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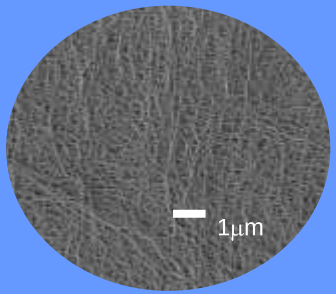
Polymer Separator Films for Lithium Ion Batteries



Patrick Brant
ExxonMobil Chemical Company

Carnegie Mellon University
Pittsburgh, PA
November 11, 2009

Overview

- ExxonMobil organization
- Polyolefin utility
- Lithium ion batteries and separator film
- Summary

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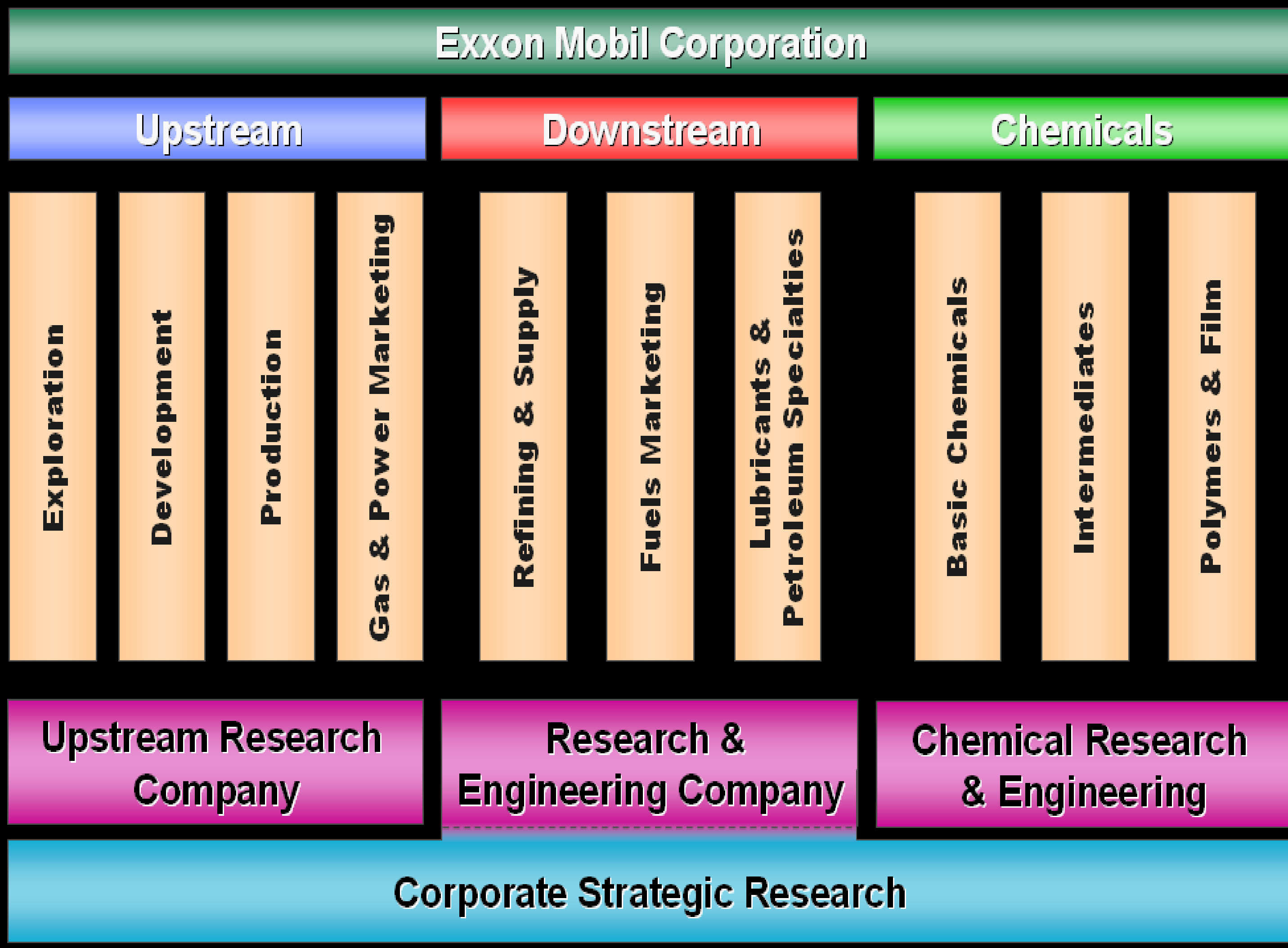
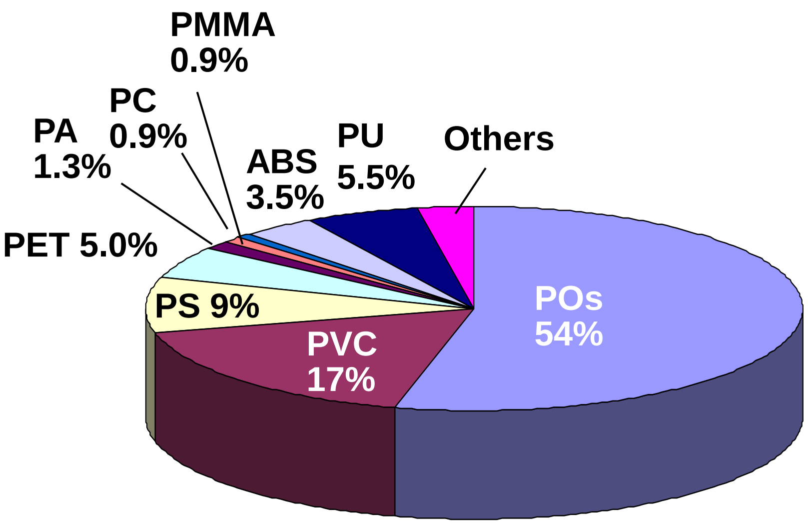


Polyolefins (POs) – Champions of Thermoplastics [a]



POs – Key Features

- Chemically Inert
- Low cost
- Recyclable / Energy Recovery
- Exceptional Fabrication & Applications Versatility

- WW Production of Thermoplastics > 350 Billion Pounds / Year
- POs > 50% of all Thermoplastics
- Sustainable? 6-7%, CO_2 [2 saved/1 produced] [b], downgauging
  - Paper or plastic? 4x more

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[a] G. Gottfreid, Polymeric Materials, Ch. 1

[b] McKinsey and Company study, reviewed by the *Öko* Institute

Polyolefins in Transportation

- About 200 lb of plastics, rubber in typical car

10% Weight Reduction –
6.6% Fuel Economy

Advanced motor oils

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Lithium Ion Battery Overview

Past → Present

- Initial motivation for work
- Battery components and brief history
- Separator structure and functions; how they are made
- Lithium ion battery benefits, impact

Future

- Drivers
- Opportunities
- EV, HEV, pHEV considerations
- Summary

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Initial Motivation for Work

- Two clear fundamental advantages
  1. Lithium is the lightest metal
  2. Lithium half reaction standard electrode potential is big †

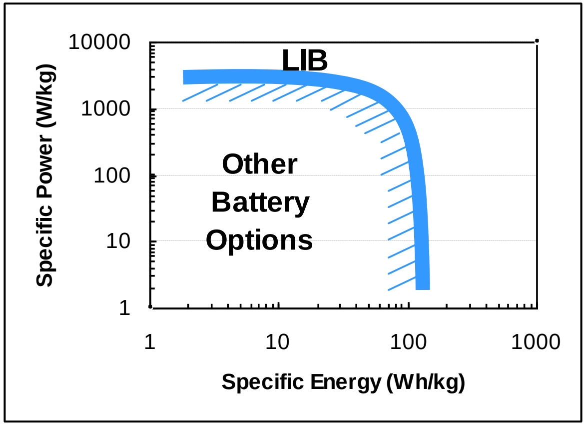
- In principal, fundamental advantages could lead to
  - Higher energy density; weight and volume advantage
  - Higher power density at a given energy density
  - Fewer cells, related parts

- Key Hurdles- beginning in 1975

Materials
  - Cathode
  - Anode
  - Electrolyte
  - Separator

Performance
  - ✓ Self-discharge performance
  - ✓ Memory
  - ✓ Cost per W-h and per W
  - ✓ Abuse resistance
  - ✓ Cold/hot behavior
  - ✓ Thermal management (safety)
  - ✓ Cycle life
  - **Markets?**

Ragone Plot



* 1 Wh = 3,600 J or 860.4 cal

† *"Electrochemical Series" in Handbook of Chemistry and Physics*

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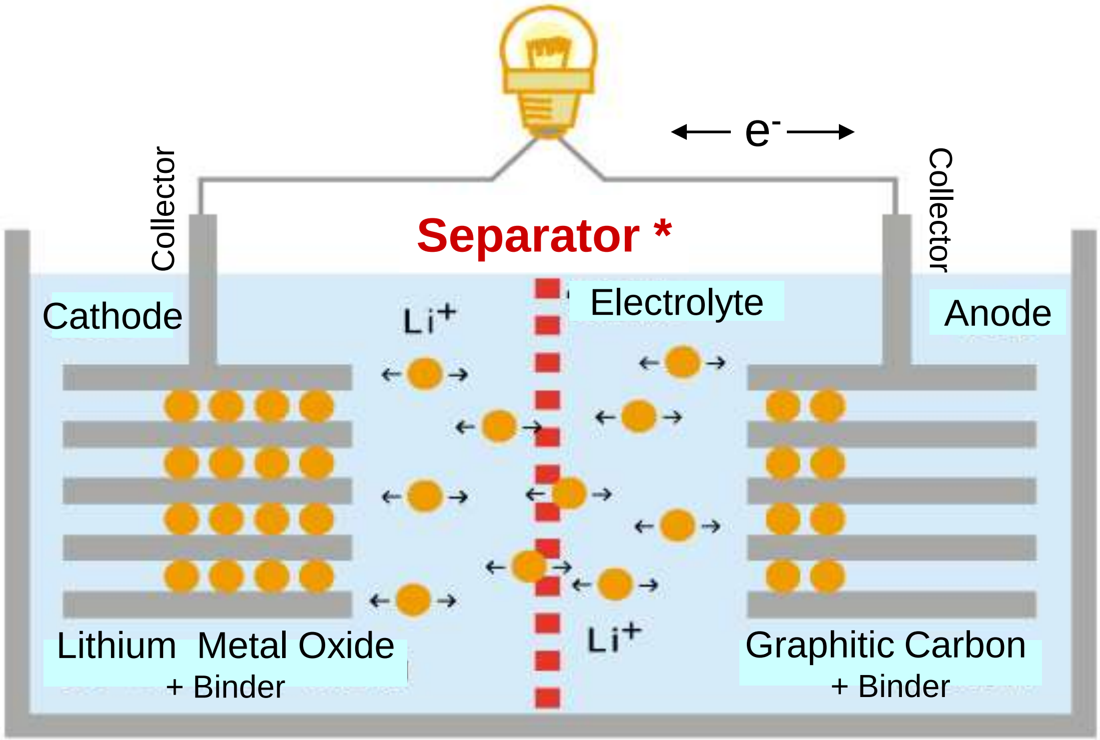
Basic Components in (Lithium Ion) Battery

Galleries for Li



*** Separator = Battery Separator Film = BSF**

Brief History

Whittin

Other Cathodes:
$Li(Ni,Mn,Co)O_2$
$Li(Ni,Co,Al)O_2$

F. Beguin and R. Yazami, Actualite Chimique 2006 295-296, 86-90

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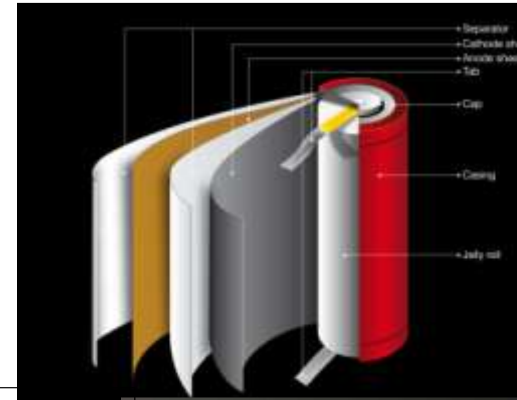
Separator Film Requirements

- Permeable (~40-50% void volume) for ready ion transport, yet insulate electrodes
  - Small pores (seive) but low resistance

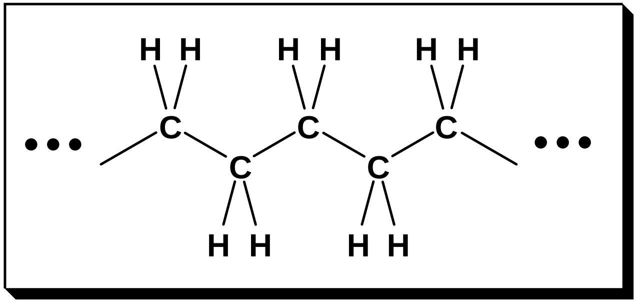
$$R_{eff} \prec \frac{\text{Tortuousity}}{\text{Porosity}}$$

- Chemically inert, uniform, free of flaws
  - 2-10+ years in highly reactive environment
- Excellent puncture strength
  - Thin (7-30μ), dimensionally stable
- Slitting, compatible w/ manufacturing equipment
- Act as safety device if cell becomes too hot
  - Safety margin: Δ = [meltdown temperature – shutdown temperature]
  - The higher the meltdown temperature the better

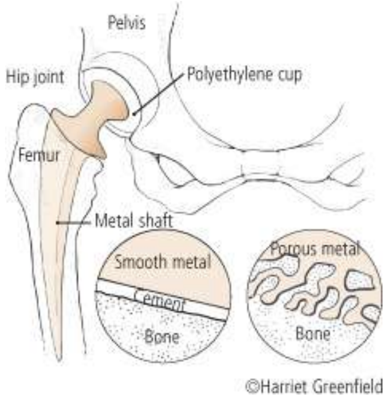


Lithium dendrite

Polyethylene – A High Performance Thermoplastic



T_g -120C T_m 132-140C



Battery Separator Film

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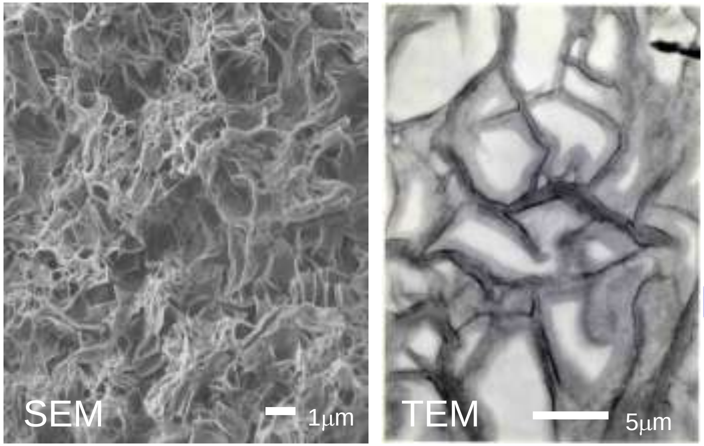
How to Make a Classic Monolayer Separator Film

- **Pennings et al, 1965 - 1979: Gel spinning and super drawing of uhmw HDPE filaments**

Solution of polyethylene dissolved in hydrocarbon

Gel sheet

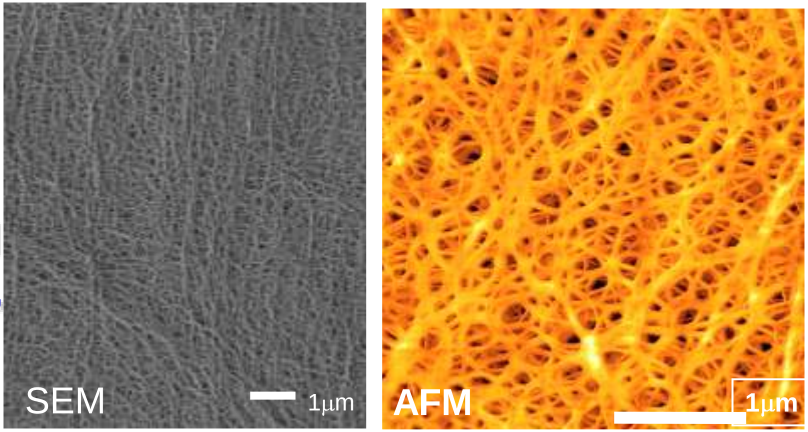
Thin wall cellular structure composed of stacked lamella crystals



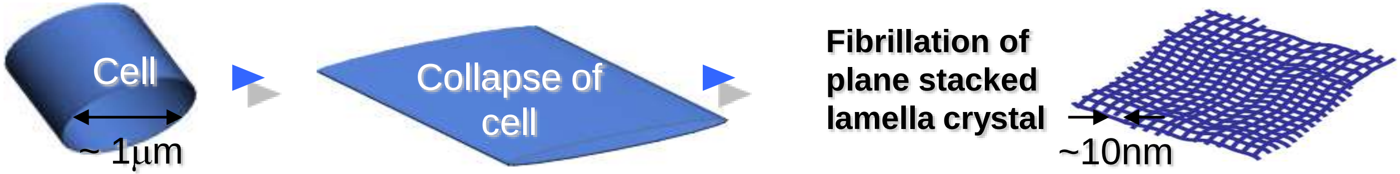
Biaxially orient, extract liquid hydrocarbon, dry

Micro-porous film

Uniform fine fibrous network composed of stacked lamella crystals



Schematic diagram



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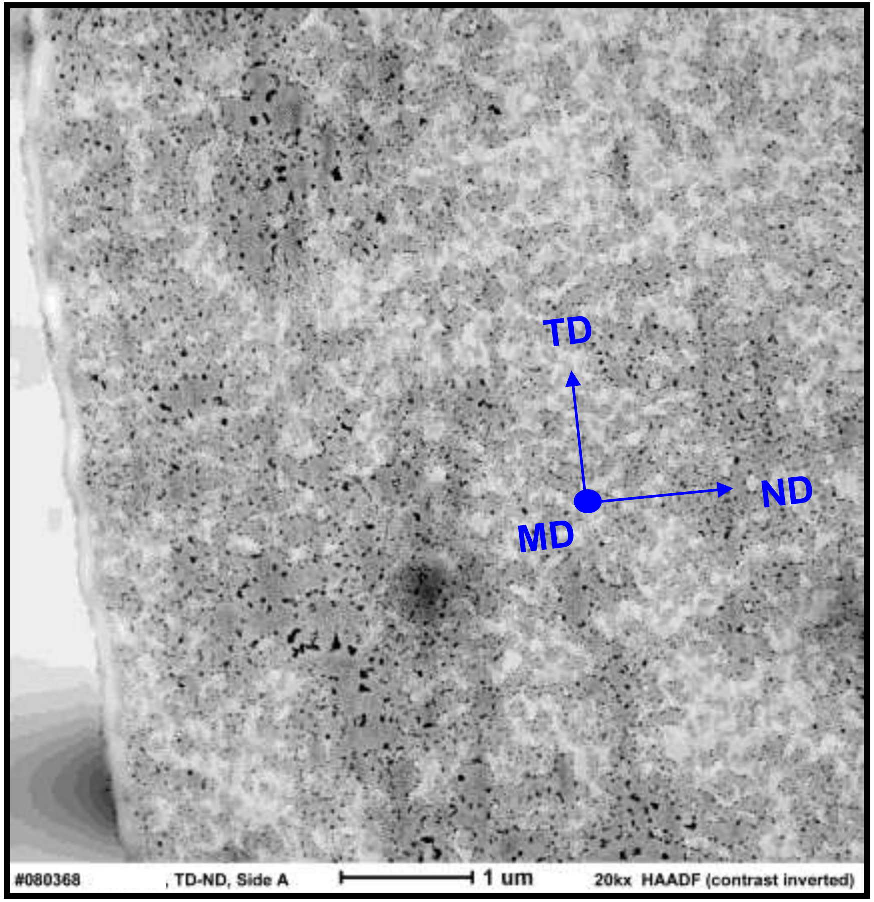
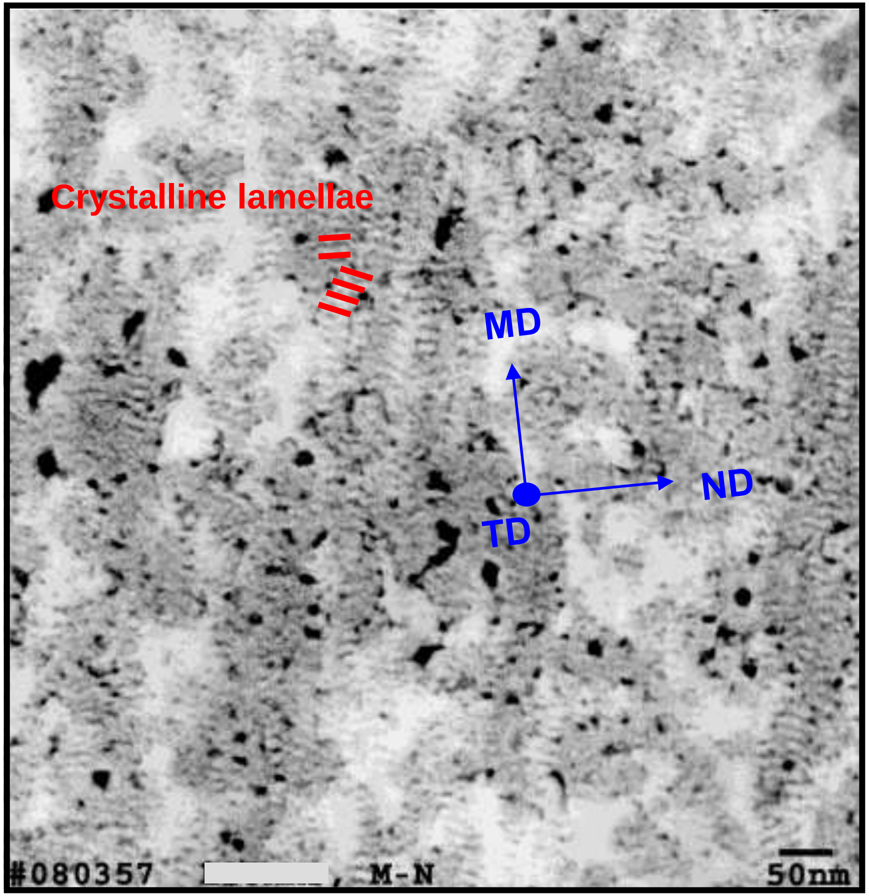
A Closer Look at Separator Morphology

TEM's of stained cross-sections show highly uniform, finely textured morphology



TD x ND plane



MD x ND plane

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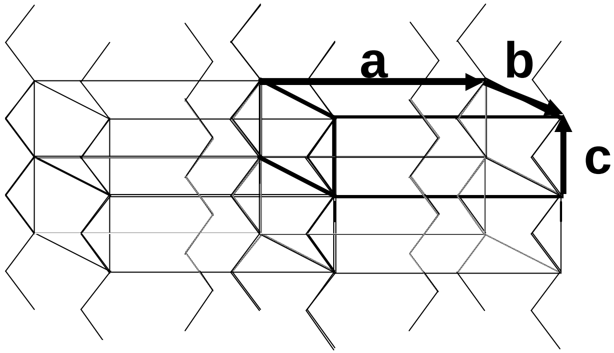
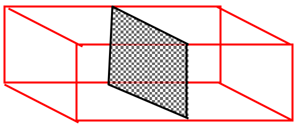
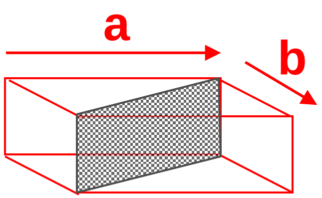
Orientation and Crystallinity *



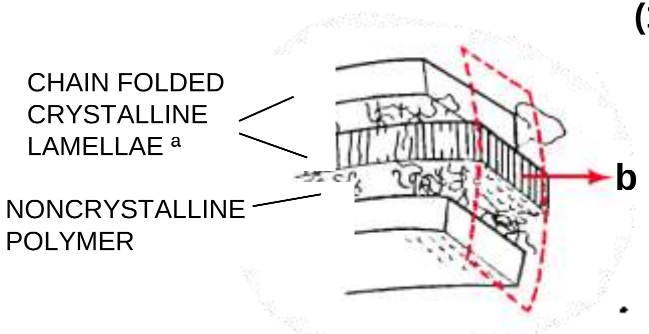


(200)

ORTHORHOMBIC
UNIT CELL:
a = 7.36 Å
b = 4.92 A
c = 2.54 Å; chain axis

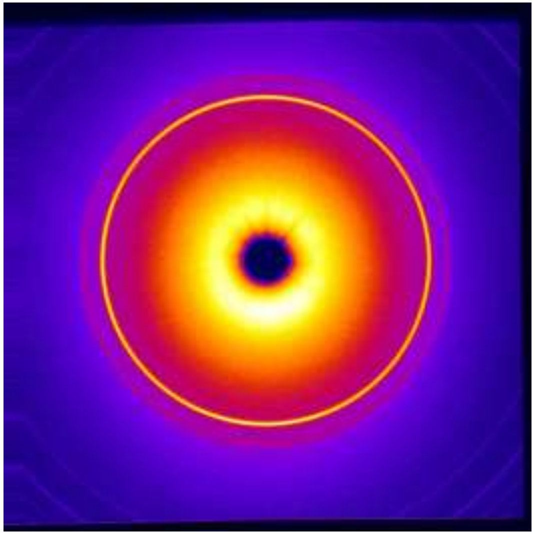


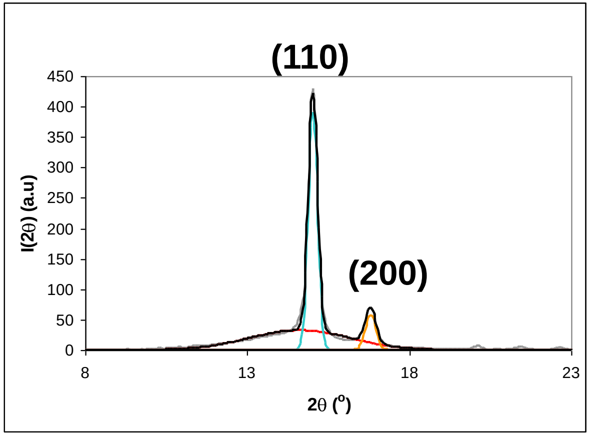
(110)



[a] Some extended chains

WAXS of a BSF



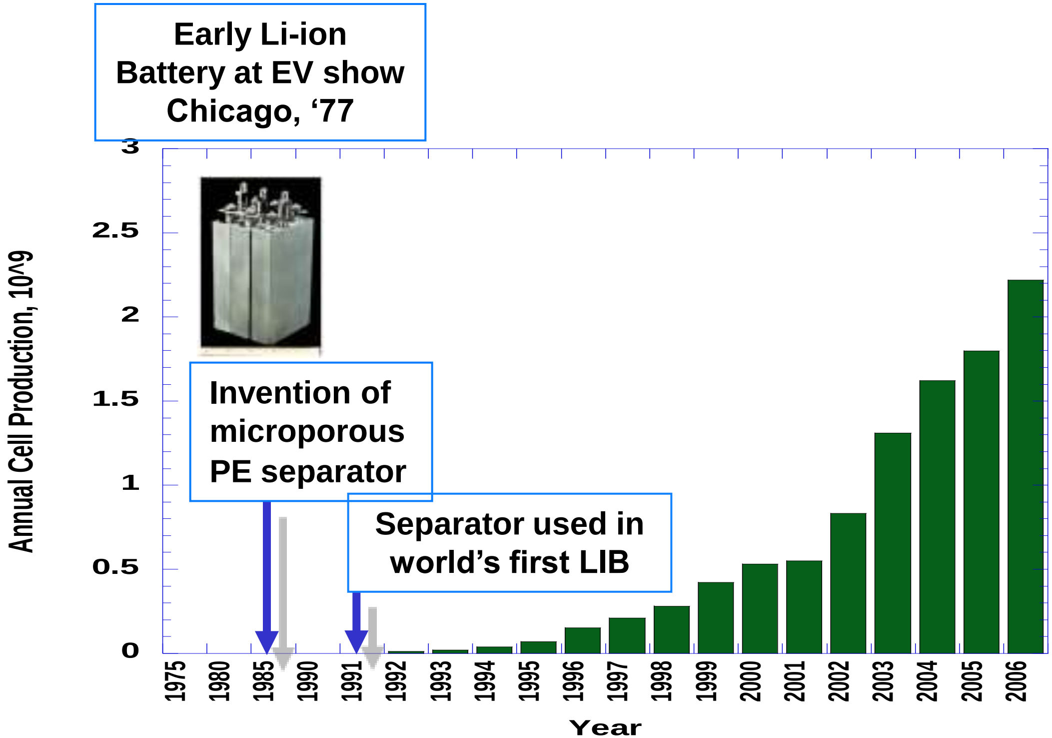


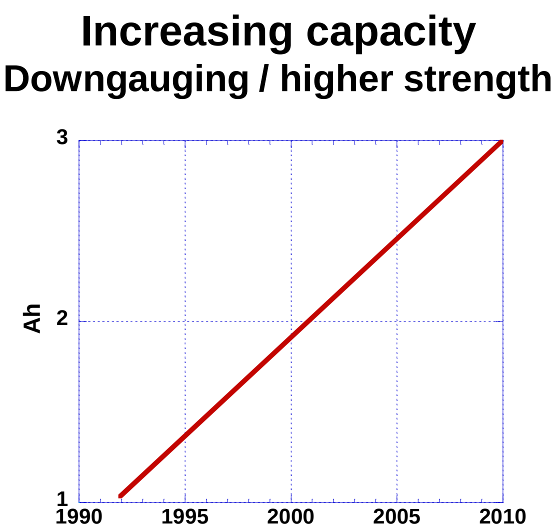
* Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886

Realizing the Benefits of Lithium Ion Batteries

- Higher energy density - nearly 2x higher than Ni-MH; weight advantage
  - Higher power density at a given energy density
- Higher voltage - ~3.6 V vs 1.2 V for Ni-Cd and Ni-MH; fewer cells, connections
- Better self-discharge performance - around one tenth of Ni-Cd and Ni-MH
- Virtually no memory effect
- Expect lower cost per W-h and per W
  - Raw material cost can be a big factor
- Other key data:
  - Abuse resistance
  - Cold/hot behavior (-40 to +40C); electrolyte viscosity
  - Thermal management
  - Cycle life

Growth of LIB Comes with Increasing Demands





Markets: Cellphone, laptop, camcorder, digital camera, power tool, *e*bikes,…

Future – Continuing Growth

- Energy and LIB
- Opportunities, challenges
- EV, HEV, pHEV considerations
- Evolving demands on separator

WSJ, August 6, 2009

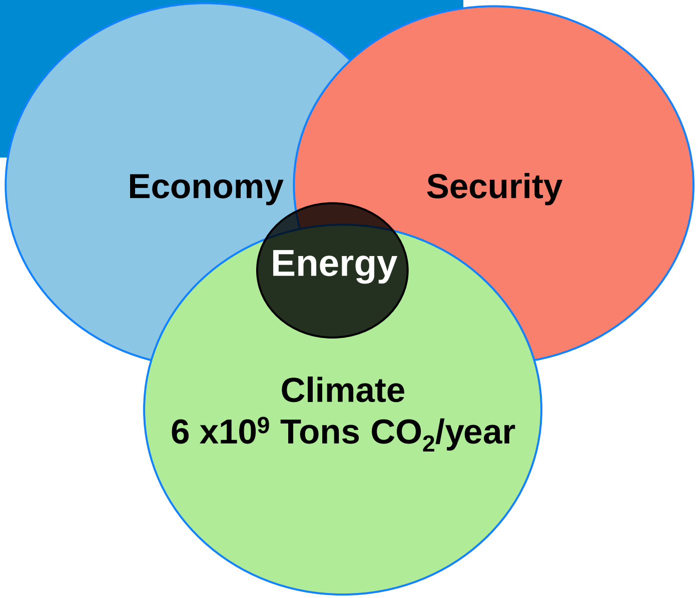
Refuel or Recharge? | How plug-in hybrids compare

	Model, price	Time spent refueling	Cost to refuel	Approximate distance traveled
Gas engine A traditional gas-fueled engine	Ford Focus Sedan $15,995	About 8 minutes to fill the gas tank	$35.24	472.5 miles
Hybrid engine [illegible]	Toyota Prius $22,000	About 5 minutes to fill the gas tank	$31.06	595 miles
Plug-in hybrid engine [illegible]	Chevy Volt $40,000 (Estimate)	About 8 hours to charge the battery	80 cents (Electricity cost only)	40 miles (Electricity only) 1,000 miles (Electricity and gasoline)
Electric motor only [illegible]	Tesla Roadster $109,000	At least 3.5 hours to charge the battery	$2.44	244 miles

Funds Flow to Electric Cars

White House Unveils $2.4 Billion in Grants to Jump-Start Industry in Midwest

By Elizabeth Williamson

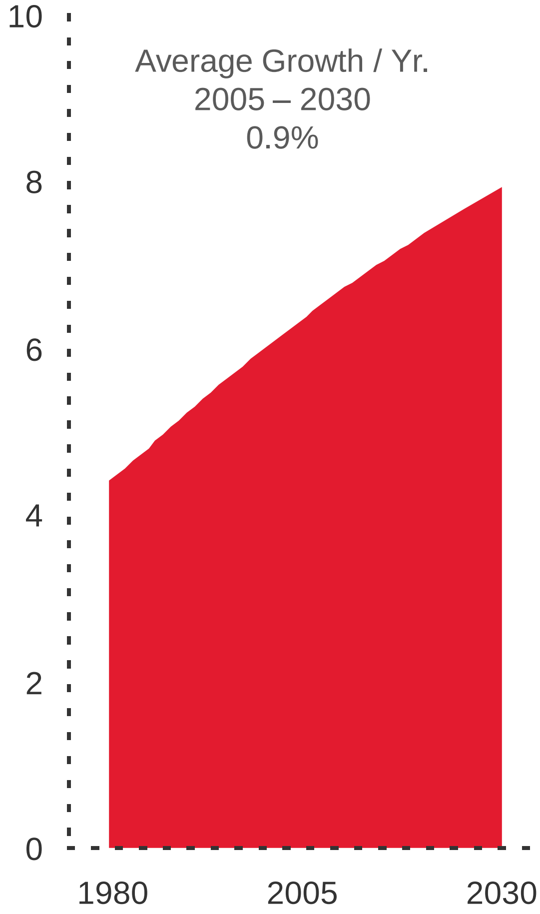


Recharging Stations in Short Supply

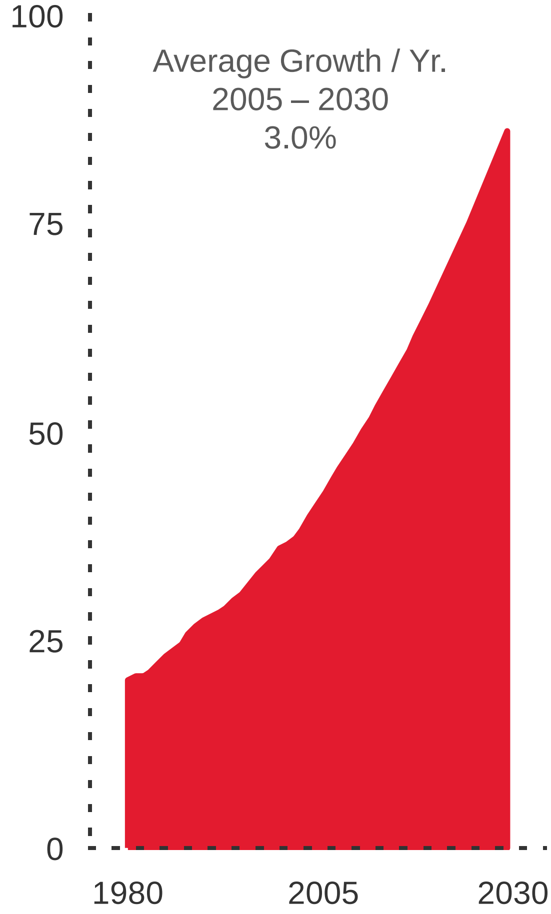
By Rebecca Smith

Global Economics and Energy

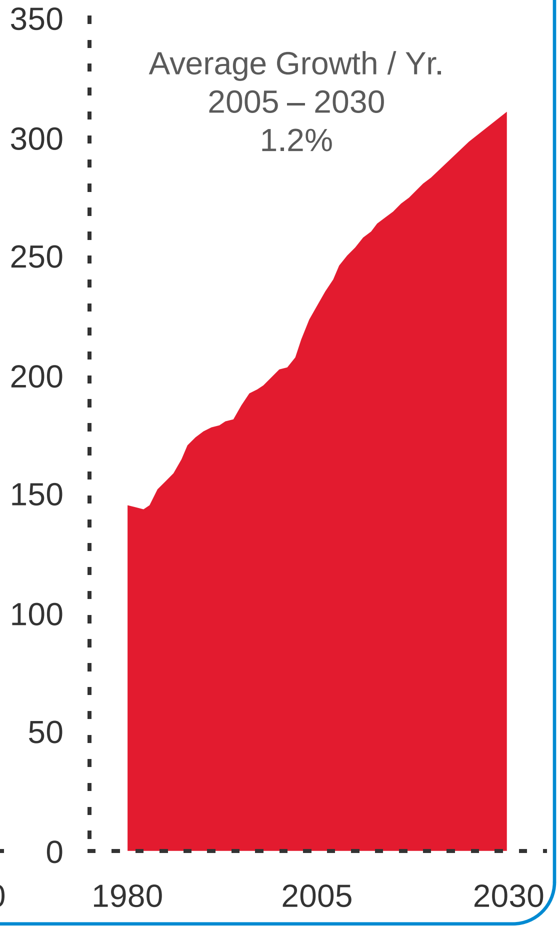
population
billion



GDP
trillion 2005$



energy demand
MBDOE



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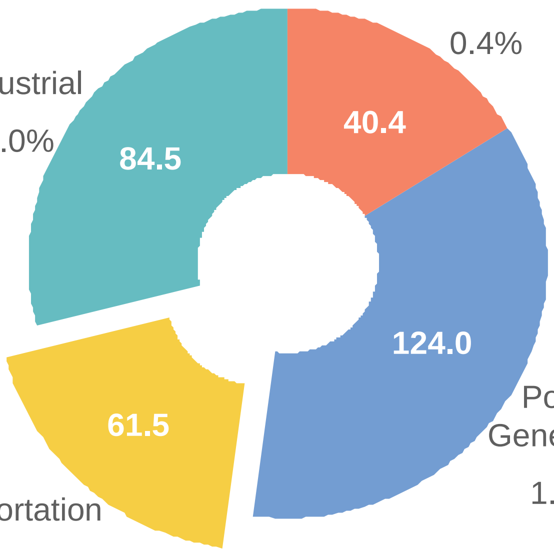
Transportation - Global

demand by sector

2030 demand in MBDOE

Average growth/Yr 2005-2030



2030: ~310 MBDOE

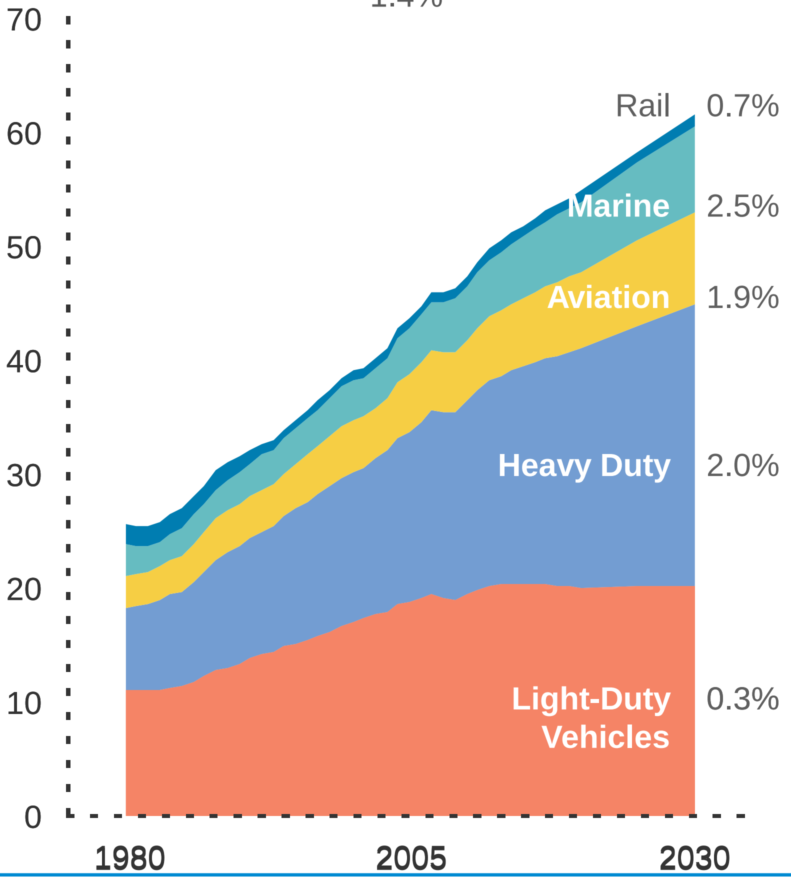
1.2%

global transportation

by sub-sector

MBDOE

Average Growth / Yr. 2005 – 2030 1.4%



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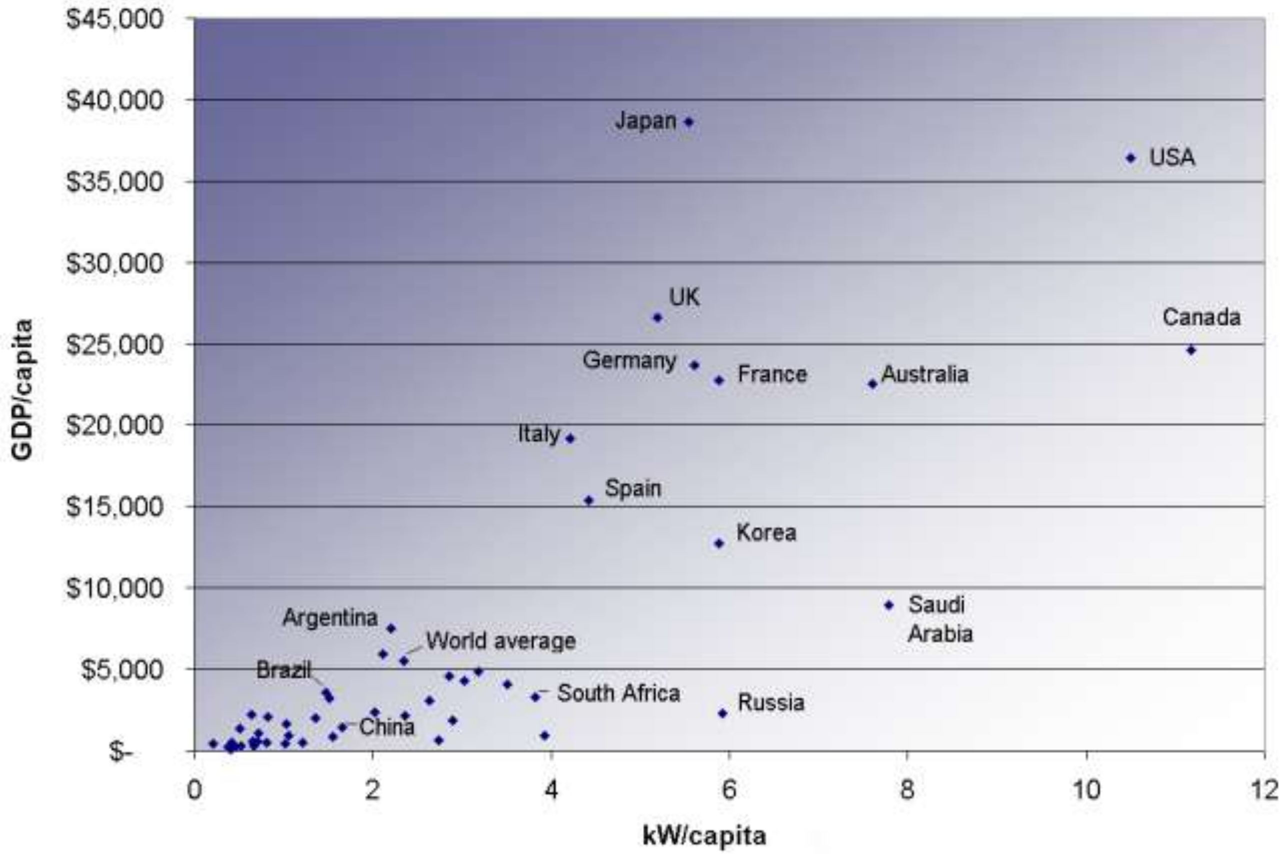
Energy Consumption and Productivity



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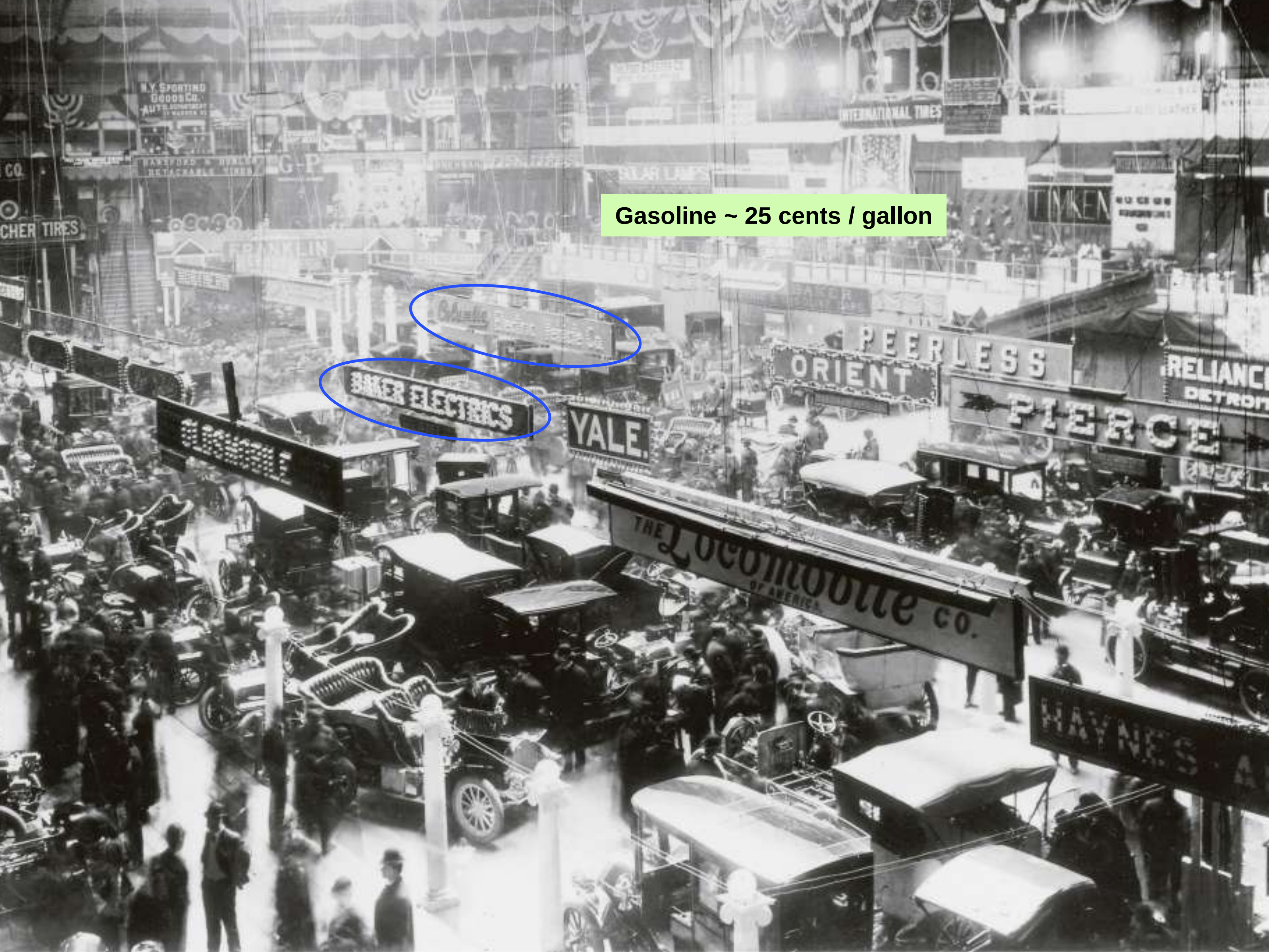
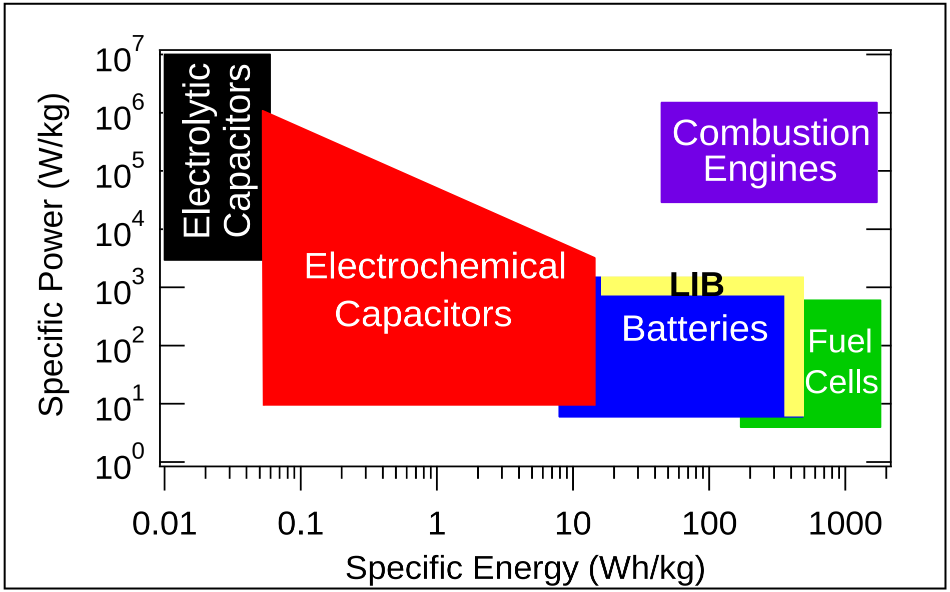

Gasoline ~ 25 cents / gallon
N.Y. SPORTING GOODS CO.
INTERNATIONAL TIRES
PEERLESS
ORIENT
RELIANCE
PIERCE
YALE
BAKER ELECTRICS
THE Locomobile CO. OF AMERICA
HAYNES

Batteries in Transportation

Ragone Plot



Gasoline versus LIB

	Gasoline	LIB
Energy Density, kWh† /kg	**13** [a*]	**0.17** *
Energy Efficiency	**~15-20%** *	**85-90%** *
Efficiency of Producing Fuel	**0.9**	**~0.4-0.5** [b]

[a] 3x the energy density of sugar
[b] For production of e^- from coal or NG
† 1 kWh = 3,600 kJ or 860.4 kcal

- Diversification and more efficient use of hydrocarbons: 13.8 MBbl oil/day for transportation in US
- Reduce carbon dioxide emissions
- Part of integrated set of solutions

* Deutsche Bank, Auto Manufacturing Electric Cars: Plugged in, 9 June 2008

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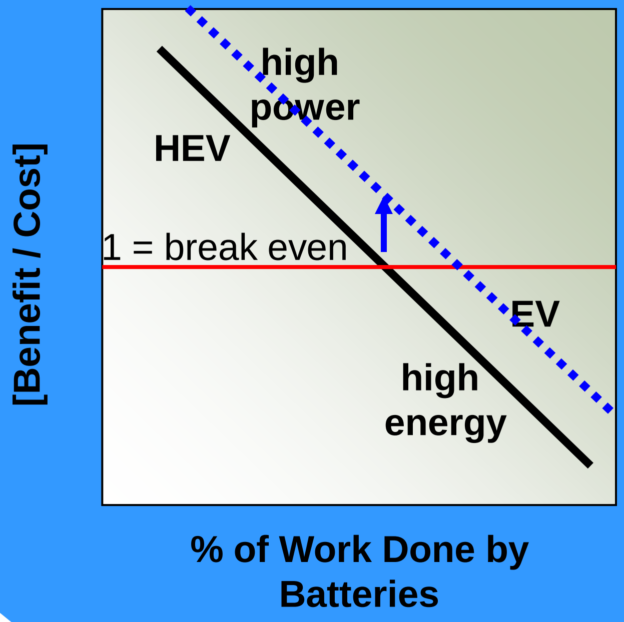
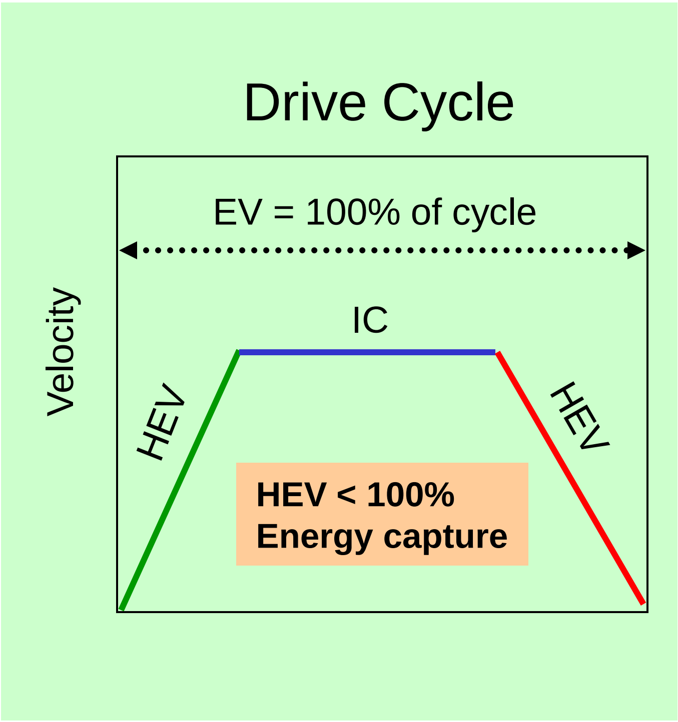
Relative LIB Benefit / Cost





Rough estimate: LIB size for EV ~200 kg (80 – 1000 V)

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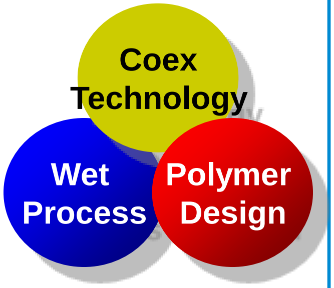
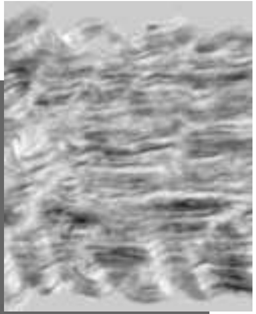
Evolving Separator Demands

for larger battery formats (stacked, prismatic), and bigger battery packs…. but emphases vary according to LIB chemistry and module or pack control

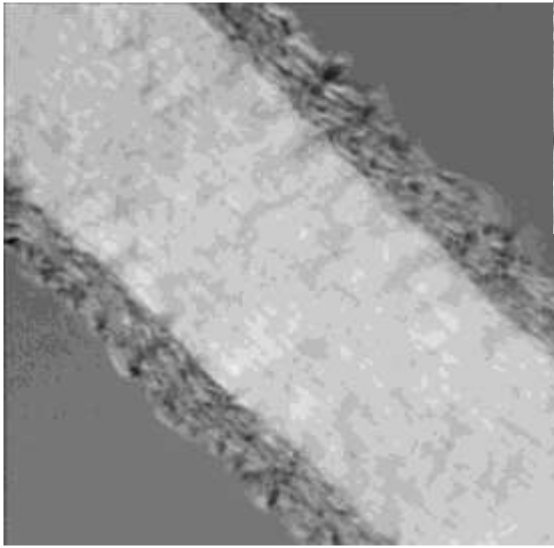


- Higher temperature stability - ~ 200 → 250+C
  - Retain sufficient dimensional stability
  - Coatings and higher temperature polymers
    - Blends, co-extrusion
- Increasing puncture resistance
  - w/ appropriate permeability
- Lower shutdown temperature
- ~10+ year life
- Delivered flawlessly at lower cost

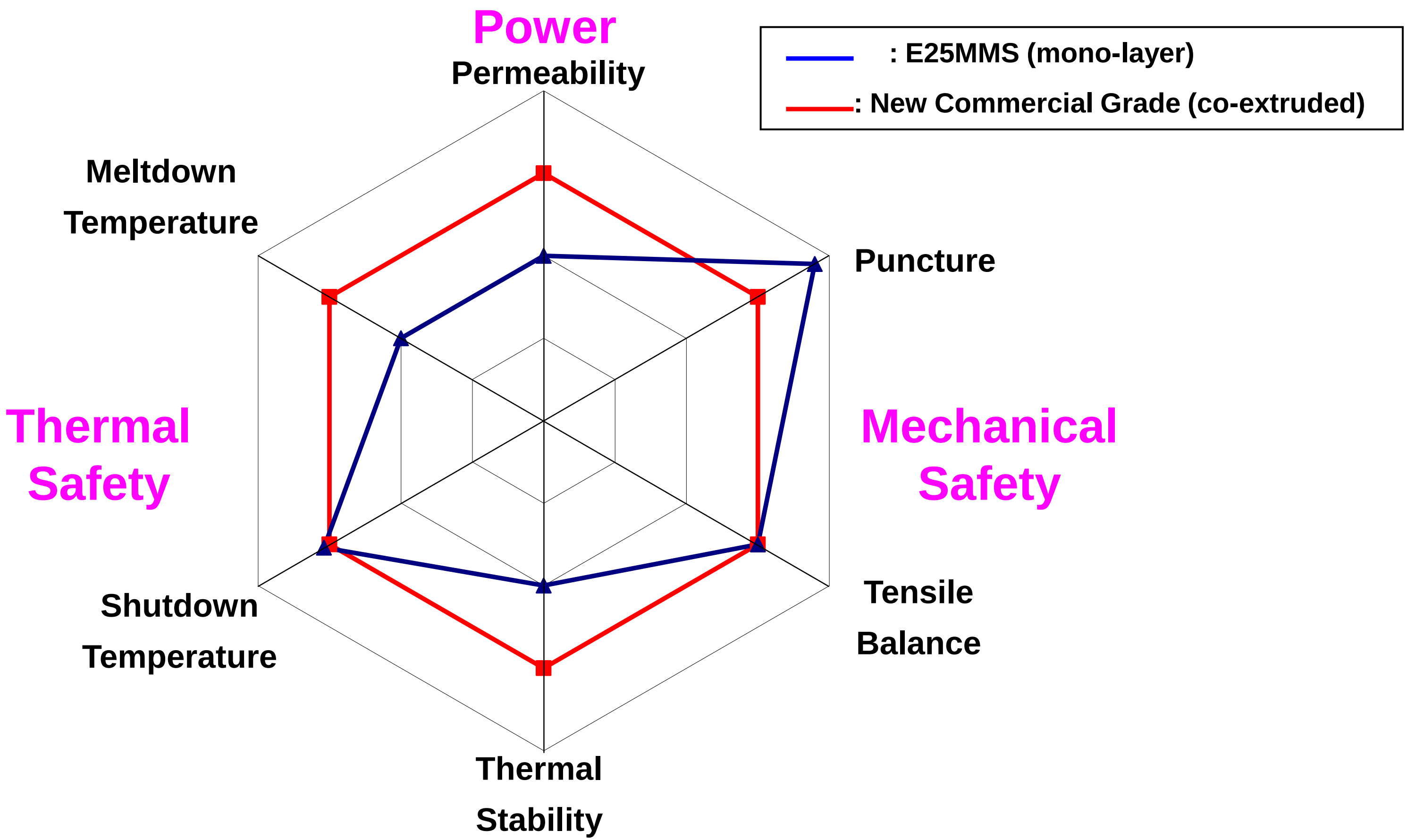
Monolayer



Co-extruded Separator



Improved Thermal Stability



New commercial grade has superior thermal stability, higher permeability and meltdown temperature than standard mono-layer

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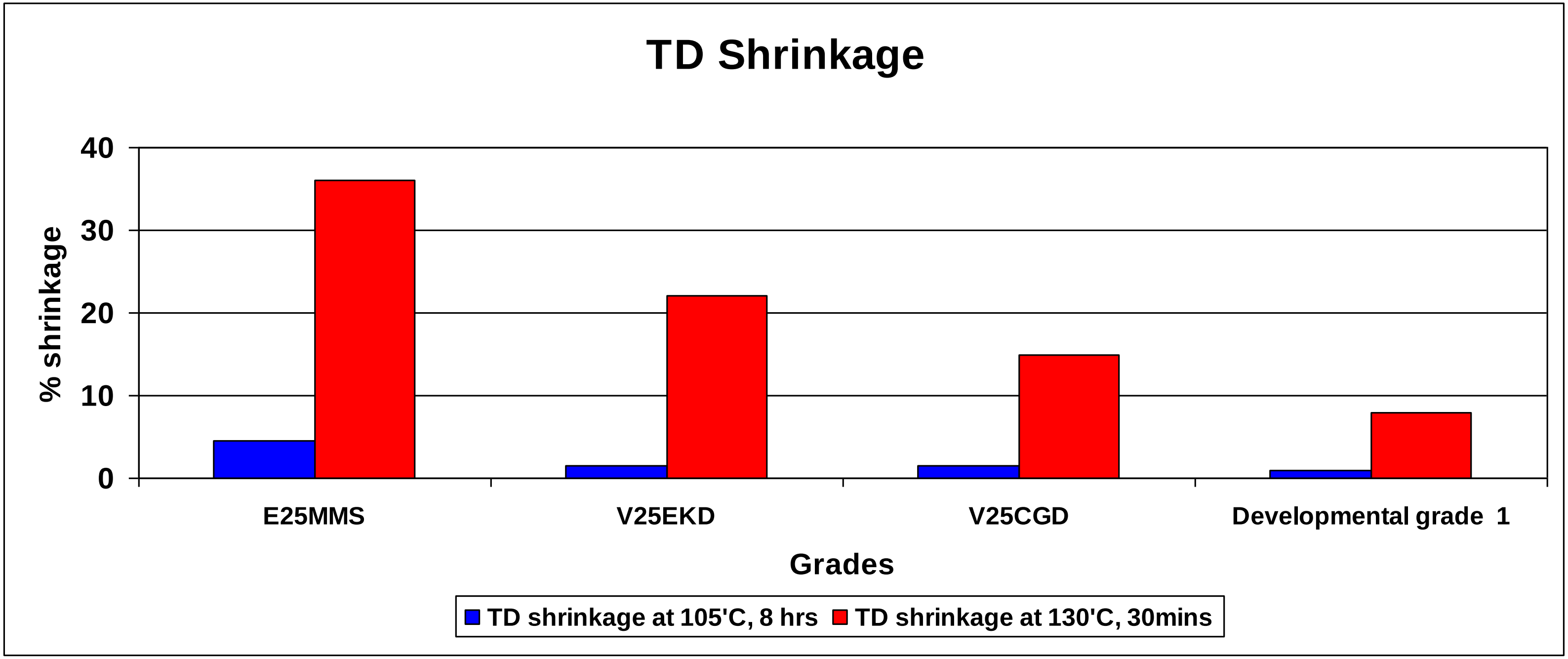
Lower TD Shrinkage



Lower TD shrinkage allows
more flexible LIB designs

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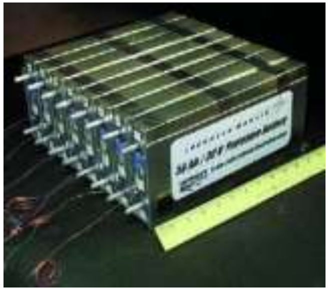
Summary

- Lithium ion batteries power the portable electronics revolution
  - Polyolefin separators a key part of this success story
- Lithium ion batteries for transportation: *e*bikes, EV/p-HEV, HEV
  - Major commitments already
    - Battery and auto manufacturer announcements
  - Continuing improvements, especially to reduce cost, increase life
    - Once again, separators critical to performance
- Can be a key part of overall drive to increase energy efficiency
  - Uninterrupted power supplies
  - Fixed energy storage
- More technology breakthroughs are critical
  - Exciting research and development opportunities



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Thank you

- Many contributors to this talk
  - JoAnn Canich, Alan Vaughan
  - Koichi Kono, Jack Tan, Takeshi Ishihara, Jeff Brinen, Zerong Lin, …..

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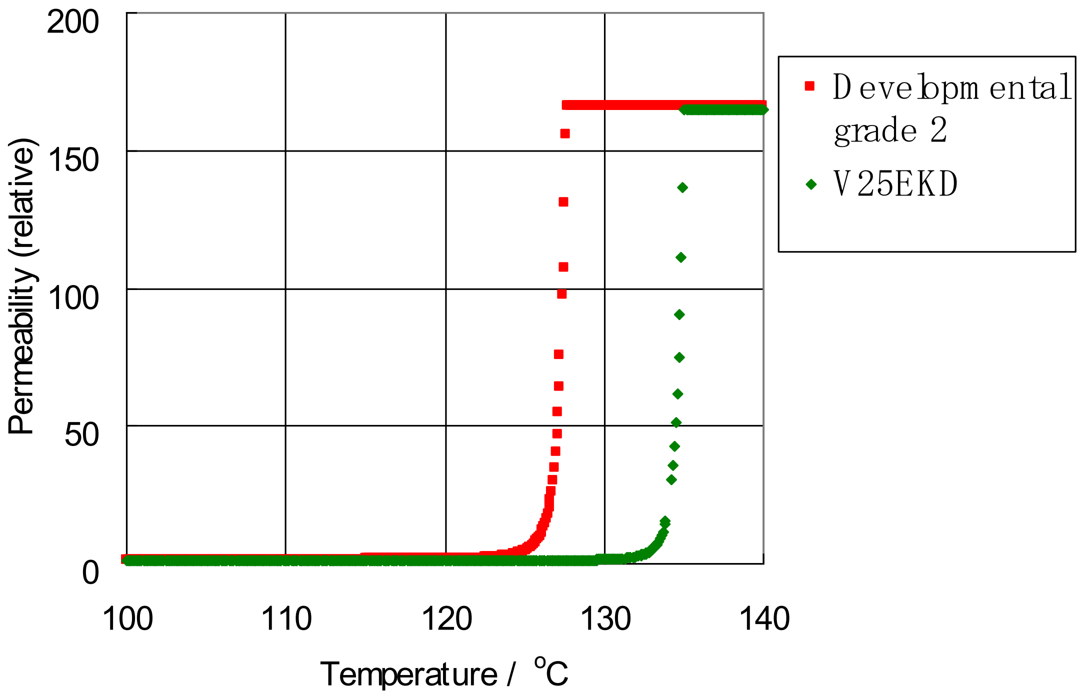
Shutdown Performance



Developmental grade 2 is designed for earlier pore closure with complete shutdown at 128˚C, potentially prevent exothermic reaction which leads to thermal runaway in the event of internal shorts or overcharging

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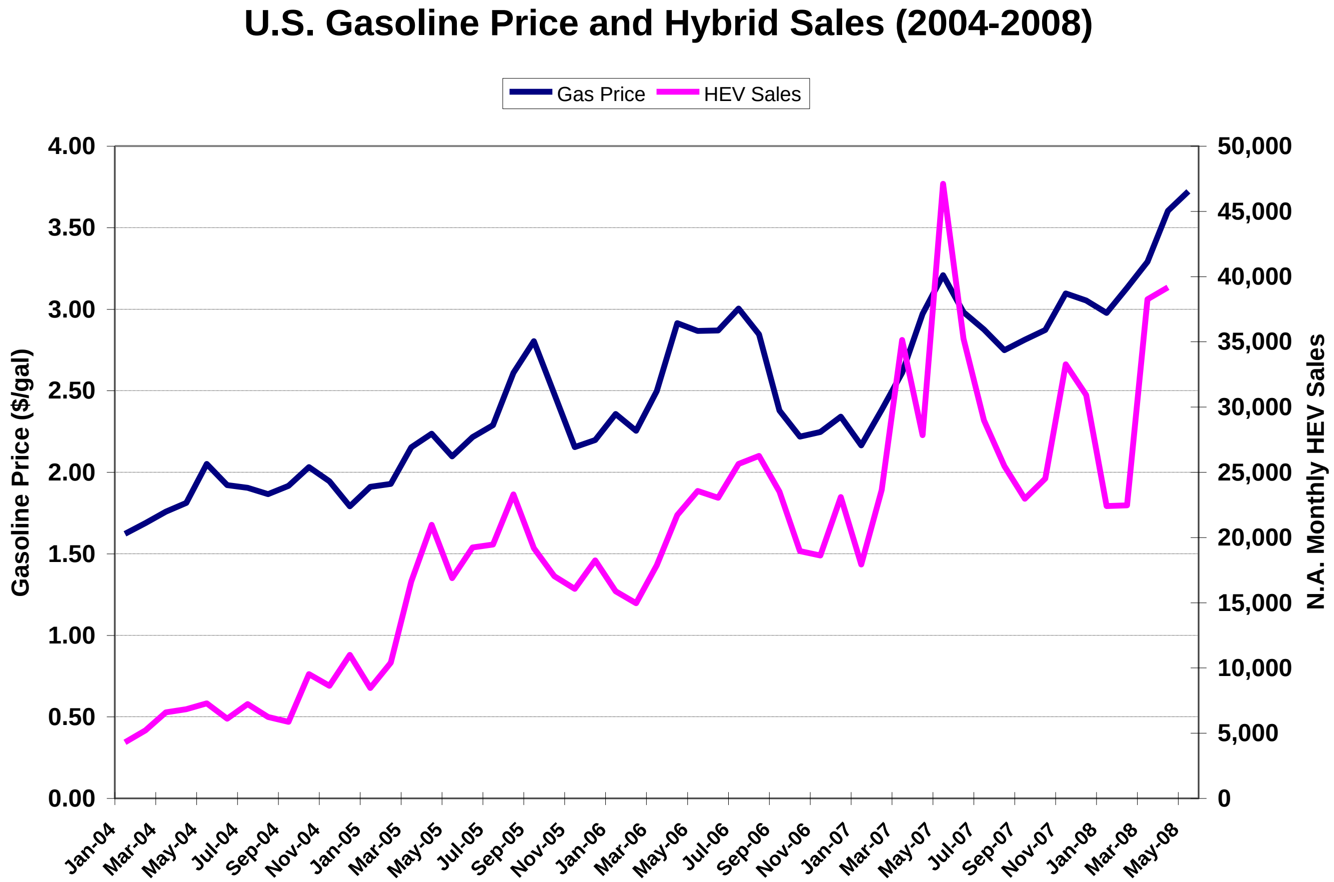
Economics Lesson: Hybrid Sales Linked to Fuel Price



- US accounts for ~70% of all HEV sales

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