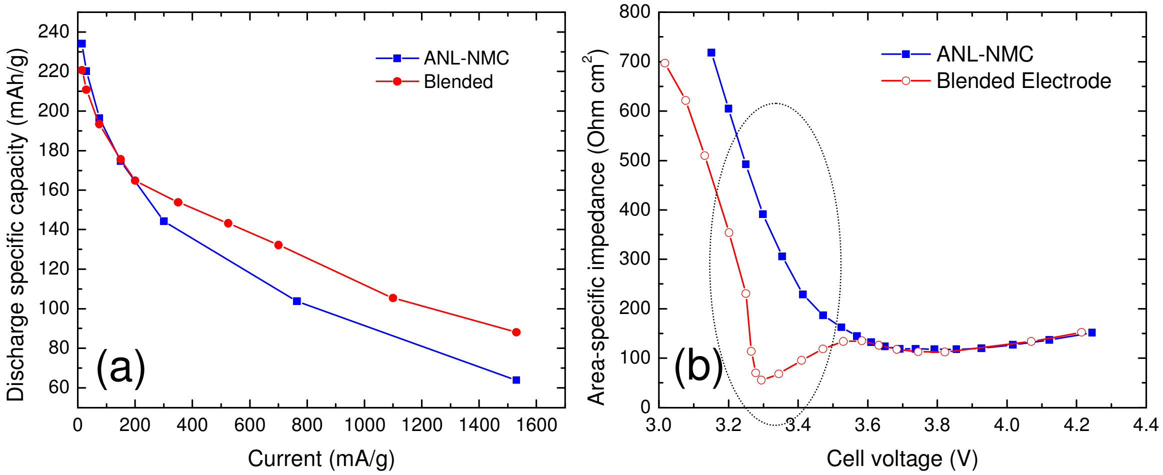


Figure 2. (a) Discharge capacity variation with discharge current of lithium cells containing ANL-NMC cathode (no olivine) and ANL-NMC/olivine blended cathode (20 wt% olivine). (b) Area specific impedance of lithium-ion cells (Mag-10 anode) containing ANL-NMC cathode (no olivine) and ANL-NMC/olivine blended cathode (20 wt% olivine), measured by 3C, 10 s pulse.

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

No publications, reports, or patents were submitted this quarter

TASK 1
Battery Cell Materials Development

Project Number: 1.1C (ES020)

Project Title: Developing High Capacity, Long Life anodes

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

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

- **Project Start/End Dates:** October 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.

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- Explore the M_aO_b-$Sn_xCo_yC_z$ system where M= Si, Sn, Mo, Ge (in term of electrochemistry, material structure investigation, binders effect); (2011-2012)
2- Prepare materials with at least 600 mAh/g capacity with cycleability more than hundred cycles (2011-2012);
3- Study the rate capability of these materials and the effect of the electrode loading on the cell performance (2011-2012);

4- Identify the best material in term of cost, voltage output, cycling performance, and deliverable capacity (2011-2012);
5- Identify the best material in term of cost, voltage output, cycling performance, and deliverable capacity (2011-2012);
6- Prepare a scalable amount of anode material (~ 100 grams) with 600 mAh/gas capacity for 100 cycles (2013);
7- 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 study the binder effect on the cycleability performance of these anode materials and we found that binders based on polyimide are the most appropriate to deal with the volume expansion of these anode material during the lithium insertion and de-insertion (see Figure 1 of the 50wt%cSiO-50wt%$Sn_{30}Co_{30}C_{40}$). (En schedule)

(b) Summary of work in the past quarter related to milestone (2)
In term of cycleability, anode materials based M_aO_b-$Sn_xCo_yC_z$ (where MO: SiO, MoO_3, GeO_2) exhibit a capacity between 600 and 800 mAh/g substantiated for more than 100 cycles (see Fig. 1)

(c) Summary of work in the past quarter related to milestone (3)
The rate capability of M_aO_b-$Sn_xCo_yC_z$ composite was evaluated as is shown in Figure 2 for 50wt%MoO_3-50wt%$Sn_{30}Co_{30}C_{40}$ anode material. The anode electrode was tested between 0.005 and 2.5V at various current densities from 50 to 2400mA.g^{-1}. This anode material exhibits superior rate capability. A capacity of about 325mhA.g^{-1} was delivered at 8C rate with outstanding charge and discharge efficiency. (En schedule)

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

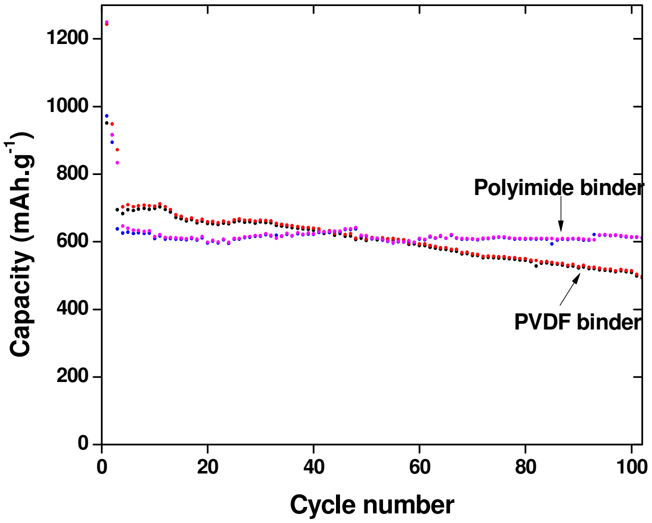


Figure 1: cycleability of Li/50wt%cSiO-50wt%$Sn_{30}Co_{30}C_{40}$ half cell using PVDF and Polyimide binder.

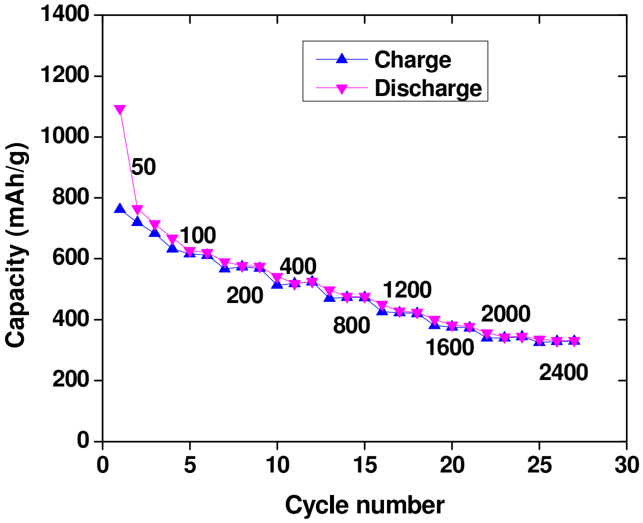


Figure 2: rate capability of Li/50wt%MO_3-50wt%$Sn_{30}Co_{30}C_{40}$ half cell.

TASK 1
Battery Cell Materials Development

Project Number: 1.1I (ES022)

Project Title: Develop Improved Methods of Making Intermetallic Anodes

Project PI, Institution: Andrew Jansen, Argonne National Laboratory

Collaborators (include industry):
Dileep Singh, Argonne National Laboratory
Jack Vaughey, Argonne National Laboratory
Wenquan Lu, Argonne National Laboratory

Project Start/End Dates: October 2008 / September 2014

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

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

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

Financial data: $300K

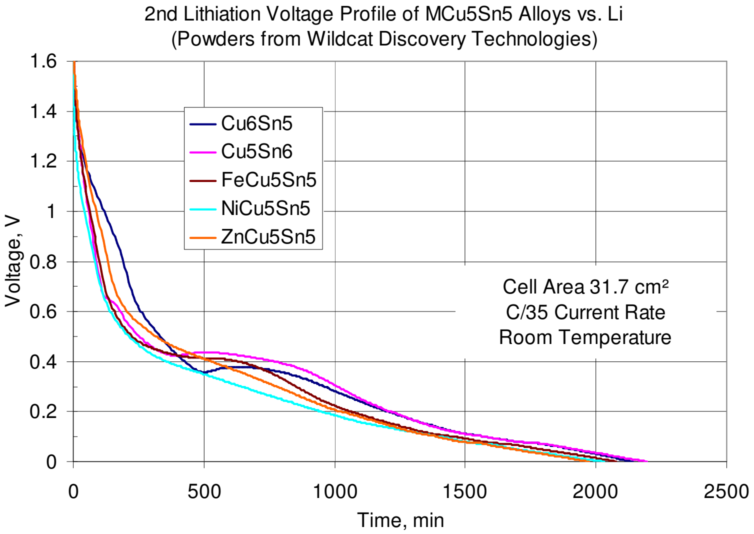
PROGRESS TOWARD MILESTONES

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

This work was completed; see Q1 report.

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

Half cells were made with electrodes based on the new smaller alloys from Wildcat Discovery Technologies. While the primary particle size is near 400 nm, many of these particles are agglomerated into secondary particles. More energetic milling and mixing will be used in the next quarter to break up these particles during the slurry making process. Nevertheless, some interesting results were obtained from these imperfect electrodes. Differences were seen in the voltage profiles for these five alloys (see the figure below).



In particular, the 0.4 volt plateau corresponding to Li_2CuSn was not seen for the Ni and Zn substituted alloys. These metals may interfere with this phase formation. The capacity of these five alloys was near, or slightly over, the theoretical capacity. An estimate of the electrode capacity density was also made based on these electrodes and is shown in the table. All of the MCu_5Sn_5 electrodes have an electrode capacity density greater than graphite electrodes, and continues to warrant further consideration.

Anode	Tap Density g/mL	2nd Delithiation Capacity of Alloy, mAh/g	Electrode Capacity Density mAh/cm^3
Cu_6Sn_5	2.05	472	544
$NiCu_5Sn_5$	2.90	434	513
$ZnCu_5Sn_5$	2.48	488	704
$FeCu_5Sn_5$	2.46	514	757
Cu_5Sn_6	2.51	557	816
Graphite	0.8 - 1.1	340	440

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

The initial batch of electrodes made with these smaller sized particles did not improve the cycle life problem. It is hoped that improved slurry processing and electrode composition and processing will improve the cycle life. But, it is possible that the poor cycle life could be due to the larger surface area (higher activity) of the smaller particles, or the primary particles are still too large, or copper displacement is preventing re-alloying. Effort will also be directed to other classes of binders (cellulose and polyimide) and more carbon (and inert) additives to help maintain porosity.

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

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

TASK 1
Battery Cell Materials Development

Project Number: 1.1H (ES023)

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

Project PI, Institution: Daniel Abraham, Argonne National Laboratory

Collaborators (include industry):
G. Cheng, Argonne National Laboratory
B. Lucht, University of Rhode Island
Alex Wei, Purdue University
Kang Xu, Army Research Laboratory

Project Start/End Dates: October 2008 / September 2014

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

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

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

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

Financial data: $300K

PROGRESS TOWARD MILESTONES

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

Furthermore, we have discovered a new family of heteroaromatics substituted carboxylic ester-based compounds that have been identified as electrolyte additives. (see examples in Fig. 1).

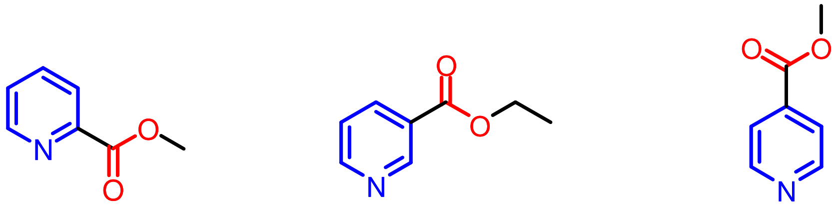


Fig. 1

Methyl Picolinate (**MP**) Ethyl Nicotinate (**EN**) Methyl Isonicotinate (**MIN**)

Our experiments show that even small amounts of these additives can significantly improve capacity retention without causing impedance rise, a common problem associated with many electrolyte additives (see Fig. 2).

Small amounts (0.3 wt%) of MP, EN and MIN addition to baseline electrolyte improves capacity retention. MIN appears to be the best performer based on initial capacity loss. It is evident that small structural changes cause significant impact on initial cycling behavior – further studies are planned to obtain information on the effect of molecular structure on SEI characteristics. Note that the additives do not significantly alter cell impedance. The graphite SEI generated by MP may have the strongest interaction with the Li-ion, which may explain why the compound displays the widest mid-frequency arc.

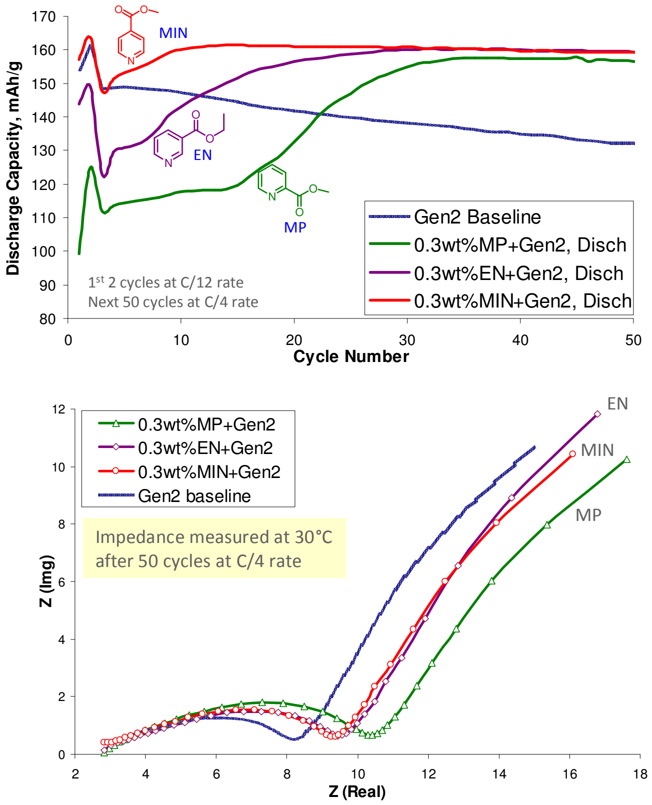


Fig. 2. Cycling and EIS data from NCA//Graphite cells comparing the effects of various additives with that of the baseline electrolyte.

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

Argonne filed a USA Patent Application on “heteroaromatics substituted carboxylic ester-based compounds as electrolyte additives” (ANL-376, Cheng, G.; Abraham, D.P.)

TASK 1
Battery Cell Materials Development

Project Number: ES024

Project Title: High Voltage Electrolytes for Li-ion Batteries

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

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

Project Start/End Dates: June 2008 / May 2011

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

Approach: Three approaches were taken.

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

Milestones:

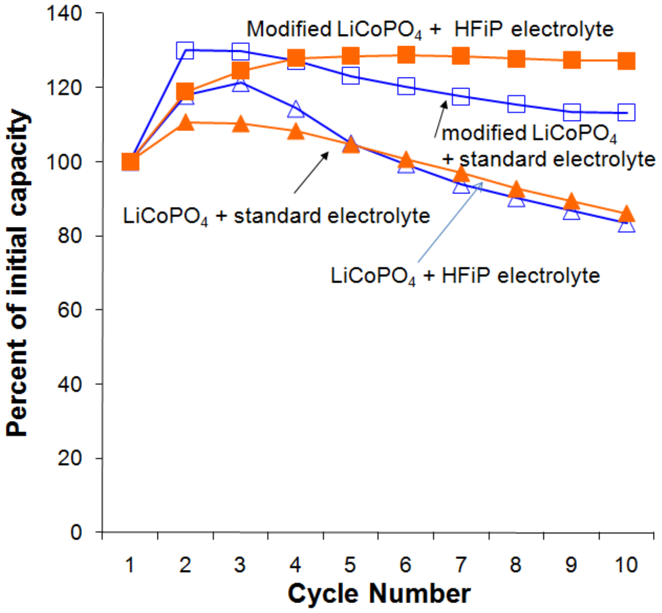
- **(a)** Explored additives that passivates cathode surfaces at high voltages, (Dec 2010)
- **(b)** Diagnostic studies: surface characterization and SEI chemistry (Dec 2010)
- **(c)** Evaluate electrolytes with additives in both half cells and full cells (May 2011)
- **(d)** Understand reactive pathways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

Financial data: $200,000/year

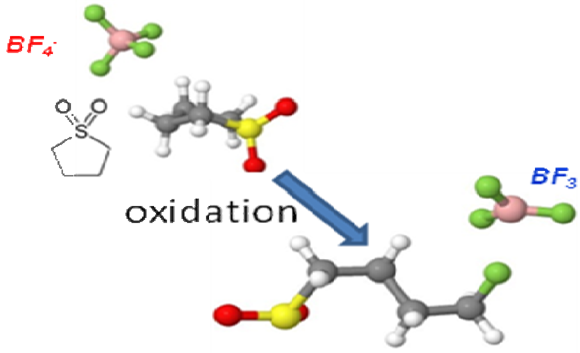
PROGRESS TOWARD MILESTONES

(a) **Test of high voltage electrolytes with high voltage $LiCoPO_4$ cathode**: To further test the effectiveness of the HFiP additive for high voltage operation, $LiCoPO_4$, a 4.8 V cathode, was cycled in baseline electrolyte, 1.0 m $LiPF_6$ in EC:EMC (3:7 wt. ratio), with and without HFiP additive. We found that the capacity of $LiCoPO_4$ was faded fast regardless of the electrolytes used as shown in the figure below. This suggests that the electronic structure of $LiCoPO_4$ is not stable enough for cycling.

(b) **Test of modified $LiCoPO_4$**: The modified $LiCoPO_4$ (m-$LiCoPO_4$) made by substituting part of Co with other metal was able to cycle significantly better than $LiCoPO_4$ as shown the figure below in baseline electrolyte, 1.0 m $LiPF_6$ in EC:EMC (3:7 wt. ratio). The cycling of m-$LiCoPO_4$ was further improved when cycled in the baseline electrolyte with and HFiP additive (see figure below). These results suggest that the success development of high energy density Li-ion batteries using high voltage cathodes will need both high voltage electrolytes and stable high voltage cathodes.



(c) **Reactivity of solvents in the presence of anion investigated by Quantum Chemistry**: The presence of anion influences the oxidation stability limits (see Q1 quarterly report). Fluorine transfer from BF_4^- or PF_6^- to solvent molecules is responsible for the reduction of the oxidation potential of electrolytes. Sulfolane and ethylene carbonate under the presence of BF_4^- anion result in very different reaction products that can influence greatly the reactivity of the solvents as shown below.



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

1. A. v. Cresce and K. Xu, “Electrolytes in Support of 5 V Li Ion Chemistry”, *J. Electrochem. Soc.* , **2011**, 158, A337-342
2. T. R. Jow, M. Marx, J. L. Allen, “Li^+ Charge Transfer Kinetics at 1. NCA/Electrolyte and Graphite/Electrolyte Interfaces, and 2. NCA/Electrolyte and LFP/Electrolyte Interfaces in Li-ion Cells,” *ECS Trans.,* **2011**, 33(23), 1-13.
3. O. Borodin, T. R. Jow, “Quantum Chemistry Studies of the Oxidative Stability of Carbonate, Sulfone and Sulfonate-Based Electrolytes Doped with BF_4^-, PF_6^- Anions,” *ECS Trans.*, **2011**, 33(28), 77-84.

TASK 1
Battery Cell Materials Development

Project Number: 1.1D (ES025)

Project Title: Development of Advanced Electrolyte Additives

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

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

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

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

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

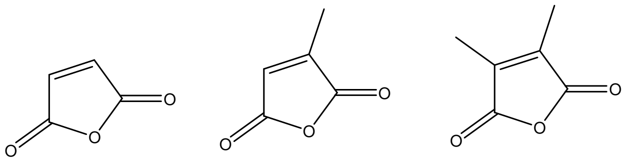
Milestones
(a) Generate screening list based on the semiempirical rule and establish valid and quick screening procedures, Mar. 2011, (Complete).
(b) Run the screening procedures to find promising additives that could bring superior features to lithium-ion cell system, Sep. 2012, (On schedule).
(c) Evaluate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

Financial data: $200K/FY2011

PROGRESS TOWARD MILESTONES

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

Degree of unsaturation of chemical structures is regarded one criterion for making screening list. Chemicals with high degree of unsaturation always have cyclic structure and double bonds, which could be beneficial to the SEI formation process. The screening process consists of formation, impedance measurements, and fast cycle test at elevated temperature. A series of new maleic anhydride derivative compounds, as shown in Fig. 1, have been screened.



5 6 7

Fig.1. Structures of maleic anhydride derivatives (5-7) as electrolyte additives.

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

Fig. 2 is the differential capacity profiles of the cells with and without 1w% Additives 5-7. Sharp peaks were observed when additives were added to the cells, suggesting the effective decomposition of additives 5-7. In the capacity retention profiles, lithium ion cells with additives showed better cyclability compared to the cells without additives.

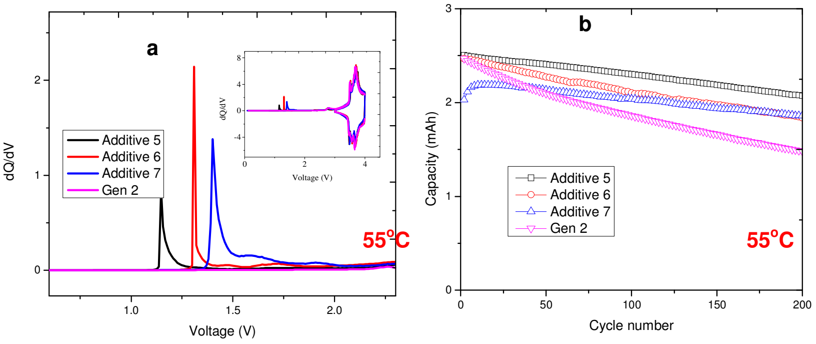


Fig. 2. (a)Differential capacity profiles of MCMB/NCM cells with electrolyte 1.2M $LiPF_6$ EC/EMC 3/7+1% additive; (b) Capacity retention of MCMB/NCM cells cycled between 2.7 and 4.2V at 55 ◦C using electrolyte of 1.2M $LiPF_6$ EC/EMC 3/7 with and without 1w% additives (5-7).

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

New succinic anhydride derivatives (5, 6, 7) shows better capacity retention at 55°C when compared to cell s without additives. Further work is ongoing to investigate the effect of additives on power and cell impedance.

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

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

TASK 1
Battery Cell Materials Development

Project Number: ES026

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

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

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

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

Objectives:

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

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

The candidate electrolytes are characterized using a number of approaches, including performing ionic conductivity and cyclic voltammetry measurements, and evaluating the performance characteristics in experimental ~ 400 mAh three electrode cells. Initially, cells will be fabricated with either (a) MCMB /$LiNi_{0.8}Co_{0.2}O_2$ or (b) graphite/$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrode couples, and later evaluated with high voltage systems. Other chemistries can be evaluated depending upon availability from collaborators . In addition to performing charge/discharge characterization over a wide range of temperatures and rates on these cells, a number of electrochemical characterization techniques will be employed, including: (1) Electrochemical Impedance Spectroscopy (EIS), (2) DC linear (micro) polarization, and (3) Tafel polarization measurements. The electrochemical evaluation in proven three electrode test cells enables electrochemical characterization of each electrode (and interface) and the identification of performance limiting mechanisms. Electrodes are easily harvested from these test cells and samples will be delivered to collaborators (i.e., URI and LBNL). In addition to evaluating candidate electrolytes in spirally wound experimental cells, studies will be performed in coin cells, most notably in conjunction with high voltage cathode materials.

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

Milestones:

Month/Year	**Milestone**
Sept. 2011	Milestone A: Prepare and characterize experimental laboratory cells containing Gen-2 electrolytes and identify performance limiting characteristics at different temperatures.
Sept. 2011	Milestone B: Demonstrate improved performance of first generation electrolyte over a wide temperature range compared with the baseline electrolyte (*i.e.*, 1 M $LiPF_6$ in EC:DEC 1:2), especially at -30^{o}C, in experimental and prototype cells

Financial data:

Total project funding:

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

Funding received:
FY'09 = 0 K
FY'10 = 175K
FY'11 = 175K

Accomplishments and Progress toward Milestones:

We have investigated a number of ester containing electrolytes, namely methyl propionate and methyl butyrate-based electrolytes, in conjunction with electrolyte additives, with the intent of providing improved low temperature performance while still delivering acceptable high temperature resilience. More specifically, we have focused upon formulations consisting of $LiPF_6$ in ethylene carbonate (EC) + ethyl methyl carbonate (EMC) + methyl propionate (MP) or methyl butyrate (MB) (20:20:60 vol %) with and without electrolyte additives, including lithium oxalate, mono-fluoroethylene carbonate (FEC), vinylene carbonate, and lithium bis(oxalate) borate (LiBOB). The identification of these esters, as well as the optimization of their concentrations in EC+EMC-based solutions, was based upon studies with MCMB-$LiNiCoO_2$ and $LiNiCoAlO_2$ systems.

In the recent quarter, we have continued to evaluate the performance of a number of A123 cells that have incorporated methyl butyrate-based electrolytes investigated under the program (i.e., specifically 1.20M $LiPF_6$ 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 part of the testing, we have performed discharge rate characterization over a wide temperature range (-60 to +20^{o}C) using a number of rates (ranging from C/20 to 11.4C rates). Although the cells with the baseline electrolytes were observed to deliver negligible capacity at -40^{o}C, excellent performance was demonstrated with the cells containing the methyl butyrate-based electrolytes, as shown in the Figure 1. The performance corresponds to over 90% of the room temperature capacity being delivered at -40^{o}C at a 11.2C discharge rate (57-59 Wh/kg under these conditions). These systems have also been observed to support up to 10C rates at temperatures as low as -50^{o}C and C rates at -60^{o}C.

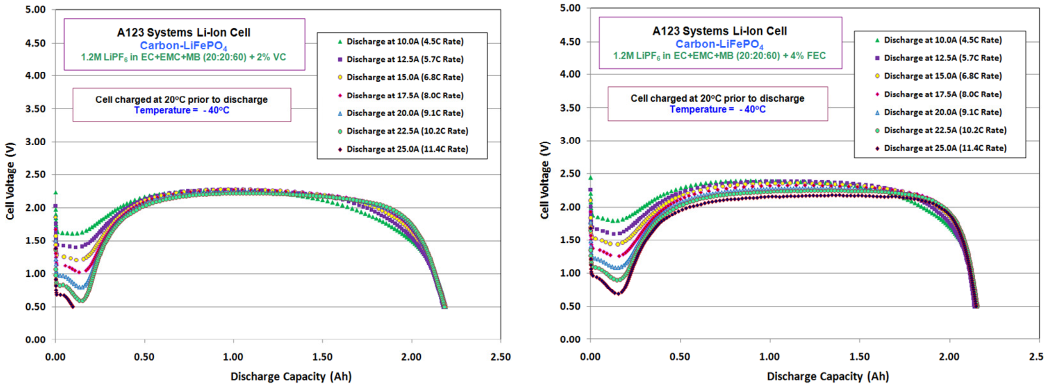


Figure 1: Discharge rate characterization of $LiFePO_4$-based A123 cells at -40^{o}C using high rate (4.5C to 11.2C) Cells containing 1.0M $LiPF_6$ EC+EMC+MB (20:20:60 vol %) with either 4%FEC or 2% VC. Cells were charged at room temperature prior to discharge.

The cycle life performance of these systems is also promising, with over 2,000 cycles being delivered at room temperature with over 90% of the initial capacity remaining (1.0C rate charge and discharge). Effort has also been focused upon evaluating the high temperature resilience of these systems by implementing a number of additional cycle life tests (i.e., at 40° and 50°C), as shown in Fig 2. Thus far, the performance is encouraging with over 400 cycles being delivered, with the cells containing the 1.20M $LiPF_6$ in EC+EMC+MB (20:20:60 vol %) + 2% VC electrolyte behaving comparably to the baseline system, and the FEC containing variant displaying modestly increased capacity fade. We have also performed tests in which the cells are cycled between two temperature extremes (i.e., +40° and -20°C) to determine the impact of the high temperature exposure upon the low temperature performance. As shown in Fig. 2, the cell containing the methyl butyrate+VC performed comparably to the baseline system, illustrating promising lifetime characteristics over harsh conditions. Future efforts will be devoted to evaluating the performance at even higher temperature (i.e., up to +60°C).

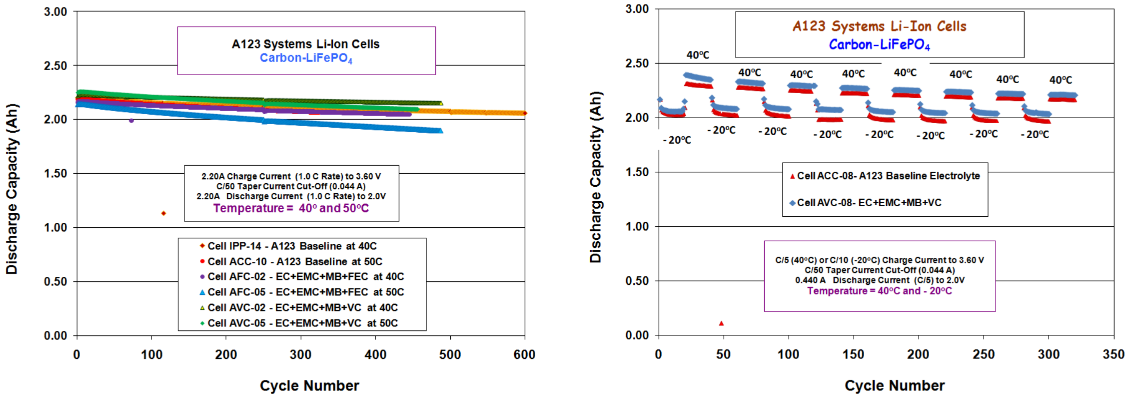


Figure 2: Cycle life performance of $LiFePO_4$-based A123 cells containing various electrolytes at +40°C and +50°C (Figure A) . Variable temperature cycling (+40° to -20°C) of $LiFePO_4$-based A123 cells containing 1.20M $LiPF_6$ EC+EMC+MB (20:20:60 vol %) + 2% VC and the baseline electrolyte (Figure B).

In the recent quarter, we have also investigated the effect of using additional lithium electrolyte salts in conjunction with $LiPF_6$ to serve as electrolyte additives, with the intent of improving the high temperature resilience of the cells. In particular, we have prepared electrolytes which contain LiBOB, lithium hexafluoro isopropoxide, and a lithium malonate borate-based salt (LiDMMDFB) developed by LBNL and the URI (Li Yang, John Kerr, and Brett Lucht). Initial results indicate that the electrolyte salts result in good reversibility with low irreversible capacity losses on formation, as shown in Fig. 3. Effort will focus upon electrochemical evaluation (i.e., EIS, linear and Tafel polarization), discharge rate characterization, and exposure to high temperature. It is anticipated that some portion of these salts will electrochemically decompose to produce favorable SEI layers at the interfacial regions, resulting in improved stability of the systems at high temperatures.

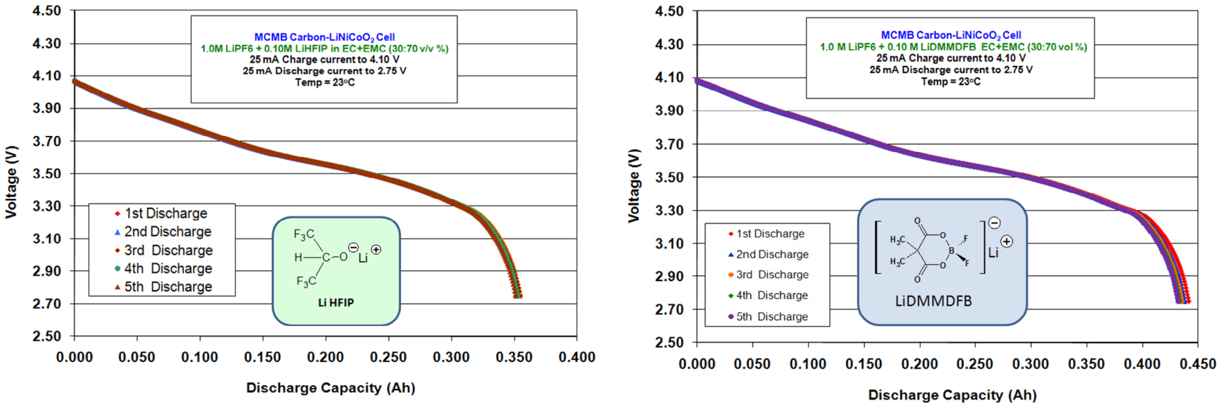


Figure 3: Formation cycling at 23°C of three electrode MCMB carbon-$LiNiCoO_2$ cells (C/20 charge and discharge rates) containing electrolytes with various lithium salts: (a) LiHFIP and (b) LiDMMDFB.

Future work will involve continuing the investigation of the use of additives in conjunction with ester-based wide operating temperature range electrolytes, with a focus upon (i) assessing other candidate additives, (ii) studying the high temperature and cycle life degradation modes, (iii) correlating electrochemical trends with performance, and (iv) identifying performance limiting aspects at extreme temperatures. Future work will also focus upon the use of fluorinated esters, especially with high voltage systems, including trifluoroethyl butyrate, ethyl trifluoroacetate, and trifluoroethyl acetate These electrolytes will be investigated using a number of different chemistries, including high voltage systems (such as graphite-$LiNiCoMnO_2$ (Toda) and the lithium titanate-spinel electrochemical system being provided by Argonne National Laboratory). Effort will also be devoted to demonstrating these systems in prototype cells, such as in $LiFePO_4$-based cells (A123) $LiNiCoAlO_2$ cells (Quallion), and $LiNiCoO_2$ cells (Yardney).

Publications:

1. N. Leifer, M. C. Smart, G. K. S. Prakash, L. Gonzalez, L. Sanchez, P. Bhalla, C. P. Grey, and S. G. Greenbaum, "^{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. F. C. Krause, M. C. Smart, R. V. Bugga, and G. K. S. Prakash, "The use of fluorinated electrolyte in lithium-ion batteries for improved safety in human-rated aerospace and terrestrial applications", 241st American Chemical Society National Meeting and Exposition, Anaheim, CA, March 28, 2011.

4. M. C. Smart, B. V. Ratnakumar, W. C. West, and E. J. Brandon, “Primary and Secondary Lithium Batteries Capable of Operating at Low Temperatures for Planetary Exploration”, Lunar Superconductor Applications, 1st International Workshop, Houston Texas, March 3-5, 2011.

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

TASK 1
Battery Cell Materials Development

Project Number: ES027 **Reporting Period:** FY 2011 Q2

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

Project PI, Institution: Kevin L. Gering, INL

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

Project Start/End Dates: Jan. 2009/Ongoing

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

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

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

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

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

- voltage stability (CV)
- flammability (flash point)
- 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%). We investigate the performance of our electrolytes with two electrode couples: LNMO/LTO and NMC/Carbon.

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

Milestones (cumulative over FY 2011):

🟩 **= 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	In progress	
i. Synthesis of newer FM series and second-generation Ionic Liquid Phosphazenes	In Progress	
Various supporting characterization and cell testing will be ongoing throughout FY 2011.		

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

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

PROGRESS TOWARD MILESTONES

(a, b) Four new compounds have been synthesized and characterized over the last quarter, including the fluorinated series FM1, FM2, FM3 and the ionic liquid PhIL-1. Representative compounds were chosen for coin cell studies with the aforementioned electrode couples. Electrolytes were blended by adding up to 20% phosphazene additives to the baseline electrolyte EC-EMC-$LiPF_6$, then subjected to a number of characterization tests.

(c) Completed 2011 Q1.

(d) Completed 2011Q1.

(e) Density Functional Theory (DFT) simulations have been performed to determine the solvent-to-lithium binding energies for key phosphazene additives, looking at the specific interaction between the phosphazene nitrogens and free lithium (see Fig.1) . While the charge neutral compounds (SM, FM series) show binding energies higher than those of conventional organic solvent compounds, the INL ionic liquid PhIL-1 shows binding that is profoundly lowered. Reducing this interaction will promote greater cell efficiency in terms of interfacial processes. DFT will continue to be a design tool for determining some molecular attributes prior to synthesis.

(f) INL electrolyte additives at levels as low as 1% provide superb thermal stabilization of the baseline electrolyte, showing practically no color change after 60 days at 60 °C, while the baseline underwent drastic changes and polymerized under these conditions. Figure 2 shows results for SM6 and SM7 additives from our second such study. Study 1 was completed July 2010, looking at SM4, SM5 and FM1, and also found that these compounds promote significant stabilization of the baseline system.

(g) Coin cell testing was completed using electrolyte blends having up to 10% SM3, SM6, FM2, or PhIL-1. Capacity-related studies are summarized in Fig. 3. While there are some polarization effects noted at some of the higher cycling rates, there is good C/10 capacity retention for cells containing the INL additives. Also to note is that the additives appear to stabilize the rate of cell aging compared to the baseline, per formation cycling and initial characterization. Testing with the LNMO/LTO electrode couple showed good, consistent performance with the additives, while the NMC/Carbon cells showed higher irreversible capacity loss. We found out post-facto that the initial set of NMC/Carbon electrodes received from SNL were not calandared. We will repeat the experimental matrix for calendared sets of this electrode couple and provide updated performance data.

(h) We are currently testing coin cells at 55 °C and a 3C rate to determine if the phosphazene compounds prolong cell life at these mildly abusive conditions.

(i) Synthesis targets have been chosen for newer generations of FM and PhIL compounds, and these will be produced in 2011 Q3.

Publications, Reports, Intellectual property

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

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

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

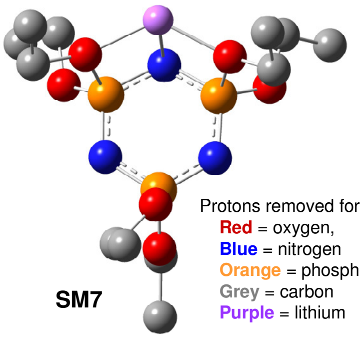
Fig. 1

DFT Modeling of Phosphazene Trimers

Looking at solvent-to-Li^+ Binding

Previous modeling (some INL) has been performed for lithium binding in phosphazene polymers (*J. Phys. Chem B* **2004**, *108*, 15694 and *J. Phys. Chem. B* **2003**, *107*, 3168), but not for phosphazene trimers.

Density functional theory performed with Gaussian03, B3LYP, 6311-G(d,p) basis set. All structures are minima (no imaginary frequencies).



SM7

Protons removed for clarity.
Red = oxygen,
Blue = nitrogen
Orange = phosphorus,
Grey = carbon
Purple = lithium

- Coordination of lithium with simple pendent groups occurs with 2 pendent oxygens and 1 ring nitrogen.
- With varying pendent groups (ethoxy, isopropoxy), the binding energy varies between **72.6 and 76.7 Kcal/mol.**

DFT Modeling of Phosphazene Trimers

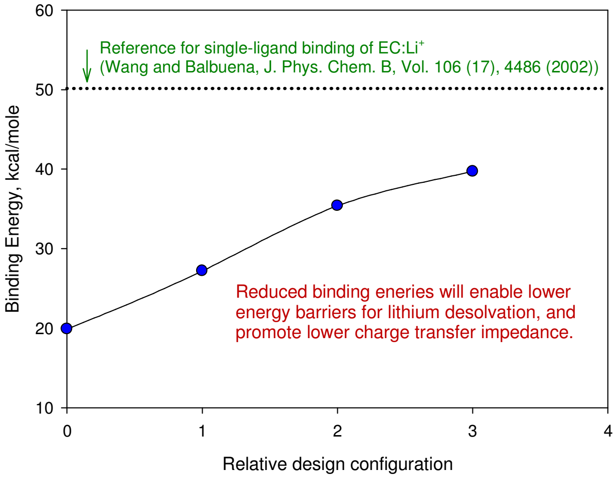
Fluorinated Trimer Binding Energy

Name (# of CF_3 groups)	# of possible isomers	**Average binding energy (Kcal/mol)**
FM1 (6)	1	**65.0**
FM2 (3)	10	**70.2**
FM3 (2)	8	**70.7**
FM4 (1)	4	**72.7**

- There is an electron withdrawing effect by adding fluorines. The lowest binding energy calculated is 62.9 Kcal/mol (3 CF_3 groups, no F-Li interaction), a decrease of ~10-15 Kcal/mol from the non-fluorinated trimers.
- Electron withdrawing effect is almost completely offset by fluorine coordination to lithium.

DFT Modeling of Phosphazene Ionic Liquids

DFT Results for Nitrogen-to-Li^+ Binding Energy for Various Design Configurations of Gen1 Ionic Liquid Phosphazene (strongest binding site shown)



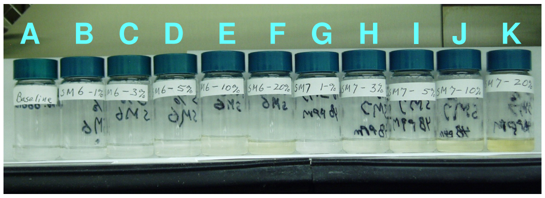
A major consideration of our Gen1 Ionic Liquid additive is to diminish the inherent association between phosphazene nitrogens and free cations (Li^+).

INL Gen1 Ionic Liquids have lower binding energies with lithium, compared to conventional organic solvents (EC).

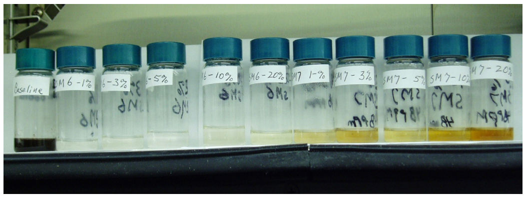
Fig. 2

Thermal Stability Testing, Study 2

Day 1

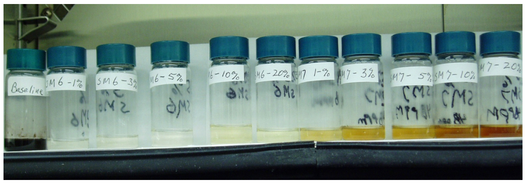


Day 40

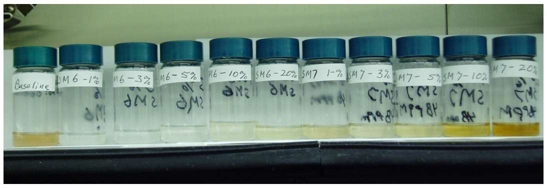


Day 8

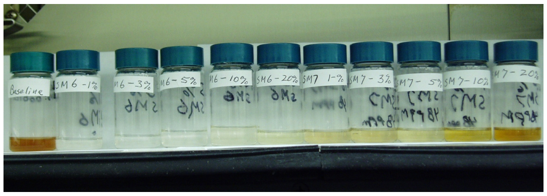
Day 62 (end)



Day 19



Day 26



A: Baseline
B: 1% SM6
C: 3% SM6
D: 5% SM6
E: 10% SM6
F: 20% SM6
G: 1% SM7
H: 3% SM7
I: 5% SM7
J: 10% SM7
K: 20% SM7

All tests at 60 °C. Baseline is 1.2M $LiPF_6$ in EC/EMC (2:8)

CONCLUSION:

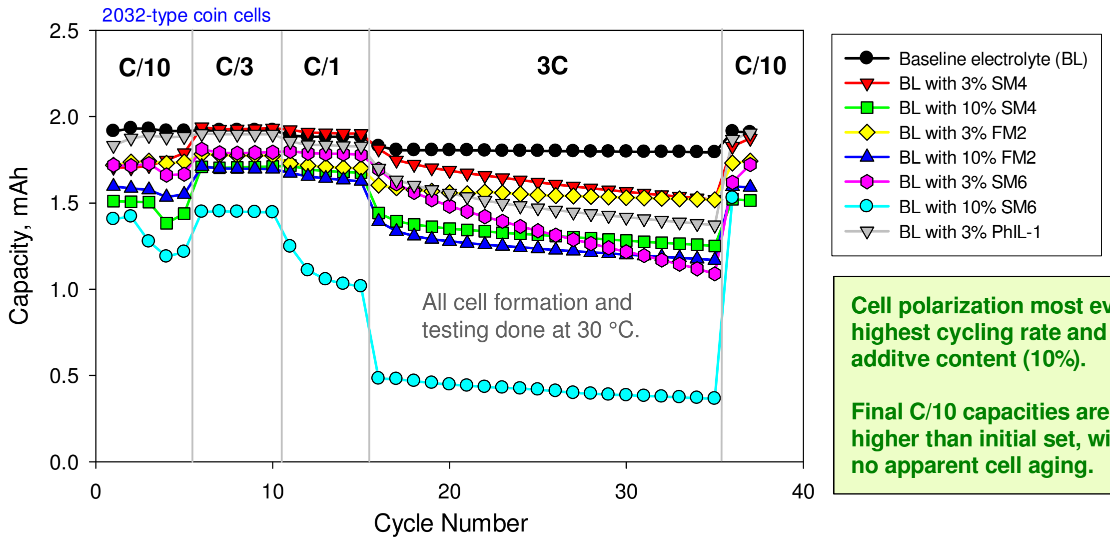
The presence of INL phosphazene SM6 has a profound effect in stabilizing the baseline electrolyte at levels as low as 1%. SM7-doped samples discolor due to suspected 40 ppm water contamination; SM7 study will be repeated.

Fig. 3

Cell Testing, Capacity Attributes

This slide might be updated at the time of the Merit Review to reflect ongoing cell aging at 3C cycling and 55 °C, done following the protocol below.

LNMO/LTO



Cell polarization most evident at highest cycling rate and highest additve content (10%).

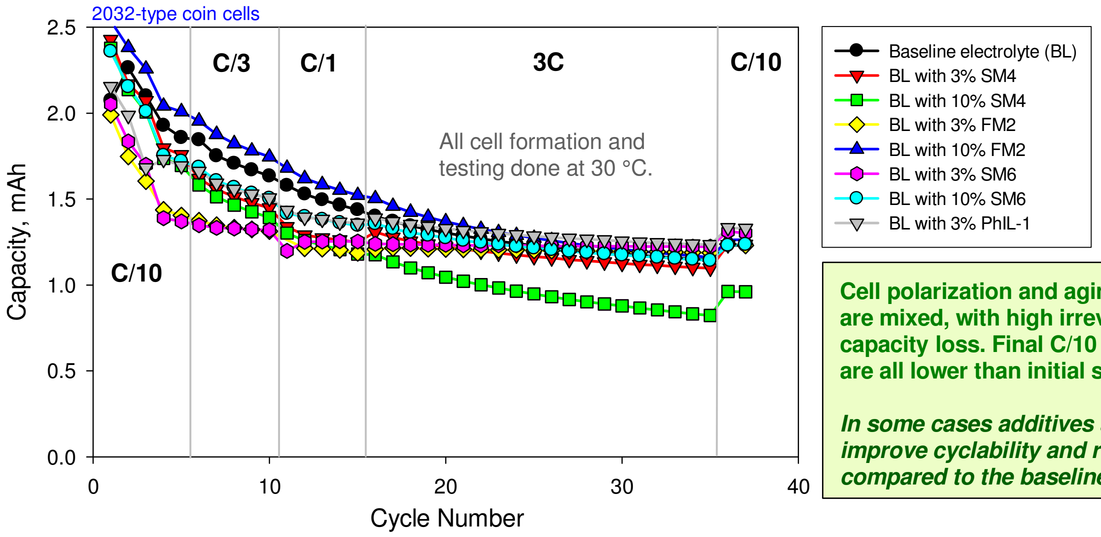
Final C/10 capacities are all higher than initial set, with no apparent cell aging.

Electrode materials provided by ANL

Cell Testing, Capacity Attributes

This slide might be updated at the time of the Merit Review to reflect ongoing cell aging at 3C cycling and 55 °C, done following the protocol below.

NMC/Carbon



Cell polarization and aging effects are mixed, with high irreversible capacity loss. Final C/10 capacities are all lower than initial set.

In some cases additives appear to improve cyclability and reduce aging, compared to the baseline.

Electrode materials provided by SNL

The NMC/Carbon results shown were obtained with uncalandared electrodes (unknown to us at the time). We are repeating this study using calandared materials.

TASK 1
Battery Cell Materials Development

2nd Quarter Report, Jan. ~ Mar. 2011

Project Number: 1.1E (ES028)

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

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

Collaborators (include industry):
Dennis Dees, Argonne National Laboratory
Jai Prakash, Illinois Institute of Technology

Project Start/End Dates: October 2008 / September 2014

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

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

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

Milestones:
(a) Electronic conductivity measurement and analysis of composite electrodes with various porosities.
(b) Conductivity network of composite electrode by SEM.
(c) Four point probe modeling of carbon coated NCM electrode.

Financial data: $300K

PROGRESS TOWARD MILESTONES

(a) Electrodes with both aluminum and polyester substrates were calendered to various porosities. The electronic conductivity was measured on composite electrode with combinations of electrode composition and porosity using 4 probe method.

(b) The composite electrodes with various compositions were cut using focus ion beam by Leica. The cross-section of the composite electrode was characterized using SEM.

(c) Four point probe model was built and validated using FlexPDF program.

(a) Summary of work in the past quarter related to milestone (a).
The resistance of the NCM3 (3% carbon coating) electrode with 1wt% additional carbon on aluminum foil shows less resistance before calendering. Resistances of both electrodes NCM0 (no carbon coating) and NCM3 on aluminum decreases after calendering. For the electrode on polyester substrate, the sheet resistance of the NCM3 electrode is higher. The electrode sheet resistance increases after calendering for both NCM0 and NCM3. Therefore, interfacial resistance is dominant for the composite electrode using aluminum substrate. The contact resistance between the particles and substrate was small for carbon coated sample.

(b) Summary of work in the past quarter related to milestone (b)
The SEM images indicated that the conductive network of composite electrode was mainly from conductive additives. The less carbon black in the composite electrode, the poor electronic conductivity was obtained. This observation is consistent to the 4 probe measurements.

(c) Summary of work in the past quarter related to milestone (c)
The four point probe modeling was programmed by D. Dees using FlexPDF software. Conductivity calculated from FlexPDF model was consistent to the 4 probe measurement. The validated model will be used to determine the interfacial resistance between the composite layer and substrate.

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

2nd Quarter Report, Jan. ~ Mar. 2011

Project Number: 1.3 (ES028)

Project Title: Screen Electrode Materials, Electrolytes, and Additives

Project PI, Institution: Wenquan Lu, Argonne National Laboratory

Collaborators (include industry):
Andrew Jansen, Argonne National Laboratory
Dennis Dees, Argonne National Laboratory
Jai Prakash, Illinois Institute of Technology

Project Start/End Dates: October 2008 / September 2014

Objectives:

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

Approach:

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

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

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

Milestones:

Materials have been investigated in 2nd Quarter:

a) Composite cathode materials:
   - ○ $1/3Li_2MnO_3 \bullet 2/3LiNi_{0.5}Mn_{0.5}O_2$ H. Wu (ANL)
   - ○ $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.37}Co_{0.24}Mn_{0.39}O_2$ from Toda Kogyo (Japan)

b) Surface modified graphite from ConocoPhillips (USA)
c) Electrodes evaluation ($LiNi_{0.5}Mn_{1.5}O_4$ and $Li_4Ti_5O_{12}$) for high voltage electrolyte development
d) Redox shuttle (3.8V vs. Li/Li^+) from ES (ANL)

Financial data: $350K

PROGRESS TOWARD MILESTONES

Evaluation on high energy density composite material, $1/3Li_2MnO_3 \bullet 2/3LiNi_{0.5}Mn_{0.5}O_2$ from ANL (H. Wu) was continued. Cycle life of this material was studies using both half cells and full cells.

A high energy composite material, $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.37}Co_{0.24}Mn_{0.39}O_2$ from Toda Kogyo (Japan), was obtained and tested in this quarter. The energy density and irreversible capacity during 1^{st} cycle have been tested. Its power and rate capability were also studied by HPPC using half cells. Its thermal property was tested using DSC. The information has been transferred to cell build project under ABR program.

On the anode site, investigation on surface modified natural graphite from ConocoPhillips was continued in terms of its cycling issue. The electrode thickness and lithium counter electrode effect were studied.

In support of the high voltage electrolyte development, high voltage spinel LNMO and LTO electrodes from Enerdel (USA) were electrochemically characterized.

In support of battery material scale up activities at ES (ANL), Redox shuttle (RS2) was received and investigated in terms of its electrochemical performance and thermal properties.

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

Composite cathode, $1/3Li_2MnO_3 \bullet 2/3LiNi_{0.5}Mn_{0.5}O_2$, from ANL (H. Wu) was tested in both half cells and full cells. In half cells, 92% capacity retention was obtained at room temperature in 50 cycles. In the full cell, coupled with SMG (Hitachi), 87% capacity retention was obtained at room temperature in 50 cycles.

Composite material, $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.37}Co_{0.24}Mn_{0.39}O_2$ from Toda Kogyo was tested as cathode material. This material showed 250mAh/g reversible capacity with 17% reversible capacity loss during 1^{st} cycle at room temperature and C/10 rate. It also showed low ASI (about 40 ohm-cm2) during 3C HPPC using half cells. The half cell capacity retention is about 97% at C/3 rate.

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

The cycling performance of A12 (surface modified graphite from Conocophillips) was investigated. The thicker electrode showed poor cycleability compared to thinner electrode in the half cells. However, much better capacity retention was obtained when A12 is coupled with NCA electrode in the full cell.

(c) Summary of work in the past quarter related to milestone (c)
The electrochemical performance of LNMO and LTO has been evaluated using 1.2M $LiPF_6$ EC/EMC (3/7) electrolyte. The reversible capacity of LNMO was determined to be 117mAh/g with 8% irreversible capacity loss during 1st cycle. The ASI value from home calendered electrode was 80 ohm-cm2. As for LTO, 89 mAh/g was obtained with almost no irreversible capacity loss. The anode to cathode capacity ratio was found to be 0.83.

(d) Summary of work in the past quarter related to milestone (d)
3.8V redox shuttle RS-2 scaled up from ES was tested using graphite/$LiFePO_4$ cells. Redox potential was determined to be around 3.8V depending on the current applied to the cell. Excellent overcharge protection was obtained using 9wt.% RS-2. However, Calorimetry test results indicated huge amount of heat generation when redox shuttle was activated.

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

1. High Voltage $LiNi_{0.5}Mn_{1.5}O_4$ Spinel and $Li_4Ti_5O_{12}$ Evaluation (EnerDel), W. Lu and N. Liu, Internal report on high voltage spinel for high voltage electrolyte development. Feb 2011.
2. Investigation of RS2 Redox Shuttle by ES, W. Lu, N. Liu, and L. Zhang, internal report on redox shuttle scaled up by ES, Feb. 2011.
3. Electrochemical and Thermal Characterization of Graphite Anode for Li-ion Batteries, W. Lu, C. Lopez, N. Liu, A. Jansen, D. Dees, 35th International Conference and Exposition on Advanced Ceramics and Composites (ICACC'11) Jan. 23rd-28th, 2011.
4. High-Energy Electrode Investigation for Plug-in Hybrid Electric Vehicles, Wenquan Lu, Andrew Jansen, Dennis Dees, Paul Nelson, Nicholas R. Veselka, and Gary Henriksen, J. Power Sources, 196, 2011, 1537-1540.

TASK 1
Battery Cell Materials Development

Project Number: 1.2.2 Electrode Material Development (ES029)

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

Project PI, Institution: Vincent Battaglia, LBNL

Collaborators (include industry): NEI Corp., Nippon Denko Co., Ltd, G. Ceder (MIT)

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

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

Approach: We will evaluate sources of $LiNi_{1/2}Mn_{3/2}O_4$ spinel for potential use in the high-voltage electrolyte effort of the ABR Program. We will utilize physical, chemical, and electrochemical techniques in this effort. An important consideration is that the spinel formulation allows the properties of the candidate electrolytes to be compared with minimal ambiguity as we make a selection. After a suitable spinel is selected, we will work on optimizing its formulation through the BATT Program and transfer the results to this project.

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

Financial data: \$240 k for FY11.

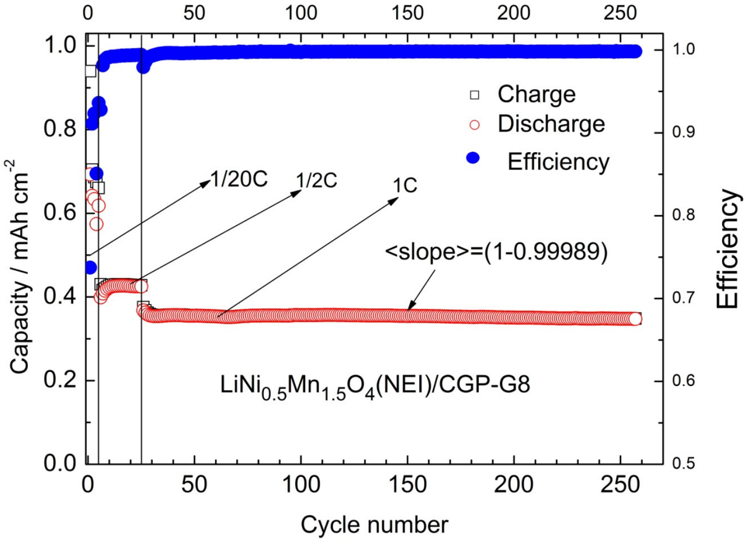
PROGRESS TOWARD MILESTONES

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

During the second quarter of FY 2011, we were able to obtain samples of $LiNi_{1/2}Mn_{3/2}O_4$ from two suppliers: NEI and Nippon Denko. Physical characterization of these materials has included SEM, TEM, EDS, XRD, PSA, and BES. Through EDS, it was determined that neither material contains any additional elements that have been used by other researchers to stabilize the native spinel. The TEM showed that the materials are very crystalline and that there are no surface coatings.

The as-supplied sample materials were also tested for solubility. 5 g of material was added to 15 g of our standard electrolyte with a composition of 1 M $LiPF_6$ in EC:DEC, 1:2 wt. ratio. After 1 week at 55°C, no Ni and some Mn were detected. For comparison, we ran a sample of $Li_{1.15}Mn_{1.85}O_4$ from Toda, America, a material known to dissolve. We found that the two Ni-spinel samples showed amounts of dissolved Mn that were about 1/3 and 2/3 of the ~0.12% of Mn that dissolved from the Toda material.

Our visiting researcher successfully prepared electrodes of the $LiNi_{1/2}Mn_{3/2}O_4$ (LiNMO) active material. These electrodes were formulated with relatively low loadings of 0.6 mAh/cm^2, and were cycled against Li, LTO, MCMB, and CGP-G8. The coulombic efficiency of each of these cells improved in the order listed. It is still not clear why cycling *versus* Li resulted in the lowest efficiency. We postulate that the cause is the poor stability of Li metal when cycled in the presence of DEC.



The graph to the left shows the cycling results achieved for the CGP-G8 Graphite / NEI $LiNi_{1/2}Mn_{3/2}O_4$ cell. The electrolyte was our standard electrolyte with no additives, and the active material was neither coated nor doped. This cell shows outstanding cycle-life stability , the best we have seen among literature reports for this material tested against graphitic electrodes. In addition, this cell shows 75% higher energy density than the LTO/LNMO cell. The cell capacity decay is 0.011% per cycle, but the cell inefficiency is 0.2% per cycle. This result suggests that not all of the side reactions in this cell are necessarily harmful.

TASK 1
Battery Cell Materials Development

Quarter 2

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

Milestones:
(a.) The source of the gassing was identified and the mechanism was proposed , (On schedule)
(b.) A solution was proposed according to the proposed mechanism. (On schedule)

Financial data: $300K

PROGRESS TOWARD MILESTONES

The in-situ GC-MS analysis indicated that the charged LTO ($Li_{4+X}Ti_5O_{12}$) directly participates in the reaction and produces the hydrogen following the equation below:
$Ti^{3+} + H^+ = Ti^{4+} + ½ H_2$
Due to the large amount of hydrogen observed, the hydrogen source should involve the carbonate solvents beside the trace amount of water in the cell.
Since the reaction involves the electron transferring from LTO to solvent, if we could cut off the electron pathway, we might be able to eliminate the gassing issue. Surface

modification of LTO either by additives or by ALD could be the possible solution. work on coating is progressing.

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

The charged LTO has directly participated in the gas evolution reaction. The GC-MS analysis shows the quantitative relation between Ti^{3+} and H_2. Carbonate solvents are the source of H^+.

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

Surface modification of LTO either by additives or ALD method is proposed.

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

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

TASK 1
Battery Cell Materials Development

Project Number: 1.1L (ES113)

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

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

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

Project Start/End Dates: October 2010 / September 2014

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

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

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

Milestones:
(a.) Material synthesis, purification and formulation, September 2011, (On schedule)
(b.) Investigation of physical properties of the Silane/Sulfone hybrid electrolytes, September 2011, (On schedule)
(c.) Complete initial evaluation of Silane/Sulfone hybrid electrolytes for LNMO/LTO chemistry, September 2011, (On schedule)

Financial data: $200K

PROGRESS TOWARD MILESTONES

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

Electrochemical stability of TMS/1NM3 mixed electrolytes was investigated by using cyclic voltammetry over a 0-6V range. A CV plot (Fig.1) of the 1.0M LiPF6 TMS/1NM3 shows that the electrolyte is stable up to 5.10V vs Li^+/Li for 5:5 ratio and 5.22V for 9:1 ratio. Compared with the good voltage stability of sulfone (5.5V vs Li+/Li) as reported by Xu et al. and silicon-based electrolyte has relatively narrow electrochemical window, which is typically in the range of 4.2-4.7V reported by Amine et al.. However, when mixed together, the oxidation potential of the mixture electrolyte shifted inwards without sacrificing the high voltage stability of TMS, which is consistent with the findings in their conductivities. The high-voltage stability of these silane/sulfone blend materials could, therefore, enable not only cathode materials such as $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, $LiMn_2O_4$ or $LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$, but also 5 V cathode materials and Argonne layered composite cathodes.

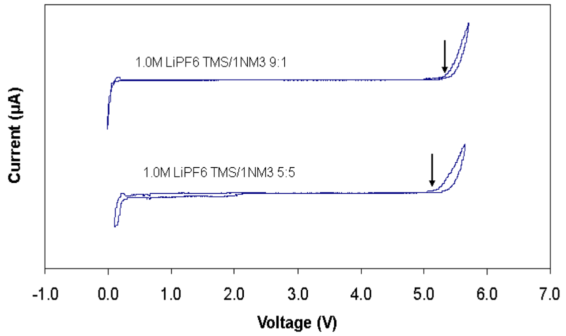


Fig.1. Cyclic voltammograms of 1.0M $LiPF_6$ hybrids with weight ratios of 9:1 and 5:5.

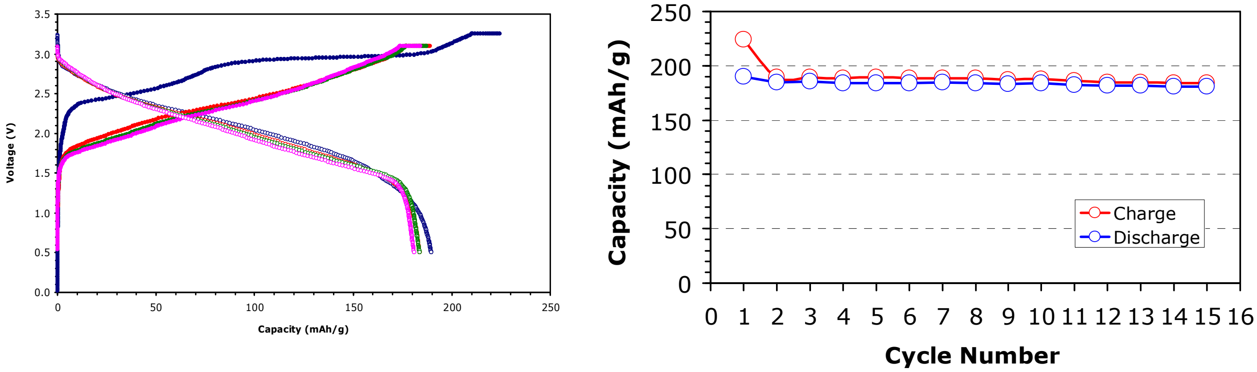


Fig.2a (left). 1st cycle charged to 3.25V as activation step; 2nd and the subsequent cycles are regular cycling: 0.5~3.1V, C/20 at room temperature; Fig.3b (right). Cycling performance of high capacity cathode/LTO cell using hybrid electrolyte.

Fig.2a shows few charge/discharge cycles of a cell based on $Li_{1.2}Ni_{0.15}Co_{0.10}Mn_{0.55}O_2$ as cathode, and $Li_4Ti_5O_{12}$ (LTO) as anode. 1.0M $LiPF_6$ TMS/1NM3 5/5 was used as electrolyte and a microporous PP/PE/PP membrane (Celgard 2325) was used as separator. After the first activation cycle to remove Li_2O, the cell was able to provide similar charge and discharge profile as in the case of organic electrolyte when cycled between 3 and 1 V at c/10 rate. The cell cycled well with 99.98% efficiency after 1st cycle and showed no capacity fade for subsequent cycles. The capacity delivered by the

$Li_{1.2}Ni_{0.15}Co_{0.10}Mn_{0.55}O_2$ electrode in this cell (190mAh/g) is similar to that delivered by the same electrode when a conventional LiPF6/EC: EMC (3:7) electrolyte is used. The initial good cycling performance indicates the sulfone/silane mixed electrolyte is suitable for the practical application for high energy lithium ion battery. Further study is ongoing to investigate the aging effect on cell performance and incorporating low viscosity high voltage stability solvent such as Fluor-ethers and esters in a 3 or 4 solvent mix.

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

Hybrid Electrolyte Patent-ANL-IN-09-039

TASK 1
Battery Cell Materials Development

Project Number: 1.2D (ES114)

Project Title: Spherical Carbon Anodes Fabricated by Autogenic Reactions

Project PI, Institution: Michael Thackeray, Argonne

Collaborators (include industry): Vilas Pol (Co-PI), Superior Graphite, General Motors

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

Objectives:
The initial objective of this project is to prepare spherically-shaped- and other rounded carbon anode particles for HEVs, PHEVs and EVs by autogenic reations to:
1) improve the abuse tolerance of carbon anodes without compromising capacity or power;
2) optimize autogenic processing conditions to enhance structural and electrochemical properties of the carbon products; and
3) evaluate electrochemical and thermal properties of the carbon materials.
The first objective of this phase of the project is to therefore to achieve a spherical carbon anode with comparable capacity (300mAh/g) and enhanced safety relative to graphite. A second objective would be to use autogenic reactions to prepare high capacity carbon-Si and carbon-Sn anode architectures that offer twice the capacity of graphite.

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

Milestones:
(a) Establish collaborative interactions with Superior Graphite and General Motors to gain access to high temperature (>2000 °C) furnaces – C*ollaborations established*
(b) Prepare carbon samples for Superior Graphite and General Motors – *First batches completed and heated - on going*
(c) Evaluate electrochemical properties of heat-treated carbon samples in lithium half cells and full cells – *Sept. 2011 – on schedule*
(d) Evaluate the relative physical, chemical and electrochemical properties of lithiated carbon spheres vs. lithiated graphite – *Sept 2011 – on schedule*
(e) Compare models of current distribution around spherically-shaped and sheet-like (graphitic) carbon particles – *Sept 2011 – on schedule.*

Financial data: $300K/year

PROGRESS TOWARD MILESTONES

Milestone (a). Establish collaborative interactions with Superior Graphite and GM: Collaborative interactions with Superior Graphite (Chicago) and General Motors have been established and are on going. However, because of delays in getting samples heated because of furnace problems, we have approached another party to assist with the heat-treatment process. An NDA is being executed – we hope to have access to their high temperature furnace soon.

Milestone (b). Prepare carbon samples for Superior Graphite and GM:
See Milestone (a)

Milestone (c). Evaluate electrochemical properties of heat-treated carbon samples: The typical morphology and electrochemical properties of autogenically-prepared hard carbon spheres before and after heat-treatment (1 hour at 2400 °C) were described in the previous report. The heat-treated spherical carbon particles (SCP-HT) delivered typically ~250 mAh/g with a first cycle capacity loss of 20%. Heating the carbon spheres for 8 hours in an inert atmosphere (Superior Graphite, SCP-HT8) did not significantly increase the graphitic component in the spheres; however, the prolonged heat treatment did provide a marginal increase in capacity (255 mAh/g) and it reduced the first-cycle capacity loss to 15% (Fig. 1)

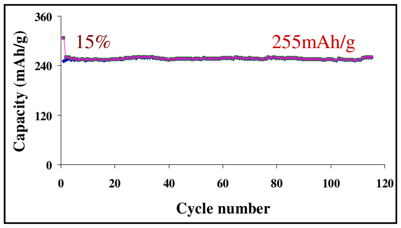


Fig. 1. Capacity vs. cycle no. plot particles of a of a Li/SCP-HT8 cell.

Spherical Carbon	Density	BET	Pore Volume
SCP (700 °C)	2.2 g/cc	4.4 m^2/g	0.0078cc/g
SCP-HT (2400 °C)	2.1 g/cc	1.1 m^2/g	0.0043cc/g

Table 1. Physical properties of spherical carbon Synthesized at 700 °C and 2400 °C.

Milestone (d). Evaluate the relative physical, chemical and electrochemical properties of lithiated carbon spheres vs. lithiated graphite:
The physical properties of heat-treated SCP-HT samples, in terms of their density, BET surface area and pore volume were determined and compared with those of untreated SCP samples (Table 1). The carbon spheres are extremely hard and dense, with a true density equivalent to that of graphite (2.1-2.2 g/cm^3). By contrast, their tap density is low (~1g/cm^3), due to the difficulty of compacting the powders because of apparent electrostatic charge between the particles. The pore volume is low, and decreases on heat-treatment as expected. An evaluation of the thermal stability and reactivity of lithiated carbon spheres has been initiated.

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

This subproject has been initiated with Dennis Dees using an electrochemical model developed for spherical secondary particles. The aim of this work is to ascertain the potential benefit of using carbon spheres vs. other forms of carbon with respect to suppressing lithium dendrite formation and enhancing the relative safety of lithium-ion cells with carbon sphere electrodes.

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

V. G. Pol, Plastics Recycling Conference, New Orleans, LA, 1-2 March 2011.
M. M. Thackeray, Fermilab Lecture Series, Batavia, IL, 4 February, 2011.

TASK 1
Battery Cell Materials Development

Project Number: 1.1V (ES115)

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

Project PI, Institution: Christopher Johnson, Argonne National Laboratory

Collaborators (include industry):
Sun-Ho Kang, Argonne National Laboratory
Wenquan Lu, Argonne National Laboratory
Stephen Hackney. Michigan Technological University

Project Start/End Dates: October 2010 / September 2016

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

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

Milestones: Materials will be produced and tested that will show progressively improved properties as the project moves forward.
(a) Synthesize new materials, September 2011, (on-schedule)
    - Optimize ion-exchange reaction conditions, March 2011 (completed)
(b) Characterize electrochemical properties of synthesized materials, September 2011, (on-schedule)
    - Demonstrate high-rate of 200 mAh/g @ 2C rate, March 2011, (completed)
(c) Characterize structure of materials, September 2011, (on-schedule)
    - Examine morphology of starting materials, and ion-exchange products, March 2011, (completed)
(d) Continue optimization of Na, Li and transition metal content ratios in materials, June 2011, (on-schedule)
(e) Initiate measurement of thermal properties of charged material in DSC, September 2011, (on-schedule)

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

PROGRESS TOWARD MILESTONES

(a) $Na_xLi_y(Ni_{0.25}Mn_{0.75})O_z$ cathode precursors were synthesized with the widest range possible: x=0.3, 0.4, 0.5, 0.6, 0.7. 0.8, 0.9, where y=0.9, 0.8, 0.7, 0.6, 0.5, 0.4, and 0.3. The x+y = 1.2 for all, and x+y/Ni+Mn = 1.2. The extent of the P2 solid solution range was examined. Optimization of Li ion-exchange reaction conditions of the above Na-Li materials is currently underway.

(b) XRD patterns were taken on starting materials and products. Also, the 2C rate capacity was measured and is above 200 mAh/g.

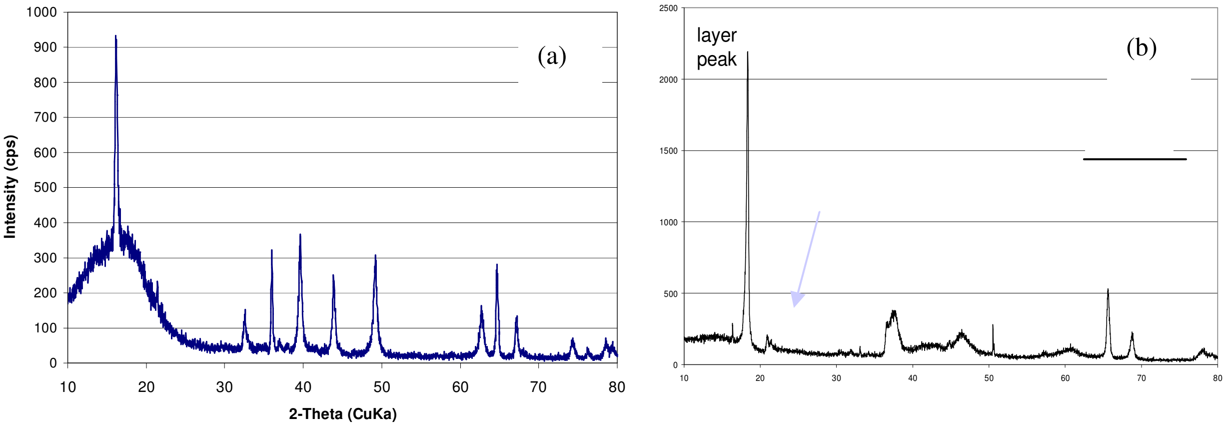
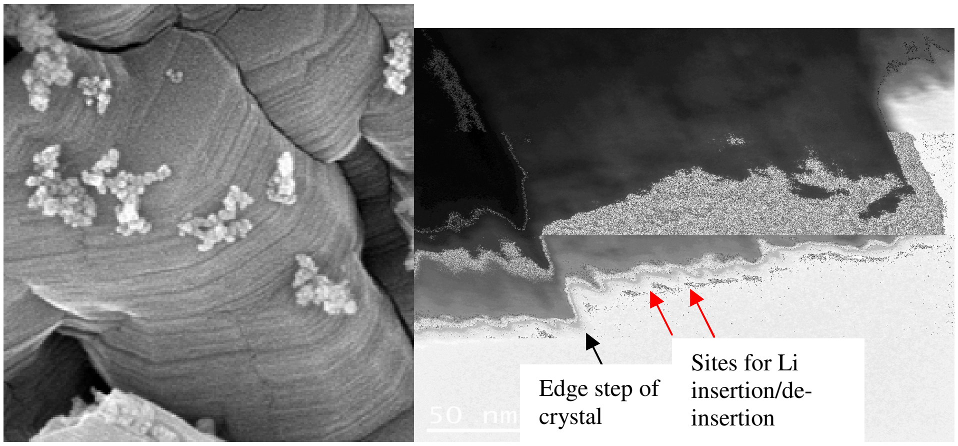


Fig. 1. XRD patterns of (a) $Na_xLi_y(Ni_{0.25}Mn_{0.75})O_z$ (P2 type) and (b) $Li_{1.06}Na_{0.02}Ni_{0.21}Mn_{0.63}O_2$ (layered compound with a number of c-direction stacking faults). The faults allow for fast insertion/de-insertion of Li cations into the structure.

(c) FESEM and HRTEM of Li ion-exchanged products were completed. The morphologies resemble a 'stack-of-cards' after the exchange, indicating that Na is pulled out of the layer and replaced concomitantly with Li.



(a) (b)

Fig. 2. (a) FESEM of $Li_{1.06}Na_{0.02}Ni_{0.21}Mn_{0.63}O_2$ (layered compound with a number of c-direction stacking faults), and (b) HRTEM of Li ion-exchanged material perpendicular to the c-axis showing points of entry for fast Li cation insertion/de-insertion.

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

(e) Thermal properties of the charged materials in milestone (a) are on-going.

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

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

TASK 1
Battery Cell Materials Development

Project Number: ES038

Project Title: High Energy Density Ultracapacitors

Project PI, Institution: Patricia Smith, NAVSEA-Carderock

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

Project Start/End Dates: FY09 to FY12

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

Approach:

Identify candidate high-performance electrolyte compositions via discussions with battery manufacturers, other DOE investigators and literature reports. Evaluate most promising systems by fabricating and cycling pouch cells (25 and -30°C). Evaluate the thermal stability of electrode materials, electrolytes, and cell design using Differential Scanning Calorimetry (DSC) and Accelerating Rate Calorimetry (ARC). Investigate the effect of negative electrode carbon graphitization on cell performance and thermal stability. Identify optimal carbon pore size for low temperature performance.

Milestones:
(a) Identification of high-performance, low-temperature electrolyte (July 2011). In progress
(b) Safety evaluation of 1st generation LIC cell technology (March 2011). Complete
(c) Safety evaluation of 2nd generation LIC cell technology (Sep 2011). In progress
(d) Initiation of negative carbon electrode graphitization study (June 2011). Delayed

Financial data: Project budget/year, amount subcontracted if appropriate
FY10: $350K, Funding Expensed 2Q FY11: $50K (This was from FY10 funding).

Progress Toward Milestones:

(a) During the last quarter, efforts continued to identify a better low temperature electrolyte than that of the first generation LIC cell technology developed by JM Energy. Two carbonate electrolytes were evaluated. The selected two electrolytes, A and B, revealed ~ 150% and ~53% higher conductivity, respectively compared to that of the 1st generation lithium ion capacitor electrolyte at -20°C (Figure 1).

(b) The safety evaluation of the first generation LIC capacitor was completed. The thermal stability of 1M $LiPF_6$ in EC:PC:DEC was studied by DSC and ARC. Fully-charged, 1st generation lithium ion capacitor anodes were found to be less thermally stable than fully-charged conventional ultracapacitor anodes. Other components of the two capacitors (e.g. fully-charged carbon cathode, separator) displayed similar thermal behavior. The ARC investigation results showed that the self heating of a 2,000F LIC cell (Figure 2a) started at ~ 90°C while no measureable self heating occurred for a conventional 2,000F ultracapacitor (Figure 2b) until the cell vented at 170°C.

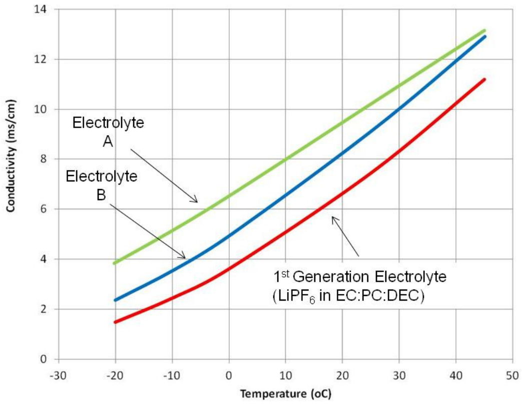
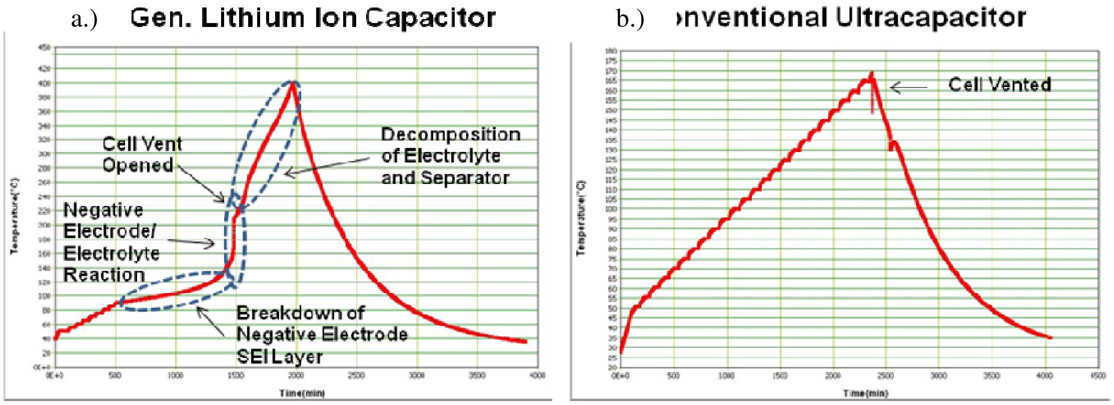


Figure 1. Conductivity of electrolyte used in first generation LIC cells and electrolyte solvent systems investigated in this effort.



a.)

b.)

Figure 2. Accelerating rate calorimetry experiments of a fully charged 2,000F (a) first generation lithium ion capacitor containing $LiPF_6$ in a mixture of ethylene carbonate, propylene carbonate and diethyl carbonate and (b) conventional ultracapacitor containing $(C_2H_5N)_4\ BF_4$ in acetonitrile.

(c) This task cannot be completed until cells are received from JM Energy. JM Energy is expected to produce their 2nd generation cells by June 2011. Individual 2nd generation electrode materials have been received and the DSC investigation will be initiated in May 2011.

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

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

Abstract submitted. P. Smith, T. Tran, and T. Jiang, “Lithium-Ion Capacitors - Performance Strengths, Limitations, and Future Directions”, AABC Europe 2011, 7 June 2011.

TASK 1
Battery Cell Materials Development

Project Number: 1.1.X

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

Project PI, Institution: Gregory Krumdick/Argonne National Laboratory

Collaborators (include industry): < none >

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

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

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

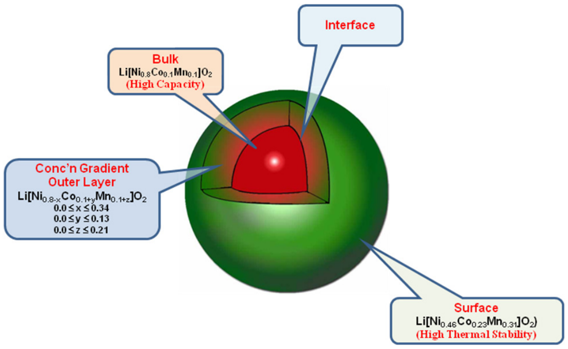


Figure 1. Schematic of positive electrode particle with Ni-rich core surrounded by concentration-gradient out layer.

Deliverables:

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

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

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

Financial data:
Total project duration: 12 mo.
Staff: $100K

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

Dr. Shin was offered a staff position on 12/23/2011 and Argonne's HR department initiated the process to obtain an H1 visa. Dr. Shin received final visa approval on 4/1/2011. Dr. Shin has made plans to relocate to the US by the end of April and will start work at Argonne on 5/2/2011. After taking the necessary orientation and safety training classes, Dr. Shin will be assigned the tasks detailed in this project.

TASK 1
Battery Cell Materials Development

Project Number: 1.1K'

Project Title: Transition Metal Precursors for High Capacity Cathode Materials

Project PI, Institution: Ilias Belharouak, Argonne National Laboratory

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

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

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

Approach: Three synthetic routes, hydroxide, carbonate, and oxalate processes, will be 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 will be made at the level of the materials morphology, physical characteristics, and electrochemical properties. Blending between materials made through the carbonate or hydroxide precursors and the same compositions made through the oxalate will be done in order to get the most use of the high packing density for high energy density and high porosity for high rate capability. The information learnt during the progress of this work will assist the ongoing effort related to the scale up of battery grade materials for high energy density lithium ion batteries.

Milestones:

a) Preparation of ($Ni_{0.3}Mn_{0.7}CO_3$) carbonate precursor was carried out using a continuous stirred tank reactor (CSTR) at the pilot scale level. (Completed).
b) The nucleation and growth of precursor particles were investigated during the CSTR process by monitoring particle size distributions, particle morphologies, chemical compositions, and structures with time. (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

Nickel sulfate, manganese sulfate, sodium carbonate, and ammonium hydroxide were used as the starting materials to prepare $Ni_{0.3}Mn_{0.7}CO_3$ precursor. A schematic of the water-jacketed CSTR (4L capacity reactor) system is shown in Figure 1. Product overflow was periodically collected during the experiment, and the particle size distribution was measured with a particle size analyzer. The precursor material, which was used to prepare the cathode materials, was collected from hour 5 to hour 8 of the process.

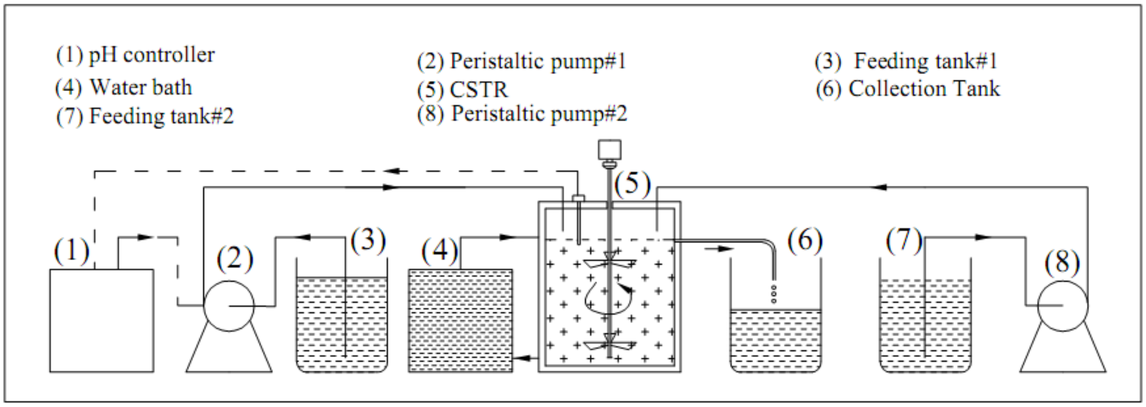


Figure 1. Schematic drawing of CSTR system used for this experiment

Figure 2 shows the particle size distribution of particles collected during the 8 hours of CSTR co-precipitation. At the very beginning, the particle distribution was unexpectedly broad, with particle sizes ranging from 1 to 80 µm. We speculated the large particles were formed by agglomeration of very small seeds which is likely due to the electrostatic force or surface tension between the seed particles. As time elapses, the particle size distribution narrowed slightly, and the distribution maximum shifted to a center around 20 µm. In addition, a small peak appeared below 1 µm, possibly due to the disintegration of the large agglomerates. After 15 min, the curve became a single distribution peak, with the maximum increasing to 8 µm (35 min), 14 µm (100 min), 16 µm (160 min), and up to 36 µm at the end of the CSTR experiment.

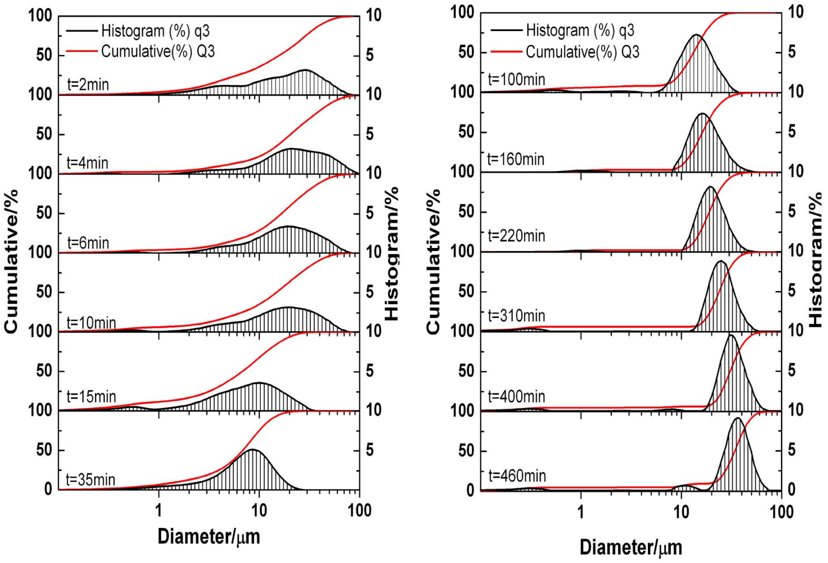


Figure 2. Particle size distribution of samples collected at different reaction times.

Fig. 3 shows SEM images of the precursors collected during the CSTR experiment. The SEM images were chosen to reflect the trend of particle nucleation and growth during the co-precipitation process. During the first minutes (2 min) of the experiment, the precursor particles were composed of large loose agglomerates with no defined shape. Thereafter, some spherical agglomerates were formed with different sizes. After 35 min, more segregation was observed within the agglomerations, and particles continued to grow with a round shape. These SEM observations were in accordance with the particle size distribution results detailed in Fig. 2. The surface of the final collected particle was apparently smooth and dense; however, a surface analysis performed by the BET method showed that these particles had a large surface area of 152 m^2/g with an average pore size of 1.7 nm. Therefore, we concluded that these spherical precursor particles were actually secondary particles composed of nano-size primary particles of the same chemical composition.

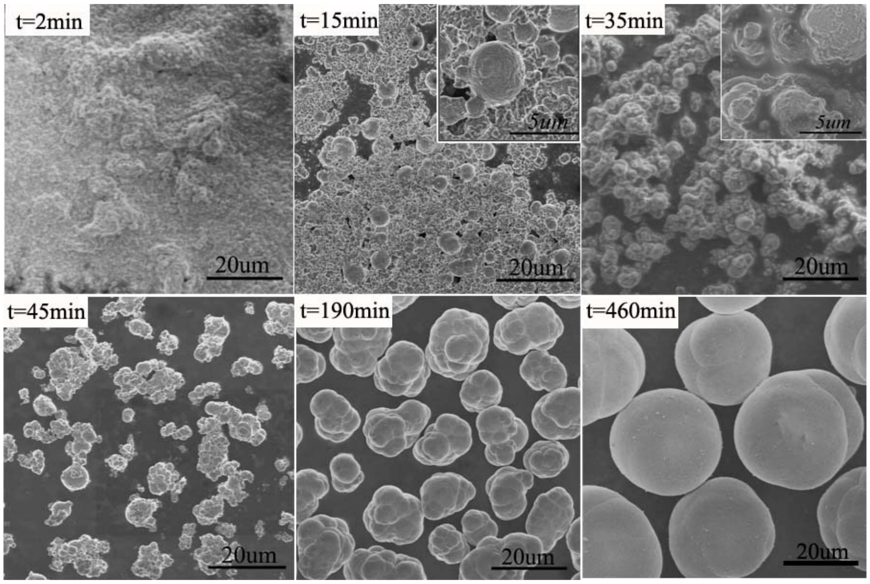


Figure 3. SEM images of samples collected at different reaction times

Publications, Reports, Intellectual property or patent application filed this quarter.
Paper accepted, Journal of Materials Chemistry.

TASK 2
Calendar & Cycle Life Studies

Project Number: ARRAVT075

Project Title: Prototype Cell Fabrication Facility

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

Collaborators (include industry):
Ilias Belharouak, Argonne National Laboratory
Wenquan Lu, Argonne National Laboratory
Bryant Polzin, Argonne National Laboratory
John Vaughey, Argonne National Laboratory

Project Start/End Dates: April 2010 / May 2011

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

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

Milestones:
(a.) Equipment identified and orders placed. August 2010, (Complete)
(b.) Equipment delivered and installed. December 2010, (Delayed)

Financial data: $1,000K in FY2010

PROGRESS TOWARD MILESTONES

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

This milestone was effectively completed in FY2010, with orders placed for all major pieces of equipment that represented approximately 97% of the total funding. The final piece of equipment (i.e. the Instron materials testing instrument) was ordered this quarter. A list of all equipment ordered is given below.

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

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

All equipment for the facility has arrived and all but two pieces of equipment has been installed. The final installations are planned for April, which will exhaust the remaining funds.

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

1. Andrew Jansen and Dennis Dees, “ANL: Prototype Cell Fabrication Facility,” To be presented at the 2011 DOE Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, May 9th-13th, 2011, Washington DC.

TASK 2
Calendar & Cycle Life Studies

Project Number: ARRAVT077

Project Title: Post-Test Facility

Project PI, Institution: Ira Bloom/Argonne National Laboratory

Collaborators (include industry): < none >

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

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

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

Milestones:

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

Financial data:
Total project duration: 21 mo.
Laboratory modifications $300K/6 mo.
Equipment: $2000K/17 mo.

PROGRESS TOWARD MILESTONES

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

An existing laboratory is being modified to accommodate the new facility. The existing laboratory was completely demolished and was brought up to current building codes. It is now ready to house the glove box and other pieces of equipment (Fig. 2).

Many other pieces of equipment rely on the glove box for proper their placement and installation of electrical and inert gas services. Since construction started about three months late and there has been a delay in the delivery of the glove box (now expected on June 10, 2011), the completion of the construction of the facility has been delayed. It is expected that construction will be complete by the end of June.

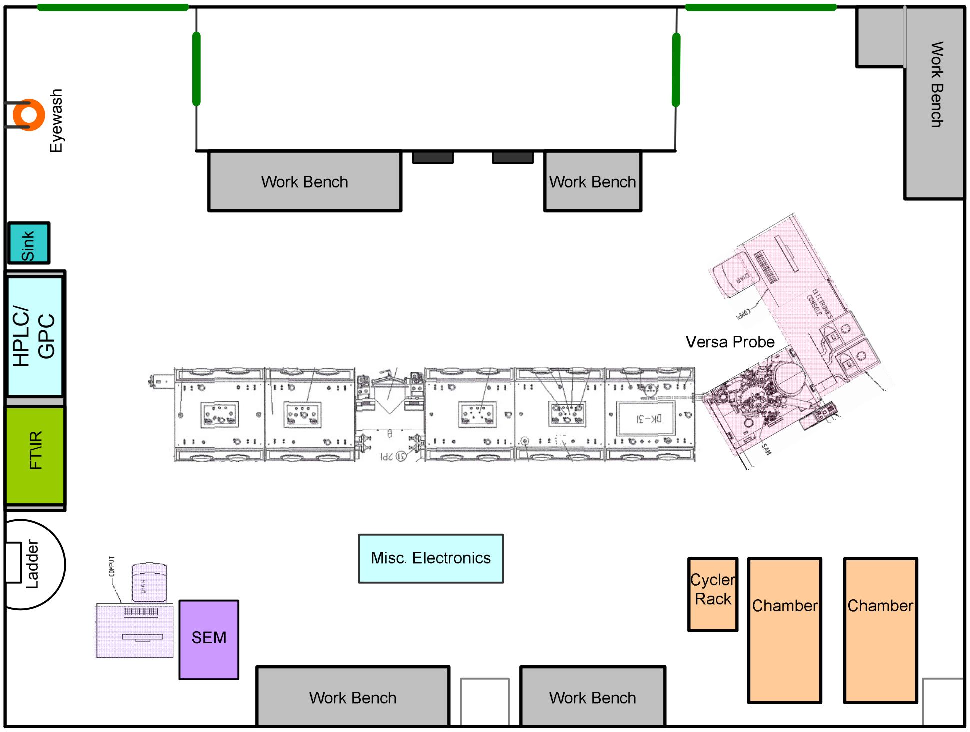


Fig. 1. Overall design of the post-test facility. The large, open area at the top of the figure is not part of the post-test facility. The VersaProbe X-ray photoelectron spectrometer (XPS) was purchased with funds from other sources.

Establishing the post-test facility will require procuring many pieces of equipment. The progress here is shown in Table 1. It should be noted that the glove box has been delayed from its original delivery date, April 15. This is due to the delay in obtaining components, such as a custom-made flange to connect the glove box to the VersaProbe XPS.

Fig. 2. Photographs showing progress in modifying the laboratory space. The picture on the reader's left shows the laboratory before the renovation started; the picture on the reader's right shows its current state.

Table 1. Status of equipment purchases.

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

TASK 2
Calendar & Cycle Life Studies

Project Number: 2.1 (ES030)

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

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

Collaborators (include industry):
Dennis Dees, Argonne National Laboratory
Sun-Ho Kang, Argonne National Laboratory
Wenquan Lu, Argonne National Laboratory

Project Start/End Dates: October 2008 / September 2014

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

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

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

Financial data: $740K

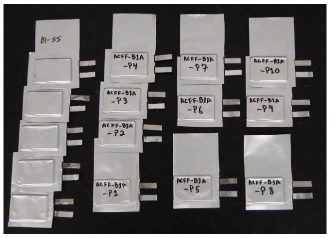
PROGRESS TOWARD MILESTONES

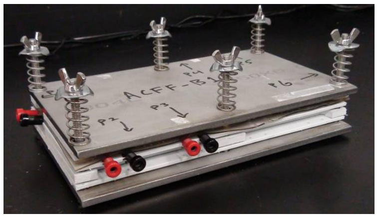
(a) Summary of work in the past quarter related to milestone (a).

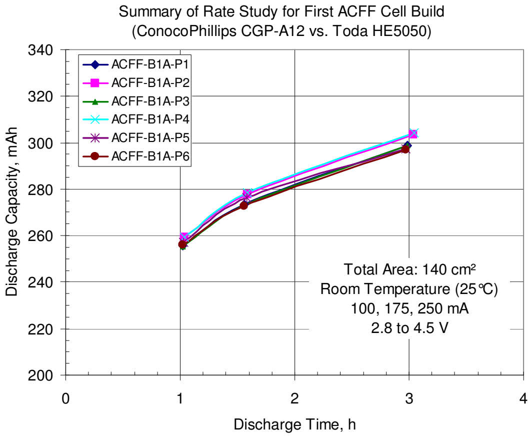
Modifications were made to several pieces of equipment to enhance safety and operation in the dry room, with final approval to operate all equipment granted in February, 2011.

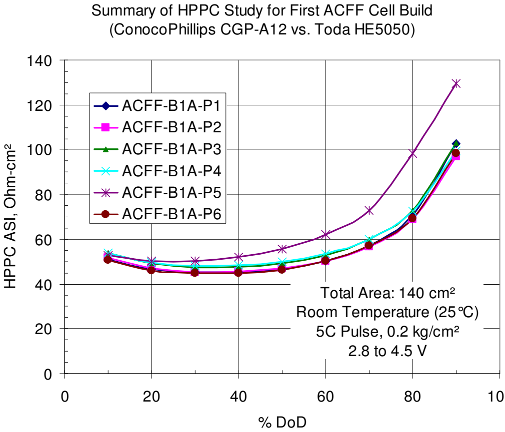
(b) Summary of work in the past quarter related to milestone (b)

Single-sided and double-sided electrodes were made with Toda' high energy cathode material, HE5050 ($Li_{1.2}Ni_{0.15}Co_{0.10}Mn_{0.55}O_2$), and with ConocoPhillips CGP-A12 high energy graphite. These electrodes were hot roll pressed to lower porosity and then punched to make electrodes for pouch cells. Over a dozen pouch cell assemblies were made with these advanced electrodes, seven of which were filled with electrolyte and then subjected to formation cycling and electrochemical performance characterization cycling. These cells performed well and were delivered to the EADL for independent verification and life testing. (One outlier was removed from further testing due to poor coulombic efficiency and higher ASI.)









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

Huiming Wu (Argonne) produced 2 kg of his high-energy NMC cathode ($Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$) in several batches. Electrode production in the cell fabrication facility is being scoped out. Trial coatings are underway.

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

Waiting for the additional 18650 cell parts, which were ordered in previous quarter. Expect these parts in April. Will begin electrode slitting trials next quarter.

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

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

TASK 2
Calendar & Cycle Life Studies

Project Number: 2.2B (ES031)

Project Title: Model Cell Chemistries (Electrochemistry Cell Model)

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

Collaborators (include industry):
Daniel Abraham, Argonne National Laboratory
Sun-Ho Kang, Argonne National Laboratory
Andrew Jansen, Argonne National Laboratory
Wenquan Lu, Argonne National Laboratory
Kevin Gering, Idaho National Laboratory

Project Start/End Dates: October 2008 / September 2014

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

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

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

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

Financial data: $400K/year

PROGRESS TOWARD MILESTONES

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

Battery design studies point out the advantages of going to thicker electrode coatings. The electrochemical model was utilized to further examine electrode thickness limitations. As shown in Figure 1, the cell discharge capacity effectively reaches a limiting capacity with increasing electrode thickness. Lowering the discharge current allows for a greater fraction of the electrode capacity to be utilized. As electrode thickness increases transport of salt in electrolyte limits the constant C-rate discharge capacity (i.e. the salt concentration in the positive electrode approaches zero). Increasing the electrode thickness also affects the current distribution in the electrodes. Because Li-ion electrodes typically have a large interfacial impedance compared to other impedance phenomena in the cell, thinner electrodes (i.e. ~≤ 150 µm for 1C discharge) have a relatively uniform current distribution. However, electrolyte transport limitations in thick electrodes shifts the initial current towards the separator, which gradually changes throughout the discharge.

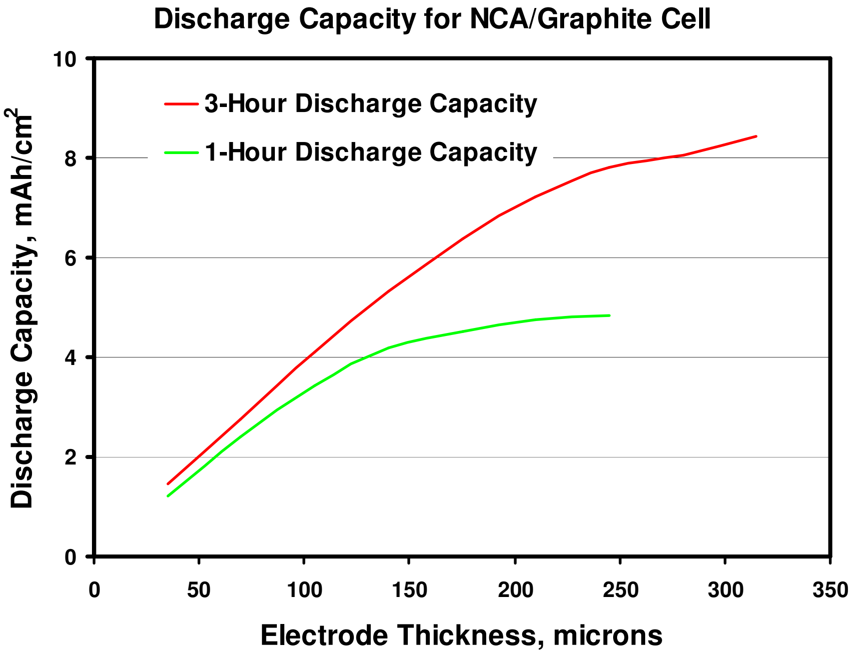


Figure 1 Li-ion cell discharge capacity as a function of electrode thickness

The electrode impedance is relatively constant over a wide thickness range. The impedance of thin electrodes increases as the active area decreases, and for thick electrodes the cell impedance increases resulting from electrolyte transport limitations. However, the primary performance limitation for thick electrodes is that thicker graphite negatives can dip below the lithium deposition voltage during regen charging pulses.

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

This project has been continually challenged by finding efficient ways to solve increasingly complex electrochemical cell models. A new differential algebraic equation solver package (PSE gPROMS) is being adopted to solve a wide variety of cell studies at the required level of complexity. Previously, coupled multi-scale problems were solved using a multi-dimensional solver. The new solver program explicitly treats each length scale to allow for greater stability and increased dynamic complexity. As an example, in the past full cell DC modeling studies with complex interfacial phenomena could not be conducted without considerable stability problems. The new solver program was able to recreate the earlier studies without the troubling stability issues. Efforts to convert existing models to the new solver are continuing.

(c) Summary of work in the past quarter related to milestone (c)
Work is progressing on implementing the SEI growth model necessary to understand power and energy fade in future Li-ion cell builds. Differing negative electrode aging behavior between Gen 2 to Gen 3 is being examined to establish a baseline set of parameters. Both technologies used graphitic negative electrodes (i.e. MAG10 for Gen 2 and MCMB for Gen 3) and layered positive electrodes (i.e. NCA for Gen 2 and NCM for Gen 3). It is believed that the continuously increasing negative electrode impedance in the Gen 3 cells can be mostly attributed to manganese dissolution from the positive and subsequent deposition on the negative.

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

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

2. Dennis Dees and Kevin Gallagher, "Electrochemistry Cell Model," To be presented at the 2011 DOE Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, May 9th-13th, 2011, Washington DC.

TASK 2
Calendar & Cycle Life Studies

Project Number: 2.3A (ES032)

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

Project PI, Institution: Daniel Abraham, Argonne National Laboratory

Collaborators:
J. Bareno, G. Cheng, S.-H. Kang, M. Balasubramanian, B. Polzin, A. Jansen, D. Dees, W. Lu, Argonne National Laboratory
J.G. Wen, M. Sardela, S. MacLaren, R. Haasch, I. Petrov, University of Illinois at Urbana-Champaign
B. Lucht, University of Rhode Island

Project Start/End Dates: October 2008 / September 2014

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

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

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

Financial data: $300K

PROGRESS TOWARD MILESTONES

Cells with the PHEV baseline chemistry contain $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$–based positive electrodes, Mag10 Graphite–based negative electrodes, Celgard 2325 separator, and EC:EMC (3:7, by wt.) + 1.2M $LiPF_6$ (baseline) electrolyte. The performance of as-prepared cells was characterized using a series electrochemical charge-discharge cycling and impedance experiments. The cells were then cycle-life aged at 45C; capacity and impedance data were obtained periodically to characterize performance degradation. Our accelerated aging tests on the PHEV baseline cells are now complete.

Figures 1a and 1b shows capacity and impedance data obtained on a cell that underwent 4000 cycles between 3.6 and 4.0V, then 2000 cycles between 3.3 and 4.0V at a C/1 rate. The figures show that the rate of capacity fade and impedance rise is greater for the 3.3-4.0V cycling compared to the 3.6-4.0V cycling. That is, cell performance degradation is greater for wider voltage cycling windows; i.e., when a larger proportion of the Li^+ inventory is shuttled between the electrodes. Wider voltage cycling windows are typical of PHEV profiles because of the need to access higher capacities that are required to drive longer distances; in comparison, shallow voltage cycles are more typical of HEV profiles, wherein the need is for high-power from cells.

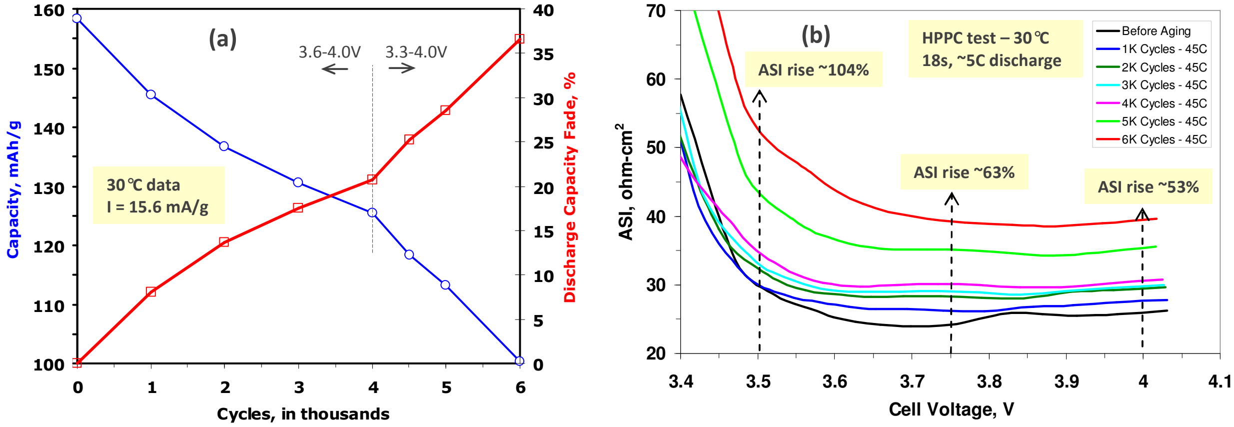


Fig 1. (a) Capacity/capacity fade data obtained from capacity-voltage plots, and (b) impedance data from HPPC tests, from a cycle-life aged cell. All data were acquired at 30°C.

To determine the source of capacity fade we conducted experiments on positive electrodes that were harvested from "formed" and "aged" full cells. The data shown in figure 2 is from a "formed" cell that was cycled three times between 3 and 4.1V at 30°C; the "aged" data is from the cell that underwent 6000 cycles at 45°C, as described earlier.

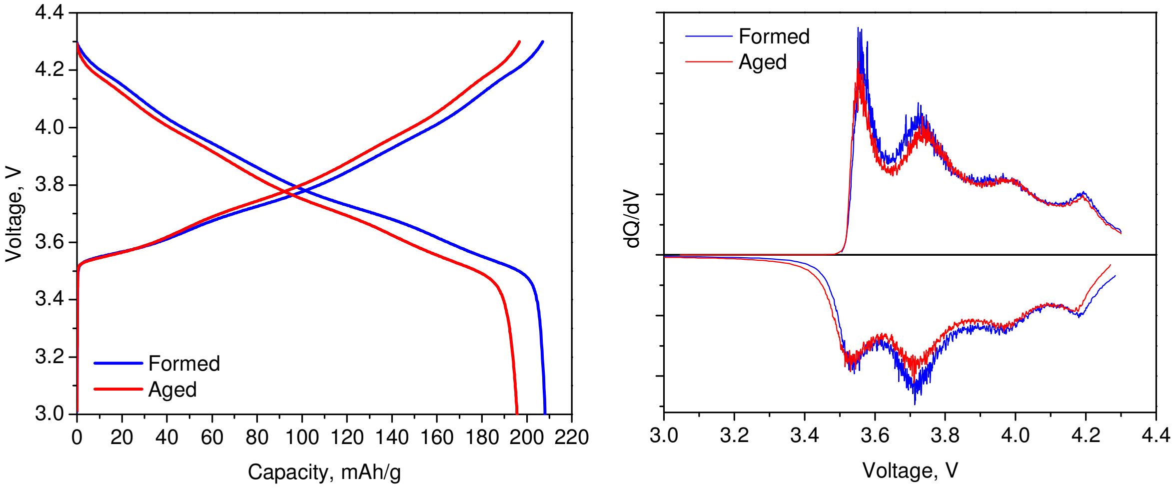


Fig 2. Capacity-voltage, and corresponding dQ/dV, plots from harvested electrode vs. Li cells.

The data shown in Fig. 2 are from coin cells containing the "harvested" positive electrode, Li metal counter electrode, and the baseline electrolyte; the data were obtained at 30°C, in the 3 – 4.3V voltage range at a ~C/30 rate. It is evident from the figure that the lithiation capacity of the aged cell electrode is only slightly (~7%) smaller than that of the formed cell electrode; furthermore, the dQ/dV profiles are also very similar. These data indicate that the "electronic isolation" of oxide particles is small, i.e., most oxide particles in the positive electrode can contribute to cell capacity when cell cycling is conducted at very slow rates. Therefore, the positive electrode contribution to "true" capacity fade is small – the cell capacity fade can be attributed to Li^+ consuming processes at the negative electrode.

Electrodes and electrode constituents for the next set of ABR PHEV cells were received towards the end of this quarter – relevant data will be reported starting next quarter.

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

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

TASK 2
Calendar & Cycle Life Studies

Project Number: 2.3B (ES032)

Project Title: Structural Investigations of Layered Oxides for PHEV Applications

Project PI, Institution: Daniel Abraham, Argonne National Laboratory

Collaborators (include industry):
J. Bareno, S.-H. Kang, M. Balasubramanian, Argonne National Laboratory
J.G. Wen, M. Sardela, S. MacLaren, I. Petrov, University of Illinois at Urbana-Champaign

Project Start/End Dates: October 2008 / September 2014

Objectives: The structure and structural rearrangements in Mn-based oxides, which show high-capacities when cycled at high-voltages, have a significant effect on cell performance, calendar-life, and safety. Our goal is to obtain a detailed structural understanding of the $Li_{1+a}(Mn_xM'_z)O_2$ family of materials: M' is typically Ni and/or Co, but other elements such as Fe, Cr, and Al, are also being studied. Our experiments are designed to answer some of the following questions: (i) What are the local atomic arrangements in the as-prepared oxides and how are these arrangements influenced by composition? (ii) What are the charge compensation mechanisms during electrochemical cycling? (iii) What phase transformations result on cycling/aging? How does this affect the oxide's capacity and rate performance?

Approach: A multi-institution effort is underway to synthesize, characterize, and model these complicated oxide structures. After synthesis, and initial examination of oxide electrochemical performance, we conduct both *exsitu* and *insitu* X-ray absorption spectroscopy (XAS) measurements that provide information on oxidation states, coordination number around the transition metal (TM) elements, and changes in these parameters during electrochemical cycling. The XAS study is complemented by Analytical Electron Microscopy (AEM), which includes high angle annular dark field electron microscopy to examine the crystal structure and electron energy loss spectroscopy to examine composition variations at near-atomic spatial resolutions. Our initial studies are on $Li_{1.2}Co_{0.4}Mn_{0.4}O_2$, which is a model compound to study the structure of $Li_{1+a}(Mn_xM'_z)O_2$ materials being considered for PHEV applications.

Milestones:
(a.) Complete structural study of as-prepared $Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$, March 2011, (met milestone)
(b.) Complete structural study of cycled $Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$, September 2011, (on schedule)
(c.) Initiate structural characterization of other $Li_{1+a}(Mn_xM'_z)O_2$ materials, September 2011, (not yet begun)

Financial data: $300K

PROGRESS TOWARD MILESTONES

The layered oxides being considered as intercalation compounds for lithium batteries display significant differences between the long range crystal structure and local arrangements around individual atoms. These differences are important because the local atomic environments affect Li-ion transport, hence the oxide's rate capability, by determining activation barriers energies, by blocking or opening Li-diffusion pathways, etc. Traditional diffraction methods provide key information on the average crystal structure. However, no single experimental technique can unequivocally determine the average long range crystal structure and the distribution of local environments over crystallographic distances while retaining atomic-scale resolution.

Therefore, in this study we have employed a combination of diffraction, microscopy, and spectroscopy techniques to investigate the long range (≈ 1 μm) and local structure (≤ 1 nm) of $Li_{1.2}Co_{0.4}Mn_{0.4}O_2$, which is a model compound for layered oxides being considered for transportation applications.

SEM and XRD revealed that the sample possesses an overall R-3m structure similar to $LiCoO_2$, and that $\approx 0.2 - 0.5$ μm primary particles agglomerate to form bigger, approximately 7 μm, secondary particles.

Electron diffraction revealed the coexistence of monoclinic Li_2MnO_3-like and rhombohedral $LiCoO_2$-like crystal structures, consistent with the HAADF-STEM observation of Li-ordering at TM planes of the host rhombohedral lattice.

X-ray absorption spectroscopy showed that $Li_{1.2}Co_{0.4}Mn_{0.4}O_2$ contains mostly Mn^{4+} in Li_2MnO_3-like atomic environments and Co^{3+} in $LiCoO_2$-like atomic environments, over length scales of, at least, 7 Å. In contrast, EELS analysis revealed a coexistence of Co and Mn on roughly equal proportion over length scales less than 1 nm.

This apparent contradiction is resolved by a proposed model consisting of well integrated $LiCoO_2$ and Li_2MnO_3 nanoclusters which, for compositions close to $0.5\ Li_2MnO_3 \cdot 0.5\ LiCoO_2 = Li_{1.2}Co_{0.4}Mn_{0.4}O_2$ presents a microstructure composed of well integrated dendritic clusters. The small width of the dendrites (≈ 1 nm) accounts both for the near perfect segregation into $LiCoO_2$ and Li_2MnO_3 at EXAFS scales and the nearly homogeneous concentration of Mn and Co at EELS scales. The dendritic nature of the clusters, allowing them to retain continuity over long distances in the TM(0001) plane accounts for the large lateral extension of the Li_2MnO_3-like contrast regions observed in HAADF-STEM. (see Fig. 1).

Because no specific atomic interactions were used in obtaining the atomistic models, we expect the proposed microstructures to be valid for other $Li_{1+a}(Mn_xM'_z)O_2$ materials that display Li-ordering within the TM(0001) planes of a host rhombohedral structure.

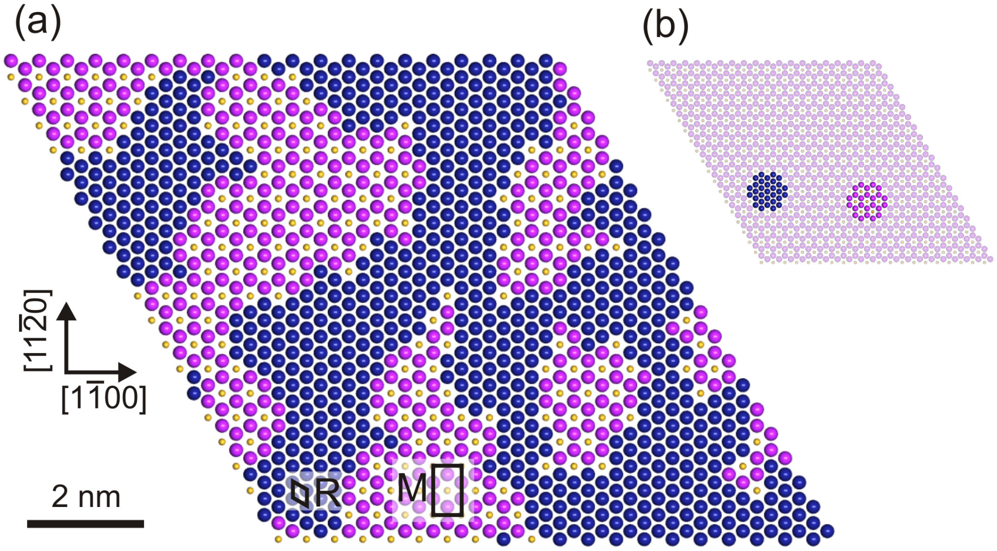


Figure 1. (a) Schematic model structure of TM plane in $Li_{1.2}Co_{0.4}Mn_{0.4}O_2$ showing coexistence of Co and $LiMn_2$ domains. Big blue and magenta spheres represent Co and Mn atoms, respectively; small yellow spheres represent Li atoms. In-plane sections of the rhombohedral (R) and monoclinic (M) unit cells are indicated in the figure. Periodic boundary conditions connect the top and left edges of the figure with the bottom and right edges, respectively. Therefore, the particular model shown contains only one Co and two $LiMn_2$ separate clusters. Additionally, projected atomic columns along <1-100> (e.g. left to right) contain approximately equal amounts of Co and X atoms, where X varies across columns following a Mn-Mn-Li sequence consistent with STEM results. (b) Illustration of the early stages of model generation showing one $LiMn_2$ and one Co cluster randomly placed on the board. Empty sites are indicated by faded colors.

Analytical electron microscopy (AEM) and X-ray absorption spectroscopy (XAS) of cycled $Li_{1.2}Mn_{0.4}Co_{0.4}O_2$ samples has been initiated.

Work on milestone (c) is yet to begin.

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

1. J.-G. Wen, J. Bareño, C. Lei, S.-H. Kang, M. Balasubramaninan, I. Petrov, D.P Abraham, Solid State Ionics 182 (2011) 98-107.
   Title: Analytical Electron Microscopy of $Li_{1.2}Co_{0.4}Mn_{0.4}O_2$ for Lithium-ion Batteries

TASK 2
Calendar & Cycle Life Studies

Project Numbers: 1.1.1 and 2.4.1 (ES033)

Project Title: Electrochemistry Diagnostics of Baseline and New Materials

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

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

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

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

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

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

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

Progress toward milestones: We determined that PF_6^- intercalation in amorphous carbons and electrolyte oxidation on carbon black additives contribute to degradation mechanisms in high-voltage cathodes. The goal of our work in the second quarter of FY11 was to investigate various carbon surface treatment processes to suppress both of these detrimental phenomena. Long-term drying at 120°C under vacuum or prolonged heat treatment at 900°C under Ar/H_2 atmosphere of various types of standard carbon black additives produced negligible improvements. We concluded that PF_6^- intercalation and electrolyte oxidation are inherently related to the carbon material bulk and surface structures and therefore a different approach is required to inhibit these processes.

Our methodology was to synthesize a conductive carbon additive with a bulk and surface structure appropriate for applications in high-voltage Li-ion systems. A polyimide polymer (Kapton, Goodfellow, Inc.) was pyrolyzed under an inert atmosphere at 1000°C. The pyrolysis process was followed by an activation process, in which the pyrolyzed carbon was exposed to CO_2 at 900°C for 1 hour. This so-called CO_2 activation process is known to increase the surface area of active materials via the $CO_2 + C \rightarrow CO$ synproportionation process. In fact, the activation process increased the surface area of the pyrolyzed carbon from 1.5 m^2/g to 535 m^2/g. Interestingly, Raman spectra of the pyrolyzed carbon and the carbon sample that was subjected to the hour-long activation process show almost no change, suggesting that the basic structure of graphene building blocks remains intact (Figure 1).

Cyclic voltammograms of the baseline pyrolyzed carbon and activated carbon electrodes are shown in Figure 2. No peaks that might be attributed to PF_6^- intercalation/deintercalation can be observed in the voltammograms of either sample. Interestingly, the activated carbon electrode significantly inhibits electrolyte oxidation. The relatively low pyrolysis temperature (1000°C) and high degree of structural disorder is responsible for suppressing PF_6^- ion intercalation. The highly amorphous carbon structure and very short Li^+ diffusion paths inhibit the intercalation process. On the other hand, the very low electrocatalytic activity of the activated carbon toward electrolyte oxidation is most likely due to formation of oxygen surface groups (carbonyl, carboxyl, hydroxyl, *etc.*) and/or the formation of a highly developed porous structure with a low concentration of high-electronic-density carbon edge atoms.

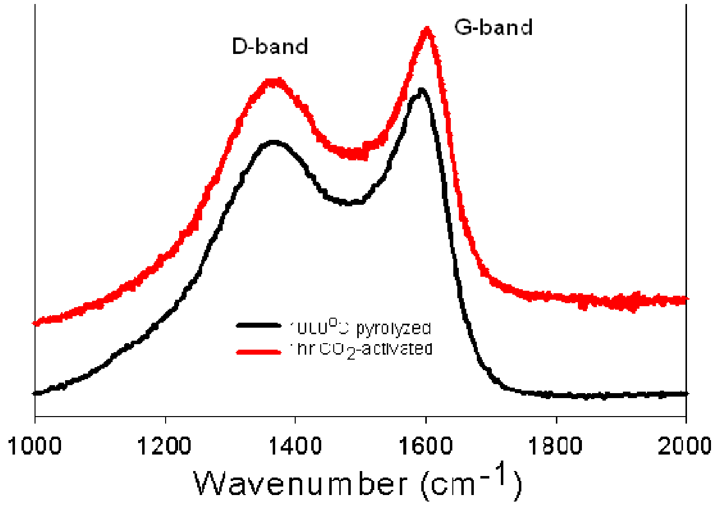


Figure 3. Raman spectra of pyrolyzed carbon and activated carbon electrodes

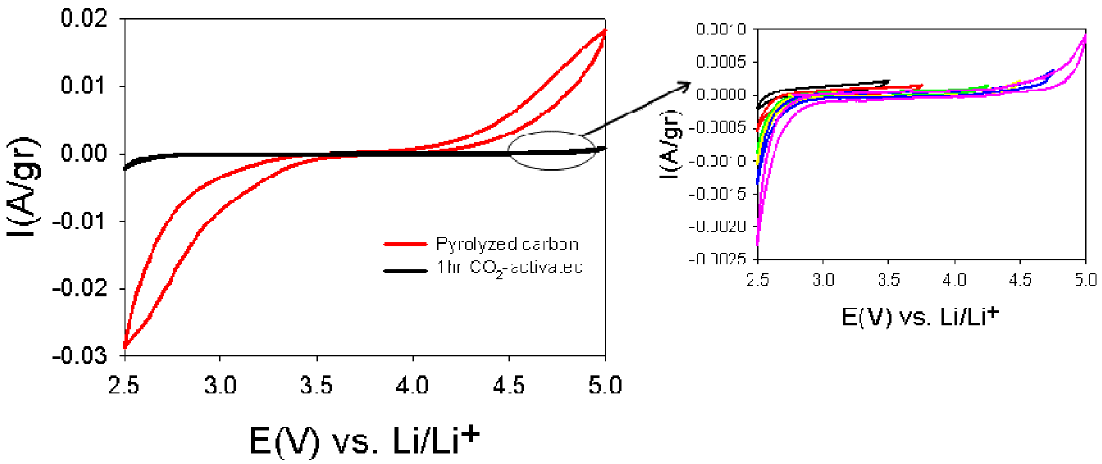


Figure 4. Cyclic voltammograms of pyrolyzed carbon and activated carbon electrodes

TASK 2
Calendar & Cycle Life Studies

Project Number: ES034

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

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

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

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

Objectives:

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

Approach:

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

Milestones:

(a) Complete the *In situ* XRD studies during charge-discharge cycling for Cr and F doped $LiMn_2O_4$ spinel as high power cathode materials in collaboration with ANL. by April 2011, **on schedule**. (b) Complete the Time resolved X-ray diffraction (TRXRD) studies of ZrO_2 coated $LiAl_{0.05}Co_{0.15}Ni_{0.8}O_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode materials during heating by April 2011, **on schedule**. (c) Report the results of in situ XRD studies of Cu or Ni doped $LiMn_2O_4$ spinel as high voltage cathode materials in collaboration with Duracell (P&G) by September, 2011, **on schedule**. (d) Start in situ XAS and TR-XRD studies of Li_2MnO_3-LMO_2 type new cathode materials during cycling and heating by September, 2011, **on schedule**.

Financial data: $350,000/year

Progress Toward Milestones:

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

The milestone (a) has been reached: The Cr and F co-substituted and Cr substituted spinel samples provided by Tronox LLC (Okalahoma City, OK 73134) have been studied by *in-situ* XRD measurements at beamline X18A of the National Synchrotron Light Source (NSLS). The *in-situ* XRD patterns obtained for Cr doped $LiMn_2O_4$ are different than the pristine $LiMn_2O_4$ reported in the literature. Peak splitting indicates the new crystal structure formed during charge. The spilt peaks re-converged into single peaks during discharge. This different phase transition behavior than the pristine $LiMn_2O_4$ spinel is originated from the Cr^{3+} substitution, and causes negative effects on electrochemical performance with lower capacity. After the co-substitution of both Cr^{3+} and F^-, both the phase transition behavior and the capacity recovered to those for the pristine $LiMn_2O_4$ spinel, but with great improvement in capacity retention. A manuscript based on these results is being prepared.

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

Progress has been made toward the milestone (b): The Time resolved X-ray diffraction (TRXRD) studies of ZrO_2 coated $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode materials during heating are underway. The preliminary results in Figure 1 show that no significant improvement in thermal stability for the ZrO_2 coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ samples in comparison with the uncoated ones, if no electrolyte is added. However, if the electrolyte is added, the ZrO_2 coated samples show quite impressive improvement in thermal stability. These results show that the improvement of thermal stability by ZrO_2 surface coating is by reducing the surface contact of the cathode material with the electrolyte.

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

Progress has been made toward milestone (c). In situ XRD spectra during charge-discharge cycling have been collected on $LiNi_{0.5}Mn_{1.5}O_4$ samples synthesized at 800 °C and 700 °C at Duracell (P&G). The results are being analyzed.

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

Progress has been made toward the milestone (d): Preliminary results of in situ TR-XRD data of Li_2MnO_3-LMO_2 type new cathode materials during heating has been collected..

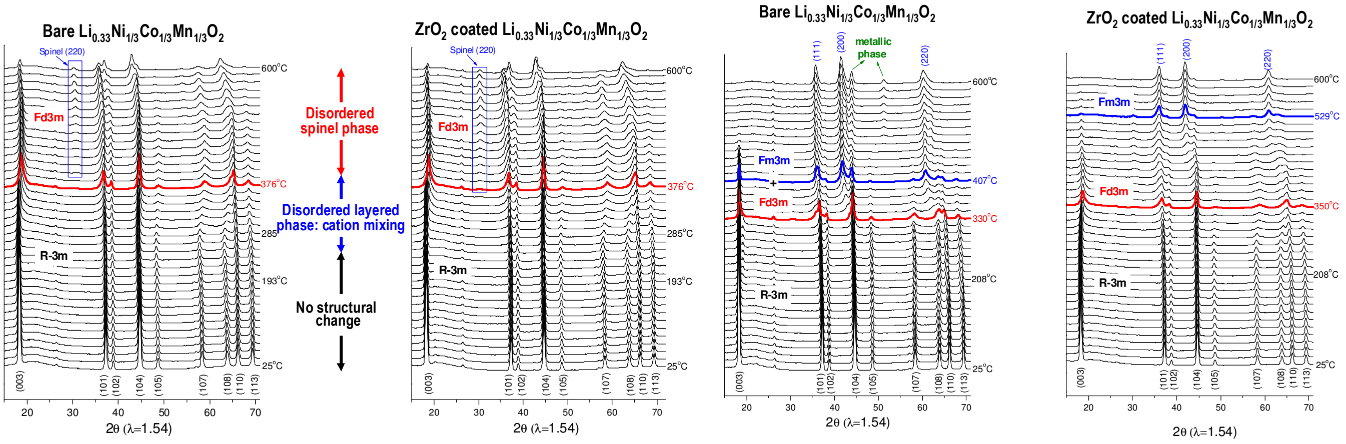


Figure 1: Time-resolved XRD of bare and ZrO_2 coated $Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ without electrolyte (left) and with electrolyte (right). The improvement of thermal stability by ZrO_2 coating is clearly demonstrated by the increased temperature of the rock-salt Fm3m phase formation in the presence of electrolyte.

Publications and presentations in this quarter:

1. X. J. Wang, Y. N. Zhou, H. S. Lee, K. W. Nam, X. Q. Yang, O. Haas, “Electrochemical investigation of Al–Li/Li_xFePO_4 cells in oligo(ethylene glycol) dimethyl ether/$LiPF_6$”, J Appl Electrochem, V41, (2011), 241-247, DOI 10.1007/s10800-010-0231-6.
2. Y. N. Zhou, X. J. Wang, H. S. Lee, K. W. Nam, X. Q. Yang, O. Haas, “Electrochemical investigation of Al–Li anode in oligo(ethylene glycol) dimethyl ether/$LiPF_6$”, J Appl Electrochem, (2011), 271-275, DOI 10.1007/s10800-010-0233-4.
3. Lijun Wu, Kyung-Wan Nam, Xiaojian Wang, Yongning Zhou, Jin-Cheng Zheng, Xiao-Qing Yang and Yimei Zhu, “Structural Evolution and Related Thermal Instability of Overcharged $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Layered Cathodes for Li-ion Batteries”, *Chemistry Materials*, submitted.
4. Xiao-Jian Wang, Hai-Yan Chen, Xiqian Yu, Lijun Wu, Kyung-Wan Nam, Jianming Bai, Hong Li, Xuejie Huang, Xiao-Qing Yang, "New in-situ synchrotron X-ray diffraction technique to study the chemical delithiation of $LiFePO_4$", *Chemical Communications*, submitted.
5. Seong-Min Bak, Kyung-Wan Nam, Chang-Wook Lee, Sang-Bok Ma, Hyun-Chul Jung, Xiao-Qing Yang and Kwang-Bum Kim, “Spinel $LiMn_2O_4$/reduced graphite oxide hybrid as cathode material for high rate lithium ion batteries”, *Chemical Communications*, submitted.

TASK 2
Calendar & Cycle Life Studies

Quarterly report FY2011/02 – Performance period Jan. 1 – March 31, 2011

Project Number: ES039

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

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

Collaborators (include industry):
University of Tennessee: Kevin Rhodes
ORNL: Melanie Kirkham, Robbie Meisner, Andrew Payzant, Chad Perish, Sergiy Kalnaus, Nancy Dudney, Zhili Feng, Xun-Li Wang, Ke An, David Wood
Argonne National Laboratory: Daniel Abraham
General Motors: Steve Harris, Yan Wu
Dow Kokam: Maneesh Bahadur, Erin O'Driscoll

Project Start/End Dates: August 2009 – September 2012

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

Approach:

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

AE has been utilized to detect, sort, and classify mechanical events such particle fracture inside of cycling LIBs [1]. In order to directly correlate the observed fracture events with strain in the active materials special in situ methods of XRD can be utilized. A novel beryllium free in situ AE-XRD cell has been devised which uses a metalized Mylar or Kapton window to allow X-ray penetration during cycling in standard coin cell hardware [2]. This provides a safe and inexpensive alternative to current in situ XRD methods. Polymer disks sputtered with a may be used in direct contact with anode materials while disks sputtered with aluminum can be used in contact with cathode materials. Studies using this combined technique will allow for further fundamental understanding of material degradation mechanisms and how they are correlated with capacity fade and cell failure.

Milestones:

- Adapt the AE-XRD technique to cathode materials and test – **In Progress (70% complete)**
- Adapt technique to be used on commercial batteries for state of health or expected life time measurement (e.g. during formation cycling) – **In Preparation**

Financial data:
$300K/year; $40K/year subcontract to UTK

PROGRESS TOWARD MILESTONES

Status

Progress in the application of AE and in situ XRD to cathode materials has included the study of $Li(Mn_{1.5}Ni_{0.5})O_4$ (MNO) [3]. MNO is an excellent candidate for high voltage LIB applications. Structural changes in MNO were monitored using in situ XRD. The first two cycles, shown in Figure 1, show a stepwise transformation between tetragonal spinel phases as Ni is oxidized or reduced during charge and discharge respectively. At low potentials a Jahn Teller distortion is observed that creates a distorted spinel phase. The volume fraction phase composition of the MNO as calculated from fitted peak areas is shown in Figure 2.

After 15 cycles the phase change behavior of the MNO changes. At after 15 cycles the Ni+3 spinel phase never completely disappears. Also, not distorted tetragonal phase was detected at lower potentials. Later the material has much less of the MNO material staying largely in the Ni+2 spinel phase during lithiation putting a limit on how much lithium can be stored. This break down in phase conversion must be related to the observed capacity fade.

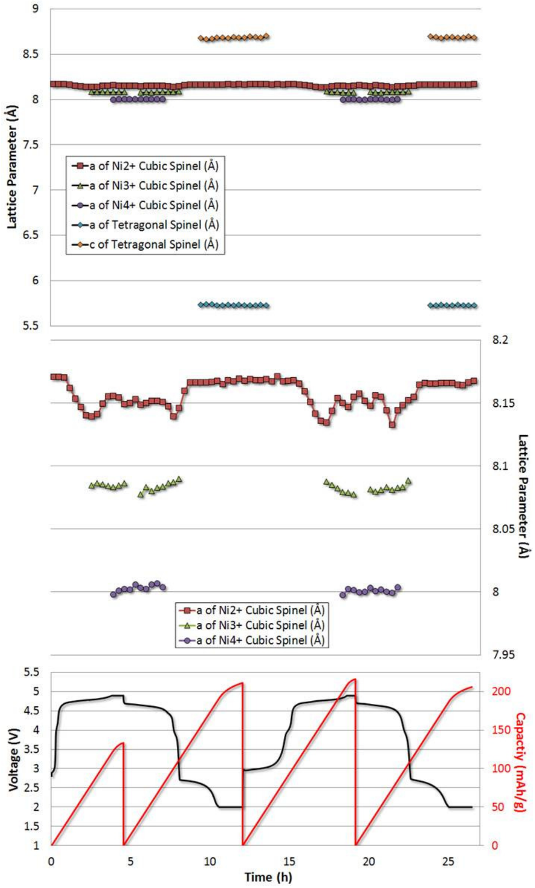


Figure 1

Currently, AE is being applied to MNO materials to detect how, when, and if particles are fracturing or if any other events may be detected. Early results show an AE response that is initially subdued but increases within the first few cycles. This may indicate particle fracture during this period which would have an important impact on the performance and path of a moving phase boundary in the particles. Collaborations to better understand the observed structural changes and how they can be influenced by particle surface coating and cycling conditions are currently underway.

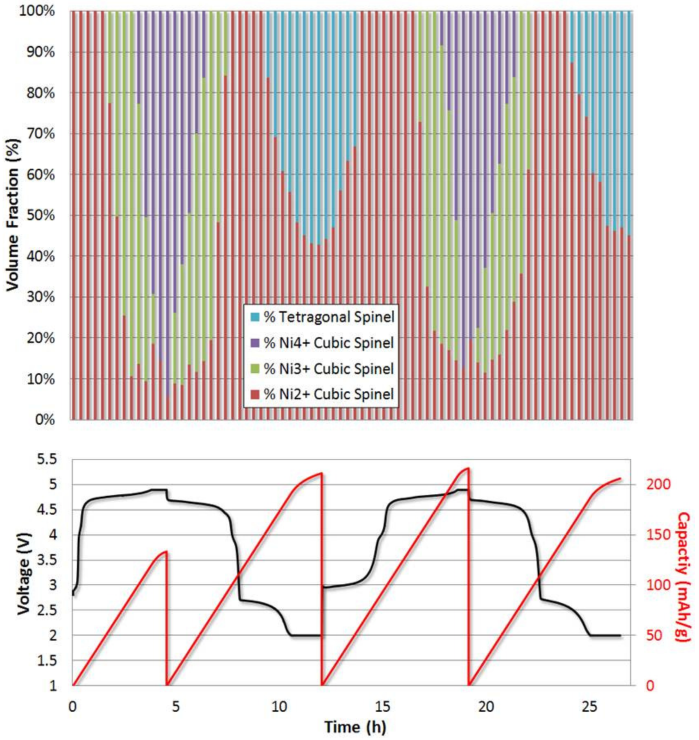


Figure 2

Publications

1. K. Rhodes et al., J. Electrochem. Soc., 157(12) A1354-A1360 (2010)
2. K. Rhodes et al., J. Electrochem. Soc., (In Review)
3. K. Rhodes et al., Rev. Sci. Instruments., (In Review)

Presentations

1. C. Daniel, K. Rhodes, S. Kalnaus, Mechano-Electrochemical Behavior of Energy Storage Materials, Materials Science and Engineering Seminar, University of North Texas, TX, April 17, 2011
2. C. Daniel, K. Rhodes, Mechanical Degradation of Insertion Electrodes, UMERC and College of Engineering Seminar, University of Maryland, College Park, MD, March 28, 2011
3. C. Daniel, K. Rhodes, Diagnostics for energy storage materials, ABR Diagnostics Workshop, Department of Energy, Argonne National Laboratory, Chicago, IL, March 1, 2011
4. J. Rhodes, M. Kirkham, R. Meisner, C. Daniel, In situ Acoustic Emission and XRD Characterization for the Development of Cathode Materials K, 219th ECS Meeting, Montreal, Canada, May 1-6, 2011

TASK 2
Calendar & Cycle Life Studies

Project Number: 2.2A (ES111)

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

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

Collaborators (include industry):
Ira Bloom, Argonne National Laboratory
Dan Santini, Argonne National Laboratory

Project Start/End Dates: August 2010/ September 2014

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

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

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

Financial data: $300K/year

PROGRESS TOWARD MILESTONES

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

(b) Documentation of assumptions and methodology: Completed draft report that explains, in detail, the assumptions and calculations that compose the battery design and cost model. Instructions and illustrated examples are provided to ease the learning curve involved with using the model.

An example of model capabilities is found in Fig 1 below. The 17 kWh PHEV batteries in the figure are designed for 50 kW of power achieved at 80 % of the open-circuit voltage at 25% state-of-charge. The potential savings are displayed from engineering advances that allow moving from a 3P-96S configuration (288 total cells) and 100 micron maximum electrode thickness to a 1P-96S configuraiton (96 total cells) and 200 micron maximum electrode thickness. The cost of a PHEV battery could be decreased by 30% from these two engineering advances alone.

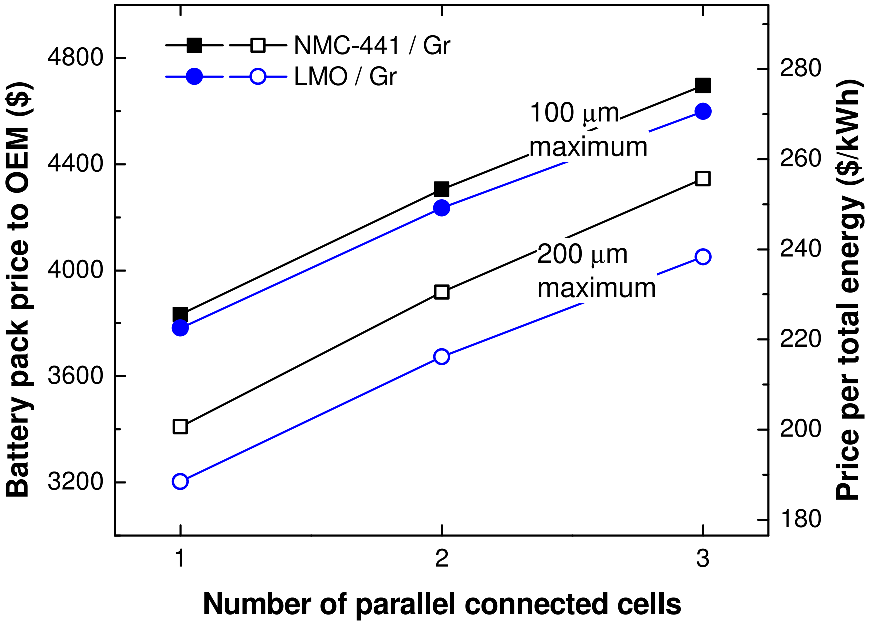


Figure 1. Battery pack price for a NMC-441 / Gr and LMO-Gr cell chemistries under different constraints: 100 or 200 micron maximum electrode thickness and 1, 2, or 3 cells connected in parallel. 1 cell in parallel means that all cells are connected in series.

(c) EPA peer-review: Answered multiple questions regarding aspects of the model that reviewers requested for clarification. Finished spreadsheet-based model and draft report to enable on-time submission of files to the EPA for peer-review. Initiated active thermal management component of design and cost model in anticipation of critques from peer-review. Approach taken is to include aluminum heat conductors between cells to increase thermal transport to module walls. The heat is then removed from the module walls through a flowing ethylene glycol – water solution.

(d) Public distribution: In the process of filing for a copyright of the stand-alone hard-coded version. Sought out and received additional review of design and cost model from unnamed domestic automaker(s). Working with other government agencies (ARPA-E) to help with implementation of model.

(e) Design & cost of advanced Li-ion: Collected relevant experimental data for the lithium and manganese rich layered transition metal oxides (LMR-NMC) and the nickel manganese "5V spinel" material (LNMO) from research actively being pursued in the ABR program. A cost calculation for the nickel, manganese, and cobalt materials synthesized by a co-precipitation process was developed to enable the calculation of active material cost for any NMC material including those in the LMR-NMC and LNMO families. The relative contributions for each raw material input, C_i, are accounted for as shown in the following equation.

$$C\left(\frac{\$}{kg}\right) = C_0 + \frac{1}{MW}\sum_i \left[x_i C_i MW_i\right]$$

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

Kevin Gallagher, Dennis Dees, and Paul Nelson "PHEV Battery Cost Assessment," To be presented at the 2011 DOE Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, May 9th-13th, 2011, Washington DC.

P.A. Nelson, K.G. Gallagher, I. Bloom, "Modeling the Performance and Cost of Lithium-Ion Batteries for Electric-Drive Vehicles," Electrochemical Energy Storage Theme, Chemical Science and Engineering Division, Argonne National Laboratory, ANL-11/XX DRAFT submitted to US Environmental Protection Agency for peer-review.

TASK 3
Abuse Tolerance Studies

Project Number: 3.1 (ES035)

Project Title: Develop & evaluate materials &additives that enhance thermal & overcharge abuse
Project PI, Institution: Khalil Amine, Argonne National Laboratory

Collaborators (include industry): Lu Zhang, Zonghai Chen, John (Zhengcheng) Zhang, Wenquan Lu, Sandia National Laboratory, EnerDel, Hitachi Chemicals, ECPRO

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

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

Approach: Three-phase strategy is adopted for the thermal property improvement, including a) securing additives and stabilized electrodes and investigating their effect on the thermal mitigation of the cell, b) developing in-house additives and shuttles that can mitigate the thermal run away and prevent *overcharge* abuse and 3) validate the effect of chemistry improvement in a full 18650 cells in collaboration with SNL synthesis

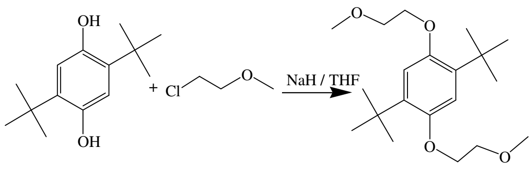
Milestones
(a) New design and synthesis of novel redox shuttle towards improved compatibility to lithium-ion cell system, Sep. 2011, (on schedule);
(b) Purification and chemical characterization of the synthesized redox shuttles, Sep. 2011, (on schedule);
(c) Evaluation and understanding of redox shuttle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

Financial data: $300K/FY2011

PROGRESS TOWARD MILESTONES

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

ANL-2 redox shuttle has been successfully synthesized with improved solubility (compatibility) in conventional EC based electrolyte with excellent overcharge performance.



ANL-2, yield 70 %

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

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

The ANL-2 redox shuttle has been fully characterized by using ^{1}H NMR and ^{13}C NMR.

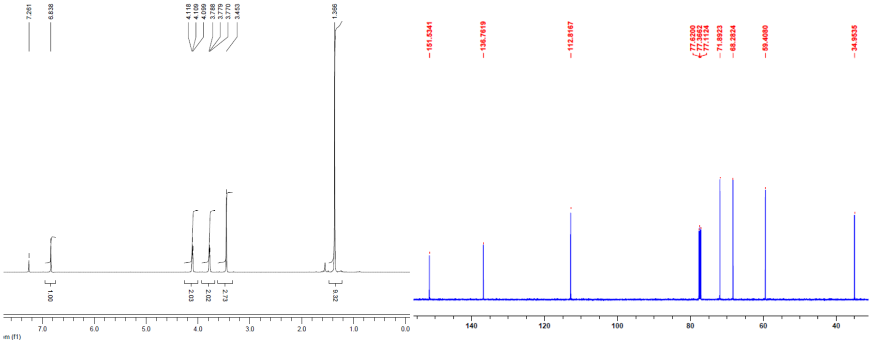


Fig 2. ^{1}H NMR and ^{13}C NMR spectra of ANL-2 redox shuttle

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

Cyclic voltammetry and coin cells evaluation have been conducted on cell using ANL-2 redox shuttle as additive. ANL-2 showed significant improvement in the overcharge protection when compared to ANL-1 redox shuttle. ANL-2 was tested in lithium-ion cells using $LiFePO_4$ as cathodes coupled with various anodes for overcharge protection evaluation. (Fig 3) The cell with the shuttle was able to survive thousands of hours overcharge abuse with no sign of decomposition of the shuttle (Fig. 4)

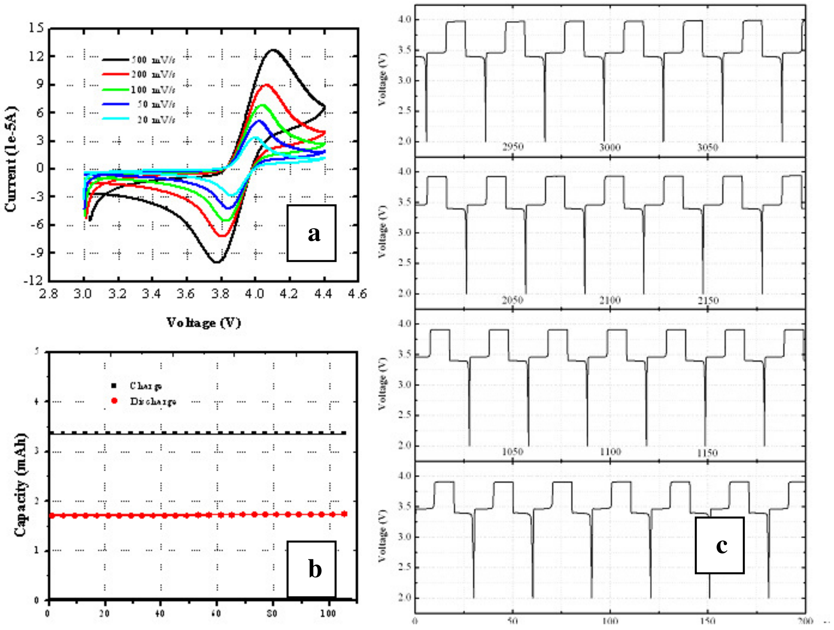


Fig 3. (a) Cyclic voltammograms of ANL-2 (10 mM) in 1.2 M $LiPF_6$ in EC/EMC (3:7 by weight) 100mV/s. (c) Voltage and (b) capacity retention profiles of $Li/LiFePO_4$ cell containing 0.1 M ANL-2 in 1.2M $LiPF_6$ in EC/EMC (3:7 by weight) during the course of 0-3000 h. Charging rate is C/10 and overcharge rate is 100%.

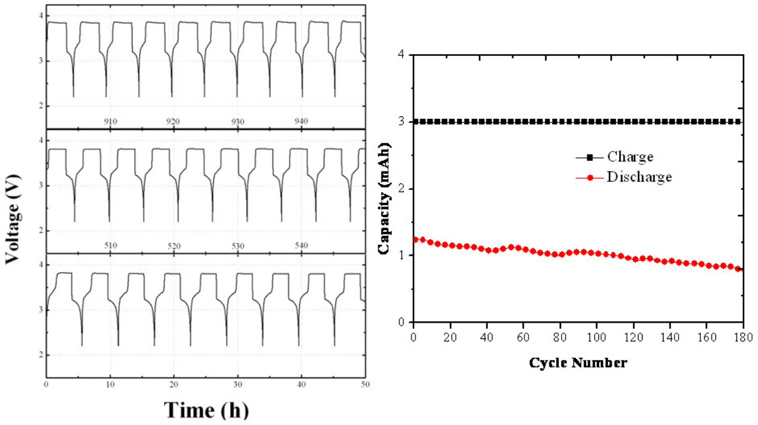


Fig 4. Voltage and capacity retention profiles of MCMB/$LiFePO_4$ cell containing 0.4 M ANL-2 in 1.2M $LiPF_6$ in EC/EMC (3:7 by weight) during the course of 0-1000 h. Charging rate is C/2 and overcharge rate is 100%.

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

IN-09-082, POLYETHER-FUNCTIONALIZED REDOX SHUTTLE ADITIVES FOR LITHIUM ION BATTERIES Zhengcheng Zhang, Lu Zhang, Khalil Amine.

TASK 3
Abuse Tolerance Studies

Project Number: 3.2 (ES036)

Project Title: Abuse Tolerance Improvements

Project PI, Institution: Chris Orendorff, Sandia National Laboratories

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

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

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

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

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

Financial data: Total budged \$1.35M; received \$592K (from SNL); \$40K subcontract to Dan Doughty (Battery Safety Consulting); \$30K subcontract to Binrad Industries (pending)

PROGRESS TOWARD MILESTONES

(a) **The effect of cell age on thermal response:** Initial targets for this work include determining the baseline thermal response of the Sanyo SA 1.25 Ah cells and age them to < 30% power fade (within the end-of-life criteria in the EV testing manual). SNL performed ARC measurements on 7 of 10 fresh cells to determine baseline response for thermal variations (onset temperature, peak heating rate, total enthalpy, etc.). Results from these experiments show very little cell-to-cell variation in terms of their thermal parameters and in the total gas generation during runaway. At INL, cells were calendar aged to ~20% power fade (60 °C storage for 2 months) and will be shipped to SNL for

ARC testing in Q3. Future work for this FY will also study the cell-to-cell variation in cycle-life aged cells and collaboration with Univ. Hawaii to determine how the thermal variations from cell-to-cell affect thermal models for entire battery systems.

(b) LiF/ABA electrolyte development: SNL has previously shown the dramatic improvement in runaway response of NMC (40% Ni) cells with the LiF/ABA electrolyte. DSC results confirm the full-cell response, showing a ~50% reduction in total heat flow for the NMC (40:30:30) cathodes in LiF/ABA electrolyte compared to the same cathode in $LiPF_6$ EC:EMC. A similar trend is also observed for other NMC chemistries (1:1:1), however, the effect is not as significant. Work will continue to develop an understanding for this mechanism of cathode passivation. Will also work with BNL to evaluate their ABA electrolytes in full cells. Moreover, a contract will be place in Q3 for Binrad/Richmond Chemical to synthesize new ABA molecules.

(c) Cell prototyping: Worked to optimize our 18650 electrode coating and cell building to support abuse testing and materials evaluation efforts. SNL has demonstrated to ability to reproducibly build 18650s with 3M NMC cathodes and Conoco Phillips G8 anodes that are 1.2 Ah in capacity (power cell design; thinner electrode, easier to reproduce). These cells will be used to support electrolyte development at SNL, ANL and INL and coated cathode work at ANL. We have also applied a similar design to $LiCoO_2$ cells to produce 1.5 Ah cells. Will continue this effort with building $LiFePO_4$ cells to support the overcharge shuttle development and testing with ANL.

(d) Overcharge shuttle evaluation in full cells: Coordinated the overcharge testing work with ANL and have outlined a test plan for the shuttle in full cells which will include two cell populations: (1) cells built at SNL with LFP provided by ANL and (2) cells built at A123. Both populations will contain control and shuttle samples. Experiments to evaluate the shuttle in cells will include constant current overcharge, C/D overvoltage cycling, isothermal calorimetry, and ARC. Work will begin in Q3 of FY11.

Publications, presentations, reports, IP, etc.

C. J. Orendorff, “Critical Safety Concerns in Lithium-ion Batteries” AABC Pasadena, CA, 1/25/2011
C. J. Orendorff, “Mitigating Catastrophic Failure in Lithium-ion Batteries” Lithium Battery Safety/Technical Group Meeting, Key West, FL, 2/16/2011

TASK 3
Abuse Tolerance Studies

Project Number: 1.2.1 (ES037)

Project Title: Overcharge Protection for PHEV Batteries

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

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

Project Start Date: March 2009

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

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

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

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

PROGRESS TOWARD MILESTONES

During this reporting period we continued to evaluate alternative electroactive polymers that may provide improved protection for 4V and higher Li-ion batteries. Polymer composite separators were prepared by impregnating a poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-phenylene)] (PFOP) solution into a Celgard membrane. Using cyclic voltammetry, PFOP was found to have an onset oxidation potential of 4.25 V, one of the highest among electroactive polymers reported so far. Fig. 1 compares the room-temperature rate performance of $Li_{1.05}Mn_{1.95}O_4$-Li cells with and without the protection of a PFOP-impregnated separator. These “Swagelok-type” cells were charged and discharged at current densities of 0.13 (0.25C), 0.26 (0.5C), 0.51 (1C), and 1.0 mA/cm2 (2C). For the protected cell, a steady-state potential was reached and maintained at each cycling rate, indicating that an electronic short was established and maintained by the conducting polymer. The potential at which the cell is shorted increases with the charging rate as the resistance across the polymer-impregnated separator varies with current density. Excellent capacity retention was observed even at the highest rate. Comparison with the unprotected cell clearly indicates that self-discharge due to the presence of the electroactive composite separator is negligible.

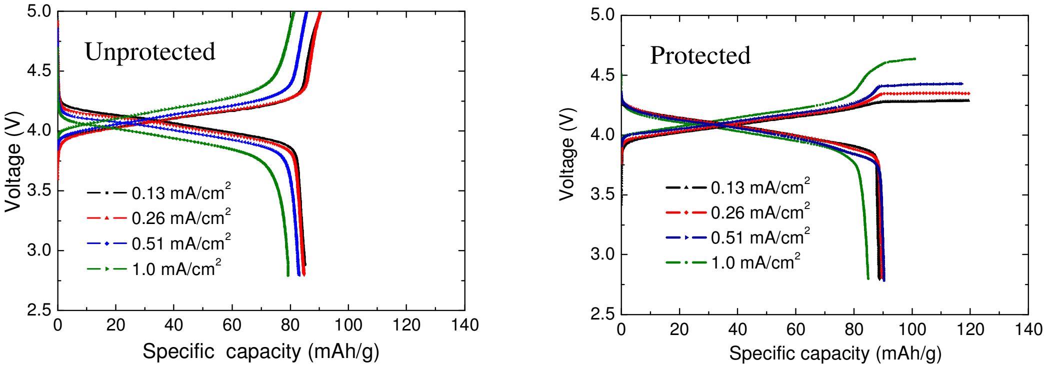


Figure 1. Variable rate charge-discharge curves for unprotected and protected $Li/Li_{1.05}Mn_{1.95}O_4$ “Swagelok-type” cells.

In an effort to scale up our approach, the performance of the electroactive polymer composite was also studied in pouch cells that had an electrode area of 3cm x 4cm, ten times larger than that in the “Swagelok-type” cells. Both “sandwich-type” and parallel cell configurations were used, wherein a composite separator was placed either between the electrodes or adjacent to the electrode assembly. At a C/7 rate and 20% overcharging, the “sandwich-type” pouch cell was reversibly protected at 4.6 V (Fig. 2a). Overcharge protection was achieved in both types of cells, although the steady-state voltage was significantly reduced in the latter case where the internal resistance was lower due to the absence of electroactive polymer between the electrodes (Fig. 2b).

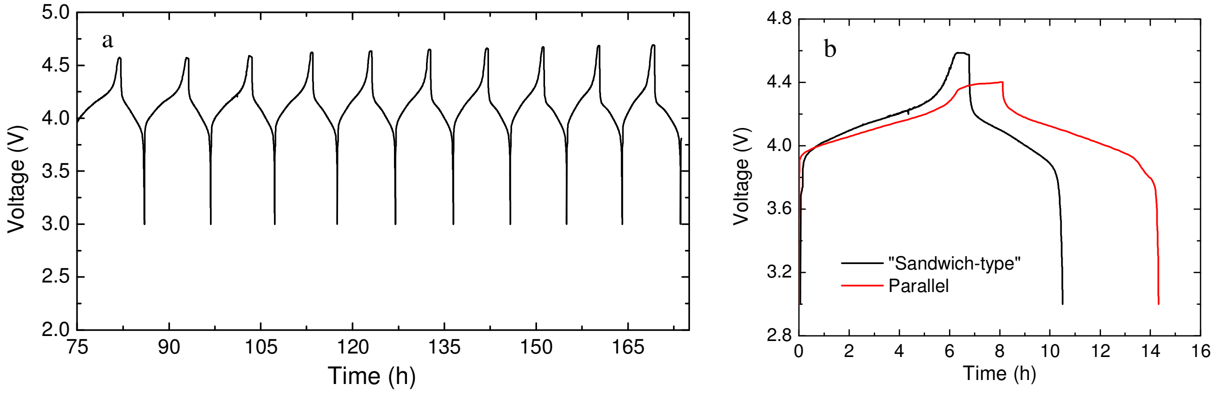


Figure 2. Polymer-protected Li/$Li_{1.05}Mn_{1.95}O_4$ pouch cells: a) charge-discharge cycling in a “sandwich-type” pouch cell and b) voltage profile comparison between the two types of pouch cells.