One Million PHEVs by 2015:
Challenges for Advanced Battery Technology

US Embassy Energy & Environment Speaker Series
Helsinki Univ. of Technology

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NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

"One million PHEVs by 2015"

Campaign pledge by presidential candidate Obama in August, 2008:

- $7000 rebate to consumers per PHEV
- Keep PHEV manufacturing in US
- 4% increases in vehicle efficiency each year

:

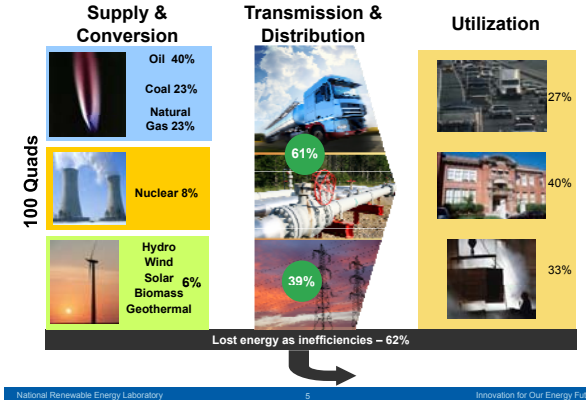
- Invest $150B in clean energy over 10 years
- 10% renewable electricity by 2012
- 25% renewable electricity by 2025
- Economy-wide cap-and-trade program to reduce CO_2 emissions 80% by 2050

U.S. Dept of Energy National Labs

NREL is the only DOE National Laboratory dedicated to renewable and energy efficient technologies

NREL is operated for DOE by the Alliance for Sustainable Energy (Midwest Research Institute and Battelle)

The United State's Energy System



A Profound Transformation is Required

Today's Energy System	Imperatives for Transformation	Sustainable Energy System
• Dependent on foreign sources • Subject to price volatility • Increasingly unreliable • 2/3 of source energy is lost • Produces 25% of the world's carbon emissions	DEFINE THE END STATES REDUCE NEW TECHNOLOGY RISK ACCELERATE ADOPTION	• Carbon neutral • Efficient • Diverse supply options • Minimal impact on resources • Creates sustainable jobs • Accessible, affordable and secure

NREL Energy Efficiency and Renewable Energy Technology Development Programs

NREL R&D Portfolio

Energy Efficiency
- Vehicle Technologies
- Building Technologies
- Industrial Technologies

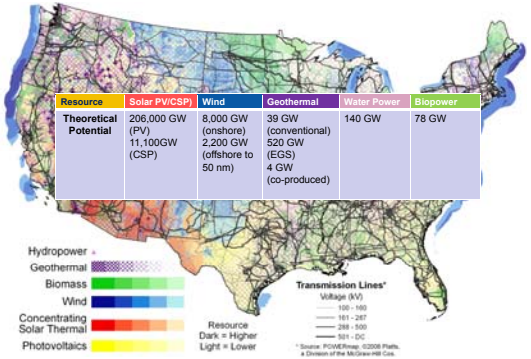
Renewable Resources
- Wind
- Solar
- Biomass
- Geothermal

Energy Delivery and Storage
- Electricity Transmission and Distribution
- Alternative Fuels
- H2 Delivery and Storage

Foundational Science and Advanced Analytics

NREL takes an integrated approach to developing clean energy solutions.

Informing Policy Makers: U.S. Renewable Resource Mapping



Resource	Solar PV/CSP)	Wind	Geothermal	Water Power	Biopower
Theoretical Potential	206,000 GW (PV) 11,100GW (CSP)	8,000 GW (onshore) 2,200 GW (offshore to 50 nm)	39 GW (conventional) 520 GW (EGS) 4 GW (co-produced)	140 GW	78 GW

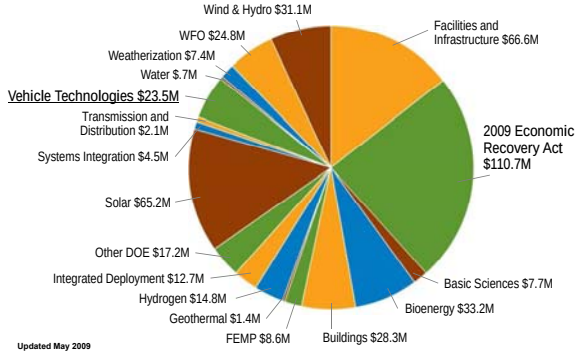
Three National Centers at NREL

National Center for Photovoltaics

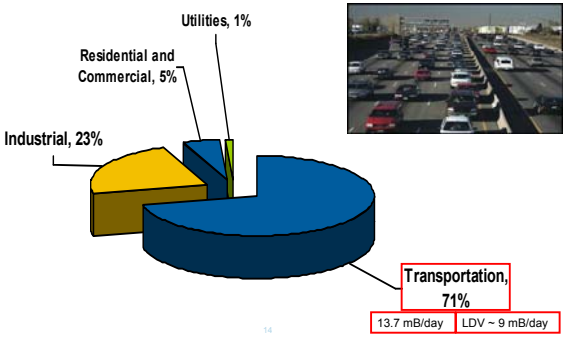
National Bioenergy Center

National Wind Technology Center

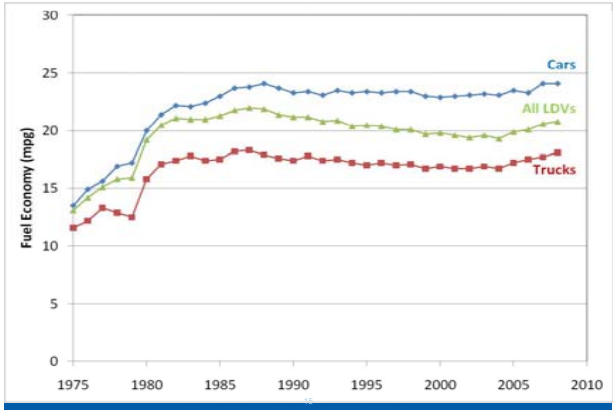
NREL Fiscal Year 2009 Program Portfolio
Estimated $460.5 Million



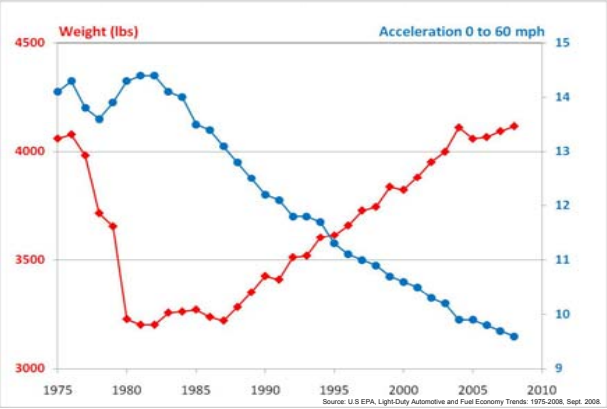
Oil Use
Globally ~86 MB/day (2007)
United States 19.4 MB/day (2008)



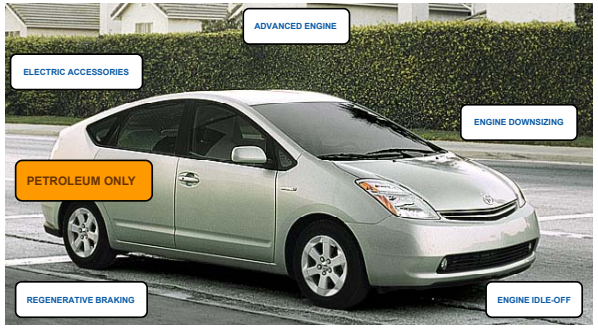
What's Happened with Fuel Economy?



Heavier and Quicker!

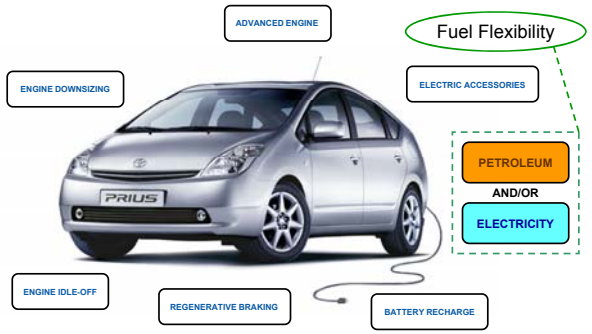


A "Full" Hybrid



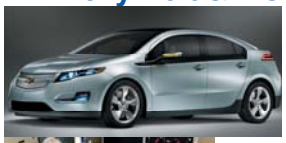
76hp gasoline engine, 67hp electric motor, 1.5kWh battery

A Plug-In Hybrid (PHEV)



76hp gasoline engine, 67hp electric motor, 9.0kWh battery (30mi)

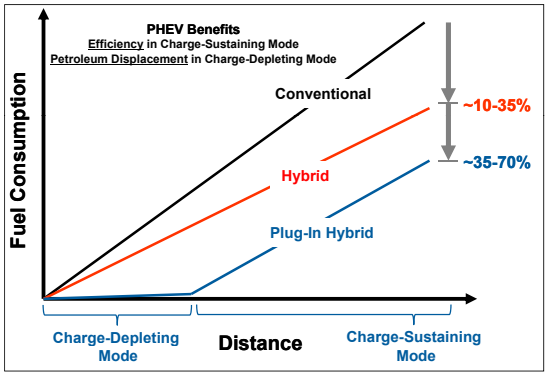
Some PHEVs coming soon… Chevy Volt & Fisker Karma



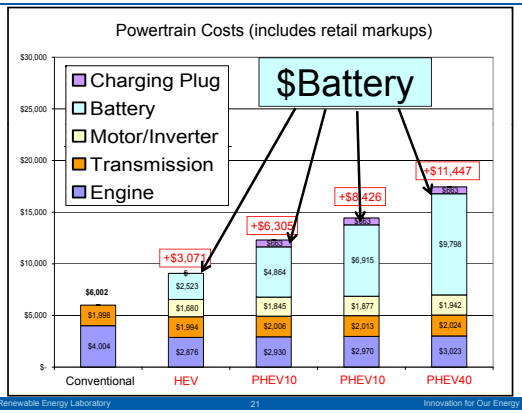
allamericanhybrid.com

www.themotorreport.com.au

PHEV Fuel Savings Tied to Usage Pattern



Powertrain Costs Comparison – Long Term



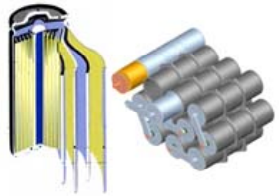
"One million PHEVs by 2015"

Following up on August 2008 campaign pledge:

- 4% increases in vehicle efficiency each year
  → 5% annual increase to 35.5 mpg (6.6 L/100km) in 2016
- $7000 rebate to consumers per PHEV
  → $2500-$7500 for 4-16 kWh battery capacity (PHEV or EV)

- Keep PHEV manufacturing in US
  → 2009 Economic Recovery Act
  $2 Billion for advanced battery manufacturing
  $400 Million for transportation electrification

U.S. Department of Energy Battery Research & Development



United States Department of Energy Energy Storage R&D

David Howell
Manager, Energy Storage R&D
Office of Vehicle Technologies
U.S. Department of Energy

CHARTER

- ❑ Advance the development of batteries and other electrochemical energy storage devices to enable a large market penetration of hybrid and electric vehicles.

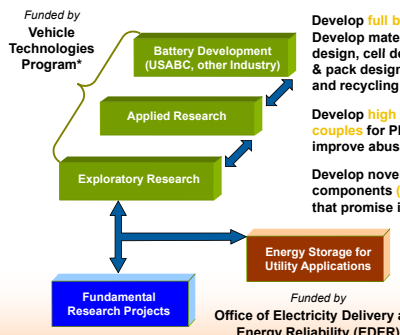
TARGET APPLICATIONS

- ❑ Power-Assist Hybrid Electric Vehicles (HEVs, FCVs)
- ❑ Plug-in Hybrid Electric Vehicles (PHEVs, FCVs)
- ❑ Battery Electric Vehicles (EVs)

GOALS

- ❑ **2010 FreedomCAR Goal (Conventional HEVs):**
  - Develop a 25 kW Power-Assist HEV battery that costs $500.
- ❑ **2014 DOE PHEV Battery Goal:**
  - Develop a PHEV battery that enables a 40 mile all-electric range and costs $3,400.

DOE Energy Storage R&D Program



Develop full battery systems with industry. Develop material specifications, electrode design, cell design & fabrication, module & pack design/fab, testing, cost modeling, and recycling studies.

Develop high energy electrochemical couples for PHEV-40 batteries and improve abuse tolerance.

Develop novel materials for battery components (cathode, anode, electrolyte) that promise increased power and energy.

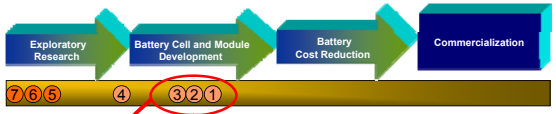
* David Howell - Manager, Energy Storage R&D
Office of Vehicle Technologies, U.S. Department of Energy

PHEV Technology Development Roadmap

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

Several lithium battery chemistries exist, including:

1. Graphite/Nickelate
2. Graphite/Iron Phosphate
3. Graphite/Manganese Spinel
4. Li-Titanate/High Voltage Nickelate
5. Li alloy/High Voltage Positive
6. Li/Sulfur
7. Li Metal/Li-ion Polymer



Lithium-ion batteries previously developed for HEV applications are in a more advanced development stage for PHEVs

PHEV Battery Targets and Challenges

Battery Attribute	Current Status	Goals	
		2012	2014
Available Energy	3.4 kWh	3.4 kWh (10 mile)	11.6 kWh (40 mile)
Cost	$1,000+/kWh	$500/kWh	$300/kWh
Cycle life (EV Cycles)	1,000+	5,000	3000-5000
Cycle life (HEV Cycles)	300,000	300,000	200,00-300,000
Calendar Life	3+ years	10+ years	10+ years
System Weight	80 kg	60 kg	120 kg
System Volume	70 liters	40 liters	80 liters

Key challenges:

- ❑ Reducing cost
- ❑ Extending life (while operating in 2 discharge modes)
- ❑ Weight and volume are additional challenges for the PHEV40

PHEV Battery Development Contracts

Pre-competitive development contracts awarded & managed by U.S. Advanced Battery Consortium (DOE + GM/Ford/Chrysler)

A123	Develop batteries using nanophase iron-phosphate.
Johnson Controls / SAFT	Develop batteries using a high energy nickelate/layered electrode.
cpi / LG Chem	Develop batteries using Manganese-spinel based chemistry.
EnerDel	Develop cells using nano-phase lithium titanate anode and a high voltage cathode.
3M	Develop advanced high-energy cathode materials for PHEV applications.
CELGARD	Develop low-cost separators with high temperature melt integrity.
ENTEK	Develop low-cost separators with high temperature melt integrity.

Total value of contracts (including industry cost-share): **$41 million**

Applied Battery Research

A multi-lab effort to develop high energy electrochemical couples for PHEV-40 batteries and abuse tolerance improvements.

Argonne, Sandia National Laboratories, INL, Berkeley Lab, Brookhaven, NREL, ARL

Activity Focus

- FY2002-2008 focused on high power battery issues such as enhanced battery life, abuse tolerance, low temperature operation, and lower cost materials.
- FY2009 focus on PHEV-40 electrochemistry development (high energy couples) and abuse tolerance improvements.

Exploratory Research

Research to Develop Novel Materials for Lithium Batteries

Activity Focus

Develop advanced cathodes, anodes, electrolytes.

Develop and apply advanced electrochemical models.

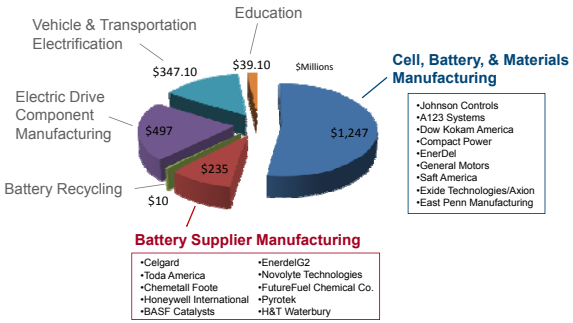
Employ advanced diagnostic tools to investigate material failure mechanisms.

Current Participants

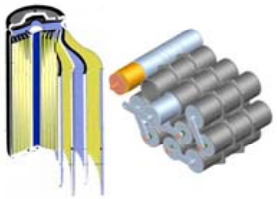
- National Laboratories
  - Lawrence Berkeley National Laboratory
  - Argonne National Laboratory
  - Brookhaven National Laboratory
  - National Renewable Energy Laboratory
  - Oak Ridge National laboratory
- Universities
  - Brigham Young University
  - Massachusetts Institute of Technology
  - State University of New York, Binghamton
  - State University of New York, Stony Brook
  - University of California, Berkeley
  - University of Michigan
  - University of Pittsburgh
  - University of Texas
  - University of Utah

2009 Economic Recovery Act

$2.4 Billion appropriation to enable domestic battery manufacturing, including electric drivetrain components & transportation electrification.



NREL Battery Research & Development



NREL believes multi-disciplinary R&D is needed to make electric-drive vehicle batteries competitive with conventional technologies

Materials

1) Develop low-cost, safe materials.

2) Optimize cell designs.

3) Size battery appropriately so as not to overstress/over-cycle, but with minimum cost and mass
   1) Accelerated calendar & cycle life testing
   2) Accurate life and DOD predictive models

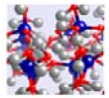
4) Minimize time spent at high temperatures
   1) Standby thermal management (vehicle parked!)
   2) Active thermal management (vehicle driving)

5) Onboard estimation, control & diagnostics

Systems

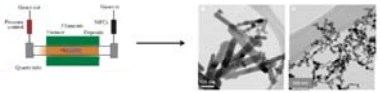
NREL Research for Safe, Low Cost, Long Life Batteries and Systems

1. Materials
2. Components
   - Computer-Aided Engineering
   - Performance & Life
   - Safety
3. Systems
   - Life-Predictive Modeling
   - Thermal Management Design
     - While Driving
     - While Parked

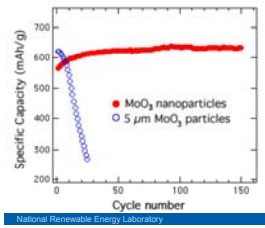


Metal Oxide Nanoparticle Anode Materials

- Synthesis by hot-wire chemical vapor deposition

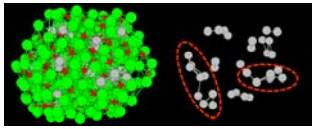


- Stable cycling enabled by nano-sized particles, as observed in experiment



- First-principles molecular dynamics simulations help explain the formation and decomposition of metal nanoclusters during cycling

$Li_6MoO_3 \leftrightarrow 3Li_2O + Mo$



Metal Oxide Nanoparticle Anode Materials

Half Cell

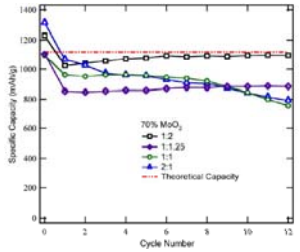
Optimized MoO_3 electrode: **1050 mAh/g**

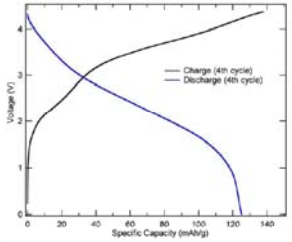
(Commercial graphite: 370 mAh/g)

Full Cell

With Li-rich NMC cathode from Argonne National Lab: **300 Wh/kg**

(Present technology: 150-200 Wh/kg)



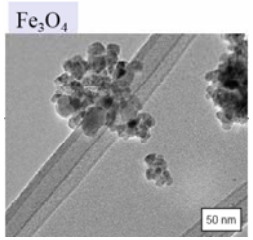


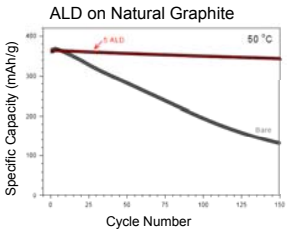
Challenges: First cycle capacity loss; voltage hysteresis

Other Recent Material Research Achievements

Fe_3O_4 nanoparticles
- Low cost
- Hydrothermal synthesis
- Achieved 1050 mAh/g

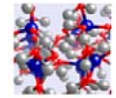
Atomic Layer Deposition Coating
- Slows down electrode surface reactions that cause degradation
- Improves cyclability of both cathode and anodes





NREL Research for Safe, Low Cost, Long Life Batteries and Systems

1. Materials
2. Components
   - Computer-Aided Engineering
   - Performance & Life
   - Safety
3. Systems
   - Life-Predictive Modeling
   - Thermal Management Design
     - While Driving
     - While Parked

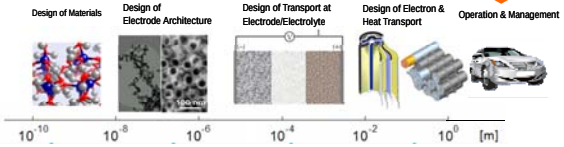


Multi-Scale Physics in Li-Ion Battery

Requirements & Resolutions

"Requirements" are usually defined in a macroscale domain and terms

Performance
Life
Cost
Safety



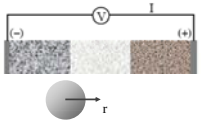
- Wide range of length and time scale physics
- Design improvements required at different scales
- Need for better understanding of interaction among different scale physics

Electrode-Scale Performance Model

Charge Transfer Kinetics at Reaction Sites

$$j^{Li} = a_s i_o \left\{ \exp\left[\frac{\alpha_a F}{RT}\eta\right] - \exp\left[-\frac{\alpha_c F}{RT}\eta\right] \right\}$$

$$i_o = k(c_e)^{\alpha_a}(c_{s,max} - c_{s,s})^{\alpha_a}(c_{s,s})^{\alpha_c} \quad \eta = (\phi_s - \phi_e) - U$$



Species Conservation

$$\frac{\partial c_s}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c_s}{\partial r}\right)$$

$$\frac{\partial(\varepsilon_e c_e)}{\partial t} = \nabla \cdot \left(D_e^{eff}\nabla c_e\right) + \frac{1 - t_+^o}{F} j^{Li} - \frac{i_e}{F} \cdot \nabla t_+^o$$

Charge Conservation

$$\nabla \cdot \left(\sigma^{eff}\nabla \phi_s\right) - j^{Li} = 0$$

$$\nabla \cdot \left(\kappa^{eff}\nabla \phi_e\right) + \nabla \cdot \left(\kappa_D^{eff}\nabla \ln c_e\right) + j^{Li} = 0$$

- Pioneered by Newman group (*Doyle, Fuller, and Newman 1993*)
- Captures *lithium diffusion dynamics* and *charge transfer kinetics*
- Predicts *current/voltage response* of a battery
- Provides design guide for thermodynamics, kinetics, and transport across electrodes

Energy Conservation

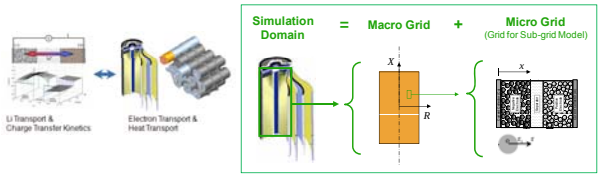
$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (k\nabla T) + q'''$$

$$q''' = j^{Li}\left(\phi_s - \phi_e - U + T\frac{\partial U}{\partial T}\right) + \sigma^{eff}\nabla\phi_s \cdot \nabla\phi_s + \kappa^{eff}\nabla\phi_e \cdot \nabla\phi_e + \kappa_D^{eff}\nabla \ln c_e \cdot \nabla\phi_e$$

- Difficult to resolve *heat* and *electron current* transport

Computer-Aided Design of Large-Format Li-ion Cells

Multi-Scale Multi-Dimensional (MSMD) Model



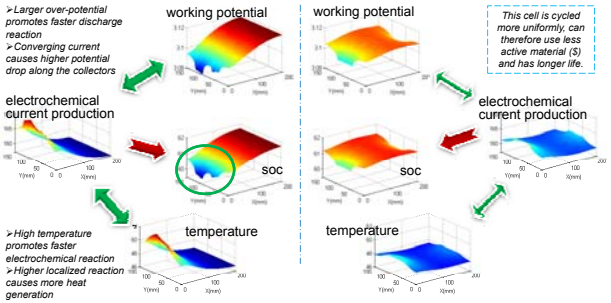
- Captures macroscopic electron/heat transports, electrode scale Li diffusion dynamics/charge transfer kinetics in separate domains
- Physically couple the solution variables defined in each domain using multi-scale modeling schemes
- Runs in tolerable calculation time, practical for battery and system engineering design

Multi-Physics Interaction

Comparison of two 40 Ah flat cell designs
2 min 5C discharge

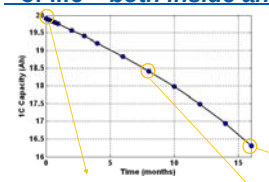
This cell is cycled more uniformly, can therefore use less active material ($) and has longer life.

➢Larger over-potential promotes faster discharge reaction
➢Converging current causes higher potential drop along the collectors



➢High temperature promotes faster electrochemical reaction
➢Higher localized reaction causes more heat generation

Model predicts cell performance at various stages of life – *both inside and outside the battery*

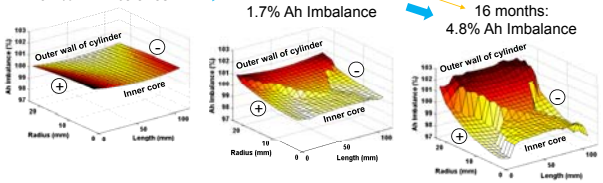


- Early in life, inner core and terminal areas are cycled the most
- Later in life, those same areas are most degraded and are cycled least

0 months:
0.7% Ah Imbalance

8 months:
1.7% Ah Imbalance

16 months:
4.8% Ah Imbalance



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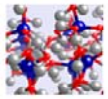
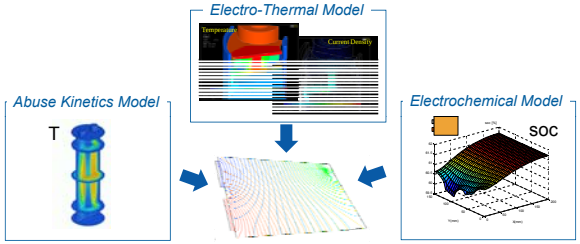


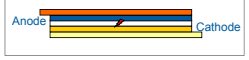
Multi-Physics Internal Short Circuit Model



Internal Short Model Study

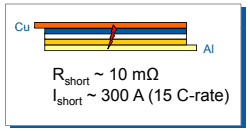
Case A:
Short between Cu and Al foils

Case B:
Short between Anode and Cathode



Case A: Short Between Al & Cu Foils

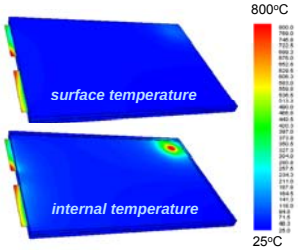
- Possible causes:
  - ✓ metal debris penetration through electrode & separator layers
  - ✓ contact between outermost bare Al foil and negative-bias can
- 20-Ah cell, 1 mm x 1 mm shorted area



R_{short} ~ 10 mΩ
I_{short} ~ 300 A (15 C-rate)

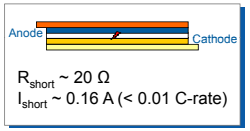
- Joule heat release is localized at converging current near short
- Localized temperature rise is observed.
- Temperature of Al tab may reach its melting temperature (~600°C)

Temperature @10 sec after short



Case B: Short Between Cathode and Anode

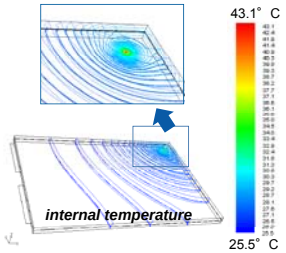
- Possible causes:
  - ✓ separator puncture or wearout
- 20-Ah cell, 1 mm x 1 mm shorted area



R_{short} ~ 20 Ω
I_{short} ~ 0.16 A (< 0.01 C-rate)

- Short current must pass through resistive electrode layers
- Large potential drop occurs across positive electrode
- Simple separator puncture not likely to lead to immediate thermal runaway

Temperatures at 20 min after Short



Case B: Short Between Cathode and Anode

Impact of Separator Structural Integrity

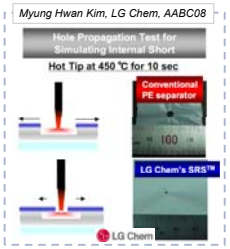
Separator Hole Propagation
1 mm x 1 mm → 3 cm x3 cm

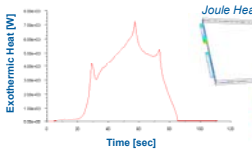
R_{short} ~ 20 Ω
I_{short} ~ 0.16 A (< 0.01 C-rate)

R_{short} ~ 0.03 Ω
I_{short} ~ 100 A (5 C)

3cm x 3cm Separator Hole

Myung Hwan Kim, LG Chem, AABC08

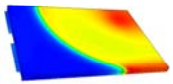




Joule Heat @ cathode layer

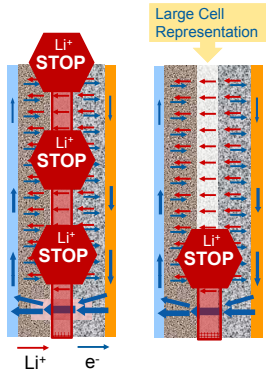
Joule Heat @ foils

Temperature at 1min after short



Shut-Down Separator

Safety devices for small cells not always adequate for large systems

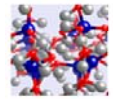


- Thermally triggered
- Block the ion current in circuit

Difficult to apply in
- Large capacity system
- High voltage system

NREL Research for Safe, Low Cost, Long Life Batteries and Systems

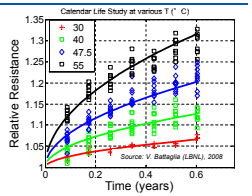
1. Materials
2. Components
   - Computer-Aided Engineering
   - Performance & Life
   - Safety
3. Systems
   - Life-Predictive Modeling
   - Thermal Management Design
     - While Driving
     - While Parked



How can we predict battery life?

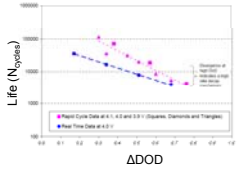
Accelerated storage tests

- Relatively well established & understood
- Mechanism: Chemical rxns → SEI growth
- Model:
  - Typical $t^{1/2}$ time dependency
  - Arrhenius relation describes T dependency



Accelerated cycling tests

- Poorly understood
- Mechanism: Mechanical stress & fracture
- Model:
  - Typical t or N dependency
  - Often correlated log(# cycles) with ΔDOD

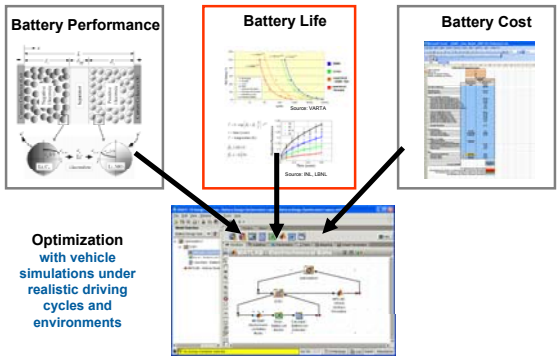


Real-world cycling & storage

- Poorly understood

PHEV Battery Design Optimization

Design/size PHEV batteries to meet USABC technical goals/requirements at minimum cost.



Optimization with vehicle simulations under realistic driving cycles and environments

Life Modeling Approach

NCA dataset fit with empirical, yet physically justifiable formulas

*K. Smith, T. Markel, A. Pesaran, "*PHEV Battery Trade-off Study and Standby Thermal Control,*" 26th International Battery Seminar & Exhibit, Fort Lauderdale, FL, March, 2009.

Calendar fade
- SEI growth (partially suppressed by cycling)
- Loss of cyclable lithium
- $a_1(\Delta DOD, T, V)$

Cycling fade
- active material structure degradation and mechanical fracture
- $a_2(\Delta DOD, T, V)$

Resistance Growth

$$R = a_1 t^{1/2} + a_2 N$$

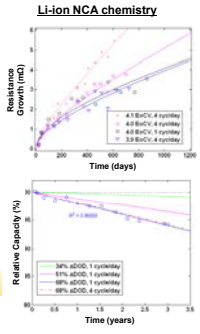
Relative Capacity

$$Q = \min(Q_{Li}, Q_{active})$$

$$Q_{Li} = d_0 + d_1 \times (a_1 t^{1/2}) \qquad Q_{active} = e_0 + e_1 \times (a_2 N)$$

Predictive model that considers effects of real-world storage and cycling scenarios

Li-ion NCA chemistry



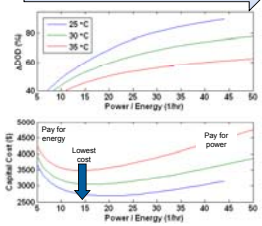
Data: John C. Hall, IECEC, 2006.

Battery life model used to understand how to size and use PHEV batteries for low cost and long life.

Impact of requirements on battery size: Useable ΔDOD and cost

PHEV10: Assumed the battery has to last 10 years at various temperatures, with 3.4 kWh, 50 kW useable at end of life

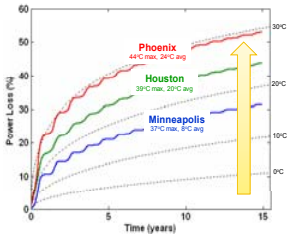
Higher P/E increases useable ΔDOD



Reducing temperature exposure from 35° C to 25° reduces PHEV10 battery cost by $1000.

Impact of climate on power fade

Calendar fade model with Typical Meteorological Year (TMY) climate dataset
Assumed battery temperature = ambient



Some Li-ion technology must be sized with significant excess power to last 15 years.

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3. Systems
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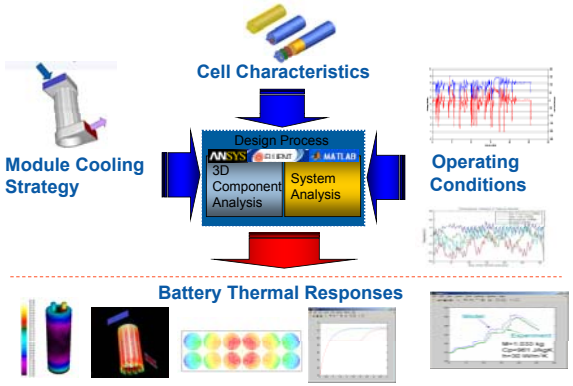
   - Thermal Management Design
     - While Driving
     - While Parked

Battery Thermal Modeling at NREL



Energy Storage Thermal Characterization Laboratory

Unique, large-size isothermal conduction calorimeters

Battery cyclers
- ABC-150 bi-directional power supply (120 kW, 8-440V, 500A)
- ABC-1000 Power conditioning unit (120 kW, 0-120 V,1000 A)
- Six Bitrode battery testers (0-12kW, 0-72V, 500A)
- Arbin battery tester (6 kW, 50 V, 120A)

Environmental chambers and isothermal baths

Infrared thermal imaging equipment

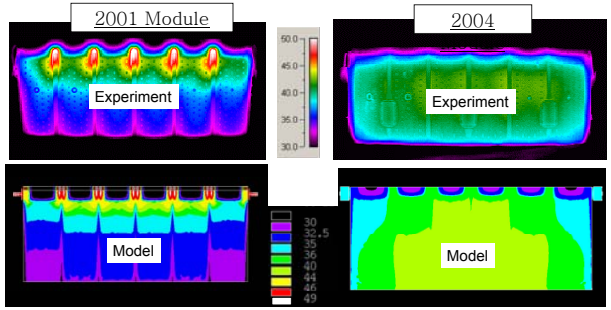
Electrochemical Impedance Spectroscopy (EIS) system

Differential Scanning Calorimeter

Accelerating Rate Calorimeter

Thermal Imaging Experiments Quantify Temperature Uniformity & Validate Models

Response of Toyota Prius module at the end of to 100A Constant Current Discharge (3 min)



The model predicts lower and more uniform temperature distribution in 2004 module.

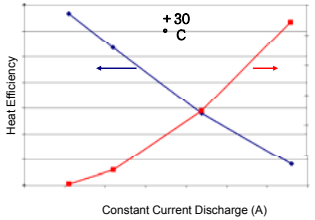
Thermal Characterization: Johnson Controls- Saft PHEV VL22M Cells

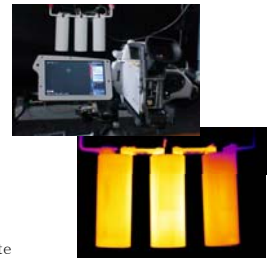
Johnson Controls

SAFT

Calorimetry
- Heat capacity & heat generation & **efficiency**
- Temperatures: -30 to +30°C
- Profiles: CC discharge

Thermal Imaging
- Temperatures: Ambient
- Profiles: 100 Amp Geometric Cycle, 5C Discharge





Heat Efficiency > 90% for currents < 5C rate at 30°C

NREL Custom-Built Calorimeter for Testing Large, Liquid-Cooled HEV & PHEV Modules

Used to measure heat generated from large batteries under real driving profiles and conditions
- Liquid cooled capability
- 40 cm x 40 cm x 60 cm test chamber

Can be used for other automotive components such as power electronics & motors.

Completed System with Heating/Cooling Unit

Flux Gauges of Test Chamber

Test Chamber

Test Chamber in Isothermal Bath

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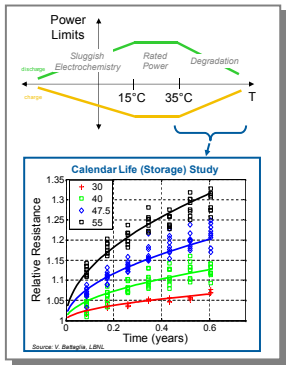
PHEV Battery Standby Thermal Management

Li-ion batteries are "comfortable" at the same temperatures as the human body.

Degradation is accelerated at high temperatures.

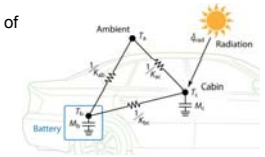
Concept:
- *Actively cool/heat batteries while vehicles are parked.*

Motivation:
- *Extend battery life → reduce cost, downsize*
- *Improve EV driving range*



Approach *Models developed to predict battery temperature fluctuations & degradation with and without standby thermal management.*

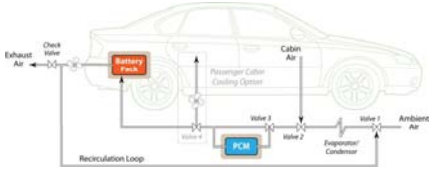
Thermal network model describes impact of ambient temperature & solar radiation on battery temperature & degradation.



Model fit to Golden, CO experiment.

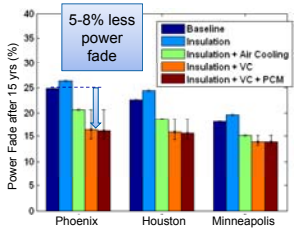
…and validated with separate data from Phoenix, AZ to within 1/2ºC.

5 candidate systems were simulated to evaluate their effectiveness at controlling battery temperature & slowing degradation.

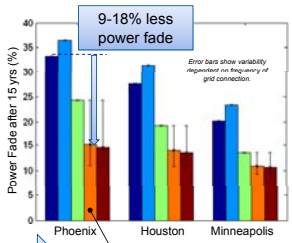


Significance: Li-ion technology can meet 15 year PHEV life goals at lower cost, *today*.

Saft HP-12LC Cell (J. Belt/INL)
• low fade rate, high cost



DOE/TLVT Cell (V. Battaglia/LBL)
• moderate fade rate, lower cost



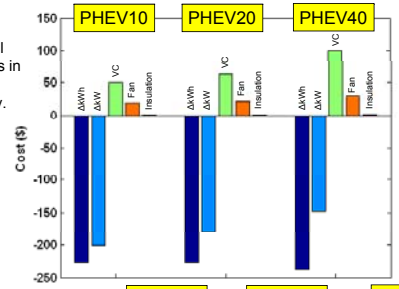
Error bars show variation in outcomes dependent upon how often the consumer plugs-in: Never, Nightly, or Whenever parked.

Cheaper overall solution.

Next slide calculates cost savings for this battery system sized for 15 year life in Phoenix, Arizona…

Savings from downsized battery expected to significantly outweigh cost of added components.

DOE/TLVT cell sized for 15 years in Phoenix, AZ, charged nightly.



Total Savings ($)

	PHEV10	PHEV20	PHEV40
Total savings assuming components represent additional cost	($360)	($320)	($250)
Total savings assuming vapor-compression and fan already exist	($430)	($410)	($390)

New NREL programs to analyze ways to reshape battery markets to overcome first cost

- Battery Ownership Modeling
  - Investigate alternative business models such as Better Place
  - Determine how investment $ used most efficiently
- Battery 2nd Use
  - Reduce initial cost of batteries through reuse (stationary storage)
  - Prevent premature disposal
  - Investigate condition and capability of PHEV & EV "end-of-life" batteries

Summary

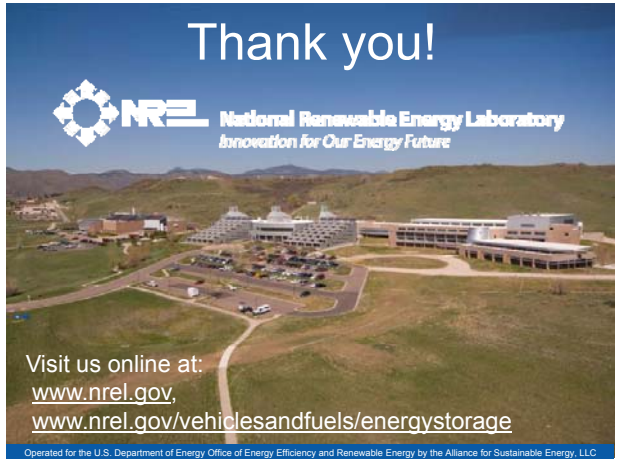
Lithium-ion batteries for HEVs have recently reached commercialization. R&D focus remains on cost reduction and improved abuse tolerance.

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

Li-ion represents the most promising chemistry for PHEVs because of its high energy density, high power capability and potential longer life & lower cost.

Lack of domestic battery manufacturing remains a significant challenge. The 2009 Economic Recovery Act provides significant funding to address it.

Long term success of PHEV & EV Li-ion batteries depends on further cost reduction and performance/life/safety improvements. Multi-physics CAE modeling is key enabler.



Operated for the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy by the Alliance for Sustainable Energy, LLC

Extra Slides

NREL Research for Safe, Low Cost, Long Life Batteries and Systems

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3. Systems
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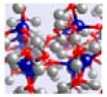
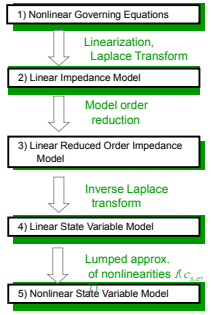
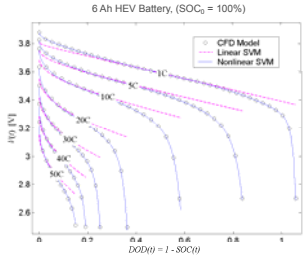
   - Thermal Management Design
     - While Driving
     - While Parked
   - Electrochemical-based Control & Diagnostics



Fast-running electrochemistry model enables real-time control of battery to less conservative limits

Electrochemical Model Reduction Procedure



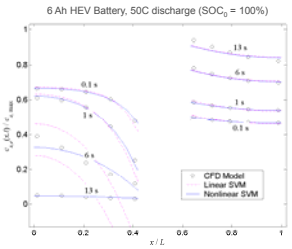


7th order nonlinear SVM
- Nearly identical current/voltage prediction compared to 313th order CFD (finite volume) model
- Explicit, executes in ~2 ms/timestep

Fast-running electrochemistry model enables real-time control of battery to less conservative limits

Model predicts chemical concentrations, potentials internal to the battery

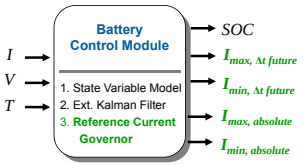
1) Nonlinear Governing Equations
- Linearization, Laplace Transform
2) Linear Impedance Model
- Model order reduction
3) Linear Reduced Order Impedance Model
- Inverse Laplace transform
4) Linear State Variable Model
- Lumped approx. of nonlinearities $f(c_{s,e})$
5) Nonlinear State Variable Model



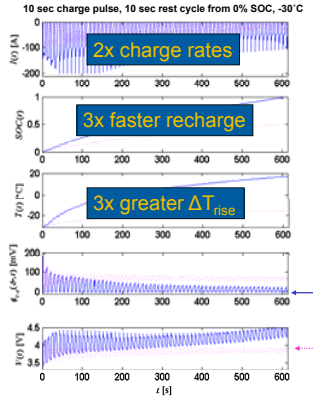
7th order nonlinear SVM
• Unlike equivalent circuit models, enables real-time prediction of internal electrochemical state

Increased power capability possible by controlling to internal electrochemical state.

- Li concentration constraints:
  $0 < \frac{c_{s,e}(x,t)}{c_{s,\max}} < 1 \qquad c_e(x,t) > 0$
  → Avoid sudden loss of power (depletion/saturation)
- Solid/electrolyte potential constraints:
  $U_{\substack{side\ rxn,\\ de-insertion}} < \phi_{s-e}(x,t) < U_{\substack{side\ rxn,\\ insertion}}$
  → Avoid damaging side reactions (such as Li plating at low T)



Example: Pulse charging to Li plating limit at cold temperatures.



$\phi_{s-e}(\delta_-,t) \geq 0\,\mathrm{V}$ — **Li plating limit.**

$V(t) \leq 3.9\,\mathrm{V}$ — **Constant V_{max} limit.**