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Current Status of D.O.E.-funded R&D on Energy Storage for Automotive Applications

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Abstract

This paper presents an overview, including highlights and accomplishments, of the energy storage R&D effort at the Vehicle Technologies Program Office of the United States Department of Energy (DOE) recently (2007–2008). DOE has supported the development of advanced automotive energy storage technologies, including batteries and ultracapacitors, over the long term. The support has involved leveraging resources and expertise from automobile manufacturers, battery developers, small businesses, national laboratories, and universities to address the technical barriers which prevent the market introduction of vehicles using advanced energy storage technologies. The energy storage research activities include the developer program, applied battery research, and focused fundamental research. The developer program is conducted in collaboration with battery developers and original equipment manufacturers (OEMs) and includes benchmark testing, technology assessments, and system development. The earlier Applied Technology Development (ATD) activity, which was focused on addressing cross-cutting barriers for high-power lithium-ion systems (which include insufficient life, inadequate low temperature performance, inability to tolerate abuse, and a high cell-level cost) has recently been completed. It has been replaced by the Applied Battery Research (ABR) activity targeting PHEV batteries. Focused Fundamental Research addresses critical problems of chemical instabilities for advanced batteries and attempts to better understand why systems fail, develops models to predict system failure and to enable optimization, and researches promising new materials. The paper also describes DOE's energy storage R&D coordination efforts with other agencies.

Keywords: Battery, On-board Energy Storage System, Li-Ion Battery, Electrolyte, Electrodes.

1 Introduction

Energy storage technologies, especially batteries, represent a critical enabling technology for the successful commercialization of a wide range of advanced, fuel-efficient, light- and heavy-duty vehicles including hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and battery electric vehicles (EVs). In 2008, U.S. consumers experienced historically high and (relatively) low gasoline prices which, for a period, rose in real terms to levels not seen since the early 1980s. Partially as a result of the high gasoline prices (approaching \$4/gallon for part of the year), sales of HEVs remained strong in 2008 – roughly at the same level as in 2007, and several automakers announced plans to introduce PHEVs as well as EVs. Total HEV sales remained about 2-3 percent of all vehicle sales. An important step for further market penetration of HEVs, as well as for the electrification of the nation's personal transportation, is the development of cost-effective, long lasting, and abuse-tolerant lithium-ion (Li-ion) batteries.

The United States Department of Energy's (DOE's) continuing research and development (R&D) into advanced batteries for transportation offers the possibility of reducing U.S. dependence on foreign oil and the potential negative impacts associated with increasing oil prices. The Vehicle Technologies (VT) Program at DOE supports R&D on advanced batteries and ultracapacitors. In fiscal year (FY) 2007, this work expanded to include a major new effort on high-energy batteries for PHEVs and underwent a relative deemphasizing of efforts on HEVs. DOE plans to help develop affordable and advanced batteries for a full range of automotive applications. The 2010 goal of the VT Program is to develop electric drive-train energy storage with a discharge power of 25 kW for 10 seconds, which can provide 300 Wh of available energy, has a 15-year life, and whose cost does not exceed \$20/kW [1]. This goal would ensure that the resulting HEVs can favorably compete with conventional vehicles on a cost and performance basis. DOE maintains a close partnership with the automotive industry through the United States Advanced Battery Consortium (USABC) to support the development of such technologies. It leverages all available resources, including those of automobile manufacturers, battery developers, small businesses, national

laboratories, and universities to address the technical barriers preventing the introduction of battery systems to the marketplace. In 1997, recognizing that most candidate battery systems suffered from similar problems of abuse tolerance, calendar life and cost; it initiated the applied research activity based at the national laboratories. This program, entitled the Advanced Technology Development (ATD), has now been completed. In FY 2009, the VT program began a new activity entitled Applied Battery Research (ABR) which is focused on PHEV battery technology. In 2000, an exploratory research activity entitled Batteries for Advanced Transportation Technologies (BATT) was set up to focus on the fundamental impediments to the development of advanced automotive batteries.

Table 1 shows the FY 2003-2008 VT budgets for energy storage R&D. For FY 2009, the budget is approximately \$69.4 million. Industrial partners funded by the USABC must share at least 50 percent of the cost of each development effort. This research effort has been highlighted in several prior EVS overview papers [e.g., 2-4].

Table 1: Recent energy storage R&D budgets

Fiscal Year	Budget (\$, Million)
2003	\$21.2
2004	\$22.3
2005	\$22.5
2006	\$24.5
2007	\$40.9
2008	\$48.3
2009	\$69.4

2 Technical barriers, targets, and current status

To accomplish the VT energy storage goals, it is necessary to set energy storage performance targets and address the technical barriers which prevent reaching those targets. Over time, it is also necessary to take stock of the status of the technologies to track their progress in overcoming the barriers.

2.1 Technical barriers and targets

It has been recognized for some time that the technical barriers to successful commercialization of advanced energy storage technologies for transportation applications are associated with cost, performance, life, and abuse tolerance. Of

these, cost is the overriding factor. The other factors also indirectly impact the battery cost. The most mature chemistries appear able to meet the cycle life requirement, although predicting calendar life remains challenging due to its dependence on many internal battery parameters and external factors. Finally, it is critical for any new vehicle technology (including advanced energy storage systems) to operate safely under both routine and extreme conditions – which can include conditions of high temperature, overcharge, or short circuit.

Technical targets for individual battery applications have been developed in collaboration with the USABC based on input from the purchasers and end-users of these technologies. A partial listing of the current targets for power assist HEVs appears in Table 2. Additional performance targets (e.g., those for EVs, ultracapacitors, and PHEVs) appear at the USABC website [5] and are also reported in the VT Energy Storage R&D annual progress report

[6]. More recently, a significant focus of the energy storage R&D is the development of batteries for PHEV applications.

2.2 Current status

For power-assist HEV applications, as described in previous EVS overview papers, e.g., [2-3], the FreedomCAR goals for key parameters like available energy, pulse power, cycle life, system weight, and system volume have all been met or exceeded by existing technologies. The Li-ion battery technology for HEVs is ready for commercialization. Among the remaining parameters, the selling price needs to be reduced by approximately a factor of two or three to reach the goals. Goals also need to be met or demonstrated for the operating temperature and calendar life.

For PHEV batteries, the cost appears to be a major barrier. Also, the impact of deep and shallow cycles on the overall life remains to be understood.

Table 2: FreedomCAR energy storage performance targets for high voltage, power-assist HEVs (Partial data from the Vehicle Technologies Energy Storage R&D annual progress report [6])

Characteristics	Minimum value	Maximum value
Pulse discharge power (kW)	25 (for 18 seconds)	40 (for 18 seconds)
Maximum regenerating pulse (18 s; kW)	20 (50 Wh pulse)	35 (97 Wh pulse)
Total available energy (kWh)	0.3	0.5
Cycle life for specified SOC increments (cycles)	300k 25-Wh cycle (7.5 MWh)	300k 50-Wh cycle (15 MWh)
Calendar life (years)	15	15
Maximum weight (kg)	40	60
Maximum volume (liters)	32	45
Production price at 100,000 units/year	\$1,700	\$3,400

Figure 1 tracks the current progress toward commercial viability for various energy storage technologies for PHEV applications. The R&D technologies supported by DOE span several development phases, including the exploratory research (as seen in the case of the Li Metal/Li-ion polymer system) and battery cell and module development (for the graphite/Mn spinel system). It is noted that the advanced energy storage technologies previously developed for HEV applications (graphite/nickelate, graphite/iron phosphate, and graphite/manganese spinel) are in a more advanced development stage for PHEV applications, too. The battery cost reduction and commercialization phases remain to be achieved for every candidate technology.

DOE's battery R&D program has evolved to focus on high-energy PHEV systems

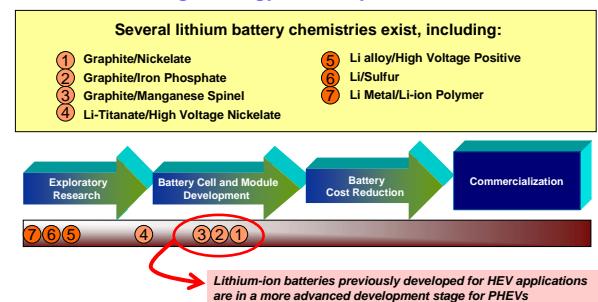


Figure 1: Status of PHEV energy storage R&D technologies

3 PHEV battery R&D

PHEVs, as distinct from current HEVs, which can only travel 1-2 mile in the battery alone mode, would run either on electricity or on gasoline and can be plugged into the electric grid at night to charge their batteries. They would cover a greater range (tens of miles) on battery power alone. Compared to HEVs, Li-ion batteries for PHEVs (and EVs) are further from commercialization. An improvement in energy density is needed to facilitate such commercialization. For PHEV batteries, the critical barriers include a high cost (currently, their cost is estimated to exceed \$1,000 per kWh versus the goal of \$500 per kWh, or less), inadequate abuse tolerance (similar to batteries for HEVs, yet potentially a more serious issue due to higher energy levels), and other issues such as too large a volume, too much weight, and insufficient life. The discharge power may also become a prominent issue, especially at low temperatures. The goal of the PHEV R&D is to reduce the cost to \$500/kWh in the short-term (by 2010) and to further reduce it to \$300/kWh in the long-term (by 2015). This cost reduction needs to take place without degradation in the battery performance. In collaboration with the USABC, VT has developed a set of PHEV battery requirements and test protocols which have been made available on the USABC website [11]. In developing those PHEV battery performance requirements, considerable modeling and simulation work was completed at ANL and NREL. State-of-the-art battery data were integrated with system models for a variety of vehicle platforms designed to operate in several “all-electric range” modes (covering 10 to 60 miles). DOE has also developed specifications for and procured state-of-the-art PHEV lithium-ion batteries that are now undergoing cycle life testing at ANL/Southern California Edison (SCE). Also, battery hardware-in-the-loop testing is taking place at ANL. DOE’s PHEV R&D activities include candidate cathodes (e.g., next-generation olivine, layered, and spinel structures) and new high capacity positive materials (having an energy density of more than 250 mAh/g).

The anode candidates include novel intermetallic alloys, nanophase metal oxides, and Li metal systems. Candidate electrolytes include high voltage electrolytes (4.5 – 5 Volts), composite electrolytes which suppress dendrite formation, and non-flammable electrolytes. In

April 2007, DOE issued, through the USABC, a \$28 million solicitation for PHEV battery development. The purpose of this solicitation was to fund battery developers to conceptualize, design, build, and test PHEV battery hardware (cells and modules) with the potential to meet the USABC PHEV energy storage performance requirements. This solicitation resulted in multiple development awards which are discussed later in this paper.

4 Energy storage R&D activities

The energy storage effort includes multiple activities – from hardware development with industry, to mid-term R&D and focused fundamental research. The activities begin by establishing technical requirements for the energy storage technologies by VT in cooperation with industry. Next, commercially available batteries are evaluated against those requirements. If requirements are unmet, additional R&D takes place, which involves either short-term directed research (applied research) by commercial developers and national laboratories, or exploratory research, generally by national laboratories and universities. The three energy storage R&D activities; the developer program, Applied Battery Research, and Focused Fundamental Research, are organized to complement each other.

4.1 The developer program

4.1.1 Background

The developer program’s goal is to support the development of a U.S. domestic advanced battery industry whose products can meet the USABC technical goals. DOE works closely with industry to develop energy storage technologies for specific applications.

4.1.2 Developer program activities

The developer program includes system development, technology assessments and benchmark testing, each of which is described below. DOE works with industry through cost-shared projects to develop electrochemical energy storage technologies which would meet FreedomCAR/USABC technical goals. The USABC provides technical and programmatic management of these projects, for which the cost is shared by the individual developer at a minimum level of 50 percent. The technologies include lithium-ion batteries, ultracapacitors, and

separators (as separators contribute significantly to the total system cost). The status and current highlights for the prominent development activities are listed in Table 3. More information on each project is available in the VT Energy Storage R&D annual progress report [6]. Additional R&D involves the thermal management issues for battery systems, which need to be addressed to avoid degradation in battery performance, reduced life, and greater likelihood of abusive conditions. Technology assessments are conducted on newly emerging technologies before developing full systems. The assessments typically represent 12-month projects to assess a developer's overall capabilities and are intended to validate the developer's technical claims. Benchmark testing of emerging technologies is important for remaining abreast of the latest industry developments. Battery technologies are evaluated according to the USABC Battery Test Procedures Manual (for EV batteries) [7], the Partnership for a New Generation of vehicles (PNGV) Battery Test Procedures Manual (for HEV batteries) [8], or the PHEV test procedure manual [11]. Additionally, the small business innovation research (SBIR) contracts have provided valuable support to EV and HEV battery development efforts over the years. Currently active Phase I and Phase II energy storage SBIR contracts represent a value of over \$8 million – utilized at the rate of \$2 – \$3 million per year. The SBIR projects are focused on the development of new battery materials and components. A list of the current SBIR contracts appears in the VT Energy Storage R&D annual progress report [6].

4.2 Applied Battery Research

Through FY 2008, the applied R&D program, entitled Applied Technology Development (ATD), was focused on assisting battery developers overcome the key barriers for the Li-ion battery technology in high-power HEV applications. Now Li-ion battery technologies have matured to a level where they could soon be introduced into the commercial HEV market. Therefore, ATD is now complete and the applied R&D program has now shifted focus to Li-ion battery technologies for PHEV applications. This new program, denoted the Applied Battery Research (ABR) Program, was initiated on October 1, 2008. Its goal is to assist the industrial developers of Li-ion batteries overcome the key barriers for this technology in

high-energy PHEV applications. Although this program is relatively new, there is general agreement on major barriers to using Li-ion batteries in PHEVs. Those include:

- Inadequate energy density and specific energy to meet the “charge-depleting” energy requirement, within the weight and volume constraints, for the 40-mile all-electric-range for a mid-size passenger PHEV
- Insufficient cycle life stability to achieve the 3,000 to 5,000 “charge-depleting” deep discharge cycles

Also, the new deep-discharge mode of operation and a need for much greater on-board energy could make it more challenging for Li-ion batteries to meet the necessary calendar life and abuse tolerance requirements. Meeting the cost target (\$300/kWh) is also a significant challenge for this technology. The new program organization is illustrated in Figure 2. Table 4 provides a list of recent highlights and accomplishments for the different focus areas of the Applied Battery Research activity. Additional details are available in the VT Energy Storage R&D annual progress report [6].

4.3 Focused Fundamental Research

The Focused Fundamental Research activity, also called the Batteries for Advanced Transportation Technologies (BATT) activity, addresses the fundamental issues of chemistries and materials associated with lithium batteries. It emphasizes the identification and mitigation of failure modes, coupled with materials synthesis and evaluation, advanced diagnostics, and improved electrochemical models. Battery chemistries are monitored continuously with periodic substitution of more-promising components based on advice from within this activity, from outside experts, and from assessments of world-wide current battery R&D. The work is carried out by a team headed by the Lawrence Berkeley National Laboratory (LBNL) and involves ANL, Brookhaven National Laboratory (BNL), the National Renewable Energy Laboratory (NREL), Oak Ridge National Laboratory (ORNL), and several universities. It has carried out investigations into three baseline systems:

Table 3: Developer program activities (summarized from the Energy Storage R&D 2008 annual progress report [6])

Application	Technology	Developer (Duration)	Highlights
Plug-in Hybrid Electric Vehicles	Li-ion (10 mile, 40 mile)	Johnson Controls Saft (24 months)	<ul style="list-style-type: none"> • Improve energy/power densities and specific power/energy at cell and pack levels, understanding typical failure modes during cycling, and achieving projected price targets.
	Li-ion Polymer (10 mile)	Compact Power/LG Chem (27 months)	<ul style="list-style-type: none"> • Blend of layered and LiMn_2O_4 spinel-based cathode. • Develop/optimize cell through calendar/cycle life testing/validation, available energy improvement and low temperature performance, abuse tolerance studies.
	Nano-Phase Iron Phosphate Battery (10 mile, 40 mile)	A123Systems (36 months)	<ul style="list-style-type: none"> • NanophosphateTM (LiFePO_4) cathode material. • Focus on cost reduction, cycle life, system weight and volume, and available energy; determine the impact of deep cycling and calendar life testing. • Cylindrical cell (PHEV-10), pouch cell (PHEV-40).
	Nano-Phase Lithium Titanate (LTO) Battery (10 mile)	EnerDel (18 months)	<ul style="list-style-type: none"> • Nano-phase LTO characterized by extremely small primary particles (10 to 20nm) agglomerated into 1 to 2 μm secondary particles. • Combination of chemistries to enable battery with the safety characteristics of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and the energy density for the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$.
Hybrid Electric Vehicles	Li-ion (40 kW)	Johnson Controls Saft (24 months)	<ul style="list-style-type: none"> • Development in Milwaukee yielded electrodes nearly identical to those produced at Saft in Bordeaux, France.
	Li-ion Polymer (25 kW) (Mn spinel-based cathode)	Compact Power/LG Chem (18 months)	<ul style="list-style-type: none"> • Li-ion polymer cell, LiMn_2O_4 spinel-based cathode. • Significant gains in calendar life estimates, currently being validated by testing at national laboratories.
	Nano-Phase Iron Phosphate Battery (25 kW)	A123Systems (36 months)	<ul style="list-style-type: none"> • Cathode material attractive due to intrinsic abuse tolerance (although the anode reactivity remains to be mitigated), high-power capabilities, and stable cycling.
	Li-ion (25 kW)	EnerDel (18 months)	<ul style="list-style-type: none"> • LTO/Mn spinel high-power cell materials. • Testing achieved 240,000 cycles and is approaching 300,000 cycles.
12V and 42V Start-Stop Systems	Ultracapacitor	NESSCAP (24 months)	<ul style="list-style-type: none"> • NESSCAP ultracapacitors extensively tested by the INL.

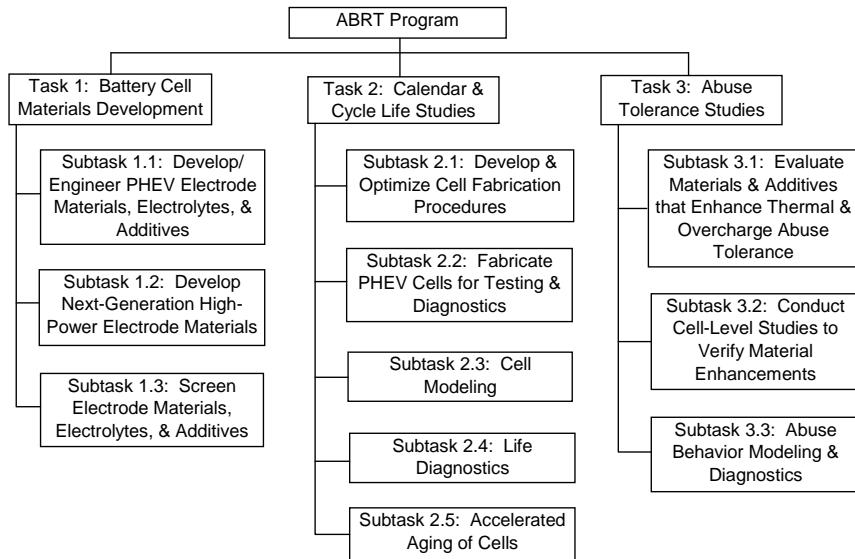


Figure 2: Organization of DOE's new ABRT Program

- The $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathode in a high-energy cell with a LiPF_6 -EC-DEC electrolyte and a carbon-coated graphite anode.
- A low cost and abuse tolerant LiFePO_4 system to develop significantly improved materials using liquid or gel electrolytes. This is regarded as a moderate-energy, low-voltage system that is inherently stable and low cost.
- A high-rate spinel system with a liquid-electrolyte, aiding work in Applied Battery Research to develop a low-cost high-power battery.

This work focuses on some of the most promising chemistries in the Li-ion battery field while also collaboratively addressing the barriers common to all of them. It was previously conducted through specific research tasks targeting cell components but was restructured about two years ago to accommodate the concept of theme-based research in addition to exploratory research. In the new structure, some members of the BATT activity are arranged around broad themes, while others continue the synthesis and characterization of new anodes, cathodes, and electrolytes for use in the next-generation Li-ion chemistries. The currently identified themes are:

- Improving the energy/life of PHEV batteries,

- Studying the impact of nanomaterials on battery behavior, with emphasis on phosphate cathodes and alloys and intermetallic anodes, and
- Understanding interfacial processes with emphasis on characterization of the solid electrolyte interphase (SEI) and on reactions in composite cathodes at potential greater than 4.3 V.

The above themes are intended to maximize BATT impact on addressing the pressing issues for PHEV commercialization, namely cost and cycle/calendar life. A 40-mile range PHEV would require an approximately 15 kWh battery and would have a high associated cost. It is possible to decrease this cost if one could increase cell energy, thus needing fewer cells. BATT pursues two approaches to achieve this: engineering existing materials to improve energy; and developing new materials with more energy per unit mass and volume. The engineering approach could yield results in the short-term and the longer-term materials research could lead to a larger impact in future. PHEV batteries may need to undergo 3,000-5,000 deep-discharge cycles over a 10-year period. BATT studies two fundamental issues limiting the life of batteries under deep discharge cycle: the formation of the SEI and its stability through the life of the battery; and the processes that occur in cathodes at a potential above 4.3 V. Table 5 lists

current R&D activities under each BATT area and the participating laboratory/university. Additional information is available in the Energy

Storage R&D annual progress report [6] and on the BATT website [9]. Table 6 lists a few recent highlights for some of those activities.

Table 4: Recent highlights from the Applied Battery Research activity (summarized from the Energy Storage R&D 2008 annual progress report [6])

Focus Area	Highlights
Understand life-limiting mechanisms and enhance life	<ul style="list-style-type: none"> Evaluation of electrolyte salts found that cell impedance varied with salt according to the trend: Lithium bis(oxolato)borate (LiBOB) > LiBF₄ > LiF₂OB > LiPF₆. Formation conditions were identified for good Gen3 battery performance: higher temperature, higher upper cutoff voltage, lower cycling rates, non-zero time at rest between cycles, and more instead of fewer total cycles. (Gen 3 is the current cell chemistry being studied and characterized.) Conclusions from cycling and aging data on cells with Gen3 electrodes included: (1) both positive and negative electrodes contribute to impedance rise when the cell contains the baseline electrolyte, (2) the LiF₂BC₂O₄ electrolyte-additive reduces capacity-fade and impedance-rise during 55°C aging, and (3) the negative electrode is the main contributor to cell impedance rise in cells containing the additive.
Understand and enhance low-temperature performance	<ul style="list-style-type: none"> It was observed that Li-ion power loss at low temperature is inherent to Li-ion kinetics and engineering approaches will most likely be necessary in the design of HEV battery systems to mitigate the effects of low temperature. Electrolyte modeling indicated that local ion and solvent concentration gradients may produce limiting conditions during cycling at low temperature that contribute to a lower rate of charge transfer at the cathode, while ion enrichment at the anode side can result in a local worsening of transport properties.
Understand and enhance inherent abuse tolerance	<ul style="list-style-type: none"> Research into the role of carbon on thermal runaway showed that a secondary SEI is formed after the breakdown of the initial SEI, then continuously broken down and reformed leading to heat generation. The accumulated heat at the anode at temperatures below 200°C may be enough to trigger a thermal runaway regardless of the cathode, especially in large batteries. Carbon with a small particle size and the highest surface area shows the largest heat when compared to carbon with larger particle size. New redox shuttle PFPTFBB showed stable overcharge from room temperature up to 55°C at least through 100 cycles. New Tonen separators showed significant improvement in shutdown properties.
Lower cell-level costs via lower cost materials, components, and technologies	<ul style="list-style-type: none"> A high-energy battery system based on a new high capacity fluorinated cathode material with 10% fluorine added delivered a reversible capacity about 70% higher than conventional Li cobalt oxide. Several advanced Materials from Asia were studied and overall, NCM type materials and their modifications demonstrate high-power capability but with appropriate Ni doping can achieve 200mAh/g.

Table 5: Overview of the current R&D tasks in the Focused Fundamental Research activity (summarized from the Energy Storage R&D 2008 annual progress report [6])

Task	Research Project (participant)
New Cathode Systems, Performance and Limitations	<p><i>LiFePO₄ and other Phosphate Systems: Performance and Limitations</i></p> <ul style="list-style-type: none"> • Simulations of LiMnPO₄ Material Properties (SUNY Stony Brook, MIT) • Phosphate Cathode Performance (LBNL) • Synthesize Nano-LiMnPO₄ and/or Li(Mn,Fe)PO₄ (LBNL) • Conductive Polymers (UT Austin) • Nano-Phosphate Processing (UT Austin) • Low Cost Synthesis of Lithium Iron Phosphate (SUNY Binghamton) • Substituted Metal Phosphates (SUNY Binghamton) • Iron Phosphate Performance and Water Contamination Effects (Hydro Quebec) <p><i>Layered Systems: Performance and Limitation</i></p> <ul style="list-style-type: none"> • Enhanced Stability with High V Cycl. of Li_xCoO₂ with “AlPO₄” coating (MIT) • Stability of Li_xNi_{0.5}Mn_{0.5}O₂ at High V (MIT) • Characterize Substituted Transition Metal Oxides (LBNL) • Layered Mixed Metal Oxides (SUNY Binghamton) • Structural Changes in Li_{1+x}M_{1-x}O₂ During Cycling (BNL) • Effect of Synthesis Conditions on the Performance of Li_xNi_{0.5}Mn_{0.5}O₂ (MIT) <p><i>Spinel and Composite Systems: Performance and Limitations</i></p> <ul style="list-style-type: none"> • Composite Layered/Spinel Cathodes, Surface Coatings (UT Austin) • High Voltage Composite Cathodes (ANL)
New Anode Materials	<ul style="list-style-type: none"> • Si/C Composite Anodes, Role of Amorphous Silicon (U Pittsburgh) • Sn and Si-based Alloys (LBNL) • MoO₃ Nanoparticles (NREL) • Intermetallic Anodes (ANL) • Alloy and LTO Anodes (SUNY Binghamton) • Cermats (LBNL) • Effects of 2D Geometry on Lithium Deposition (LBNL) • Lithium Anode Investigation (ORNL) • Li Metal Dendrite Research (Columbia U) • Sulfide and Sulfochloride Anode Materials (UT Austin)
Novel Electrolytes and Their Characterization	<ul style="list-style-type: none"> • Composite Polymer Electrolytes (LBNL) • Optimize Interfacial Impedance and Minimize Side Reactions (LBNL) • Single-ion Conducting (SIC) Polymer Electrolytes (LBNL) • Molecular Dynamics Simulations of Bulk Electrolytes (U Utah) • Ionic Liquid (IL) Electrolytes for High V Cathodes (Clemson U) • Electrolytes using Li₂O or Li₂O₂ and Tris(pentafluorophenyl) Borane as Boron-based Anion Receptor (BNL)
Li-Ion Modeling, Diagnostics, and Cell Analysis	<ul style="list-style-type: none"> • In situ NMR Diagnostics (SUNY Stony Brook, MIT) • Models of Si Anodes (LBNL) • Behavior of Interfaces, EC and VC Decomposition Products (U Utah) • Electrode Engineering Studies (LBNL) • Performance of Graphite Anodes and Additives (Hydro Quebec) • Modeling—Optimization (U Michigan) • Graphite Current Collectors (ORNL) • Transport-Property Measurement and Performance of Hybrid Capacitors (LBNL) • Quantifying Capacity Usage and Battery Size in HEVs and PHEVs (LBNL) • The Effect of Transport Restrictions in Separators, transport Limitations in Porous Cathodes, evaluation of the effect of fibers (BYU)

Table 6: Recent highlight samples from the Focused Fundamental Research activity (from [6])

Task	Highlight
New Cathode Systems, Performance and Limitations	<ul style="list-style-type: none"> Investigated surface energies, equilibrium particle morphology, and surface redox potentials for LiMnPO_4. Working with hydrothermally prepared crystals, it was found that un-substituted LiMnPO_4 crystals undergo severe decrepitation (seen in Figure 3) and a decrease in crystallographic domain size, although the only new phase was MnPO_4. Substitution of Al for Co was previously shown to enhance the rate capabilities of $\text{LiNi}_{0.4}\text{Co}_{0.2-y}\text{Al}_y\text{Mn}_{0.4}\text{O}_2$ substantially, even though Al decreases the electronic conductivity. High-energy composite cathode technology has been licensed to Toda, Inc. Work on high-power cathode materials has led to the formation of Actacell, a new high-power battery company headquartered in Austin, TX.
New Anode Materials	<ul style="list-style-type: none"> Intra-type Si/C nano-composites, with $\sim 700\text{ mAh/g}$, have been synthesized by high energy mechanical milling (HEMM) using graphite, Si and polyacrylonitrile (PAN) polymer following heat-treatment at $\sim 1073\text{ K}$-1173 K. μm-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) was produced having a conductivity six orders of magnitude higher than the nano-sized material. It shows $\sim 100\%$ capacity and 100% efficiency over extended cycling. The effects of two common additives, VC and vinylene triacetoxymethylsilane (VS), on dendrite initiation and propagation were investigated.
Novel Electrolytes and Their Characterization	<ul style="list-style-type: none"> Work on composite polymers has resulted in the formation of SEEO, Inc., a new high-energy battery company in Berkeley, CA. Both LiPF_6 and LiTFSI electrolyte solutions were prepared and subjected to water contamination tests.
Li-Ion Modeling, Diagnostics, and Cell Analysis	<ul style="list-style-type: none"> A new <i>in situ</i> NMR has been constructed to permit studies of operating batteries based on design of Letellier and co-workers. MD simulations of the interface between a LiFePO_4 cathode and two electrolytes of interest revealed a highly structured interface, a high potential barrier for Li^+ transport to the surface, and a large negative potential at the electrode surface.

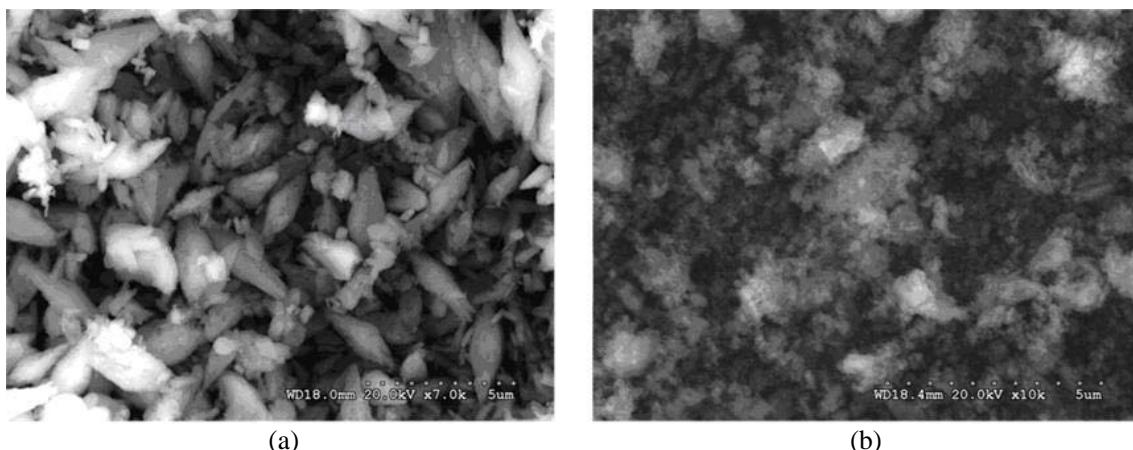


Figure 3: SEM images of LiMnPO_4 crystals (a) before and (b) after chemical delithiation

5 Energy storage collaborative activities

The DOE coordination efforts with other government agencies are extensive and comprehensive. Such efforts include membership and participation in the Chemical Working Group of the Interagency Advanced Power Group (IAPG), active participation in program reviews and technical meetings sponsored by other government agencies, and coordinating the participation of representatives from other government agencies in the contract and program reviews of DOE-sponsored efforts. Recent attendees have included representatives from such agencies as the U.S. Army-TACOM, U.S. Army-CERDEC, NRO, CIA, ONR, NSWC, NASA, and JPL. While no other Federal agency has the same set of performance and cost requirements for energy storage systems as VT, other agencies do have similar interests at the level of early R&D. DOE carefully coordinates R&D efforts to maximize effectiveness and avoid any duplication of effort. Recent examples of such cooperation include:

- The Navy and DOE jointly funding studies of capacitors and large batteries (built from small, commercially available cells) under abusive conditions.
- DOE contracts for developing conductive polymer electrolytes building up on work originally funded by the Army/Air Force.
- The Army, Navy, and Air Force awarding contracts to battery suppliers for development and production of batteries using technology developed with DOE support, including the Army TACOM/ManTech funding to Saft, Air Force and Navy funding to EEI, and Navy funding to several developers

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Internationally, the U.S. cooperates with other countries, including Japan (specifically, with the Lithium Battery Energy Storage Research Association). DOE is a member of the Executive Committee of the International Energy Agency (IEA) Implementing Agreement on Hybrid and Electric Vehicles and participates in various Annexes of the Implementing Agreement. It currently participates in Annex I: "Information Exchange", Annex VII: "Hybrid Vehicles", Annex X: "Electro Chemistry" and Annex XI: "Two-wheeled Electric Vehicles". It attends the Executive Committee meetings held in various countries and provides status updates on other implementing agreements. In addition to monitoring world-wide developmental activities, DOE also keeps abreast of legislative and regulatory mandates that could impact EVs, HEVs, and PHEVs in the U.S.

6 Conclusion

DOE Vehicle Technologies R&D activities in energy storage are focused on advanced batteries for transportation applications and they currently emphasize PHEVs. The past successful commercialization of DOE-funded batteries is a testimony to the success already achieved by the DOE-USABC cooperative program. Future advances in energy storage technologies will be leveraged with the significant progress in other enabling technologies (e.g., heat engines, lightweight materials, power electronics, and fuels) to reach the challenging VT goals. The Program office will continue to reassess longer-term technologies which promise performance, life, and cost benefits over prior technologies as candidates for future development and use in propulsion systems.

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