FreedomCAR and Fuel Partnership

2007

Highlights of Technical Accomplishments

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Preface

This report contains brief summaries of key technical accomplishments of the FreedomCAR and Fuel Partnership program for 2007. This program was initiated in 2002 as the FreedomCAR Partnership between the United States Department of Energy (DOE) and the United States Council for Automotive Research LLC (USCAR), the latter being a consortium comprised of Chrysler LLC, Ford Motor Company and General Motors Corporation. In his 2003 State of the Union address, President George W. Bush announced a national Hydrogen Initiative. In response to this, the FreedomCAR Partnership was expanded in September 2003 to include five energy companies (BP America, Chevron Corporation, ConocoPhillips, ExxonMobil Corporation and Shell Hydrogen LLC (US)) and became the FreedomCAR and Fuel Partnership.

The accomplishments described in this report support the overall FreedomCAR and Fuel Partnership goals and the progress being made. These goals are the “Freedoms” originally embraced by the FreedomCAR Partnership:

- Freedom from dependence on imported oil
- Freedom from pollutant emissions
- Freedom for Americans to choose the kind of vehicle they want to drive, and to drive where they want, when they want and
- Freedom to obtain fuel affordably and conveniently.

Previous annual reports are available on the FreedomCAR and Fuel Partnership page on the USCAR website at www.uscar.org.

The material for the 2007 Highlights of Technical Accomplishments Report was selected from the many hundreds of projects now active and put into the form of single page accounts, arranged by subject matter corresponding to the various technical teams formed by the partnership. The Technical Teams are listed below:

Vehicle Technical Teams (Members from USCAR and DOE)
- Advanced Combustion & Emissions Control
- Electrical and Electronics
- Electrochemical Energy Storage
- Fuel Cells
- Materials
- Vehicle Systems Analysis

Joint Technical Teams (Members from USCAR, the energy partners and DOE)
- Codes and Standards
- Onboard Hydrogen Storage

Energy Technical Teams (Members from the energy partners and DOE)

- Hydrogen Production
- Hydrogen Delivery
- Fuel Pathway Integration

An accomplishment from the DOE Hydrogen Learning Demonstration Program has also been included in this report because the data generated by this project are used by several of the technical teams to prioritize their research endeavors.

Each of the accomplishments summarized in this report was selected by the relevant technical team as representing a significant milestone reached, or breakthrough made, in 2007. It represents achievements in work that may well have begun in previous years but does not necessarily indicate that the final goals of a particular project have yet been met.

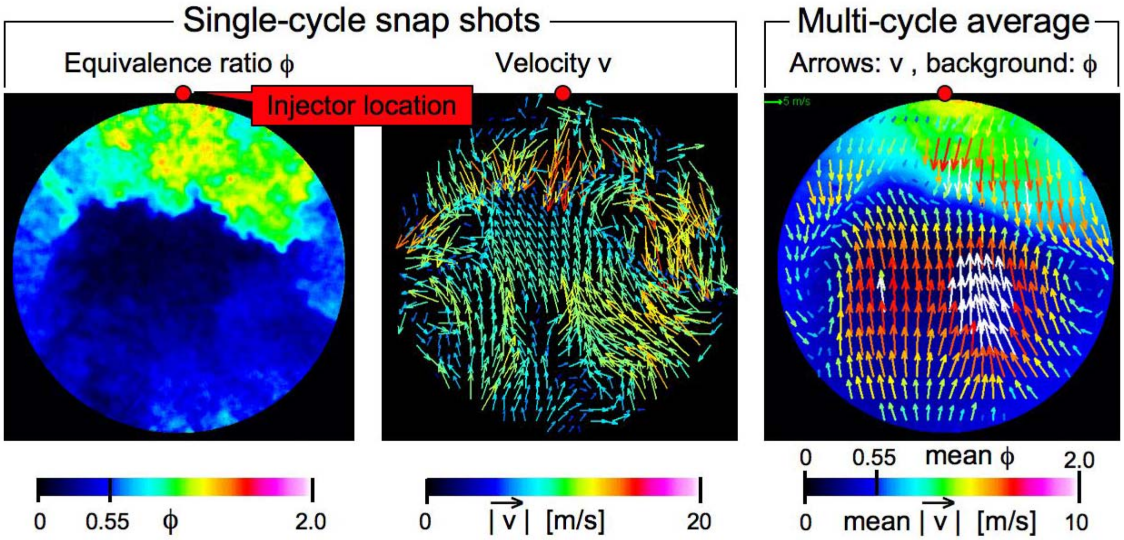
2007 FreedomCAR and Fuel Partnership Highlight

Injection Timing Strongly Impacts H_2 - Air Mixing in a Direct-Injection Hydrogen Engine

Sandia National Laboratories

The hydrogen-fueled internal combustion engine (H_2ICE) is a promising power plant that bridges to future propulsion technologies. These engines are expected to match the efficiency, NO_x-emissions, and power density of modern hydrocarbon-fueled engines. Direct injection (DI) of the hydrogen gas into the cylinder is a key element in achieving these performance goals. Detailed knowledge about the impact of DI on the charge preparation during the compression stroke, which controls ensuing combustion in the power stroke, is essential.

The influence of the injection event on the in-cylinder flow and hydrogen-air mixing was studied by applying laser-based measurements to our optically accessible DI-H_2ICE. The quantitative images of fuel concentration and charge motion (velocity) show that, as compared to conventional port injection, direct injection totally changes the flow field. In the case of injection late in the compression stroke (shown in the figure below), the observed substantial fuel stratification is caused by a relatively stable counter-flow situation created by interaction between the H_2 injection and the combustion chamber wall. Proper fuel stratification can be a good way to achieve power density while avoiding pre-ignition. For the current injector location/geometry, fuel is located close to the cylinder wall. Future work in collaboration with Ford and Argonne National Laboratory focuses on injector geometry/location and injection strategies to optimize air-fuel mixing. Additionally, the measurements will be used to validate advanced engine simulation tools under development at Sandia.



Fuel distribution and charge motion in a plane parallel to the piston top at 32° before top dead center after H_2 injection from 90° to 40°. Left: Fuel is located near the injector just after the end of injection. Center: Instantaneous gas-flow field showing turbulent flow structures. Right: Cycle-average flow field. Flow diagrams show that highly turbulent fuel from the top encounters unmixed air from the bottom.

2007 FreedomCAR and Fuel Partnership Highlight

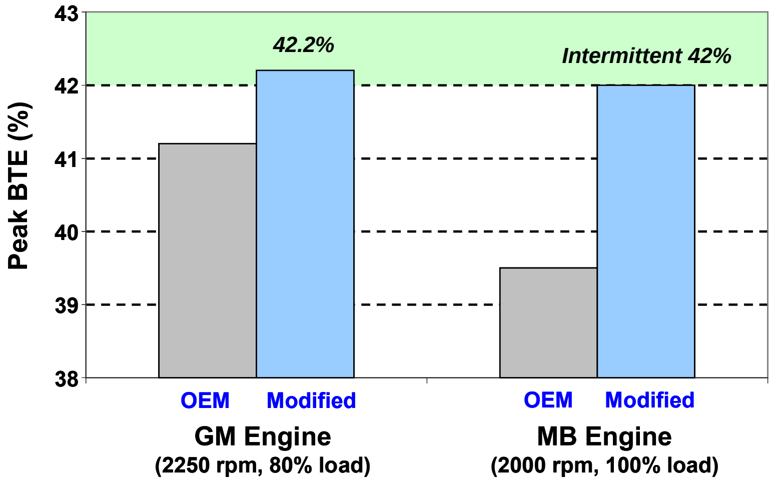
Demonstrated 2007 Engine Efficiency Milestone of 42% Peak Brake Thermal Efficiency

Oak Ridge National Laboratory

A peak brake thermal efficiency (BTE) of 42% was demonstrated on a modified General Motors (GM) 1.9-L diesel engine and a modified Mercedes-Benz (MB) 1.7-L diesel engine. Demonstration of this efficiency is an interim milestone to the 2010 FreedomCAR goals of 45% peak BTE with Tier 2 Bin 5 emissions in a light-duty engine.

The approach used to achieve 42% BTE was developed through improved thermodynamic analysis, full-engine simulation, and modifications to engine hardware and/or calibrations. Analysis routines developed as part of these activities use the thermodynamic concept of availability for identifying and explaining efficiency opportunities. Hardware modifications for the MB engine included a variable geometry turbocharger, electronic EGR valve, and EGR cooler. Calibration changes for both engines included better control of the turbocharger boost and fuel-injection phasing. A flexible microprocessor-based integrated control system enabled these system enhancements.

Future work to further improve BTE includes a combination of thermodynamic analysis, engine modeling, and experiments. Specific enablers under consideration include low temperature combustion, waste heat recovery, friction reducers, and improved thermal management of engine working fluids.



A peak BTE of 42% was achieved on two light-duty diesel engines.

Kinetic Mechanism for Diesel Lean NO_x Trap Regeneration

Sandia National Laboratories and Oak Ridge National Laboratory

Improved emissions controls are essential for utilizing high-efficiency, lean-burn engines that comply with US Tier 2 emission standards. Lean NO_x Traps (LNTs) are one of the most promising new technologies for controlling nitrogen oxide (NO_x) emissions from these engines. One major technical hurdle to commercial LNT implementation is the lack of accurate kinetic models for simulating the complex catalytic chemistry involved in adsorbing NO_x and reducing NO_x to nitrogen. Such models are critical for optimizing the fuel efficiency of the emissions controls and powertrain.

A key deficiency in previous LNT models is accurate prediction of product selectivity during LNT "regeneration" that is required periodically to keep LNT operating properly. Two byproducts of particular concern are nitrous oxide (N_2O) and ammonia (NH_3), which can create undesired emissions and decrease fuel efficiency. Based on extensive experimental measurements of an LNT catalyst by Oak Ridge National Laboratory, Sandia National Laboratories developed a detailed kinetic model that correctly captures the formation of these byproducts over a wide range of temperatures and fuel concentrations.

The figure below shows the measured and simulated gas concentrations for reduction of NO by H_2 with constant inlet gas flows at different operating temperatures. The good agreement between measured and predicted LNT product concentrations shows that the model accurately captures the regeneration kinetics. SNL and ORNL are currently combining the regeneration kinetics with an existing NO_x adsorption model to complete simulation of the entire LNT cycle. This cycle integrated model will be used to study sulfation and desulfation of LNTs and combination of LNTs with NH_3 selective catalytic reduction (SCR) catalysts. Such a hybrid catalyst system is expected to have a wider temperature operating window than typical LNTs and avoids the need for urea injection normally used in SCR systems.

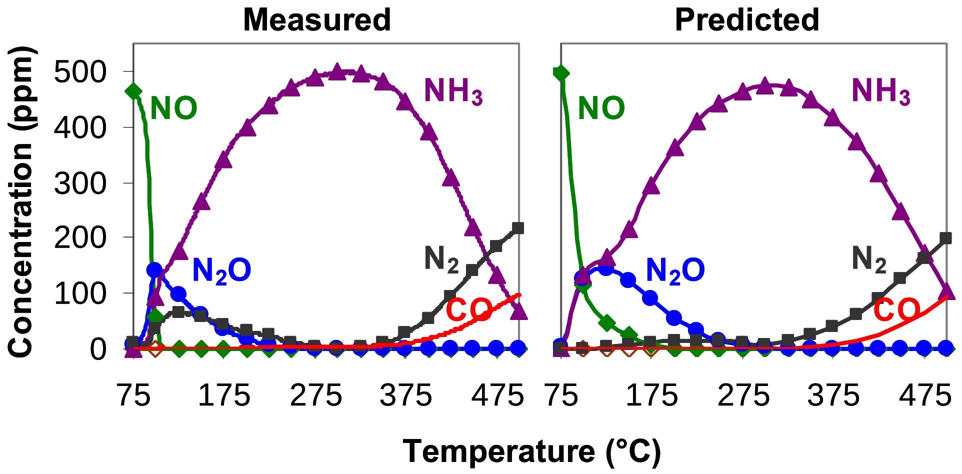


Illustration of the good correlation between experimental measurements and kinetic model predictions of the products formed in an LNT catalyst during reduction of nitric oxide (NO) by hydrogen over a wide range of temperatures.

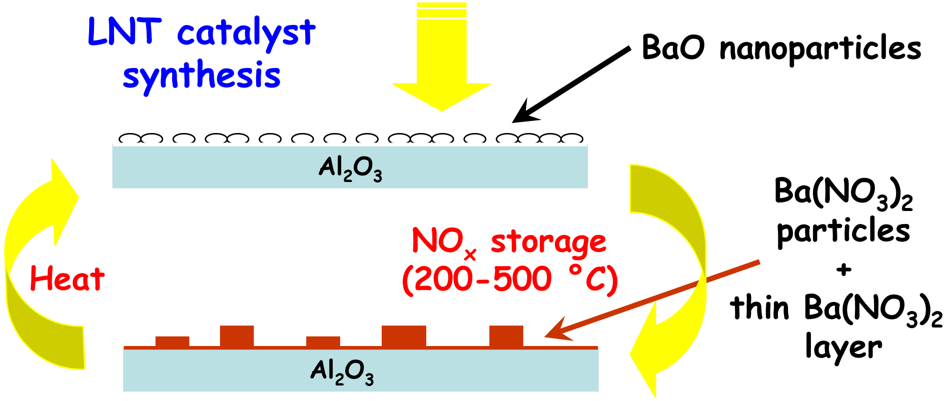
Studies of Lean NO_x Trap Aftertreatment Contribute to Diesel Vehicle Commercialization

Cummins, Johnson Matthey, Pacific Northwest National Laboratory and Oak Ridge National Laboratory

Successful market penetration of vehicles with diesel engines is challenged by NO_x emissions regulations. CRADAs between Cummins, Johnson Matthey and Pacific Northwest National Laboratory (PNNL), and between Cummins and Oak Ridge National Laboratory developed fundamental understandings of Lean NO_x Trap (LNT) technology. These understandings include determination of the chemical reaction mechanisms correlated with catalyst material characterization and understanding the causes of catalyst deactivation due to high temperatures and the presence of sulfur species in the exhaust.

The figure below shows the morphology cycle of the LNT catalyst surface during NO_2 uptake and release. During uptake, the catalyst structure changes from small barium oxide nanoparticles to larger barium nitrate particles. Regeneration of the LNT liberates the stored NO_x and restores the original Ba-based catalyst morphology. If sulfur is present on the catalyst (as sulfates), these species are not removed and the number of NO_x adsorbing sites is decreased. A quantitative model for these processes was developed and used to determine the appropriate operating conditions for the catalyst in a vehicle and to develop protocols and tools for failure analysis of used catalysts. Future work will refine these tools using additional field-tested materials.

These research contributions led to the successful commercialization of the LNT technology in the aftertreatment system of the 2007 Dodge Ram heavy-duty pickup truck powered by a Cummins 6.7L diesel engine. A press release from Cummins in January 2007 cited the DOE/EE/VT program-funded activities as being "key to interpreting many features of these uniquely complex catalytic systems".



Adapted from PNNL Published work, see:
J. Phys. Chem. B **109** (2005) 7339-7344.

The morphology cycle of BaO/Al_2O_3 in NO_x uptake/release

2007 FreedomCAR and Fuel Partnership Highlight

Floating Loop Inverter

Oak Ridge National Laboratory

Vehicle thermal management systems are typically designed to enable vehicles to operate at their highest power levels and lowest cost while minimizing cost and additional weight. Hybrid and fuel cell vehicles operate with multiple cooling systems that include cooling the motor, power electronics, batteries, internal combustion engine, transmission, and fuel cell system.

Oak Ridge National Laboratory (ORNL) engineers have developed and tested a floating loop integrated cooling system for advanced vehicle applications. This approach integrates the existing passenger air conditioning system, using R134a as the coolant, to provide cooling for the power electronics and electric motors. Tying into the existing air conditioning system and sharing components, the floating loop taps off the high side of the compressor to cool the high current, heat producing power electronics and traction motor. This system operates independently of the air conditioning compressor and requires minimal power to operate.

ORNL has incorporated this cooling concept in an inverter design that demonstrates significant weight and volume reductions from that of a traditional baseline inverter. It utilizes a unique geometry to provide double-sided direct die cooling in the R134a coolant, thereby keeping the silicon and capacitors cooler, enabling the use of less semiconductor material and capacitor film.

The ORNL Floating Loop Inverter shown in Figure 1 achieved a power density of 25kW/liter, significantly higher than the commercial baseline inverter's 9kW/liter. The high dielectric and direct contact cooling enables very tight packaging. Cost reduction is expected to be proportional to the reduction of weight and volume. The floating loop concept is a major step toward reducing the size and cost, and increasing the component reliability and life of the traction drive power electronics through operation at lower temperature while maintaining the net power output. Cooler electronics can be operated longer and have proven to be more durable and reliable as they are not subjected to thermal runaway conditions.

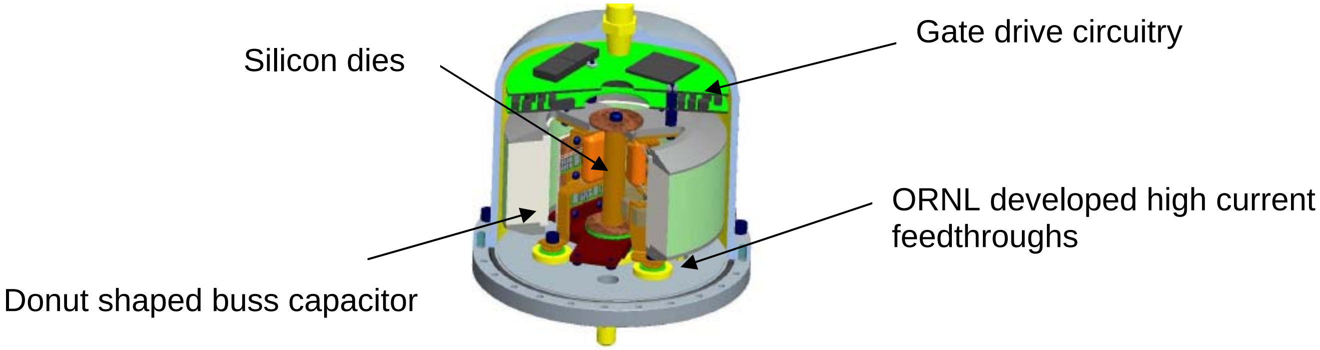


Figure 1: ORNL Floating Loop Inverter

2007 FreedomCAR and Fuel Partnership Highlight

Sintered Die Attachment

Semikron

Power electronics utilized in traction drives for hybrid, plug-in hybrid, and fuel cell vehicles are subjected to rigorous environmental stresses. Varying ambient temperature conditions, coupled with high current and power requirements all lead to extreme temperature excursions experienced by the silicon dies. Vibration and shock additionally add stresses. All of these will be exacerbated by the transition to higher coolant temperatures as efforts are made to reduce costs through the elimination of secondary cooling loops and use of the 105ºC engine cooling system.

Traditional power modules utilize solder contacts for die attachment to the Direct Bonded Copper (DBC) substrate connection. Power cycling capability is significantly reduced with these solder bonds due to the difference in the Coefficient of Thermal Expansion (CTE) between the materials. As the module is subjected to thermal cycling, the mismatch in the rate and degree of expansion between the solder and the die on one side and the DBC on the other side causes stress and solder fatigue. This results in an increase in thermal resistance and module failure.

Semikron has developed a process which involves sintering (see Figure 1) to make these connections. It is a low temperature technology which utilizes a connecting layer of silver, which has a melting point approximately three times that of solder. Due to the elevated melting point of silver, the typical fatigue effects associated with the solder bonds are mitigated.

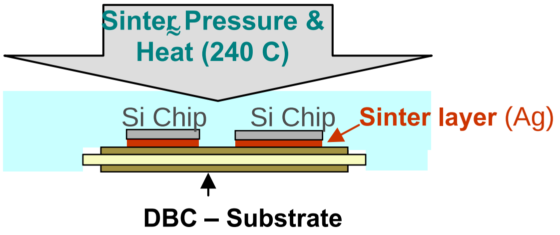


Figure 1: DBC, sintering layer and silicon chips

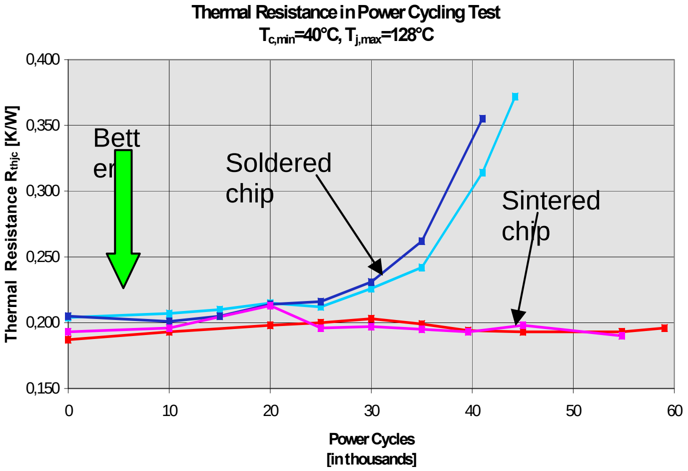


Figure 2: Effects of Power Cycling on Thermal Resistance

This process has been proven through tests conducted at Semikron (see Figure 2). Results over many thousands of power cycles prove the thermal resistance is maintained at a much lower level than traditional soldered chips. The lower thermal resistance leads to increased reliability and durability for the power electronics. This bonding technique is being implemented in Semikron’s automotive power module products.

2007 FreedomCAR and Fuel Partnership Highlight

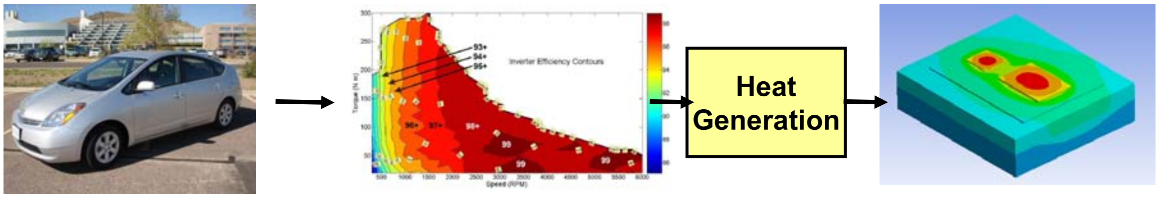
Thermal Systems Analysis for Advanced Vehicle Power Electronics

National Renewable Energy Laboratory

Power electronics are a critical yet expensive subsystem required for the operation of hybrid electric (HEV), plug-in hybrid electric (PHEV) and fuel cell (FCV) vehicles. Thermal management is key to achieving the FreedomCAR program targets for cost, weight, volume, and a 15-year life for power electronics. In 2007, the National Renewable Energy Laboratory (NREL) led efforts to predict the heat generated in existing power electronic modules and applied integrated systems modeling techniques to study how heat can be removed from advanced designs. The analysis shows the feasibility and tradeoffs for achieving program targets using high-temperature-tolerant semiconductor materials and novel heat-removal technologies being developed at NREL.

NREL researchers used parametric finite element analysis to examine three power inverter packaging concepts (using advanced interface materials, direct backside cooling, and an integrated heat sink). The analysis showed that using engine coolant at 105°C, which eliminates a costly dedicated cooling loop, will require advanced cooling technologies. NREL researchers are currently working with the FreedomCAR and Fuel Partnership to develop these technologies. The Institute of Electrical and Electronics Engineers recognized this effort with a "Best Paper" award at the 2007 Vehicle Power and Propulsion Conference for the paper "*A Comparison of Hybrid Electric Vehicle Power Electronics Cooling Options*".

These efforts leverage power electronics thermal management work at Oak Ridge National Laboratory (ORNL) and Argonne National Laboratory (ANL). For example, the figure below depicts a 2007 effort to study the heat generation of power electronic components in the Toyota Prius HEV. NREL used a validated computer model of the Prius created by ANL together with component test data from ORNL to estimate when and how much heat is generated during various driving conditions. NREL then applied this information in detailed thermal models of the power electronics to evaluate the various cooling technologies.



Vehicle Test Data & Models (ANL/NREL)

Power Electronics Test Data (ORNL)

Thermal Models (NREL)

Figure 1: An integrated thermal system model

2007 FreedomCAR and Fuel Partnership Highlight

High Temperature DC Bus Capacitors

Pennsylvania State University, Argonne National Laboratory
and Sandia National Laboratories

One of the major challenges in meeting the aggressive FreedomCAR electric traction drive goals is high temperature operation. The traction drive inverter DC bus capacitor is presently one of the limiting factors to meeting the higher operating temperature targets, as well as reducing overall system volume, weight and cost.

A team of researchers has integrated commercial flat panel display glass and glass-ceramic materials into high energy-density capacitors for the DC electric bus on hybrid electric vehicles. These new capacitors have excellent performance characteristics at and above temperatures of 200°C, almost double the temperature limit of current capacitors in traction drive inverters.

Capacitors presently occupy about 35% of the total traction drive inverter volume and initial laboratory samples show further potential to reduce that volume by 25% while meeting the same requirements for high temperature operation.

The team is collaborating with industry to transition flat panel display glass manufacturing concepts to large-scale power capacitor production.

Left Figure: Flexible glass - Penn State researchers are collaborating with flat panel display manufacturers Schott Glass U.S.A. and Corning to incorporate flexible glass sheets into high temperature capacitors. **Right Figure:** Glass ceramic synthesis at Penn State for volume efficient power capacitors.

2007 FreedomCAR and Fuel Partnership Highlight

First Generation Li-ion Cells Meet Life Cycling Goals and Pilot Production Line Completion

A123 Systems

A123, a U.S. based company headquartered in Watertown Mass, is the developer of a novel proprietary iron-based doped nanophosphate positive material that exhibits a combination of superior abuse tolerance, high power capability, and long life. The material was originally developed at MIT and is exclusively licensed to A123 Systems.

Argonne National Lab (ANL) recently completed testing the first generation of A123's commercial cells (26650-M1). The cells have been cycled past the USABC target of 300,000 cycles, with still plenty of margin in power and energy. The current generation of the cells, 32113 *Ultra,* were delivered to ANL in December 2007 to undergo similar testing for performance and life. The initial characterization tests indicate an excellent power capability of >500W for the cells. Cells were also delivered to the National Renewable Energy Laboratory for thermal characterization and more cells are scheduled for shipment to Sandia National Laboratories for abuse testing and risk assessment.

Anticipating similar test results with the 3.6 Ah- 32113 cell, A123 completed building a pilot production line in 2007 for this automotive specific application with an initial production capability of 120,000 cells annually. The plant production capacity will be increased to accommodate customer demand in the coming months. Figures 1 & 2 show images of the 90-feet long drying machine used to treat the electrodes and the coated rolls of electrode in the A123 plant.

Figure1-2: Automotive cell fabrication dryer & coated rolls in A123's plant.

Calendar Life/Cell Performance Improvements

Compact Power/LG Chem

Life *(cycle and calendar)* and cost are major challenges for most Li-ion based hybrid electric vehicle batteries. Compact Power/LG Chem *(CPI/LGC)* delivered a cell design that utilizes a reduced cost and volatility cathode material, while implementing an alternative binder electrode formulation that has resulted in continued and sustained long-term improvement in cell calendar life.

The CPI/LGC cell *(Li-ion with a manganese oxide spinel-based cathode)* has excellent cycle life capability, shows favorable abuse tolerance at the cell level, and offers improved cost stability when compared to some other alternative Li-ion chemistries. By implementing an alternative electrode binder polymer, associated coating process, and coating solvent base, significant calendar life improvement has been demonstrated.

The beneficial effect of the new electrode formulation on prolonging calendar life continues to be proven in long-term storage tests. Based on the results from cells aged more than 1.5 years, significant and sustained improvement in available power retention has been demonstrated over a significant range of elevated storage temperatures.

Future improvements will be made to increase low temperature power, while maintaining or advancing life capability.

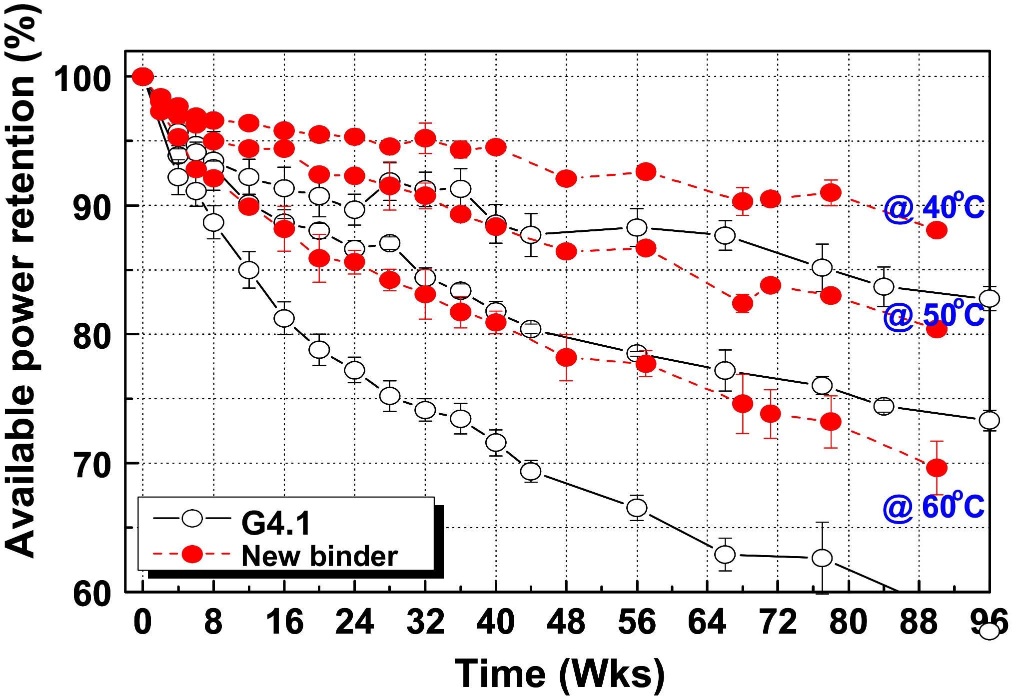


Figure: Calendar Life Improvement - The new electrode formulation results in significant improvement @ 40 ºC in terms of available power retention.

Performance Improvements of Li-ion Cells with new $Li_4Ti_5O_{12}$ Anodes

EnerDel

The United States Advanced Battery Consortium (USABC) selected EnerDel to advance Lithium Titanate (LTO)/ Mn-Spinel based technology toward the performance goals necessary for the automotive market.

During Phase 1 of the program, EnerDel achieved significant gains with their Gen 1 cells towards the FreedomCAR goals by demonstrating improved power and energy levels. EnerDel then transferred the lessons learned from the Gen1 cells, which utilized commercially available $Li_4Ti_5O_{12}$ (LTO) anode material, to cells termed Gen 2.0 and Gen 2.1. The Gen 2.0 and Gen 2.1 cells utilized $Li_4Ti_5O_{12}$ anode and $LiMn_2O_4$ (LMO) spinel cathode material synthesized by Argonne National Lab (ANL). The second generation cell with ANL material, demonstrated more power capability than the Gen 1 cells. The initial results show that this LTO/LMO chemistry exceeded the USABC's power and energy requirements as shown in Figure 1. The horizontal line represents the USABC's minimum usable energy goal of 300 W. The vertical line represents the USABC's minimum allowed discharge power of 25 kW. As shown in the figure, the Gen 2.0 and Gen 2.1 cells exceeded the usable energy goals until peak discharge power levels 80% higher (40kW) than the USABC goals.

Phase II of the project, which also started in 2007, will strive to achieve the life, safety validation and cost reduction goals.

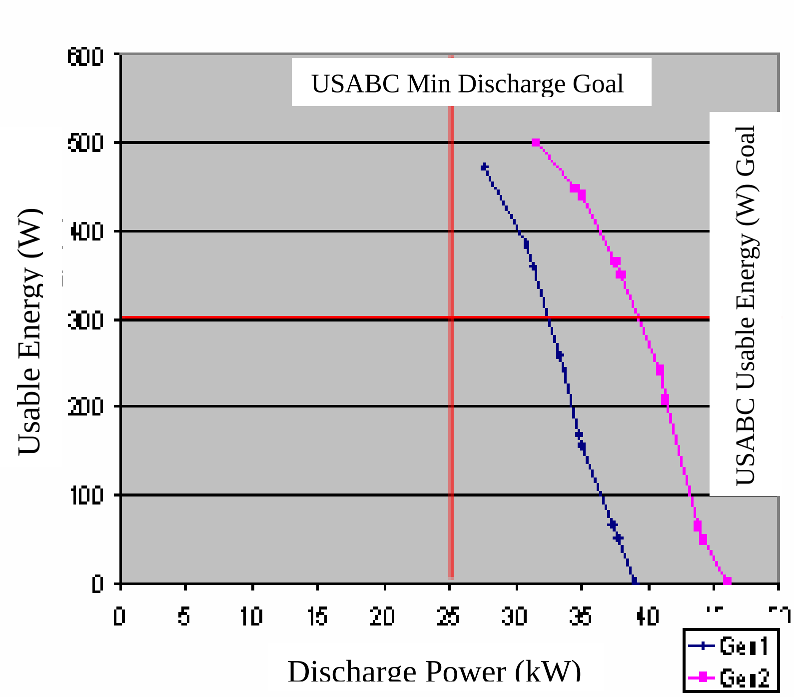


Figure 1: Usable Energy vs. Power for the Gen 1 and Gen 2 Cells.

Novel High-Capacity Tin-Carbon Composite Anode Synthesized using a Microwave Technique

Lawrence Berkeley National Laboratory

Lithium-alloying metals, like tin, have been the focus of a great deal of research because of their promise of increasing the energy density of batteries due to their large specific capacities (>1000 mAh/g *versus* 372 mAh/g for graphite). However, it is known that particles of these metals expand as much as 3 times their initial volume upon the inclusion of Li, resulting in cracking of the particles and capacity fade with cycling.

One method of alleviating the effect of expansion is to make the particles small and embed them into an inactive matrix like carbon. Lawrence Berkeley National Laboratory (LBNL) has developed a novel microwave technique to synthesize carbon-tin composites that show reversible capacities of 400 mAh/g with long-term cycling stability that far exceeds that of tin anodes prepared by other techniques. LBNL's method, which has since been patented, makes use of microwaves to embed 1 to 8 nm sized tin particles into a matrix of carbon as shown below in Figure 1. Electrodes made from these materials show reasonable capacity retention with excellent rate behavior, with capacities as high as 300 mAh/g at a 5C discharge rate. The improvement in cycle life shown using this synthesis technique is a big step forward in identifying the next generation of high-energy systems that can meet the needs of plug-in hybrid electric vehicles. The study has proven the concept of using a microwave technique to make composite anodes.

Efforts are now underway to study the impact of changes to the microstructure on capacity and capacity retention during cycling and to synthesize larger batches of samples to enable more extensive evaluation.

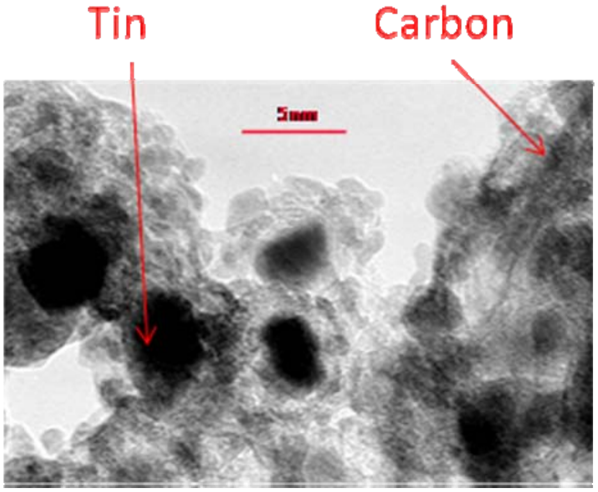


Figure 1: 1 to 8 nm sized tin particles into a matrix of carbon

2007 FreedomCAR and Fuel Partnership Highlight

Battery Life Prediction Model and Software

Sandia National Laboratories
Argonne National Laboratory
Idaho National Laboratory
Lawrence Berkeley National Laboratory

Predicting the life of a battery from physical data accumulated in less than two years, for a battery that is expected to last for 15 years, is a non-trivial exercise. Participants have combined efforts to develop a calendar life prediction model and a supporting software package that allows for the estimate of calendar life with 90% confidence.

High-power cells designed specifically for hybrid electric vehicle applications were aged in thermal chambers at different temperatures for as much as one year. A model with three parameters was found to fit the three testing conditions over the lifetime of the cells. A second model was formulated that assesses the variance of the data as a function of the relative level of cell impedance. This model consists of a cell manufacturing variation dependence and a measurement error dependence.

The first model can be used to predict calendar life at any temperature or for a varying temperature. The next step is to develop a methodology for estimating battery life under different use and environmental conditions.

To arrive at the confidence limit of the life prediction, both models are used in a Monte Carlo simulation. Below one sees the results of the fitting of the model to actual data and of the life predictions of 1000 Monte Carlo simulations of the cell test conditions.

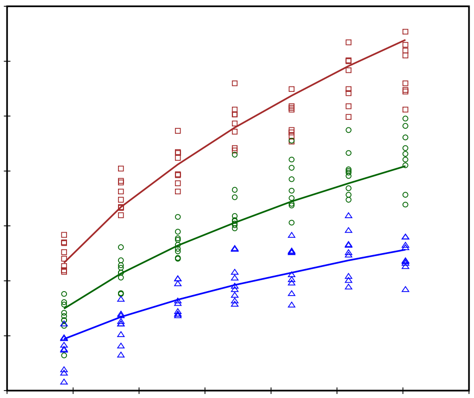


Figure 1: Model fit to test data (temp in K)

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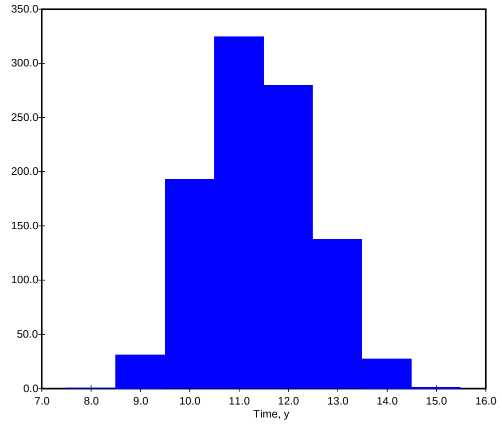

Figure 2: Shows the results of the Monte Carlo Simulation of 1000 trials from which one derives an estimate of the mean life and of the 90% confidence limit.

Stabilizing Interfaces with Electrolyte Additives

Argonne National Laboratory

As part of DOE's Advanced Technology Development Program, Argonne National Laboratory is developing electrolyte additives that help stabilize the electrode/electrolyte interfaces of lithiated graphite anodes and delithiated metal oxide cathodes. These additives decompose during the initial charge to produce passivation films that are more stable then the passivation films that form with conventional Li-Ion electrolyte systems. By forming more stable passivation films, these additives help to stabilize the cell chemistry, leading to reduced rates of capacity fade and power fade. This results in a longer calendar life compared to cells with the same basic chemistry that do not employ the additives. One of the major challenges is to create these more stable passivation films without introducing added impedance into the cells.

One of Argonne's more promising electrolyte additives is difluoro (oxalate) borate. When used as an electrolyte additive, this material helps to stabilize cell chemistries comprised of a graphite anode, an NMC cathode, and several conventional electrolyte systems. Figure 1 provides accelerated aging data (cell capacity and impedance vs. time and charge/discharge cycles) at an elevated temperature (55^{o}C) for cells with and without this electrolyte additive. When used at the 2-3 weight percent level in the electrolyte, this additive exhibits a significant stabilizing effect on this cell chemistry. Figure 2 compares AC impedance data for cells with and without the additive. This data shows that the stabilization with this additive is achieved without significantly increasing the cell impedance.
Efforts continue to develop optimal additives for use in different lithium ion cell chemistries.

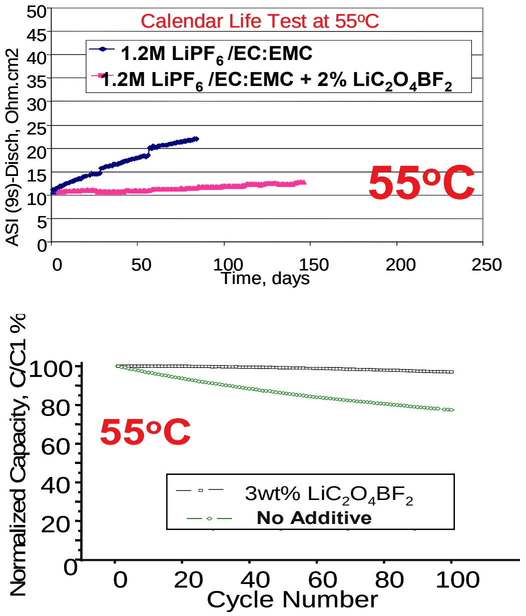

Figure 1: More stable impedance & capacity are achieved with additive.

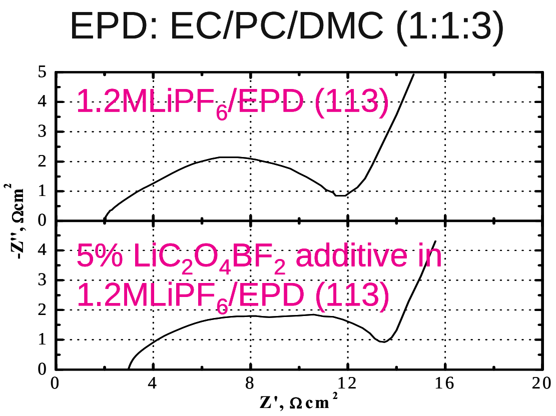

Figure 2: Similar cell impedance values are achieved with &

2007 FreedomCAR and Fuel Partnership Highlight

More Stable Li-ion Layered Cathode Materials

Argonne National Laboratory

As part of the DOE's Advanced Technology Development Program and its Batteries for Advanced Transportation Technologies Program, Argonne National Laboratory has developed new lithium metal oxide cathode materials that are more structurally and chemically stable. This results in a cathode material that possesses much higher capacity per unit mass (more than 65% greater capacity) then conventional materials. This type of new cathode material could significantly increase the energy density of Li-ion batteries, while simultaneously enhancing their inherent thermal abuse tolerance.

The structural integration of non-electrochemically active Li_2MnO_3 with electrochemically active $LiMO_2$ components, produce layered cathode materials that exhibit enhanced structural stability, when fully charged. Some members of this family of materials exhibit stability at voltages up to 4.6 volts vs. metallic lithium. Materials of this type are being refined to increase their particle density and rate capability, in an effort to enhance Li-ion battery performance, life, and abuse tolerance for PHEV applications. Also, processing conditions are being optimized to achieve these high stable discharge capacities, as shown in Figure 1.

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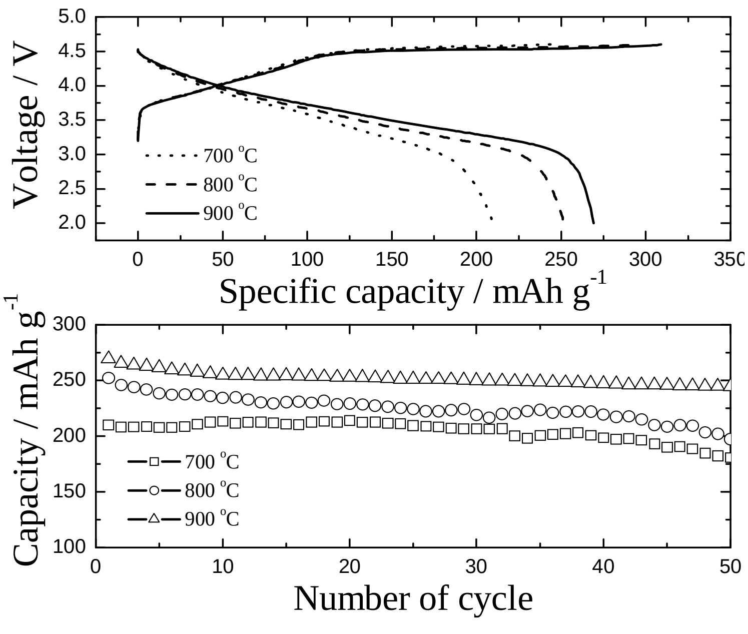


Figure 1: Stable high capacities achieved by optimizing processing conditions.

Identification of Water Transport-Related Failure Modes in Gas Diffusion Media

Los Alamos National Laboratory

Advancing the performance of automotive fuel cells relies upon understanding and minimizing the mass transport limitations caused by the presence of liquid water or ice. Gas diffusion layers (GDLs) are the fuel cell components that are most responsible for managing the removal of water from gas-flow pathways, as well as for helping to maintain water in those components where humidification is needed (e.g. the membrane). A thorough understanding of water transport properties in the context of GDL design parameters has been lacking.

Los Alamos National Laboratory (LANL) has been able to demonstrate that GDL design parameters such as polytetrafluoroethylene (PTFE) loading in the microporous layer (MPL) have effects on the *in situ* performance of the fuel cell; these effects can be related to the accumulation of liquid water in the cell, which is observable using neutron imaging, as shown in figure 1 below. Contact angle techniques were used to show the effect of fiber graphitization on the resulting GDL hydrophobicity. Although many degradation failure modes are well-known for catalysts and membranes, isolating GDL degradation mechanisms is difficult while testing *in situ*. The effort reported here has developed experimental techniques for isolating the effects of GDL degradation. Freeze/thaw cycling of paper-based GDLs has revealed that fiber breakage at channel/land interfaces is a possible failure mechanism. Elemental composition analyses of GDL materials following drive cycle testing have shown oxygen enrichment on the flow field side of the cathode GDL.

Additionally, LANL is preparing three-dimensional, two-phase models that incorporate known GDL properties to predict fuel cell performance. The GDL failure modes noted in this study will be used as motivation for future work to fabricate materials resistive to degradation.

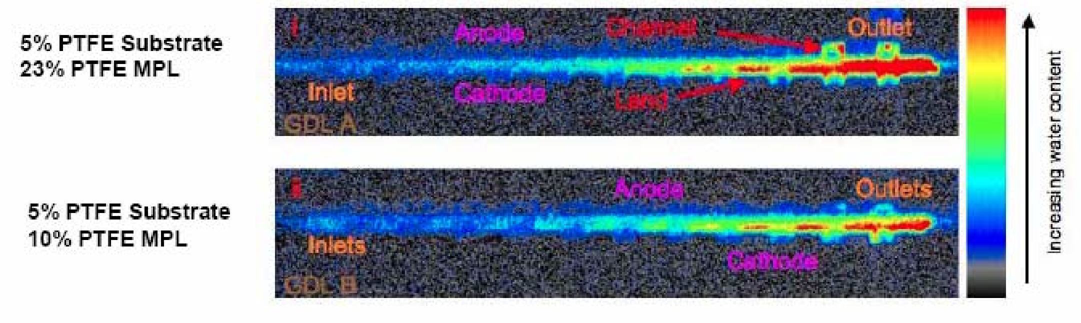


Figure 1: Water accumulation detected by neutron imaging in two cells with different microporous layer PTFE loading.

2007 FreedomCAR and Fuel Partnership Highlight

Multi-Block Copolymers Show Potential for Low Cost, High Temperature Membranes

Virginia Tech

Significant progress was made in 2006 on improving the durability of perflourosulfonic acid (PFSA) Nafion-like membranes (i.e., DuPont, 3M). These membranes, however, are unlikely to meet the DOE targets for cost or high-temperature performance. Virginia Tech has developed multi-block partially-fluorinated polyaromatic copolymers that have shown higher conductivity than Nafion over a wide range of relative humidities and temperatures. These membranes are also expected to be significantly less expensive than PFSA membranes. This family of membranes has proven to be stable in accelerated fuel cell tests that cause non-stabilized Nafion to chemically degrade. By tailoring the molecular weights of the hydrophobic and hydrophilic blocks of the copolymer, Virginia Tech has been able to increase the self diffusion coefficient of water, which leads to high proton conductivity and reduces in-plane membrane swelling, which is expected to lead to improved mechanical durability. Figure 1 shows that after the block copolymers are saturated with water, they retain more water upon heating than the random copolymers do, and much more than Nafion. These polymers have been heated to 200ºC while retaining 15 water molecules per sulfonic acid group (Figure 1). This ability to retain water is considered a possible enabler for high temperature (120ºC), low relative humidity fuel cell operation. Atomic Force Microscopy was used to show that these polymers maintain their two-phase structure at temperatures up to 160ºC. While the ex-situ data is very encouraging, both performance and durability still need to be demonstrated in an operating fuel cell.

Virginia Tech has developed a continuous process using film-casting to make thin block copolymer membranes, and plans to provide samples for external testing. Additionally, the discovery that membrane properties can be optimized by tailoring block size should be valuable to others developing novel polymer electrolyte membranes.

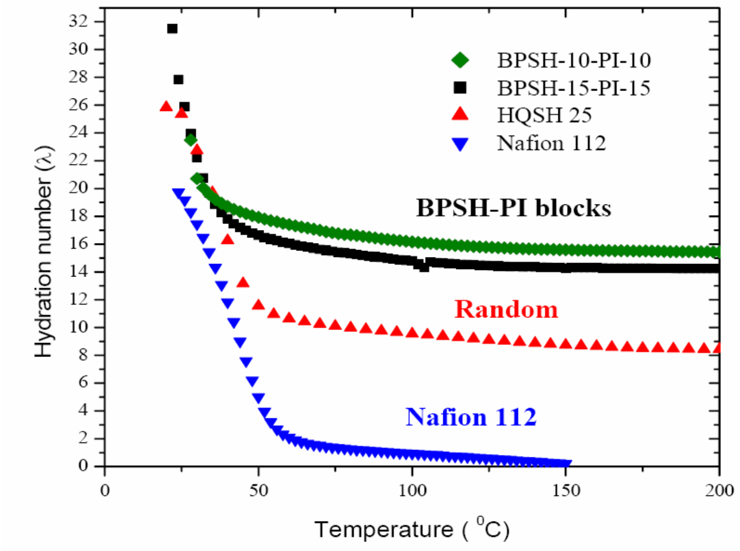


Figure 1: Water content of Virginia Tech and Nafion membranes vs. temperature

2007 FreedomCAR and Fuel Partnership Highlight

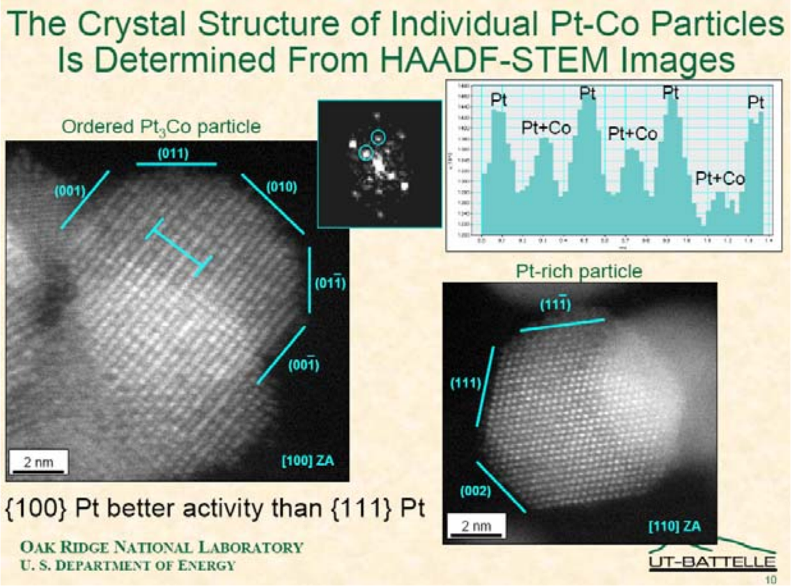
Microstructural Characterization of PEM Fuel Cell Membrane-Electrode Assemblies (MEAs)

Oak Ridge National Laboratory

The most effective way to reduce fuel cell cost is to get more power out of a given-sized fuel cell. To do so requires improved catalyst-layer electrode structures that allow hydrogen and air to more readily reach the catalysts and that allow product water to more readily drain away. Polymer electrolyte membrane (PEM) fuel cell MEA catalyst-layers contain platinum (Pt) for catalyst activity, carbon for electrical conductivity, ion-conducting polymer (ionomer) for ionic conduction, and open porosity for transport of reactants and products. There is a critical need to develop methods to visualize, on the nano-scale, which types of catalyst-layer microstructures result in optimum fuel cell performance and durability.

Oak Ridge National Laboratory has developed preparation, imaging, and compositional analysis techniques, utilizing transmission electron microscopy (TEM), to elucidate the complex nano-scale structure of PEM fuel cell catalyst layers. High-resolution imaging and microanalysis of cross-sectional, intact, MEAs allows for differentiation between the different materials comprising the catalyst layers, i.e., the carbon support, ionomer regions, catalyst particles, porosity, and membrane.

The Scanning Transmission Electron Microscopy (STEM) images below show the crystal structure of individual platinum cobalt (Pt-Co) catalyst covering the carbon support, which is in turn covered with an inhomogeneous layer of ionomer. The lower right region of the TEM image shows a Pt-rich particle located within a thick region of ionomer. These Pt-Co particles are important to characterize for the potential reduction of Pt usage in the catalyst through alloying. Nanoscale imaging is critical to advance fuel cell technology.



The Crystal Structure of Individual Pt-Co Particles Is Determined From HAADF-STEM Images

{100} Pt better activity than {111} Pt

OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

UT-BATTELLE

Theory Guiding Experimental Efforts: The Story of Calcium Borohydride

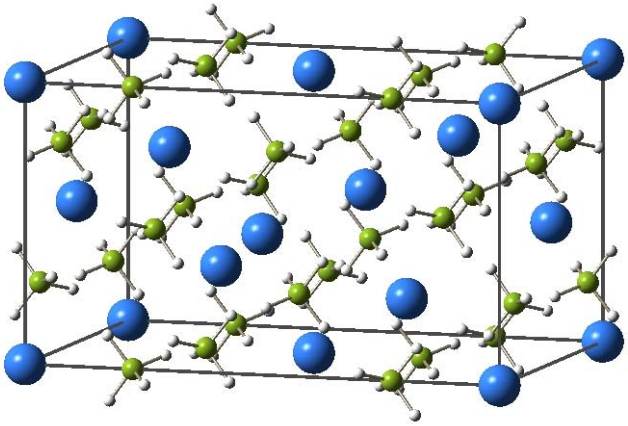
Sandia National Laboratories

Traditionally new inorganic materials discovery has often benefited from the experimentalist's intuition and serendipity. In order to more efficiently direct experimental efforts in new materials discovery, it would be valuable to use theoretical modeling to predict reactions that may lead to new materials with the desired characteristics. Theoreticians have therefore developed density functional theory (DFT) to the state that it can accurately predict the thermodynamic properties of new chemical compounds. One drawback of DFT is that the structure or atomic arrangement of the new species needs to be known to accurately predict the thermodynamic properties.

Researchers at Sandia National Laboratories developed an algorithm using a Monte Carlo approach to predict the most probable stable structure of new hydrogen storage materials. By coupling their Monte Carlo approach with DFT, they have been able to predict some potential reactions with thermodynamic properties favorable for hydrogen storage. One potential reaction of interest was a solid-state reaction pathway involving calcium borohydride [$Ca(BH_4)_2$]:

$$3\,Ca(BH_4)_2 \leftrightarrow CaB_6 + 2\,CaH_2 + 10\,H_2 \qquad \text{(Reaction 1)}$$

The reaction has a predicted hydrogen storage capacity of 9.6 wt.% and reaction enthalpy of ~53 kJ/mol. Based on this prediction, experimentalists at Sandia National Laboratories were able to find the conditions to carry out the synthesis reaction of $Ca(BH_4)_2$. While the synthesis conditions are demanding, 400°C and 700 bar H_2 pressure, the 60% yield is substantially improved over other solid-state methods. Thermogravimetric analysis of the reaction product has demonstrated 9.6 wt.% (105 g/L) hydrogen release. Furthermore Raman spectroscopy, neutron vibrational spectroscopy and X-ray diffraction analysis, carried out at Metal Hydride Center of Excellence partners National Institute of Science and Technology and University of Nevada-Reno, as well as at Sandia National Laboratories, have confirmed the reaction product to be $Ca(BH_4)_2$. Work is continuing on searching for catalysts that might aid the hydrogenation reaction to achieve higher yields and at milder reaction conditions. Although the energetics for hydrogen release from this material are too high, the approach used in its discovery is amenable to other more promising materials.



The structure of $Ca(BH_4)_2$

E. Ronnebro, E. Majzoub et al. Sandia, *Phys Rev B 74, 155122 (2006)*

2007 FreedomCAR and Fuel Partnership Highlight

Chemical Hydride: Improved Hydrogen Release from Aminoborane with Additives

University of Pennsylvania

Efficient on-board storage of hydrogen requires a system that: a) provides hydrogen at high densities by volume and weight, b) allows removal of the H_2 with modest or no energy input, and c) uses a simple, low-cost method to recharge the material back to its original state. Ammonia borane, NH_3BH_3, is one emerging hydrogen storage material candidate that has recently received a great deal of attention due to its high hydrogen content (approximately 18% weight on a material basis). Unfortunately, it releases hydrogen too slowly, and it is very difficult to replace the hydrogen to re-form ammonia borane.

Researchers at the University of Pennsylvania (in conjunction with the DOE Chemical Hydrogen Storage Center of Excellence) have recently improved on several previous methods to increase the rate (or lower the temperatures) of H_2 release from this material. Specifically, chemical additives, such as ionic liquids, ammonia triborane and a proprietary material known as a “proton sponge” have increased the rate and extent of hydrogen release from pure ammonia borane. These new additives have improved the gravimetric density of released H_2 from 5.9 wt% to 6.5 in 3 hrs and improved the volumetric density of H_2 released from 47 to 60 g H_2/L.

In order to utilize NH_3BH_3 as an on-board storage technology, more research is still required. The highest priority is to develop a practical method to regenerate the spent material back into NH_3BH_3. Finally, the infrastructure implications of a solid-state hydride storage option, that is not rechargeable on-board the vehicle, need to be evaluated.

AB: ammonia borane
AT: ammonia triborane
PS: proton sponge
bmimCl: an ionic liquid

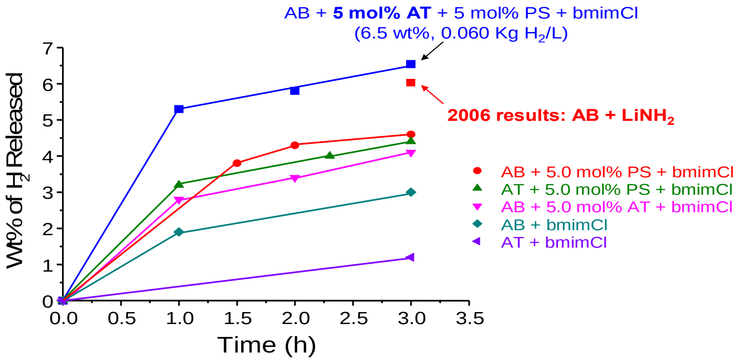


Figure 1: Dehydrogenation of ammonia borane at 85^{o}C with added ionic liquids, ammonia triborane and a proprietary material known as a “proton sponge”.

2007 FreedomCAR and Fuel Partnership Highlight
Hydrogen Storage Sodium Borohydride Go/No-Go Decision

To focus available resources on the most promising technologies, periodic Go/No-Go decision reviews are conducted to determine if specific approaches have potential to meet the FreedomCAR and Fuel Partnership technical targets. In 2007, there was a decision point on the continued R&D of sodium borohydride (SBH) hydrolysis-based systems, for on-board vehicular hydrogen storage.

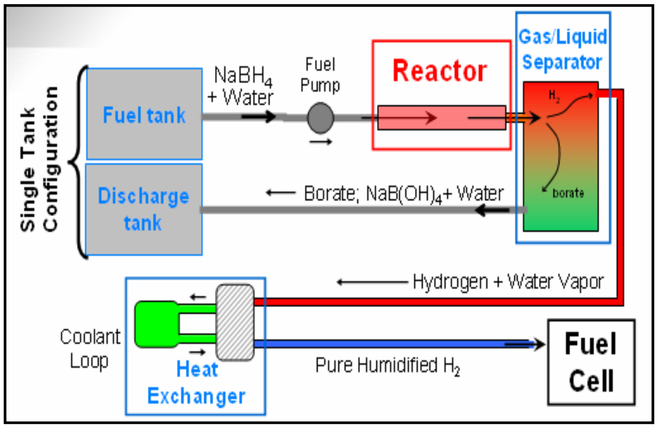
An Independent Review Panel reviewed R&D progress in the subject area during September 2007. Based on the review criteria of cost, capacities and spent fuel regeneration efficiency, the Panel recommended:

- No-Go for the hydrolysis of SBH for on-board vehicular hydrogen storage applications, and
- Retaining work applicable to cost effective production of amineboranes for aminoborane hydrogen storage systems (a key focus for the Chemical Hydrogen Storage Center of Excellence) particularly because SBH is a starting material for producing amineboranes.

The SBH hydrolysis system releases hydrogen via reaction with water. The resulting spent fuel, sodium borate, solidifies at the SBH fuel concentration necessary to meet the storage capacity targets. This issue not only limits the storage capacities, but also causes significant engineering challenges. Solidification makes the removal of spent fuel difficult as demonstrated by Chrysler in their Natrium vehicle. Chrysler had also determined that regenerating SBH is more energy intensive than producing liquid or compressed hydrogen.

The key issues leading to the No-Go recommendation are similar to the findings found with the Chrysler Natrium vehicle and related to: 1) the amount of fuel carrier that can be stored on-board to meet the near term hydrogen storage targets without causing major engineering issues; and 2) the significant energy required to rehydrogenate the fuel.

The panel members stated that the researchers made progress towards the targets, but determined that the status of the technology did not meet the short-term storage capacities, cost targets or the spent fuel regeneration efficiency goal. Additionally, for the on-board system, the panel believed the improvements have reached the maximum possible capacities and there is no clear path towards meeting the long-term targets.



Schematic of SBH On-Board System

These recommendations and the subsequent decision by DOE will allow resources to be focused on more promising materials while retaining R&D on other boron-containing systems.

2007 FreedomCAR and Fuel Partnership Highlight

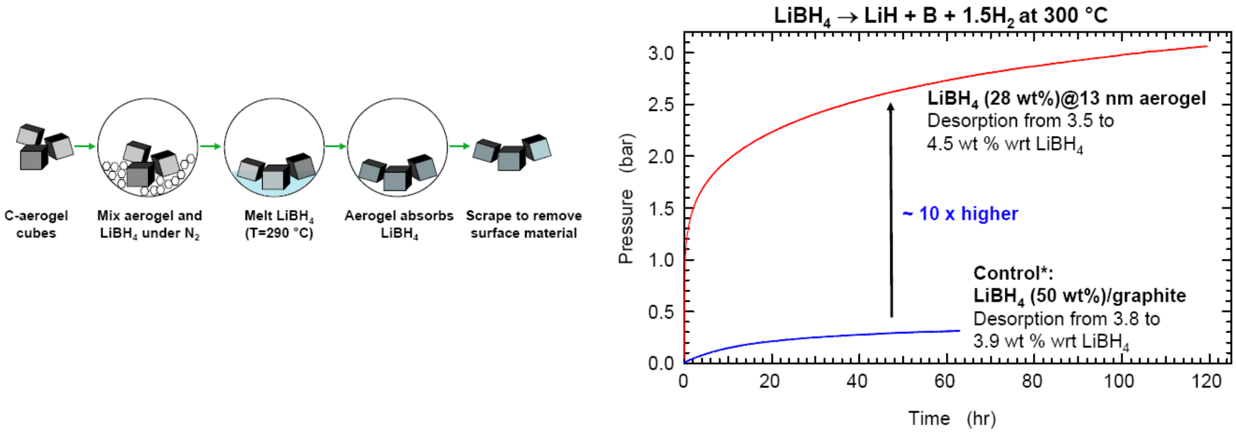
Aerogels Improve Performance of Complex Hydrides

HRL and Lawrence Livermore National Laboratory (LLNL)

Complex hydrides are materials that store hydrogen by reacting with hydrogen to make a new molecule or species. They are of interest because some of them will hold a relatively large amount of hydrogen, and once they have released their hydrogen they can be regenerated with hydrogen gas on-board the vehicle. The highest capacity hydrides tend to react at higher than desired temperatures (greater than 80°C), and at slower than desired rates. In some cases, the addition of certain metals, particularly titanium, has been helpful in reducing the temperature of hydrogen release and the reversibility and speed with which hydrogen enters and leaves the hydride. However, in some cases, this method has not worked.

Researchers at HRL and LLNL as part of the DOE's Metal Hydride Center of Excellence have demonstrated a new method to achieve 10 times better hydrogen uptake than achieved previously. Using aerogels, a very open type of molecular scaffolding, as a framework for a complex hydride, they were able to increase the rate at which hydrogen went into and out of the complex hydride and also lowered the temperature required. To achieve this performance the HRL team first had to get the hydride into the aerogel. This was accomplished by melting the hydrides in a sealed, air-free container and allowing them to soak into the aerogel, similar to a sponge. These researchers are now working on ways to further improve hydride performance by achieving the best distribution of pore sizes inside the aerogel. They are also extending the method to hydrides that are repelled by aerogels by first coating the aerogel with nickel to allow the hydride to soak in.

In addition to progress in hydrogen storage, this program also illustrates the power of cooperation between teams and between Centers of Excellence. The HRL team, a leader in complex hydrides and a part of the Metal Hydride Center, benefited from the specially tailored aerogels made by LLNL, a part of the Hydrogen Sorption Center and a leader in aerogel technology.



The complex hydride $LiBH_4$ can be caused to nearly fill an aerogel framework, improving its performance by lowering the temperature of hydrogen release and increasing hydrogen uptake.

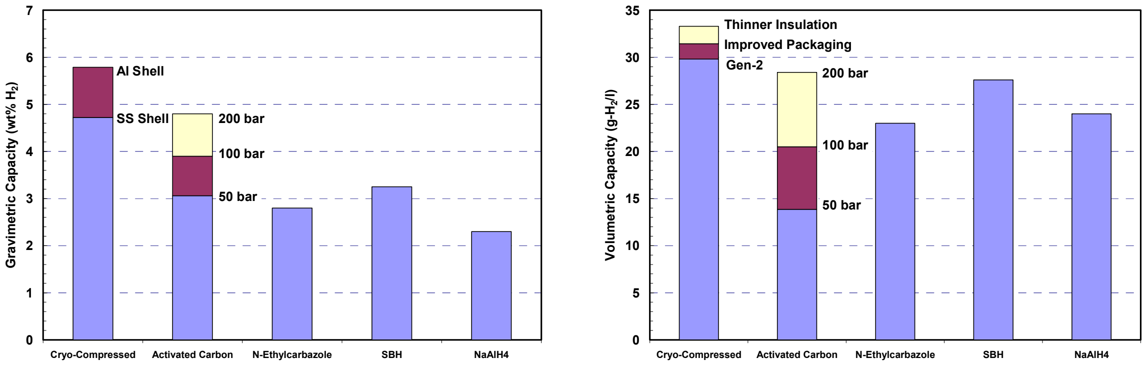
Systems Level Analysis of Different Hydrogen Storage Options

Argonne National Laboratory

A number of materials with the potential to store enough hydrogen for a driving range of more than 300 miles are being investigated. Each class of materials would likely have a very different configuration when used on a vehicle, and it is important to know how these materials would perform as part of a complete fuel system. A viable fuel system would satisfy not only the targets for weight, volume and cost, but also the constraints such as minimum delivery pressure of hydrogen, minimum flow rate of hydrogen and refueling time. It is important to determine the performance of the overall storage system as opposed to the performance of the storage material alone.

Argonne National Laboratory (ANL) has completed a baseline analysis of various storage options and determined system weights and volumes assuming the above constraints are met. ANL evaluated the cryo-compressed concept developed by Lawrence Livermore National Laboratory (LLNL), which can use liquid hydrogen in a tank that is also capable of storing gaseous hydrogen at 350-bar pressure and is being demonstrated by LLNL on a modified hydrogen fueled hybrid vehicle. As shown in the figures below, the cryo-compressed tank appears to have the highest capacity according to these preliminary analyses. For lower pressure options, a low-temperature activated carbon system appears promising but will require moderate pressures (50-200 bar) and low temperature (77K). Organic liquid carriers (such as N-ethylcarbazol), that are being developed by Air Products and Chemicals appear to have high volumetric energy density, as do sodium borohydride developed by Millennium Cell and sodium alanate which was demonstrated by United Technologies Research Center.

These system analysis studies provide important information on the performance expected from materials currently under study. They have also provided insight into subsystem and component characteristics needed to minimize system weight, volume and cost. The results will be further refined as more performance data such as kinetic and thermodynamic parameters become available.



Preliminary results for gravimetric and volumetric capacities of different storage concepts are shown. Refer to the complete ANL documents for assumptions made in analyses and limitations of the results as presented.

2007 FreedomCAR and Fuel Partnership Highlight

Room Temperature Hydrogen Storage in Spillover Materials

University of Michigan

High surface area materials have received considerable attention in the area of hydrogen storage. Interest in these materials stems from the following prototypical attributes: a) potential for room temperature storage, b) favorable hydrogen uptake/release rates, c) reversibility for storage, and d) potential for low-cost synthetic scalability. A promising family of materials in this class is metal organic frameworks (MOFs), large networks composed of metal ions and organic molecules. For example, a recent record of more than 7 percent by weight and 35 g/L (material basis) at 77K (~liquid nitrogen temperature) was achieved at UCLA. While significant progress has been demonstrated, MOFs and other materials which physically adsorb hydrogen exhibit low heats of adsorption (up to 6 kJ/mol·H_2) and thus require cryogenic conditions (77K) to obtain reasonable hydrogen uptake. Successful strategies for achieving higher binding energy are an essential step toward reaching room temperature storage at moderate pressure.

To realize enhanced binding energies in MOFs, researchers at the University of Michigan (DOE Hydrogen Sorption Center of Excellence) have implemented a novel technique, termed “bridged hydrogen spillover.” This approach involves a supported catalyst, a high surface area receptor (e.g. MOF), and catalyst-receptor bridge material that results in hydrogen binding of more than 20 kJ/mol·H_2 (3 times that of pure MOF). This augmented binding translates to room temperature storage of ~3 wt% at 100 bar (material basis), a breakthrough for materials which typically require cryogenic conditions. Samples independently prepared by the Institute of Nuclear Energy Research (INER), Taiwan, and tested by Southwest Research Institute (SwRI), corroborate this result. This noteworthy accomplishment represents the first time this level of hydrogen capacity has been achieved at room temperature.

Although the hydrogen uptake/release process was found to be fully reversible at room temperature, the kinetics for uptake and release must be improved for practical application. Additionally, in order to apply this approach generally to cryogenic materials, synthesis reproducibility and an enhanced understanding of the sorption mechanism must be achieved.

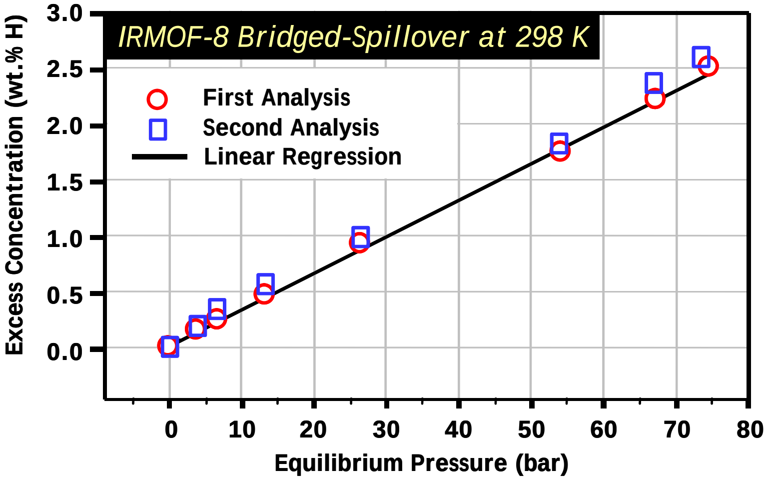


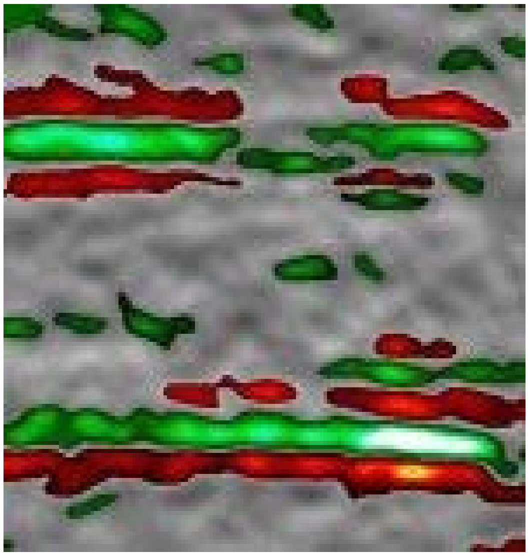
Figure 1: High-pressure hydrogen uptake (wt%) at 298 K for IRMOF-8 bridged-spillover. The first analysis (red circles), synthesized and tested at UM, was then corroborated via a second analysis (blue squares) synthesized and tested by the INER and SwRI respectively.

Development of a Tool to Quantify the Severity of Bond-Line Read-Through

Automotive Composites Consortium

Bond-line read-through (BLRT) is an appearance defect that has no impact on the performance of automotive body panels, yet diminishes a customer's perception of the quality of a vehicle. The sources of this defect are poorly understood; consequently, automakers cannot predict when this defect will occur. They first manifest themselves when parts are produced, at a point in the design process when there are few options for eliminating the defect. Frequently, panel thickness is increased to eliminate this defect, adding weight for appearance. A better understanding of the causes of this defect could allow immediate weight reduction in some vehicle panels with no reduction in part performance. In the case of outer panels made using sheet molding compound (SMC), OEMs could achieve a 25% weight reduction if this defect could be eliminated through design changes other than increasing the panel thickness. Furthermore, when an affordable, automotive-grade carbon fiber becomes available, understanding of this phenomenon is likely to be a critical enabler for implementing minimum thickness (minimum weight) carbon fiber SMC exterior panels.

One reason BLRT is so poorly understood is that a measurement system that could objectively quantify the severity of this defect did not exist. Consequently, a technique based on the existing ONDULO™ imaging technology was developed. The graphical output from the system is illustrated in the example of a BLRT "Score" map. The gray "background" of the image is the curvature value at each point on the surface. The red and green areas highlight the regions determined to be objectionable. The size and square of the average curvature of each defect are used to quantify its severity. This measurement was shown to correlate well with visual assessments of defect severity.



Now that quantitative, objective data is available, a series of experiments will be completed to understand the root causes of the defect. That information will then be used to create a computer aided engineering tool that will allow automakers to predict, early in the design phase, whether this defect will occur, and to use that knowledge to develop minimum thickness (minimum weight) part designs that also meet customer's appearance expectations.

2007 FreedomCAR and Fuel Partnership Highlight

Recycling End-Of Life Vehicles of the Future

Argonne National Laboratory, Vehicle Recycling Partnership and American Chemistry Council - Plastics Division

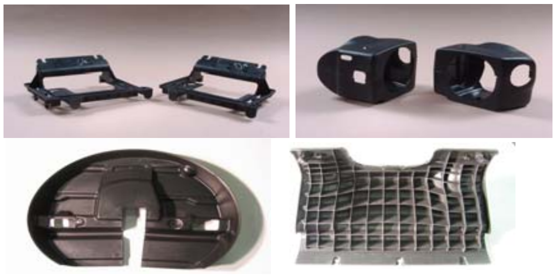
The Recycling End-of-Life Vehicles (ELV) of the Future project demonstrates and develops post-shredding recovery technologies. The project goals and objectives include: 1) establishing the feasibility of materials and resource recovery from end-of-life vehicles, and 2) increasing the use of recyclable renewable materials. Accomplishments shown below include: 1) demonstrated effective recovery of high-quality polyolefins (at greater than 90% yield) from shredder residue, 2) developed process conditions for selective recovery of Acrylonitrile Butadiene Styrene (ABS), Polystyrene (PS) and Polycarbonate (PC) from shredder residue, and 3) established technical feasibility of converting ELV shredder residue to fuels and chemicals [(Changing World Technologies (pyrolysis to high carbon chain fuel) and Troy Polymers Inc. (glycolysis of urethane to polyols)]. These results are significant because they establish that recovery and reuse of polymers and materials from ELV will: 1) increase materials supply options, 2) decrease costs for automakers and 3) decrease the carbon footprint of light-weighting materials over product life-cycle. A production-scale validation project will be initiated in 2008.

In 2007, the ELV CRADA Team received the Society of Plastics Engineers, Environmental Division Global Plastics Environmental Conference (GPEC) award for "Enabling Technologies and Processes" acknowledging the team's contribution to development of ELV recycling technology to remove recycling barriers that might preclude the use of advanced light-weighting materials.

Argonne Physical Separation Experimental Plant

Argonne Plastics Recovery Experimental Facility

Polyolefins recovery at Argonne



Auto parts made with 100% recycled polyolefins recovered from "post-shred" residue

2007 FreedomCAR and Fuel Partnership Highlight

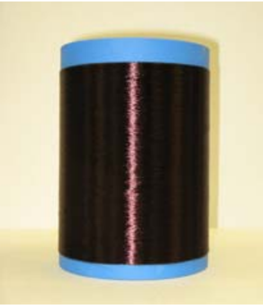
Lignin Based Precursors for Lower Cost Carbon Fibers

Oak Ridge National Laboratory (ORNL)

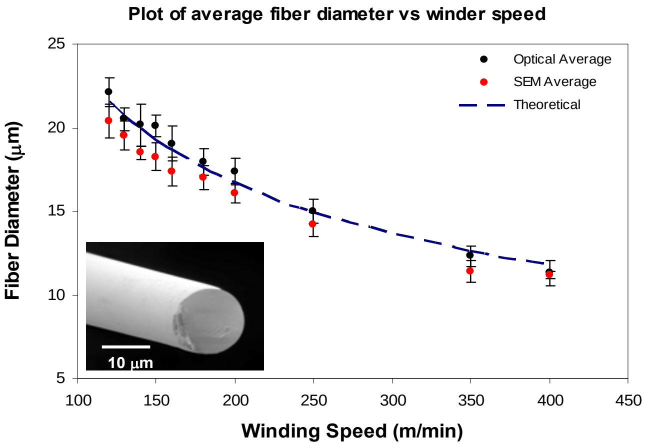
Carbon fibers offer significant weight saving potential because of their high strength, high modulus, and low density. The use of carbon fibers is currently restricted by its high cost, which is $8 to $15 per pound, of which fifty percent is attributable to the cost of the precursor.

ORNL developed the baseline technology necessary to use lignin (a by-product of the paper making process) as a very low cost feedstock for carbon fiber precursors. First the lignin must be purified to a satisfactory level and then spun into a suitable precursor fiber. Custom-designed melt spinning equipment was acquired, installed, and commissioned at ORNL. The equipment is being used to establish appropriate process conditions for melt spinning of lignin fiber tows, from both hardwood and softwood lignins. The focus in FY07 has been on scaling up the melt spinning operation for production of lignin-based carbon fiber. Experimental work is focused on deriving a fundamental understanding of factors which influence the melt spinnability of lignin. Key are factors that affect rheological and thermal stability properties of lignins; and which control process boundary limits for the melt spinning operation.

MeadWestvaco Corporation has applied solvent-extraction techniques to purify hardwood lignin and provided ORNL with a one kg sample. ORNL confirmed that the organic-purified lignin exhibited excellent viscosity and melt spinnability characteristics. The purified lignin was melt-spun, stretched, and wound onto a spool, as shown, utilizing a bench-top, single filament unit. No plasticizer or co-polymer was needed to facilitate melt spinning. After an additional 2-kg batch of the purified lignin was supplied, ORNL successfully melt spun and wound the organic-purified lignin as a 12-filament tow without the need for any additives. Steady state conditions were established and fiber spinning was uniform for relatively long periods of time.



Fiber diameter was purposefully varied from 22 to 11 microns by varying take up speed, as shown in the diagram to the right. These results closely correlated to the theoretical and demonstrated that purified hardwood lignin can be continuously melt-spun into fiber form. This constitutes a significant step towards the overall objective of producing low cost carbon fibers from a renewable resource.



2007 FreedomCAR and Fuel Partnership Highlight

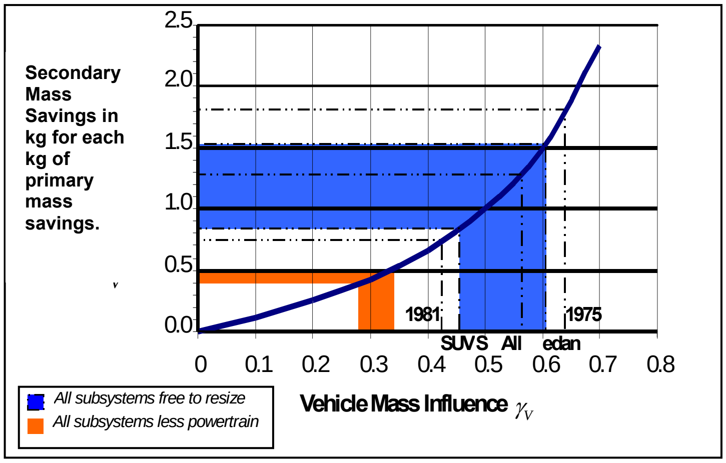
Mass Compounding

Auto/Steel Partnership

A mass increase in a component, during vehicle design, has a ripple effect throughout the vehicle: other components need to be resized increasing vehicle mass even more. The phrase “mass begets mass” describes this phenomenon. A more encouraging view considers a reduction in the mass of a component, enabled by a new technology, resulting in a greater mass reduction ripple effect.

The Auto/Steel Partnership (A/SP) developed a method to quantify opportunities for secondary mass savings of contemporary vehicles. Project accomplishments include a mass compounding influence coefficients database, and development of a calculator to estimate secondary mass savings for typical baseline vehicles. The need for such a tool was identified earlier in an addendum study of the Lightweight Front End Structures project, which demonstrated 30% structural mass reduction using optimized advanced high-strength steel designs. The study indicated additional structural mass reduction is enabled when mass reduction technologies are applied to other vehicle systems (powertrain, interior, etc.). This effect, known as mass compounding, helped identify the need for a systematic approach to quantify this effect. The tool developed by this mass compounding project will assist in achieving FreedomCAR mass reduction targets.

The results are summarized in the chart shown at right, which plots vehicle mass influence as a function of secondary mass savings per unit of primary mass savings. The secondary mass change is the additional mass reduction resulting from primary mass reduction by the implementing mass reduction technology. When all sub-systems can be resized, the secondary mass savings is from 0.8 to 1.5 kg/kg (1.25kg/kg is the estimate for the all vehicle group). When the powertrain is fixed and not available for resizing, the secondary mass savings is from 0.4 to 0.5 kg/kg (0.5 kg/kg is the estimate for the all vehicle group).



The study concludes that a 50% mass reduction of a contemporary sedan may only require a 20% primary mass reduction of individual systems and identifies steel’s potential for achieving FreedomCAR goals. Realizing this potential requires additional technology development and is challenged by mass increases resulting from trends in increased safety requirements, alternative powertrains and additional passenger amenities.

2007 FreedomCAR and Fuel Partnership Highlight

High Integrity Magnesium Automotive Castings

Automotive Metals Division

The goal of the High Integrity Magnesium Automotive Castings (HIMAC) project is to develop the metal casting process technologies to cost-effectively manufacture high integrity cast magnesium automotive chassis components that demonstrate high ductility and strength, low porosity, and are free of objectionable oxides and inclusions. HIMAC investigated emerging casting ablation and T Mag processes, and developed enabling technologies critical to increased cast magnesium automotive applications including: microstructure control, porosity and hot tearing computer models, thermal treatments, and controlled mold filling.

Project accomplishments include design and construction of manufacturing cells (including tooling) for the squeeze casting process, development of aluminum low-pressure permanent mold and squeeze casting processes for the production of magnesium structural castings (Figure 1), the low pressure permanent mold and ablation process (Figure 2), and production of Front lower control arms (Figure 3).

Figure 1: Contech Squeeze Casting Cell

Figure 2: CMI E&E Low Pressure Casting Cell

Figure 3: Magnesium Front Lower Control Arm

The new casting processes address the critical barriers to magnesium casting implementation, as stated in the *Magnesium Vision 2020 Document.* Specifically, the processes provide industry with higher integrity Mg automotive castings for applications such as control arms, knuckles, and wheels that may enable weight savings of 35 to 60%. They reduce magnesium component processing and facility costs, and they enable the production of high integrity magnesium castings.

The use of controlled molten metal transfer and filling (electromagnetic pump) will eliminate many of the production and environmental issues associated with the standard cover gas over magnesium melts and yield higher quality castings.

In addition to all of the above, the HIMAC project will provide technical support to the Magnesium Front End Research and Development Project.

2007 FreedomCAR and Fuel Partnership Highlight

Hybrid Electric Vehicle (HEV) Fuel Economy Over a Wide Range of Battery Temperatures

Argonne National Laboratory

The energy storage device in an HEV, typically a battery, is a very key component that enables HEV operation. When the battery is outside of its proper operating temperature, the functionality is greatly reduced which results in the vehicle operating more as a conventional internal combustion engine (ICE) vehicle and less as an HEV. This results in lower fuel economy.

Argonne tested two advanced HEVs, the Toyota Camry HEV and the Ford Escape HEV over a wide range of battery temperatures to determine the impact on fuel economy and battery utilization. Figure 1 shows the dependency of fuel economy on battery power. As battery temperature increases from -12°C to 25°C, battery power increases by 4X, and the fuel economy increases by nearly 2X. Figure 2 shows that it takes approximately 40 minutes of driving to raise the fuel economy to the optimum of 35 mpg at ambient temp of -14°C.

Higher battery power enhanced engine start/stop operation, increased regenerative braking, and increased overall engine operating efficiency by using the engine only in high efficiency regions. At excessively high battery temperatures, above 40°C, the battery charging limit greatly decreased, which reduced the regenerative braking energy that could be recovered.

Similar results were demonstrated at low battery temperatures with both vehicles even though they are quite dissimilar in vehicle size and classification. Since the Escape HEV uses air conditioning to cool the batteries, rather than cabin air as with the Camry HEV, battery temperatures for the Escape never exceeded 35°C, which resulted in no reduction in regenerative braking.

PHEVs utilize the battery energy storage system even more than HEVs. Given the fuel consumption dependency of HEVs on battery temperature as shown in this study, future work will investigate the fuel consumption and electrical energy utilization of PHEVs as a function of battery temperature.

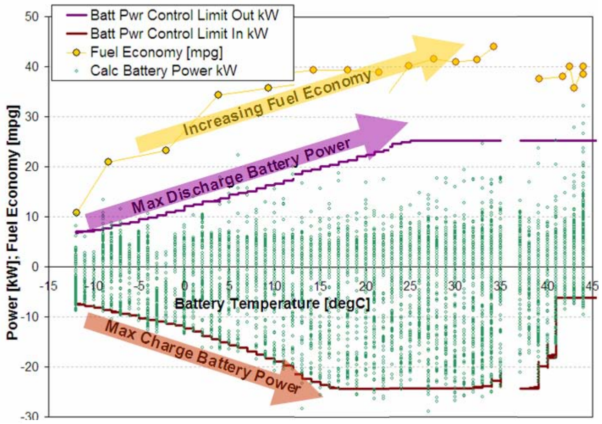


Figure 1: Hybrid battery functionality is not realized until battery reaches 15 to 25 deg. C.

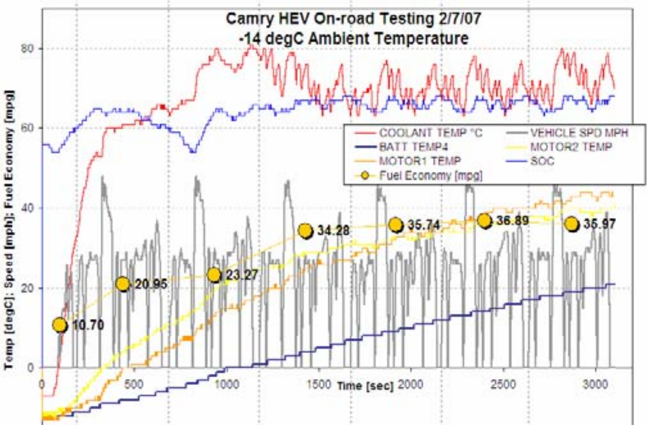


Figure 2: Fuel economy is raised to the optimum of 35 mpg after 40 minutes (2400 seconds) of driving, at ambient temp of -14 deg C.

2007 FreedomCAR and Fuel Partnership Highlight

Energy Storage System Requirements for PHEVs

Argonne National Laboratory

Working with FreedomCAR energy storage and vehicle experts, Argonne National Laboratory (ANL) researchers have evaluated the energy storage system power and energy requirements of several vehicle platforms to follow the UDDS (Urban Dyno Drive Schedule) in electric mode. The PSAT vehicle simulation results were used by the United States Advanced Battery Consortium (USABC) to define the battery requirements for plug-in hybrid electric vehicle (PHEV) applications.

Based on battery test data, a battery model with two time constants was developed at ANL to represent a typical PHEV battery. The utility of the model was further extended to include cells of the same chemistry, but with capacities in the range of 10–100 Ah and capacity-to-power ratios (C/P) of 0.75–3.0 times with no constraint on the number of cells. The sizing algorithm developed was then used to develop design-specific batteries for several vehicle platforms (midsize car, small SUV and large SUV) and all electric ranges (AER).

All the results were generated for a pre-transmission parallel HEV on the UDDS drive cycle. The simulation results demonstrated that most of the other standard drive cycles (Japan1015, HWFET, NEDC) would lead to similar electrical energy requirements. However, more aggressive city/highway drive cycles, such as the LA92, may require up to 20% more energy. The study also demonstrated that electrical accessories, such as air conditioning, would consume 10 Wh/mile for every additional 100 W, meaning the AER could be decreased as much as 40%. The following Energy and Power graphs do not include accessory losses, which can be substantial.

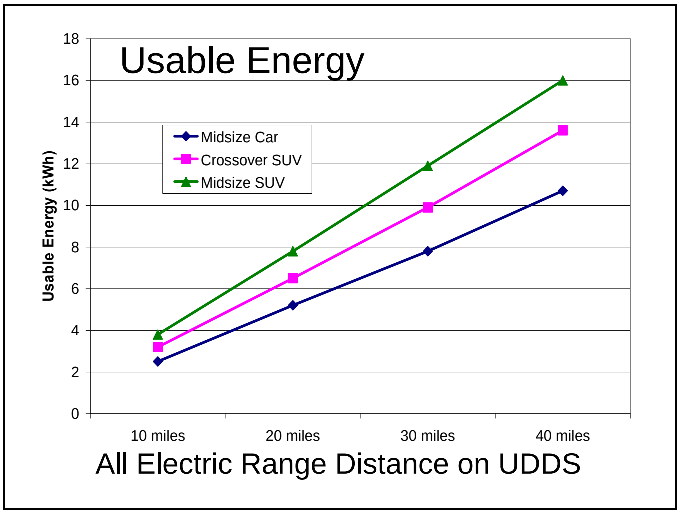


Figure 1: Battery energy required, as a function of, vehicle mass and driving distance, within the cycle

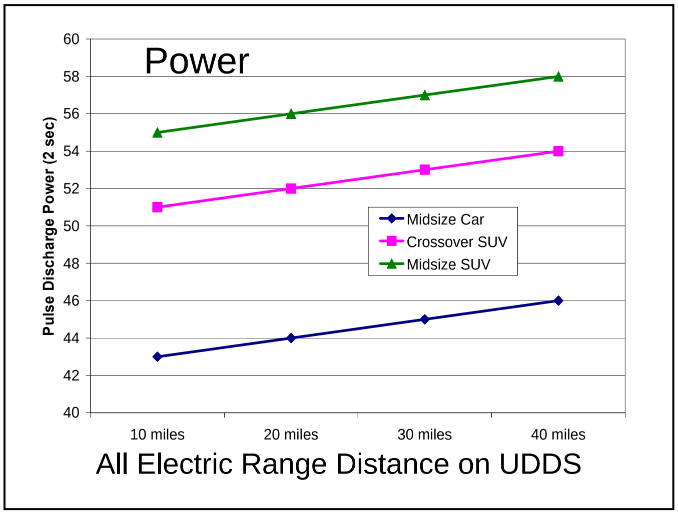


Figure 2: Battery power required during a 2 second acceleration, of max power demand, within the cycle

Final PHEV requirements selected by the USABC:

* Short term: 10 miles AER (3.4 kWh, 50 kW) * Long term: 40 miles AER (11.6 kWh, 46 kW)

Fuel Pathways Integration Technical Team

Well-to-Wheels

Well-to-wheels (WTW) analysis is used to estimate energy use and emissions for complete hydrogen pathways, from feedstock production to vehicle fuel use. The Fuel Pathways Integration Technical Team (FPITT) continually reviews the Department of Energy's WTW analysis process and the assumptions and data used to conduct such analysis with the goal of identifying issues and gaps. Several gaps and opportunities were found in the modeling and analysis of distributed hydrogen production by reforming of natural gas:

1. A system for documenting the assumptions and data used in WTW analysis is needed to ensure transparency and capability to compare WTW analyses.
2. An analysis of the effects of changing on-board hydrogen pressure from 5,000 psi to 10,000 psi is needed.
3. Additional analysis on necessary storage at the forecourt facility is needed.

Resource Analysis

In addition, the team has developed estimates, on a WTW basis, of water use and other resource needs for various hydrogen and competing petroleum-based pathways. Resources such as water, electricity, and platinum may constitute limitations to implementation of hydrogen technologies and facilities. By analyzing the resource needs for each element of various hydrogen pathways, the team is able to identify which hydrogen production pathways are most likely to face resource limitations, as well as which resources represent the greatest barrier to development of a hydrogen economy.

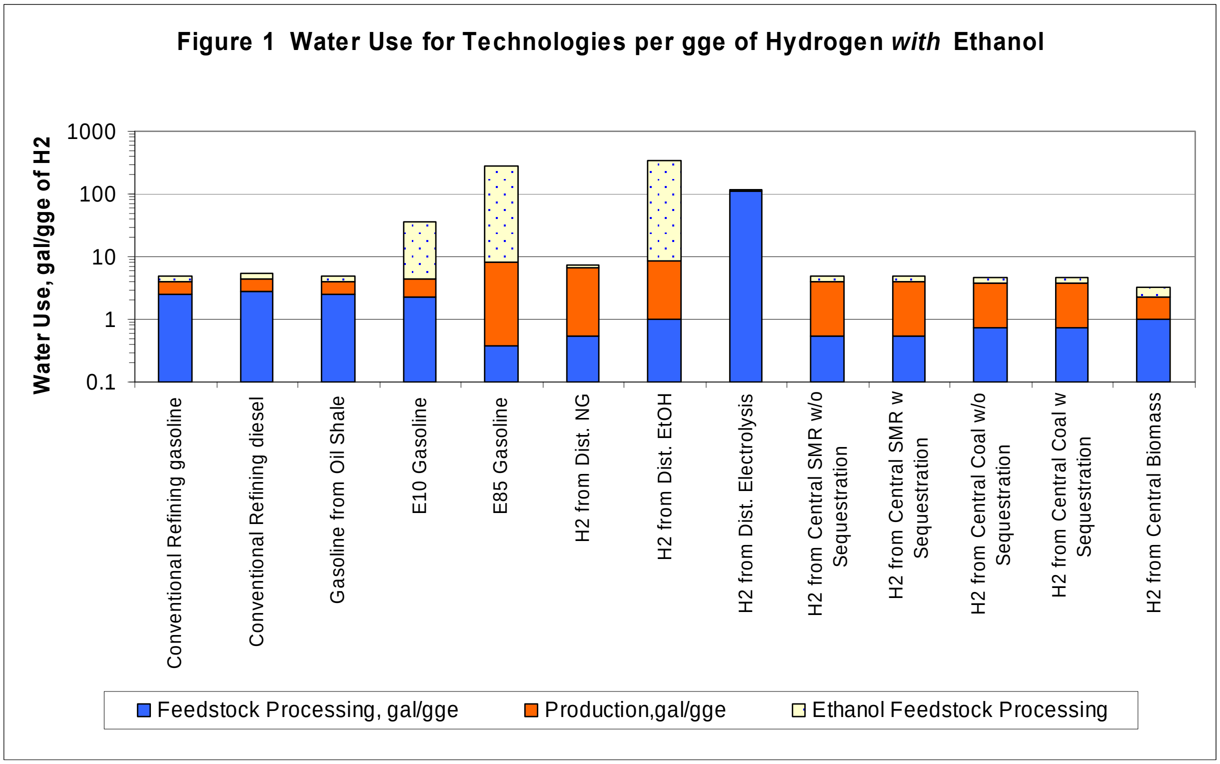


Figure 1: Water consumption for various hydrogen production pathways.

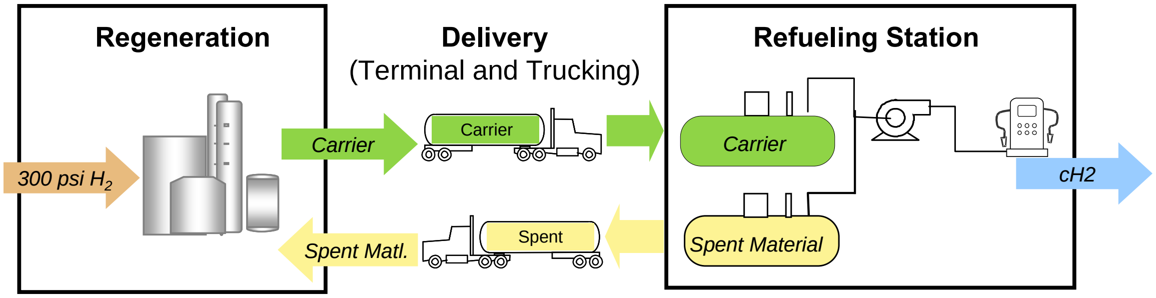
Carriers for Hydrogen Delivery

TIAX and Air Products

Low cost and energy efficient delivery of hydrogen from central production facilities is an essential enabler for widespread use of hydrogen fuel cell vehicles. There are a number of options for hydrogen delivery including gaseous hydrogen delivery in pipelines or high pressure tube trailers, liquefaction and transport of liquid hydrogen in cryogenic trucks, and the use of novel carriers such as metal hydrides, absorbents, or chemical hydrides. Until this year, little work had been done to understand the potential application of novel carriers for hydrogen delivery, and little research had been devoted to this application of novel hydrogen carriers.

As part of a larger project on hydrogen delivery analysis, TIAX initiated a systematic analysis of novel carrier material classes (metal hydrides, absorbents, chemical carriers) and delivery modes (truck, pipeline) to understand the key variables and parameters that dictate the costs and energy efficiencies of carrier delivery pathways where the hydrogen is released at the refueling site for dispensing to the vehicle. This effort included modifying and expanding the H2A Delivery models to accommodate analysis of carrier delivery pathways. Although this effort is not yet completed, the initial results and analysis tools are already proving valuable to begin guiding the strategy for the potential use of carriers for hydrogen delivery.

In a separate effort, under a collaborative agreement with DOE, Air Products has been researching a novel liquid hydrocarbon carrier that would be hydrogenated at a large central plant, delivered by truck or pipeline, and dehydrogenated either at the refueling site or potentially on-board the vehicle. This project made significant progress this year on the dehydrogenation operation, and the initial cost analysis of this system is promising.



Example carrier pathway

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H2A Hydrogen Delivery Models

Nexant, TIAX, GTI, Chevron, Argonne National Laboratory, National Renewable Energy Laboratory and Pacific Northwest National Laboratory

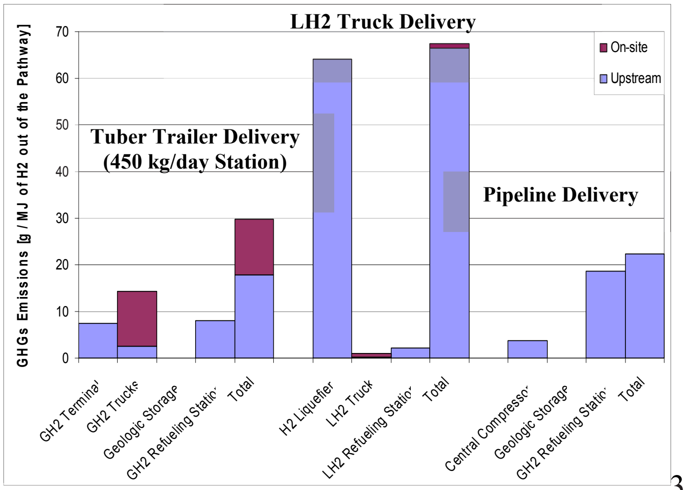
Low cost and energy efficient delivery of hydrogen from central production facilities is an essential enabler for widespread use of hydrogen fuel cell vehicles. There are a number of options for hydrogen delivery, including gaseous hydrogen delivery in pipelines or high pressure tube trailers, liquefaction and transport of liquid hydrogen in cryogenic trucks, and the use of novel carriers such as metal hydrides, absorbents, or chemical hydrides. Full infrastructure costs, energy efficiencies, and greenhouse gas (GHG) emissions are a complex function of the technology and the geographic layout of the infrastructure.

In order to guide the research needed, it is necessary to fully understand the major factors that drive the cost, efficiency, and emissions of hydrogen delivery. A team of researchers from Nexant, GTI, Chevron, TIAX, Argonne National Laboratory, National Renewable Energy Laboratory, and Pacific Northwest National Laboratory, under a cooperative agreement funded by DOE, dramatically improved and expanded our understanding of hydrogen delivery infrastructure needs and technologies and incorporated this into much improved H2A Delivery Models (Version 2).

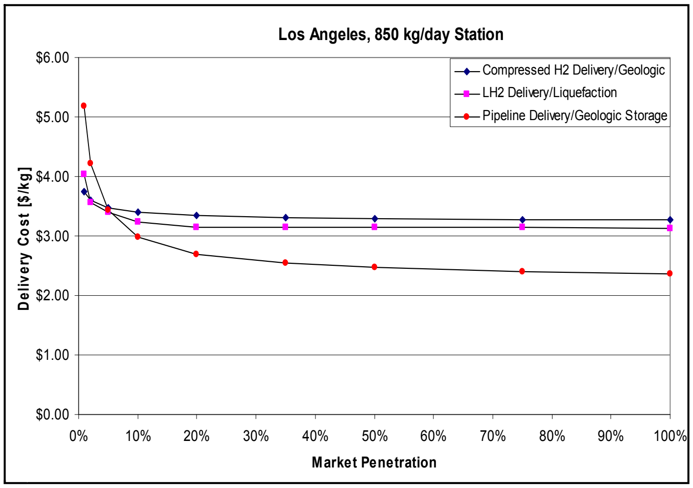
The improvements made to the Models include:

- A detailed analysis of the system supply and demand hourly, daily, and seasonal variations and the optimization of the infrastructure storage needs to handle these variations.
- Improved capital operating cost information for all of the components in the infrastructure.
- The inclusion of Well-to-Vehicle energy efficiencies and GHG emissions.
- The comparability to analyze refueling station sizes from 50 kg/day to 6,000 kg/day (initial demonstration stations to stations 2x current large gasoline stations).

The improved H2A Delivery Models are proving invaluable in the refining of the hydrogen delivery research strategy and the targets for the DOE Hydrogen Delivery Program element.



20% Market Penetration, 100 kg/day Station, 62 miles to City



Distributed Hydrogen Production from Natural Gas through Advanced Reforming

GE Global Research and H2 Gen Innovations Inc.

Advances in distributed hydrogen production from natural gas have been realized through the integration of key subcomponents into one vessel for process intensification and expected reductions in station footprint size. Advances in heat integration have increased the energy efficiency of small-scale hydrogen production.

- GE Global Research pressure tested a "Short Contact Partial Oxidation Reactor." Testing occurred up to 180 psi absolute pressure, varying space velocities and steam to carbon ratios at a production rate of 800 kg/day using a baseline catalyst formulation. A high pressure reformer with water gas shift is being tested at 60 kg/day scale. (Figure 1)

- H2Gen Innovations Inc. manufactured and installed a hydrogen generator capable of generating 565 kg/day. Remote monitoring and operation, reliability, heat recovery and integration, and better than 99.999% hydrogen purity are key features of this new small-scale unit. (Figure 2)

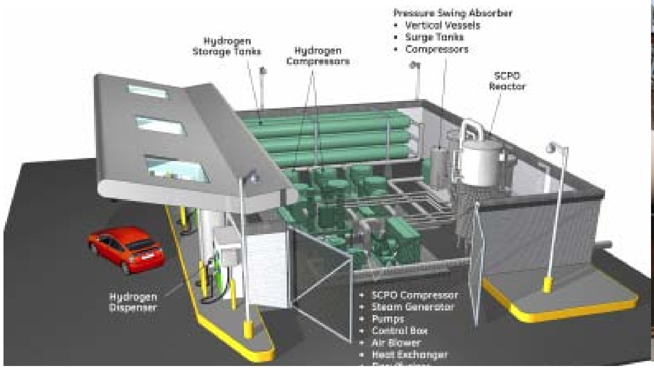


Figure 1: GE Global Research rendering of a production unit integrated into 1,500 kg/day hydrogen refueling station

Figure 2: H2 Gen Innovations 565 kg / day steam methane reformer actual installation

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Distributed Hydrogen Production from Bio-Derived Liquids through Aqueous Phase Reforming

Virent Energy Systems Inc. and Pacific Northwest National Laboratory

One of the main challenges to realizing the environmental benefits of hydrogen energy applications is reducing the greenhouse gas emissions associated with hydrogen production from fossil fuels. Depending on the type of biomass used, an on-site aqueous phase reforming system has been identified that has the potential to produce hydrogen for less than $3.80 per gasoline gallon equivalent by 2012. A pilot plant for hydrogen production from glycerol is in operation, and a plant using sugar is being developed as part of a DOE-funded program.

Several significant milestones were achieved:

- A 10 kg/day pilot plant for hydrogen production from glycerol is in operation and a plant using sugar is under development at Virent Energy Systems in Madison, Wisconsin. Trademarked as “BioForming” this new distributed bio-derived liquids technology for hydrogen production has been reduced to practice.

- Researchers at the Pacific Northwest National Laboratory have doubled hydrogen production from their baseline by improving reactor engineering and conditions of aqueous phase reforming. The improvements are a result of advanced catalysts and incorporation of microtechnology to overcome mass transfer barriers.

Figure 1: Virent Energy Systems – 10 kg/day aqueous phase reforming pilot plant

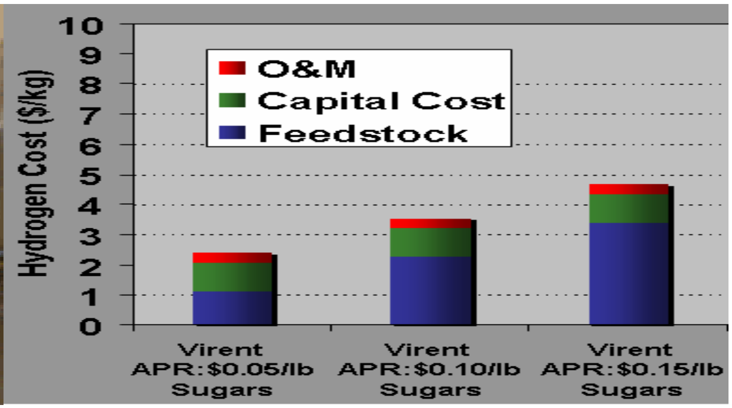

Figure 2: Virent Energy Systems – process economics at sugar costs of $.05-.15/lb

2007 FreedomCAR and Fuel Partnership Highlight
Hydrogen Safety Best Practices Manual

Pacific Northwest National Laboratory and
Los Alamos National Laboratory

Hydrogen has been produced, transported, stored and used for decades in a variety of industrial, aerospace and other settings. A wealth of knowledge related to the safe use and handling of hydrogen exists as a result of this extensive experience.

The online Hydrogen Safety Best Practices Manual is intended to be a resource for people who are working with hydrogen and related systems, especially those less familiar with the properties, hazards, and practices associated with the use of hydrogen. The noted historical experience with hydrogen has been integrated with learnings from the work conducted by the Hydrogen Safety Panel on behalf of the DOE Hydrogen Program to form the basis for content.

A best practice is a technique or methodology that has reliably led to a desired result. Utilizing best practices is a commitment to apply available knowledge and technology to achieve success. For the online manual, best practices are organized under the following eight sections:

- Safety Culture
- Safety Planning
- Consideration for the Design of Facilities and Equipment
- Equipment Maintenance and Integrity
- Hydrogen Storage and Piping Systems
- Development of Operating Procedures
- Communications
- Incident Procedures

The manual includes downloadable references and links to safety event records from the Hydrogen Incident Reporting Tool (www.h2incidents.org) that provides "lessons learned" of relevance to best practices content. The website containing the manual was released for limited access review in September, 2007 to a group of approximately 40 reviewers. A technical team reviewed and took action on all feedback comments followed by public release of the Manual in December, 2007.

Figure 1: Online Hydrogen Safety Best Practices Manual sample page

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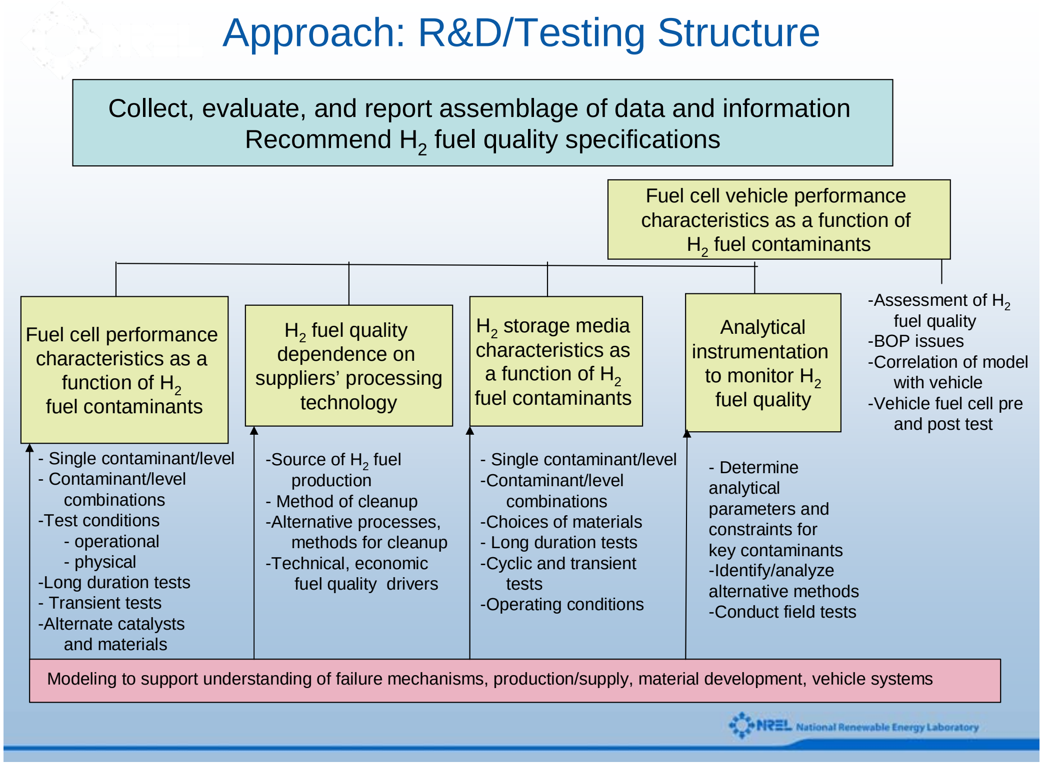
Hydrogen Fuel Quality – PEMFC Road Vehicles

National Renewable Energy Laboratory

Hydrogen fuel quality must be quantified at the vehicle-station interface and must consider how the presence of small amounts of contaminants affect the performance and durability of fuel cells and balance of plant, material compatibility of on-board and stationary hydrogen storage systems, and the operation and maintenance of hydrogen production, purification, and delivery systems.

Fuel quality guidelines based on available data and information have been issued by the International Organization for Standardization (ISO TS14687-2) and the Society of Automotive Engineers (SAE J2719). Before these guidelines can become standards, a comprehensive, structured R&D and testing effort is needed to determine the effects – especially degradation mechanisms – of various contaminants on fuel cell electrodes and membranes. Implications of fuel quality on the complexity, performance, and durability of fuel cell systems and upstream infrastructure, as well as on the cost of fuel, must be understood so that critical trade-offs can be assessed.

To help develop a consensus testing and R&D effort under ISO and SAE, DOE formed a team of hydrogen and fuel cell experts from industry, universities, and national laboratories in the U.S. and Canada. The team is implementing a comprehensive approach to R&D and testing to obtain data required to modify the guidelines into standards over the next three years. That approach is shown in Figure 1 below.



Approach: R&D/Testing Structure

Collect, evaluate, and report assemblage of data and information
Recommend H_2 fuel quality specifications

Fuel cell vehicle performance characteristics as a function of H_2 fuel contaminants

- Assessment of H_2 fuel quality
- BOP issues
- Correlation of model with vehicle
- Vehicle fuel cell pre and post test

Fuel cell performance characteristics as a function of H_2 fuel contaminants

- Single contaminant/level
- Contaminant/level combinations
- Test conditions
  - operational
  - physical
- Long duration tests
- Transient tests
- Alternate catalysts and materials

H_2 fuel quality dependence on suppliers' processing technology

- Source of H_2 fuel production
- Method of cleanup
- Alternative processes, methods for cleanup
- Technical, economic fuel quality drivers

H_2 storage media characteristics as a function of H_2 fuel contaminants

- Single contaminant/level
- Contaminant/level combinations
- Choices of materials
- Long duration tests
- Cyclic and transient tests
- Operating conditions

Analytical instrumentation to monitor H_2 fuel quality

- Determine analytical parameters and constraints for key contaminants
- Identify/analyze alternative methods
- Conduct field tests

Modeling to support understanding of failure mechanisms, production/supply, material development, vehicle systems

NREL National Renewable Energy Laboratory

Figure 1: Hydrogen Quality R&D Approach

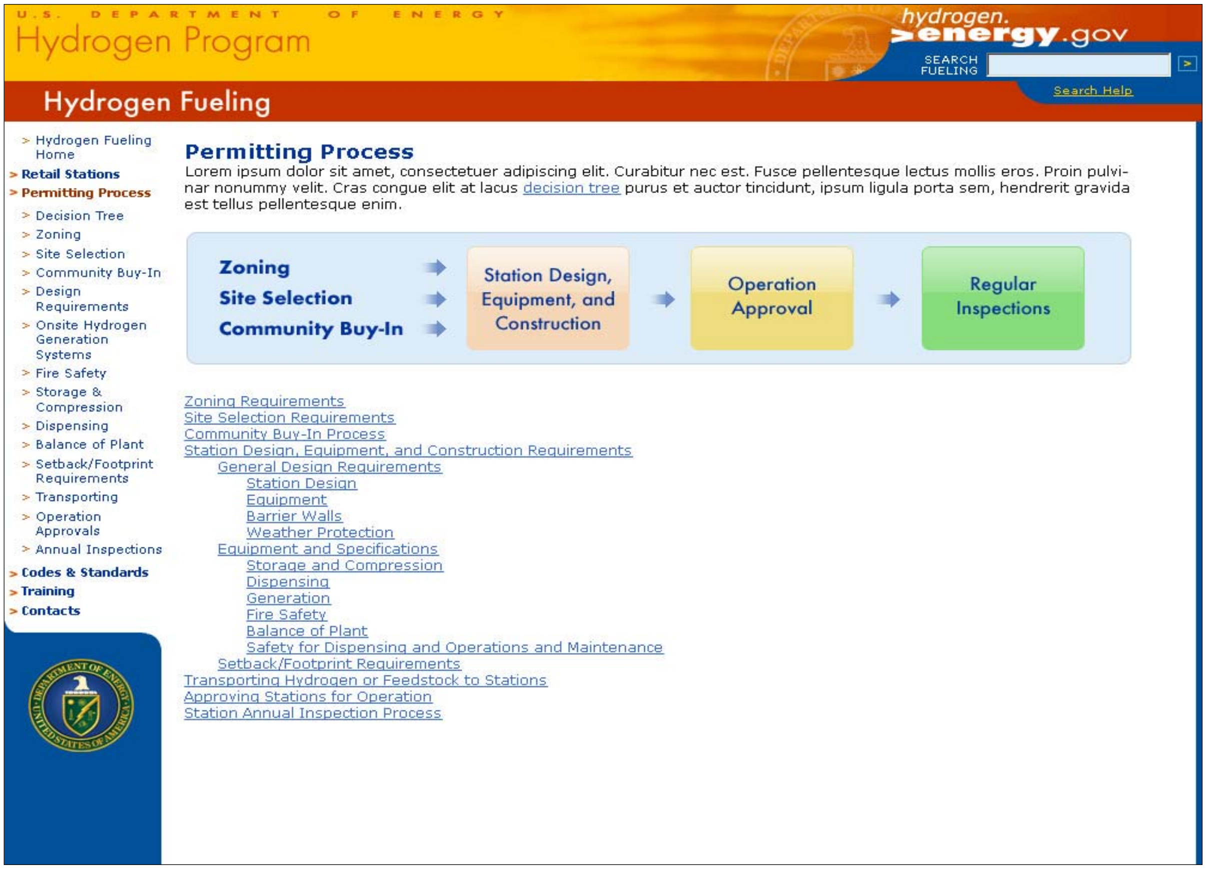
2007 FreedomCAR and Fuel Partnership Highlight

Hydrogen Fueling Station Permitting Compendium

National Renewable Energy Laboratory (NREL)

Facilitating the permitting of Hydrogen Fueling Stations (HFS) is a high priority for both the Partnership and the Secretary of Energy's Hydrogen Technical Advisory Panel. NREL conducted national and regional workshops with HFS developers and code officials and launched the development of a web-based information compendium to meet the needs and recommendations of the developers and code officials at the workshops. The compendium identifies the applicable codes and standards to permit a HFS and includes a database containing the specific permitting requirements from those codes and standards. The compendium also contains fact sheets on hydrogen technologies and key HFS equipment, a network chart of code officials who have previously permitted HFS, process flowcharts for permitting HFS that will help both developers and code officials navigate the permitting process, and best practices for the application of codes and standards for advanced HFS technologies and configurations. The compendium provides a one-stop information source that will facilitate the permitting of HFS and help make the permitting process more timely and cost-effective.

A sample page from the compendium is shown in Figure 1 below.



Permitting Process

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- Zoning Requirements
- Site Selection Requirements
- Community Buy-In Process
- Station Design, Equipment, and Construction Requirements
  - General Design Requirements
    - Station Design
    - Equipment
    - Barrier Walls
    - Weather Protection
  - Equipment and Specifications
    - Storage and Compression
    - Dispensing
    - Generation
    - Fire Safety
    - Balance of Plant
    - Safety for Dispensing and Operations and Maintenance
  - Setback/Footprint Requirements
- Transporting Hydrogen or Feedstock to Stations
- Approving Stations for Operation
- Station Annual Inspection Process

Figure 1: Hydrogen Fueling Station Permitting Compendium sample page

2007 FreedomCAR and Fuel Partnership Highlight

DOE Hydrogen Learning Demonstration

Government-Industry Partnership

Successful commercialization of any new technology requires real-world testing and data collection. The data collected through this 50-50 industry cost-shared project will be used to evaluate progress toward technical targets for fuel cell durability and range, efficiency and hydrogen cost, and it will also provide important lessons learned about community acceptance, safety, permitting, and codes and standards issues.

The Demonstration Project, started in 2004, has completed three full years of vehicle and refueling station operation. The four teams in the project; GM/Shell, Chevron/Hyundai-Kia, Ford/BP and Chrysler (DaimlerChrysler)/BP, have been operating vehicles in Southern and Northern California, Michigan, Florida and Washington, D.C. In addition, vehicles will also be operated in the New York area. Data from 77 vehicles now in fleet operation and 14 project refueling stations in use has been analyzed, and results include 149,000 individual vehicle trips covering 821,000 miles traveled and 30,000 kg H2 produced or dispensed.

On-road fuel cell durability has been determined by analyzing voltage degradation of the fuel cell, resulting in an individual team-average high of over 1,600 hours with the 4-team average over 800 hours. Fuel cell system efficiency at ¼-power has also been determined and compared to the DOE target of 60%; system efficiency results from the four teams ranged between 52% and 58%.

Generation 2 vehicles will be introduced into the program and will include more advanced fuel cells and 10,000 psi storage technology. The generation 2 vehicles will help meet the 2009 targets of 2,000 hour fuel cell durability and 250 mile range.

A variety of hydrogen refueling pathways have been incorporated into the project, including delivered hydrogen, hydrogen produced from natural gas and hydrogen produced by electrolysis using grid and solar-based electricity. The hydrogen production target to be met in 2009 in the Learning Demonstration is $3/gge.

Learning demonstration participants (clockwise from upper left): BP, Ford Edge, Chrysler-Daimler B Class, Shell, Chevron & Hyundai-Kia, GM Equinox