Electrochemical energy storage and extended-range electric vehicles

Mark Verbrugge

Director, Materials and Processes Lab

General Motors Research & Development Center

Saturn Vue
10 ZEV
Plug-in HEV

Volt concept
40 ZEV
Extended-range EV

National Science Foundation workshop: "Drug Discovery Approach to Breakthroughs in Batteries," 8-9 September 2008.

❑ Outline

- Automotive trends and technology drivers
- GM roll-out plan for
  - Hybrid Electric Vehicle (HEV)
  - Plug-In Hybrid Electric Vehicle (PHEV)
  - Extended Range- Electric Vehicle (EREV)
  - Fuel Cell Electric Vehicle (FCEV)
- EFlex Rechargeable Energy Storage System (RESS)
  - Requirements, Status, Outlook
- How might we address battery life issues…a research problem
- Summary

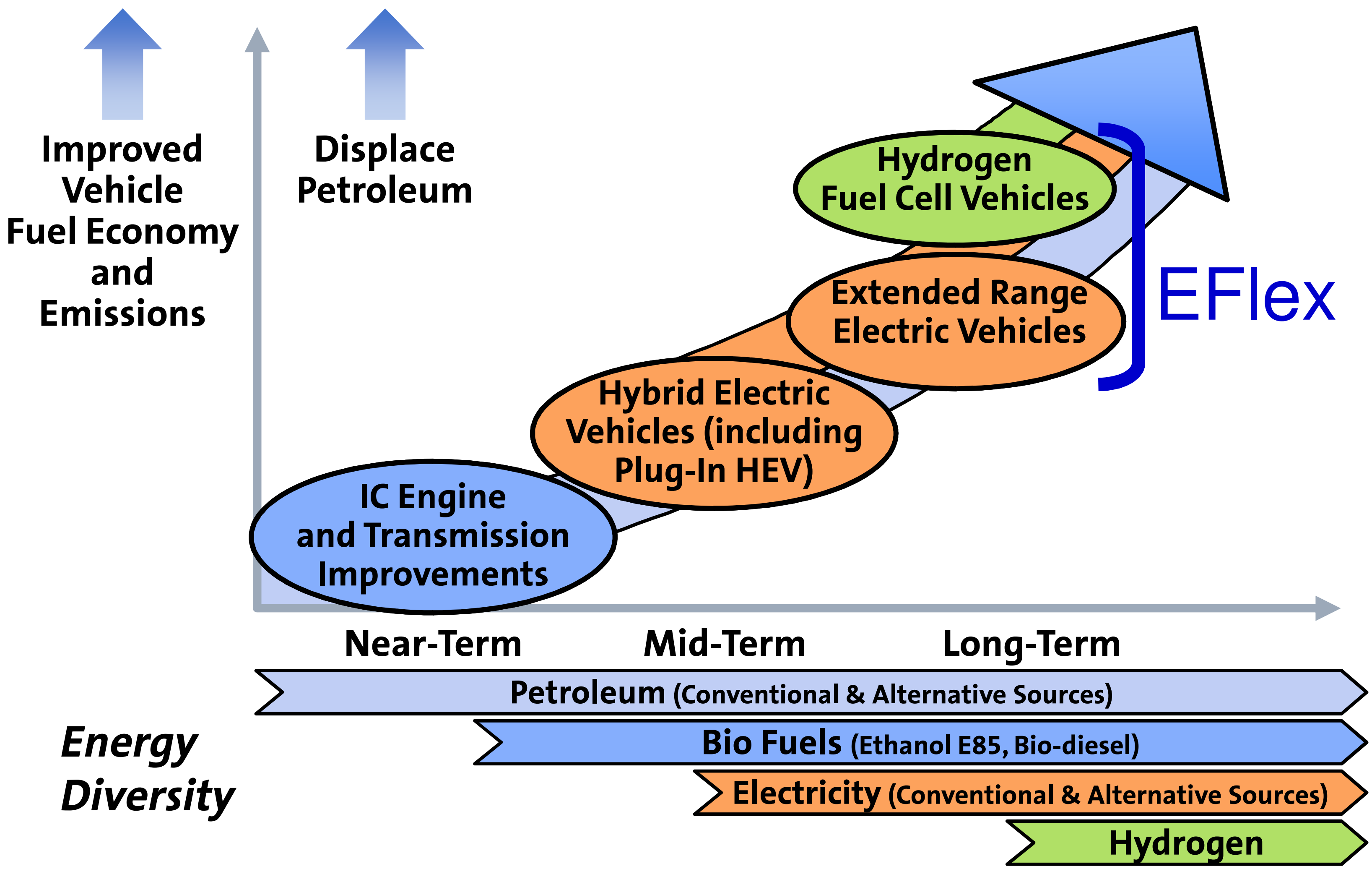
Opportunity

- Personal vehicles: a growth industry
  - 2007: 71M sales
  - 2017: 98M sales

Challenge: Sustainability

- Energy
- Environment
- Safety
- Congestion

Advanced Propulsion Technology Strategy



GM E-Flex

Common drivetrain system uses electricity created and stored on-board the vehicle

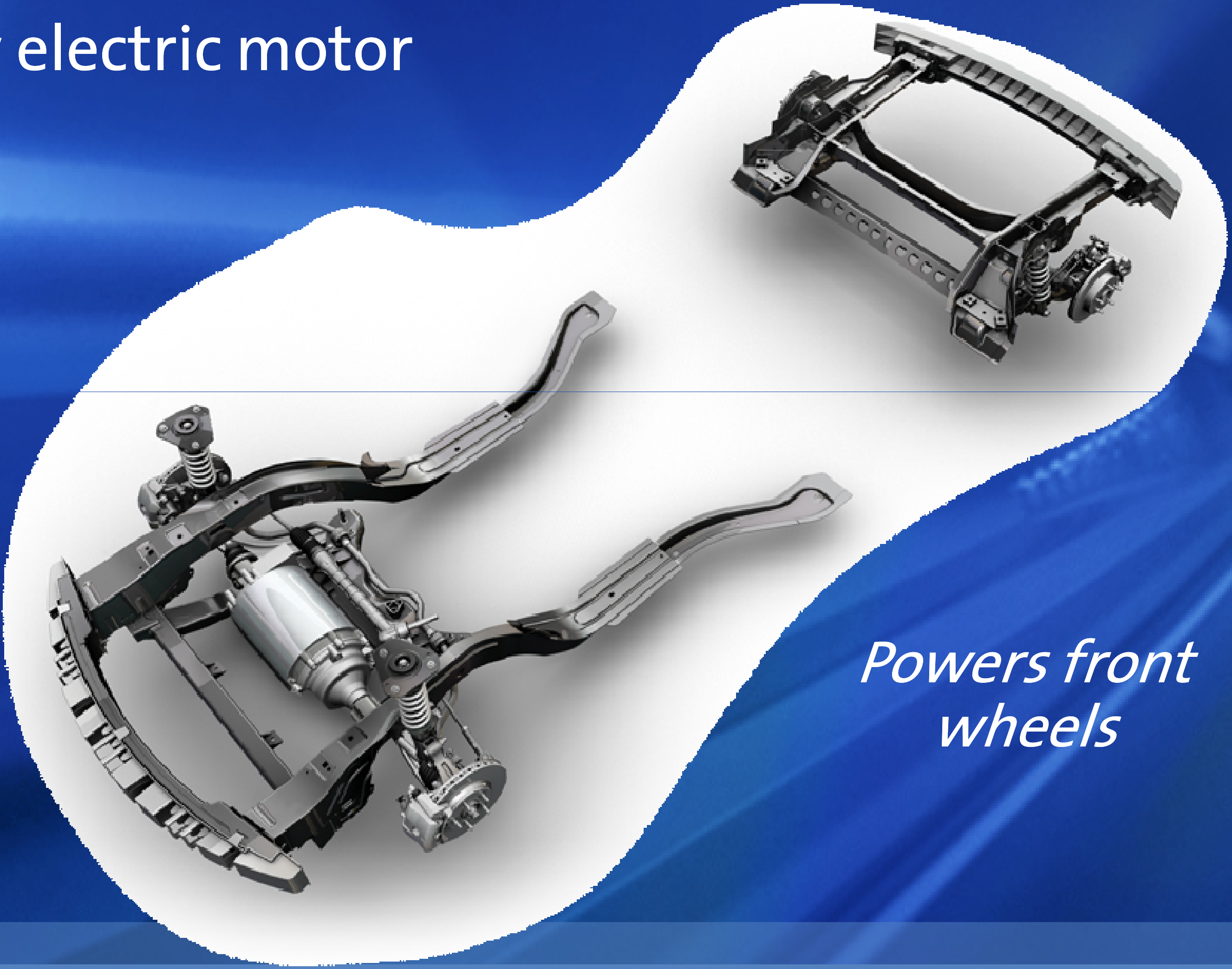
- Engine-generator
- Hydrogen fuel cell
- Advanced battery
- Plug-in capable

Electricity can be generated from a wide range of energy sources

E-Flex enables energy diversity

Extended-Range Electric Vehicle (E-REV)

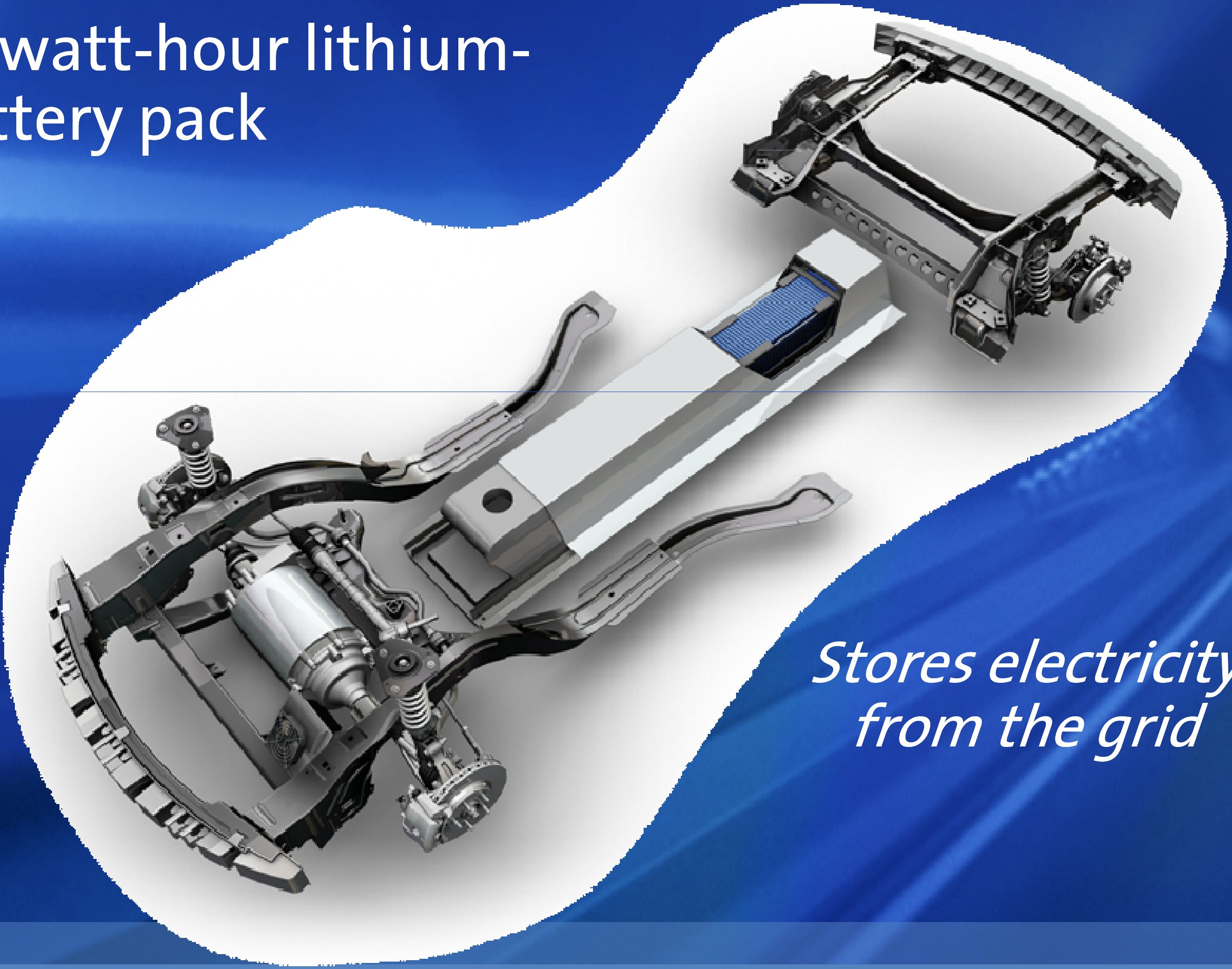
120kw electric motor



Powers front wheels

Extended-Range Electric Vehicle (E-REV)

16 kilowatt-hour lithium-ion battery pack

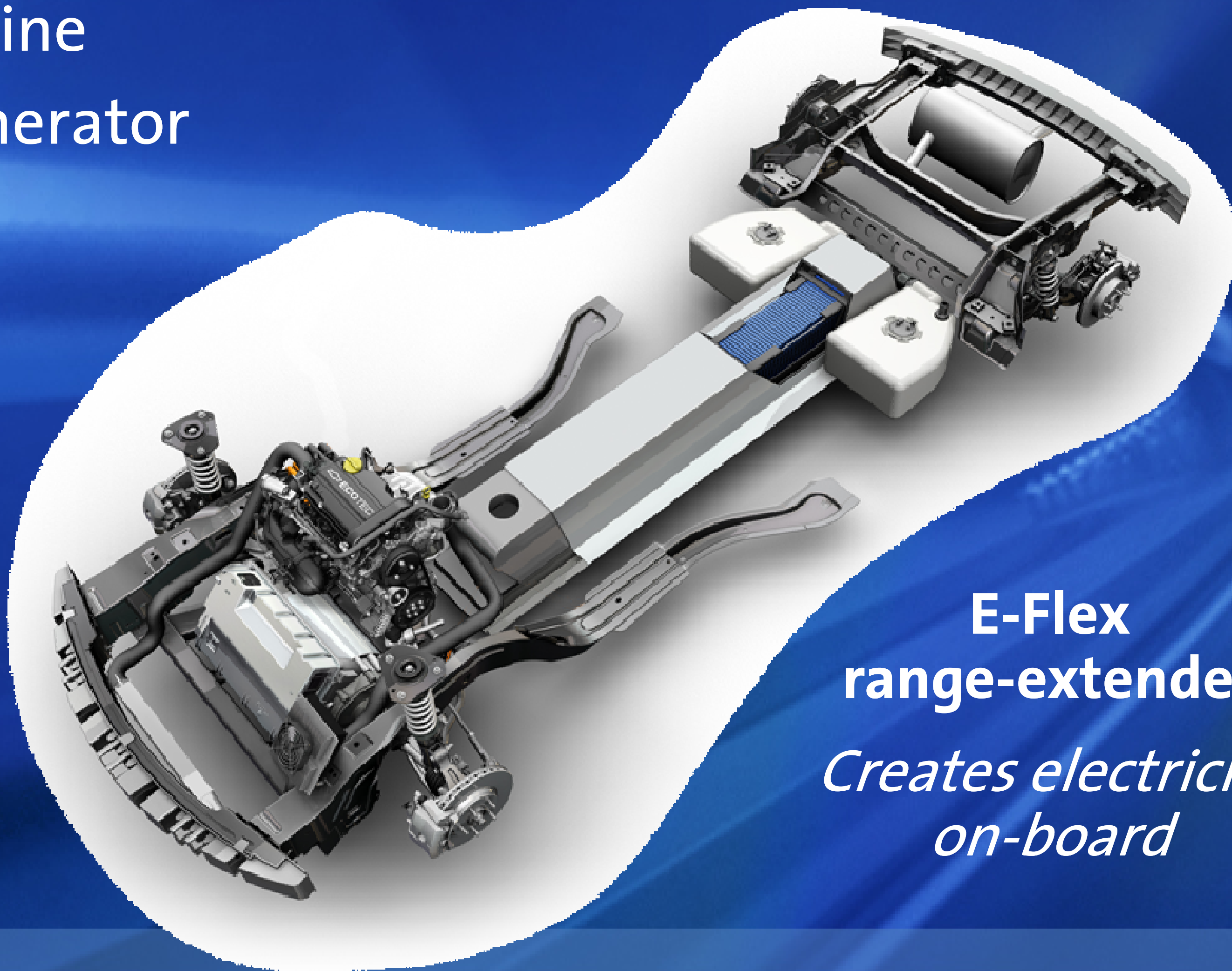


Stores electricity from the grid

Extended-Range Electric Vehicle (E-REV)

74 Hp engine

53 kW generator

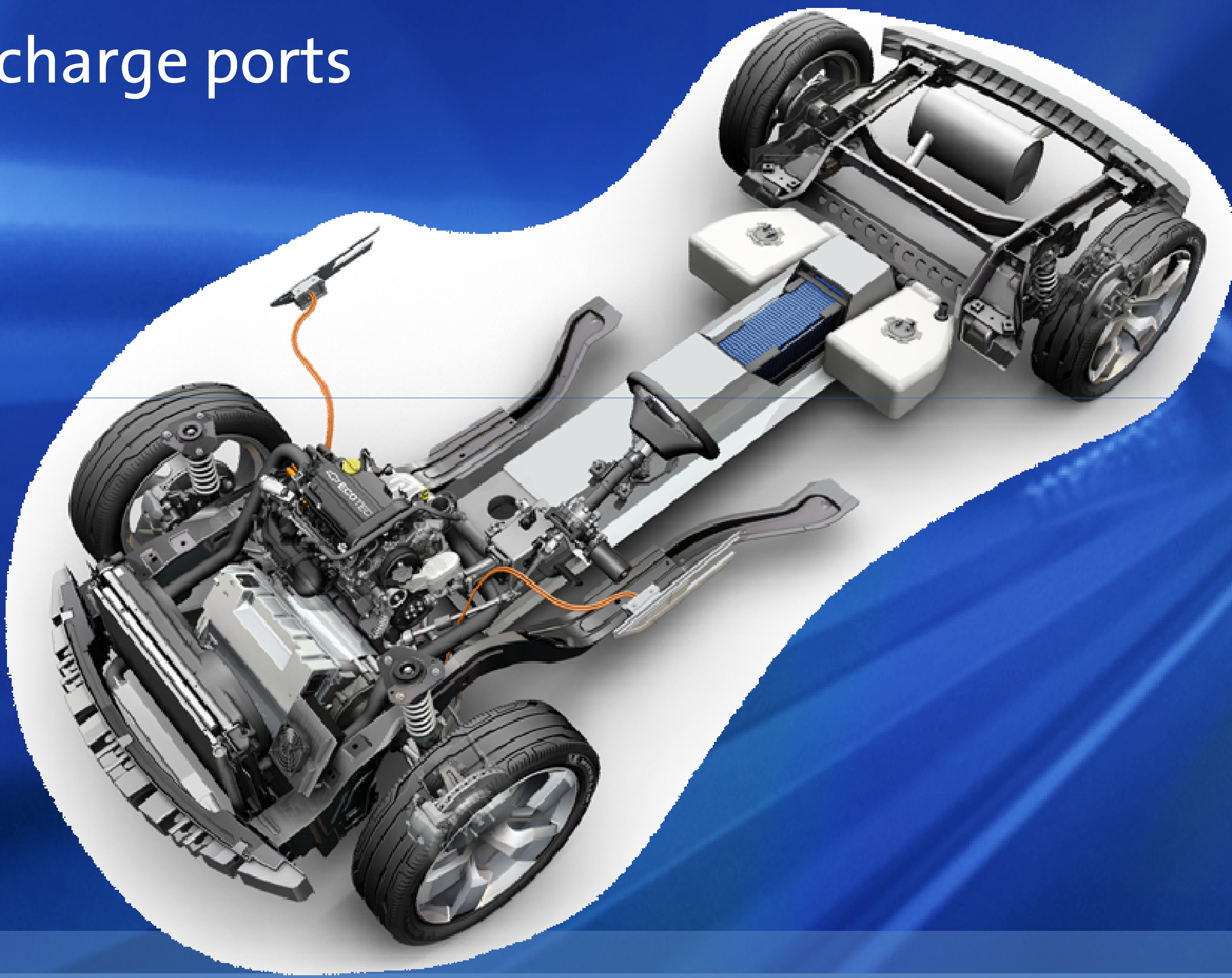


E-Flex range-extender

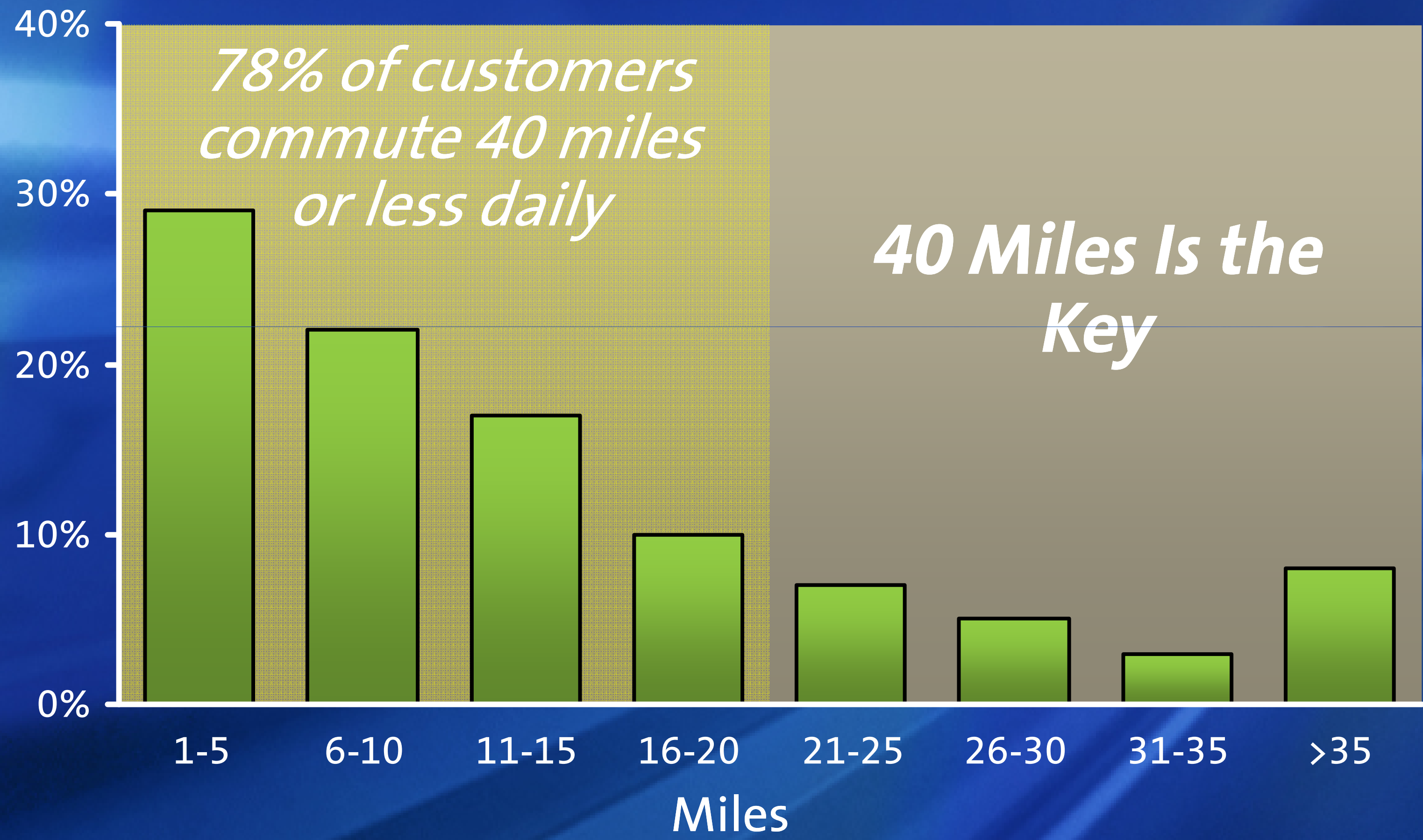
Creates electricity on-board

Extended-Range Electric Vehicle (E-REV)

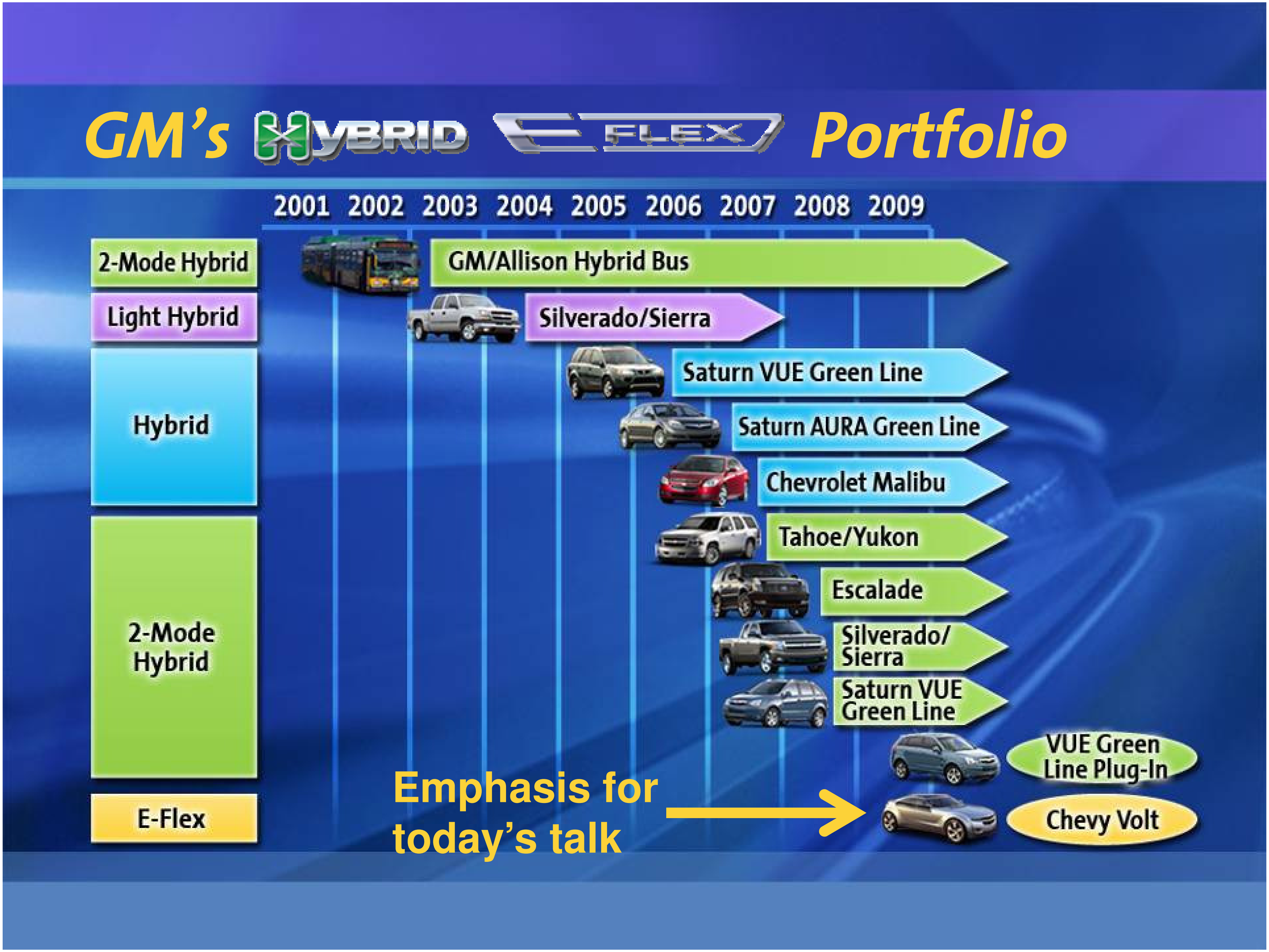
E-REV charge ports



Typical One-Way Miles From Home To Work



Based on OmniStats Data posted by the U.S. Bureau of Transportation


GM's HYBRID E-FLEX Portfolio
2001 2002 2003 2004 2005 2006 2007 2008 2009
2-Mode Hybrid
GM/Allison Hybrid Bus
Light Hybrid
Silverado/Sierra
Hybrid
Saturn VUE Green Line
Saturn AURA Green Line
Chevrolet Malibu
2-Mode Hybrid
Tahoe/Yukon
Escalade
Silverado/Sierra
Saturn VUE Green Line
VUE Green Line Plug-In
E-Flex
Chevy Volt
Emphasis for today's talk

Rechargeable Energy Storage System (RESS) for the EFLEX program

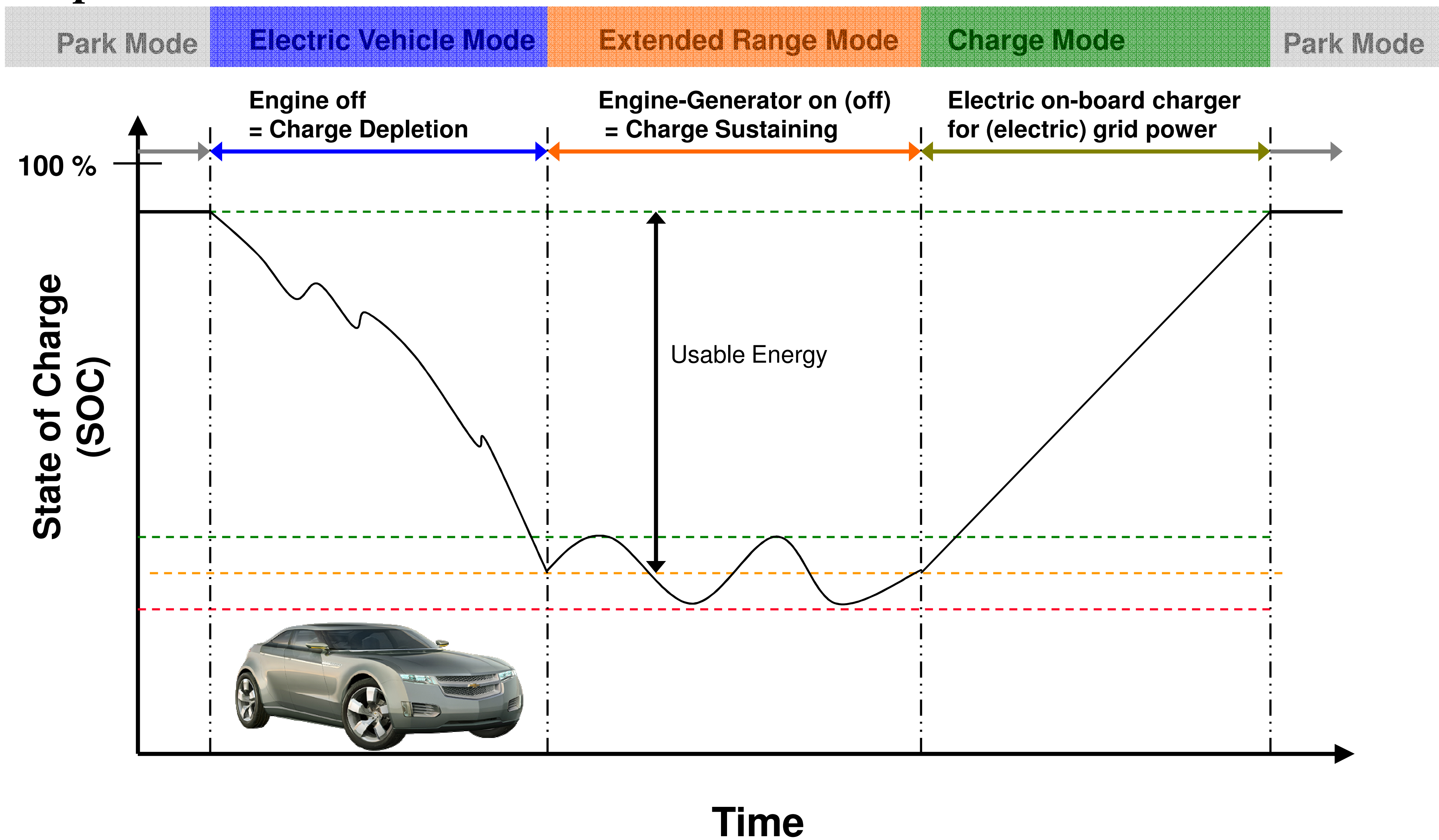
- **Two System Suppliers contracts were awarded (June 2007):**
  - Compact Power Inc. (CPI) subsidiary of LG Chem
    - Integrating LG Chem cells
  - Continental Automotive (Conti)
    - Integrating A123 Systems cells

- **Cell development contract awarded to A123 Systems (Aug 2007)**

EFLEX RESS Test Status

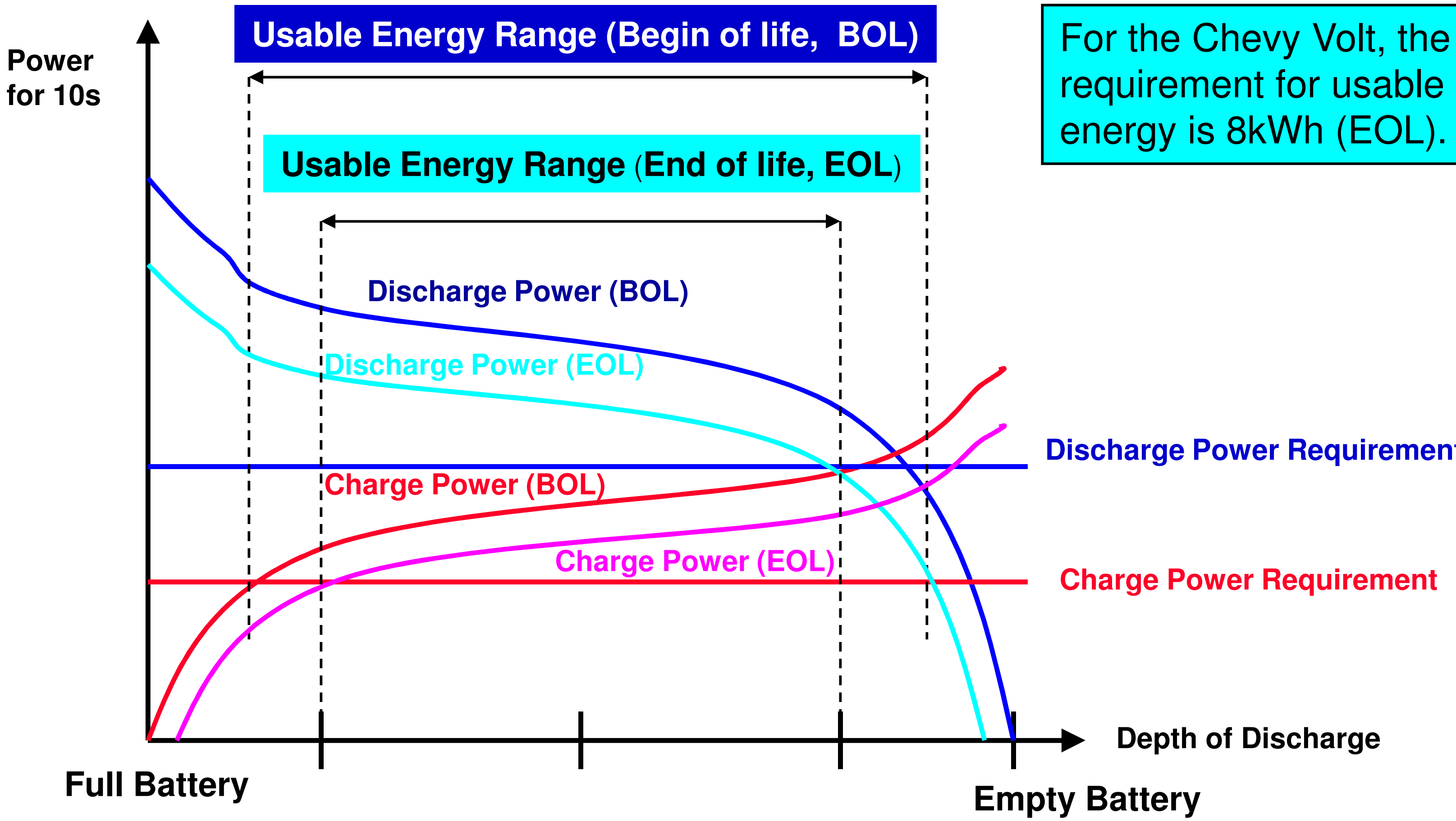
- **Tested successfully on pack level**
  - Power
  - Energy
  - Efficiency
  - Thermal systems
  - Controls
- **Tested successfully on the cell level**
  - All of the above
  - Accelerated Life
  - Abuse

Extended Range Electric Vehicle Operation Modes



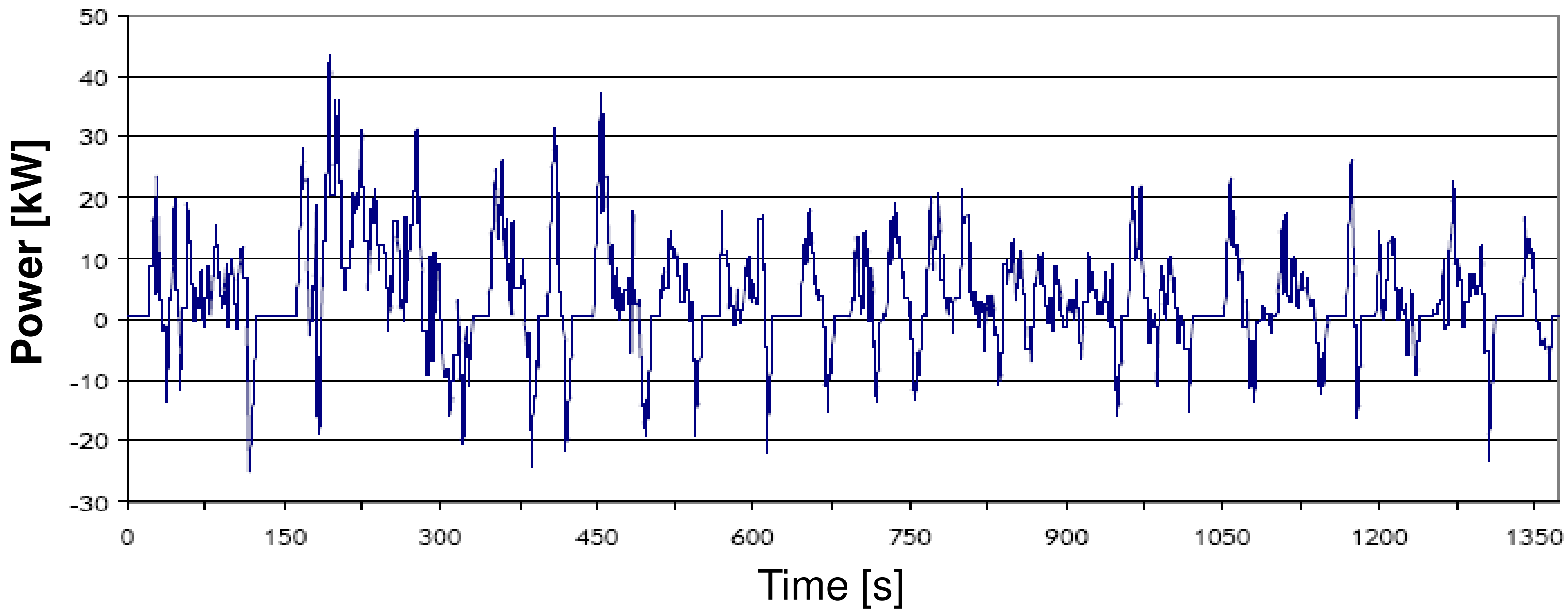
Usable Energy definition

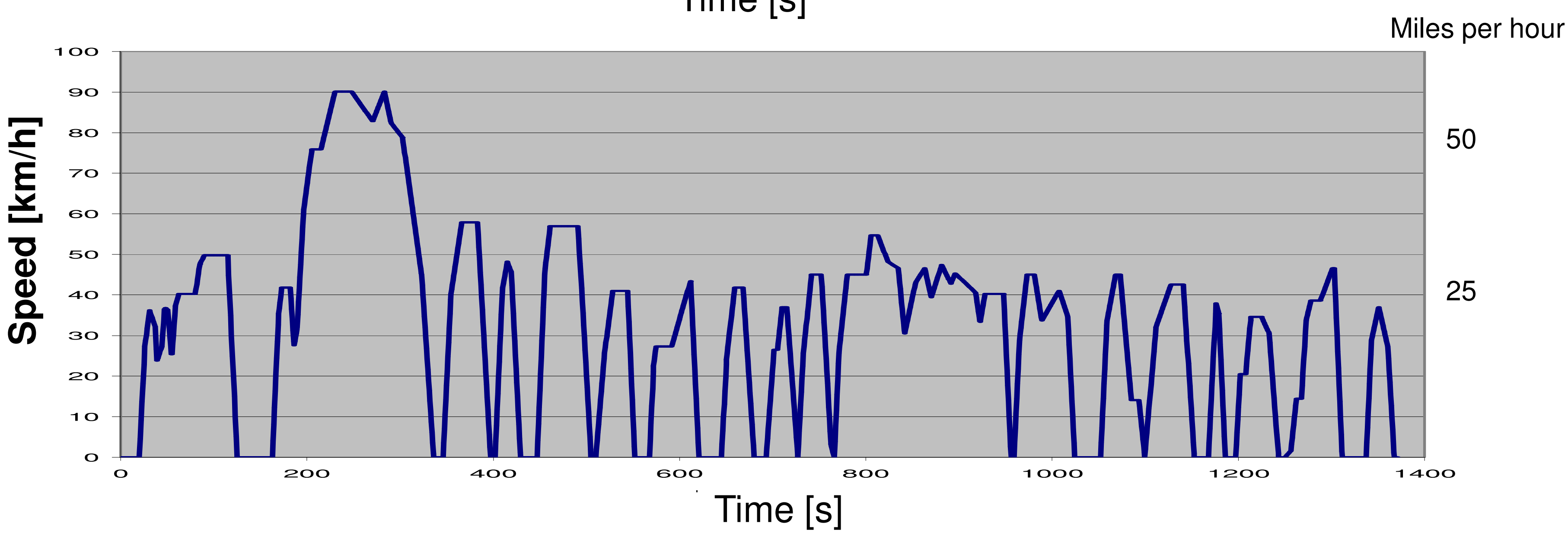
For the Chevy Volt, the requirement for usable energy is 8kWh (EOL).



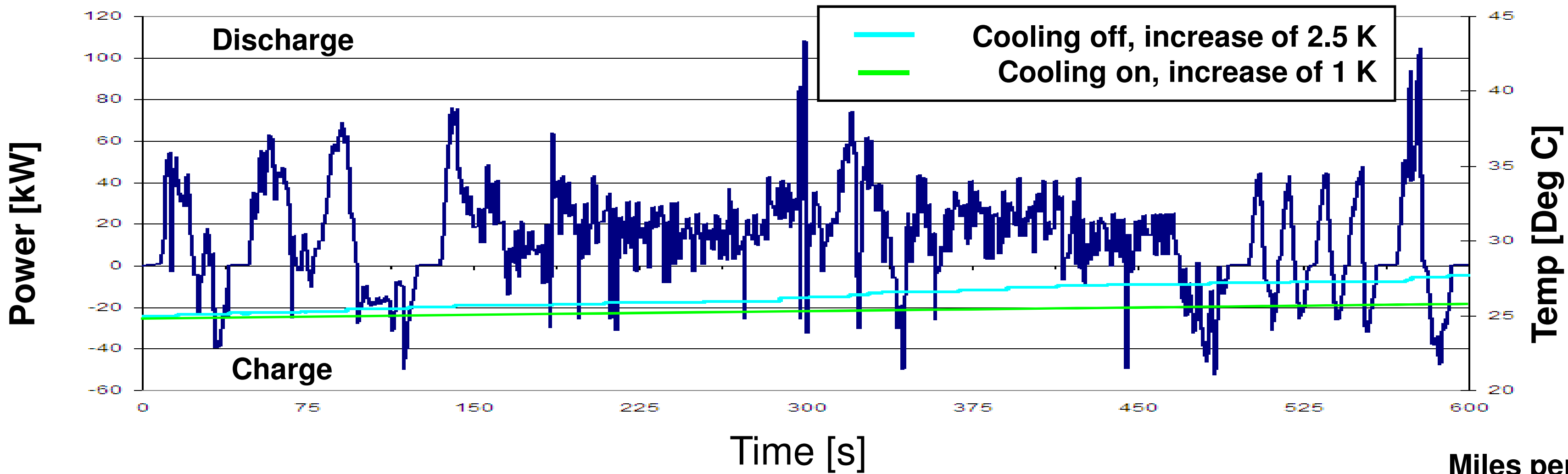
Usable Energy is defined by the operating range over which the charge and discharge power requirements are fulfilled at end of life (Battery Temperature: 20°C). ***This enables predictable vehicle performance in EV mode.***

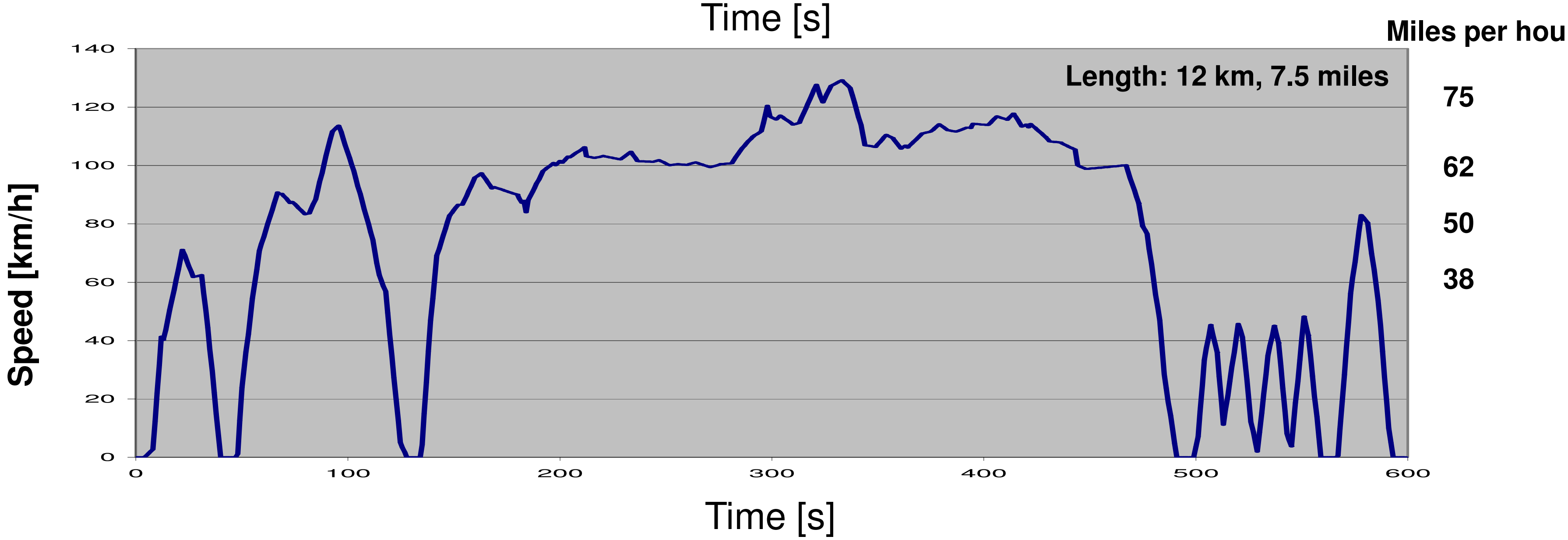
EFLEX: Power required to drive City Cycle in charge depletion (EV) mode





Power profile in US06 cycle EFLEX charge depletion mode (EV)





US06 drive cycle power profile exceeds the average power of more than 95% of drivers surveyed in a study in California.

Comparison of GM's requirements to USABC specs

UNITED STATES ADVANCED BATTERY CONSORTIUM

FreedomCAR & Fuel Partnership

Requirements of End of Life Energy Storage Systems for PHEVs

Characteristics at EOL (End of Life)		High Power/Energy Ratio Battery	GM 2-Mode PHEV (EFLEX FCEV)	High Energy/Power Ratio Battery	EFLEX EREV
Reference Equivalent Electric Range	miles	10	10	40	40
Peak Pulse Discharge Power - 2 Sec / 10 Sec	kW	50 / 45	50/45	46 / 38	115/110
Peak Regen Pulse Power (10 sec)	kW	30	27	25	60
Available Energy for CD (Charge Depleting) Mode, 10 kW Rate	kWh	3.4	3.5	11.6	8
Available Energy for CS (Charge Sustaining) Mode	kWh	0.5	0.3	0.3	0.35
Minimum Round-trip Energy Efficiency (USABC HEV Cycle)	%	90	90	90	90
Cold cranking power at -30℃, 2 sec - 3 Pulses	kW	7	7	7	8
CD Life / Discharge Throughput	Cycles/MWh	5,000 / 17		5,000 / 58	4700 / 54
CS HEV Cycle Life, 50 Wh Profile	Cycles	300,000		300,000	
Calendar Life, 35℃	year	15	10	15	10
Maximum System Weight	kg	60	90	120	160
Maximum System Volume	Liter	40	TBD	80	100
Maximum Operating Voltage	Vdc	400	420	400	410
Minimum Operating Voltage	Vdc	>0.55 x Vmax	170	>0.55 x Vmax	232
Maximum Self-discharge	Wh/day	50		50	5% in 60 Days
System Recharge Rate at 30℃	kW	1.4 (120V/15A)	1.4	1.4 (120V/15A)	3.6 (230V/16 A)
Unassisted Operating & Charging Temperature Range	℃	-30 to +52	-30 to +52	-30 to +52	-30 to +52
Survival Temperature Range	℃	-46 to +66	-46 to +66	-46 to +66	-46 to +66
Maximum System Production Price @ 100k units/yr	$	$1,700		$3,400	

EFLEX EREV requires 2.5 times the power of USABC requirements

Batteries for extended range EV's and plug in Hybrids…future focus

- **Cost**
  - Can we size pack closer to end-of-life requirements?
  - Can we reduce materials & processes costs?
- **Life**
  - How do electrodes fail?
  - Can we develop an accelerated life test?
- **Temperature tolerance**
  - Can we improve low temperature power?
  - Why is battery life shorter at higher temperatures?

1

Research questions around degradation phenomena

Formation of Lithium-Graphite Intercalation Compounds in Nonaqueous Electrolytes and Their Application as a Negative Electrode for a Lithium Ion (Shuttlecock) Cell

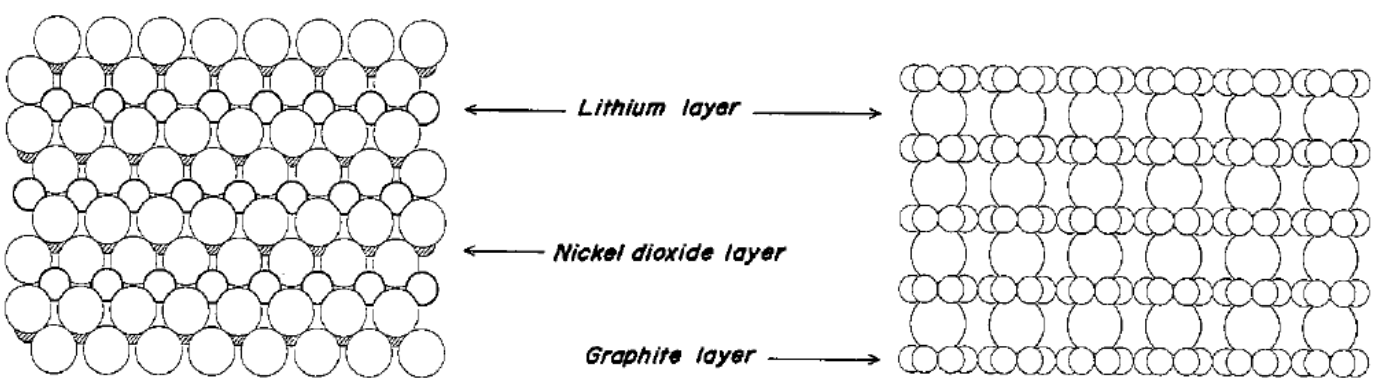
Tsutomu Ohzuku,* Yasunobu Iwakoshi, and Keijiro Sawai

Electrochemistry and Inorganic Chemistry Laboratory, Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi, Osaka 558, Japan

J. Electrochem. Soc., Vol. 140, No. 9, September 1993

$$\underset{(1.19\ \mathrm{cm^3 \cdot Ah^{-1}})}{\square C_6} + \underset{(0.76\ \mathrm{cm^3 \cdot Ah^{-1}})}{LiNiO_2} \rightleftarrows \underset{(1.34\ \mathrm{cm^3 \cdot Ah^{-1}})}{LiC_6} + \underset{(0.69\ \mathrm{cm^3 \cdot Ah^{-1}})}{\square NiO_2}$$

Total volume of $\square C_6$ and $LiNiO_2$ in the discharged state is $1.95\ \mathrm{cm^3 \cdot Ah^{-1}}$, and that of LiC_6 and $\square NiO_2$ in charged state is $2.03\ \mathrm{cm^3 \cdot Ah^{-1}}$. Therefore, the volume change of the ma-



What governs the durability and reliability of lithium ion cells? Reactions, transport phenomena, and fracture within insertion electrodes.

Mark Verbrugge
with YT Cheng
and many others
inside and outside
GM

Playa with mud cracks, dawn. Black Rock Desert, Nevada, USA
http://www.terragalleria.com/pictures-subjects/dried-mud/picture.dried-mud.usnv9106.html

Crack (fracture) propagation takes place during drying (moisture extraction) when the surface undergoes tensile contraction.

Structural modifications of disordered mesocarbon microbeads with lower temperatures of heat treatment

Prathap Haridoss, Francisco A. Uribe, Fernando H. Garzon, and Thomas A. Zawodzinski, Jr.
Electronic and Electrochemical Materials and Devices Group, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

J. Mater. Res., Vol. 13, No. 7, Jul 1998

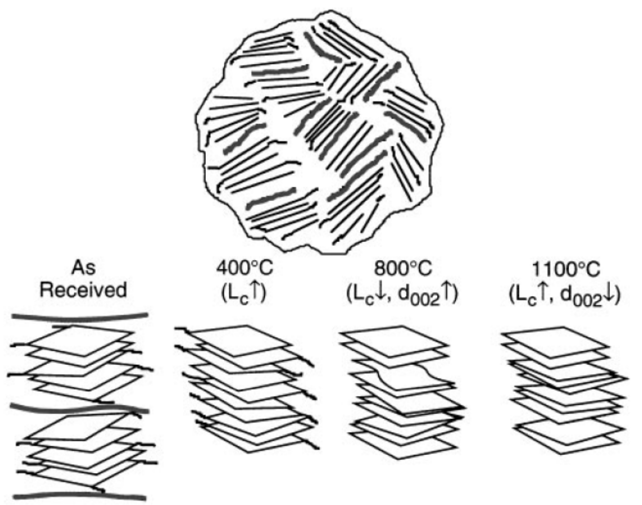


FIG. 12. Schematic representation of structural changes resulting from heat treatment.

Mesocarbon microbeads (MCMB's) are spherical carbon particles that are produced from mesophase pitch or coal tar.[20] These carbon particles have a size range of about 1–80 μm. As a result, they have low surface to volume ratios which reduces the total irreversible capacity loss due to passivating film formation on the surface. The electrochemical properties of mesocarbon

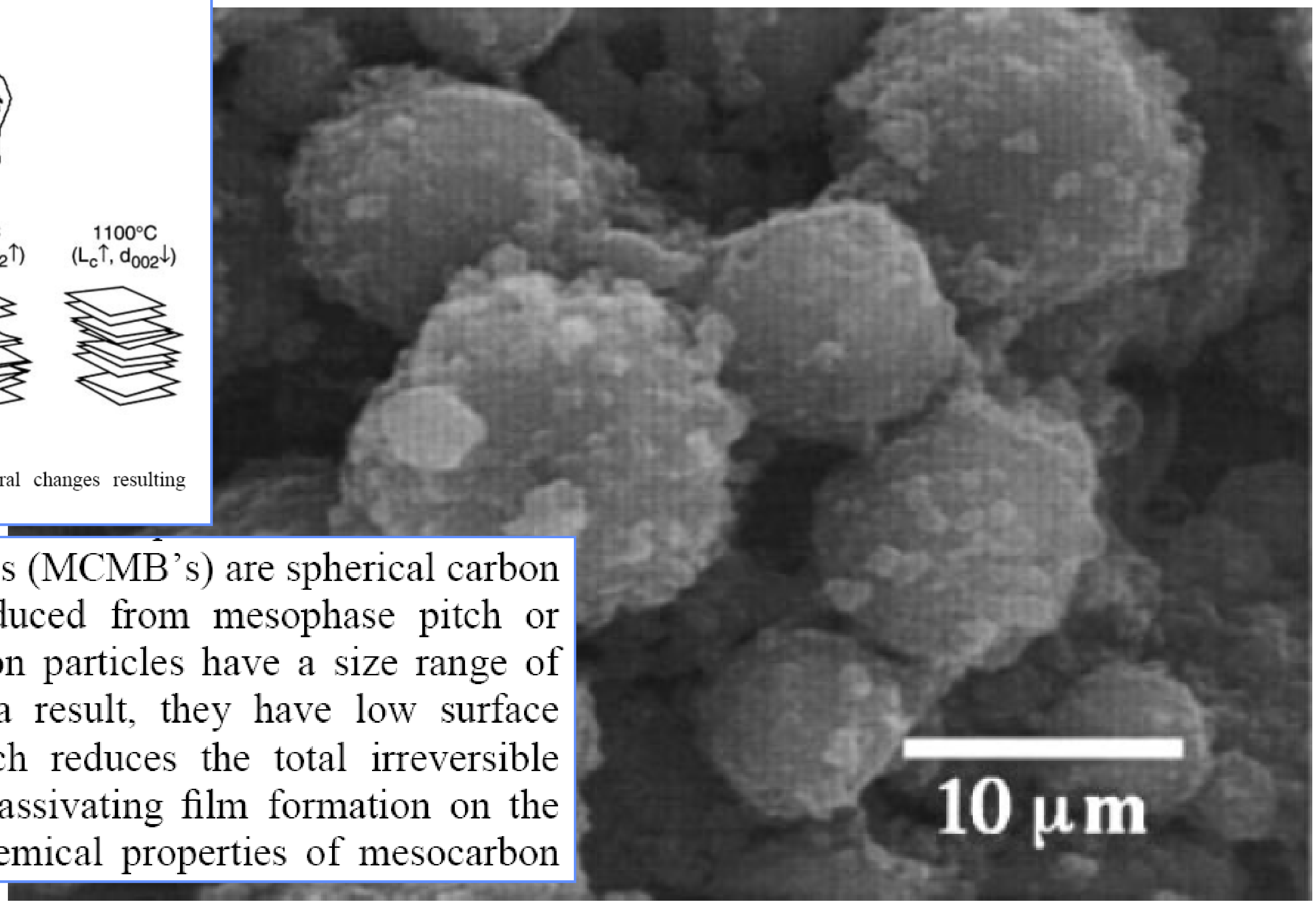
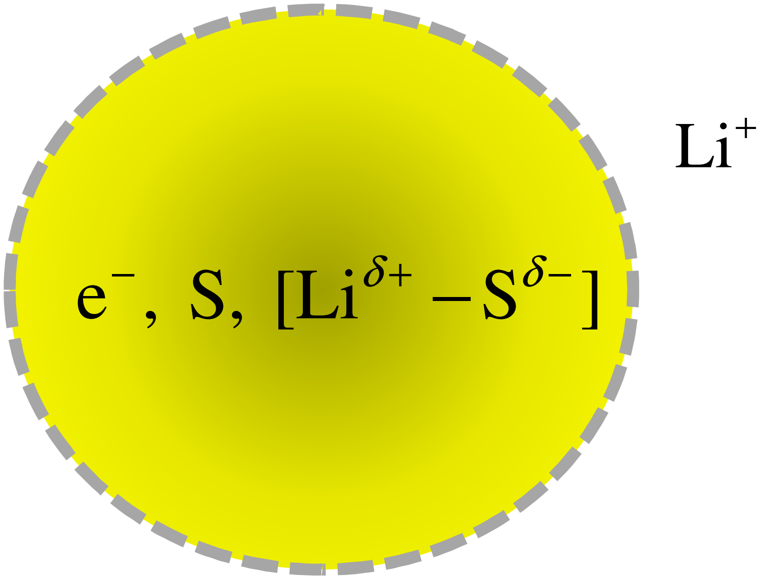


FIG. 1. SEM micrograph of MCMB 6-G as received.

Intercalation process



Typically 10% expansion for negatives (carbons) and 5 to 10% for positives (metal phosphates or oxides)

contraction

← Negative (carbon) discharge

$$Li^+ + S + e^- = [Li^{\delta+} - S^{\delta-}]$$

Negative (carbon) charge →

expansion

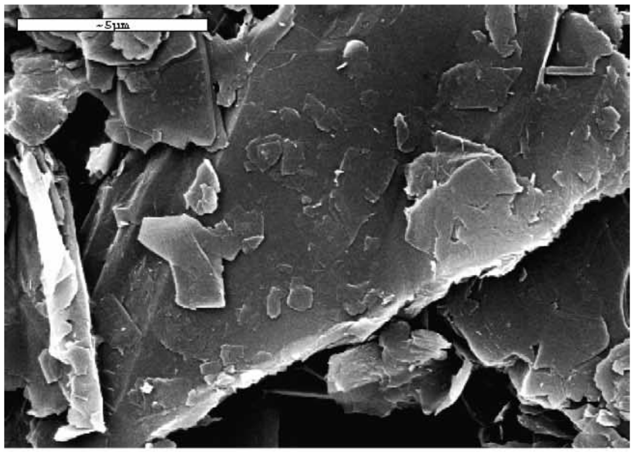
Capacity fading of lithiated graphite electrodes studied by a combination of electroanalytical methods, Raman spectroscopy and SEM

E. Markervich, G. Salitra, M.D. Levi, D. Aurbach *

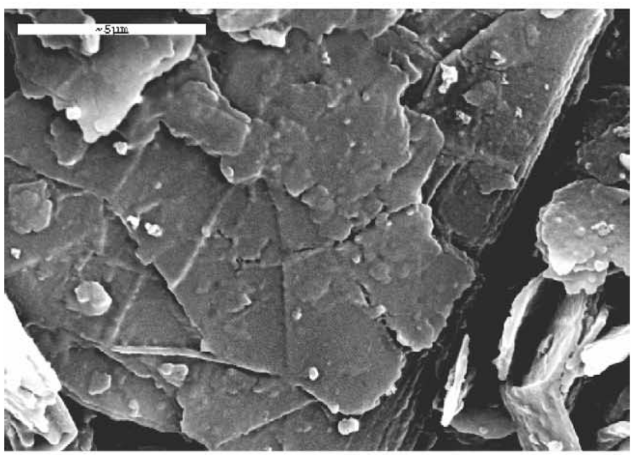
Department of Chemistry, Bar-Ilan University, 52900 Ramat-Gan, Israel

NEGATIVE ELECTRODE

Journal of Power Sources 146 (2005) 146–150



(a)



(b)

SEM images of the surface of the KS-15 composite pristine electrode (a) and the same electrode after 140 intercalation–deintercalation cycles at 25 ◦C (b and c).

During cycling, graphite particles crack into smaller pieces that are less oriented than the original platelets, with the possible filling of the cracks thus formed by the reduction products of the electrolyte solution. In addition, the average crystalline size (estimated by Raman spectroscopy) decreases as cycling progresses.

Electrochemical and Solid-State Letters, **4** (9) A137-A140 (2001)
1099-0062/2001/4(9)/A137/4/$7.00 © The Electrochemical Society, Inc.

Colossal Reversible Volume Changes in Lithium Alloys

L. Y. Beaulieu,[a,*] K. W. Eberman,[b,**] R. L. Turner,[b,**] L. J. Krause,[b,**] and J. R. Dahn[a,c,**,z]

NEGATIVE ELECTRODE

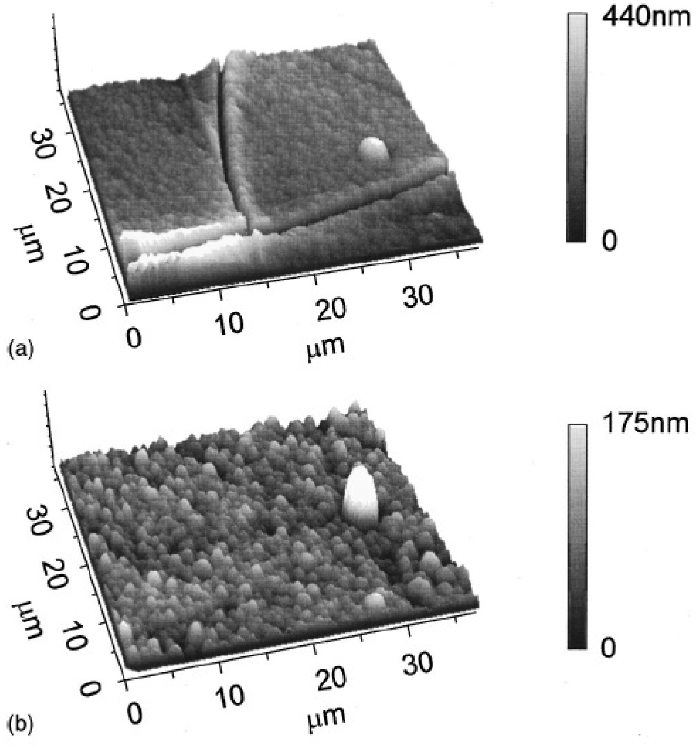


Figure 4. Three dimensional views of (a) image 2h and (b) image 2i. The out-of-plane distance is shown using the contrast scale given to the right of each image.

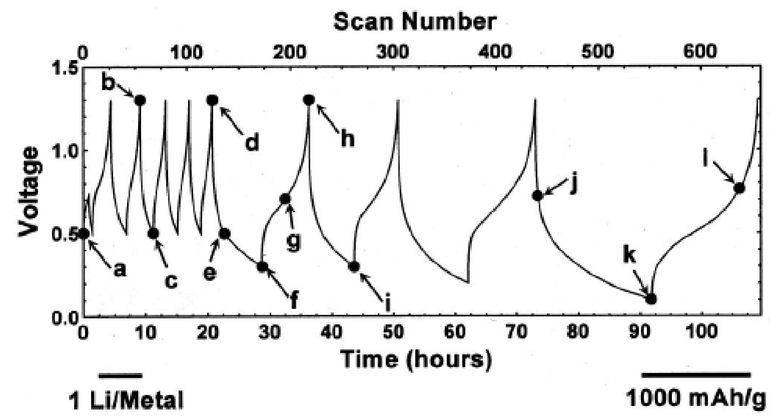


Figure 3. Selected AFM images with scan ranges and contrasts given in Table II. The images a-l were collected at the corresponding points indicated in the voltage-time curve. A scale bar displays the length of time that corresponds to a charge transfer of 1000 mAh/g and another scale bar displays the time that corresponds to the reaction of 1 mol Li per mole M.

Video Clip

Video Clip

Performance of $LiNiCoO_2$ materials for advanced lithium-ion batteries

POSITIVE ELECTRODE

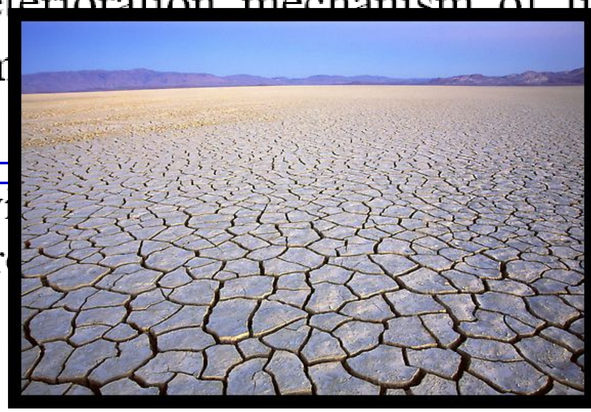
Yuichi Itou, Yoshio Ukyo *

Toyota Central R&D Labs Inc., Nagakute, Aichi 480-1192, Japan

Available online 8 August 2005

Journal of Power Sources 146 (2005) 39–44

In this study, the de... lithium- ion batteries using com... O_2 as the positive electrode ... . The



are formed in particles w... e
resistance at positive electr...
tronic conduction, due to ... r
to verify this mechanism, ...

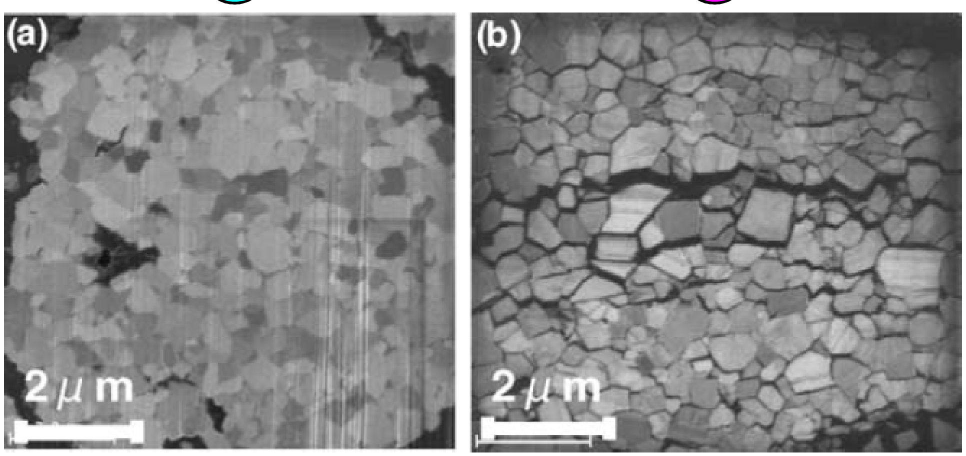
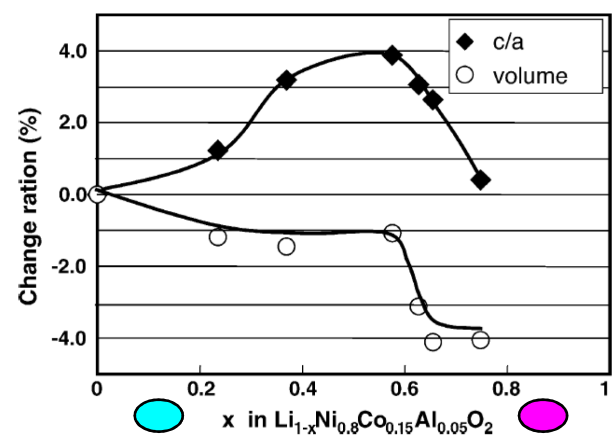


Fig. 9. Morphology of positive particle: (a) state of discharge, (b) state of charge.

"This result indicates volume change causes the increase in resistance."



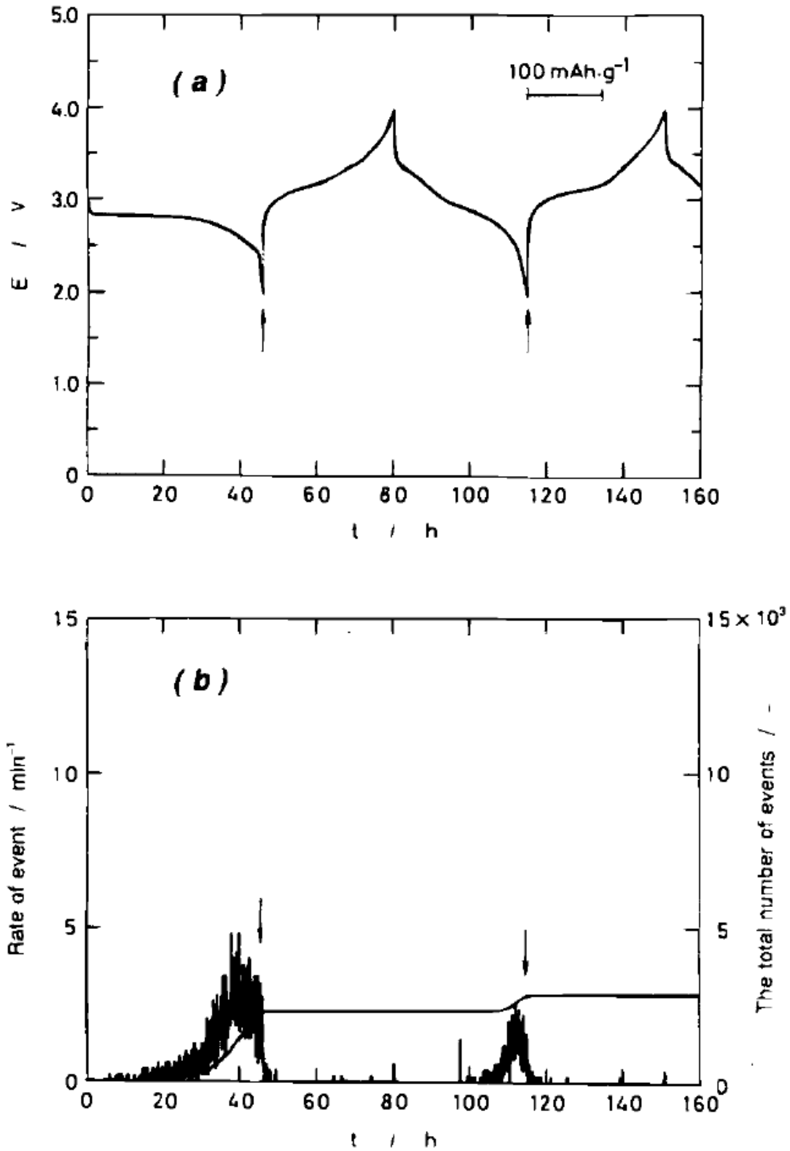


Fig. 5. Acoustic emission observed during the continuous charge and discharge of a Li/HEMD(400) cell in a voltage range of 2.0 to 4.0 V at a rate of 0.1 mA cm^{-2}; (a) charge and discharge curves for the initial two cycles and (b) the rate of acoustic events in counts per min together with the total number of events. The positive electrode was prepared by pasting a mix (74 mg), consisting of 80 w/o HEMD(400), 10 w/o acetylene black, and 10 w/o Teflon on an aluminum screen.

POSITIVE ELECTRODE

Monitoring of Particle Fracture by Acoustic Emission during Charge and Discharge of Li/MnO_2 Cells

Tsutomu Ohzuku,* Hirohiko Tomura, and Keijiro Sawai*

J. Electrochem. Soc., Vol. 144, No. 10, October 1997

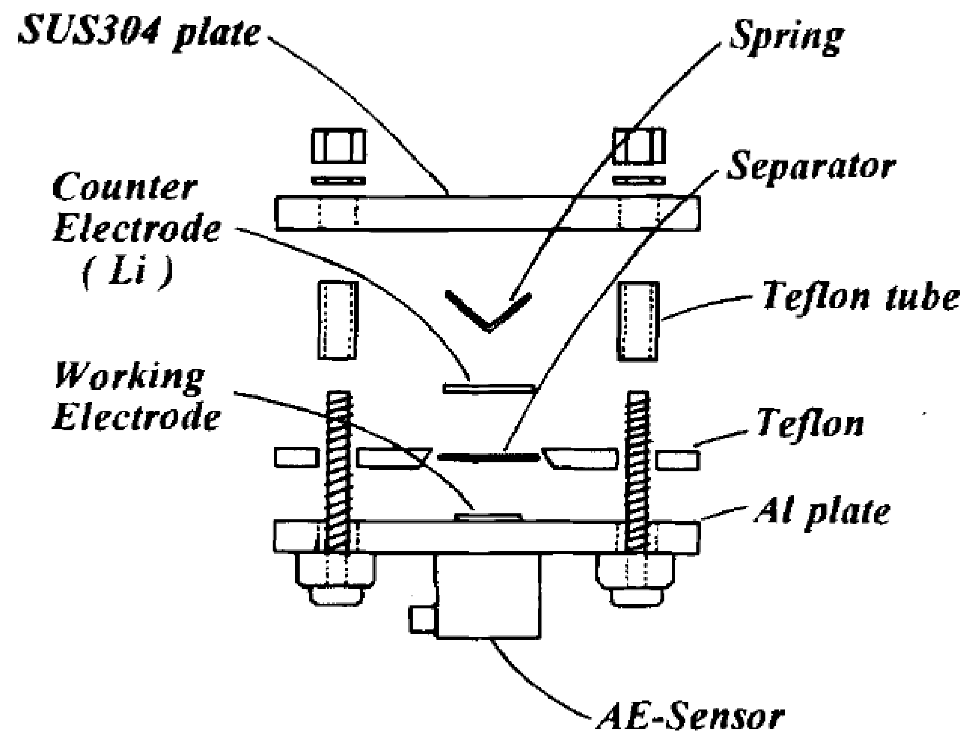


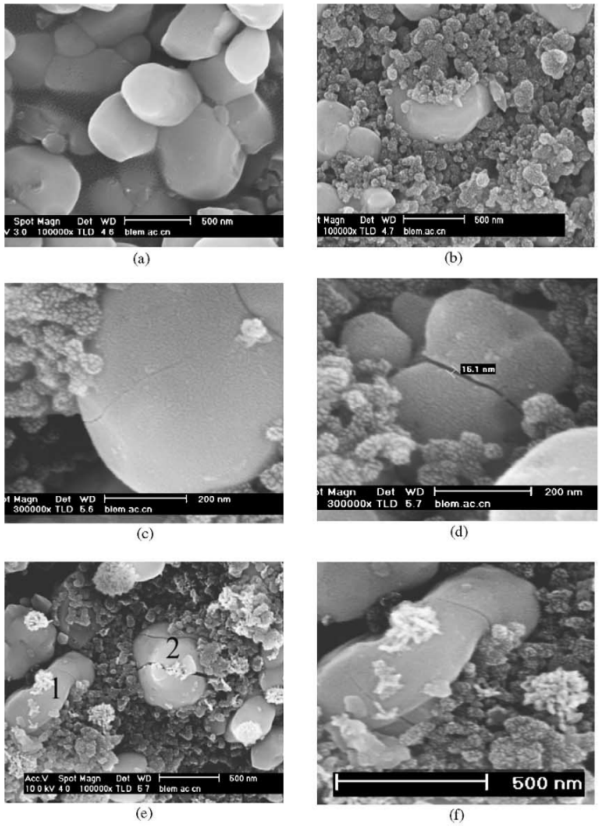
Fig. 1. Schematic illustration of electrochemical cell used for monitoring acoustic emission.

Cracking causing cyclic instability of $LiFePO_4$ cathode material

Deyu Wang, Xiaodong Wu, Zhaoxiang Wang, Liquan Chen*

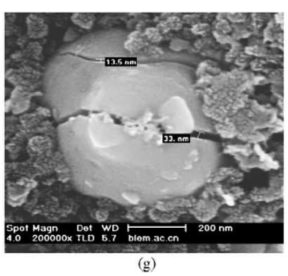
Journal of Power Sources 140 (2005) 125–128

POSITIVE ELECTRODE



Cycles	
0'	0
10	30
60	60_p1
60_p2	

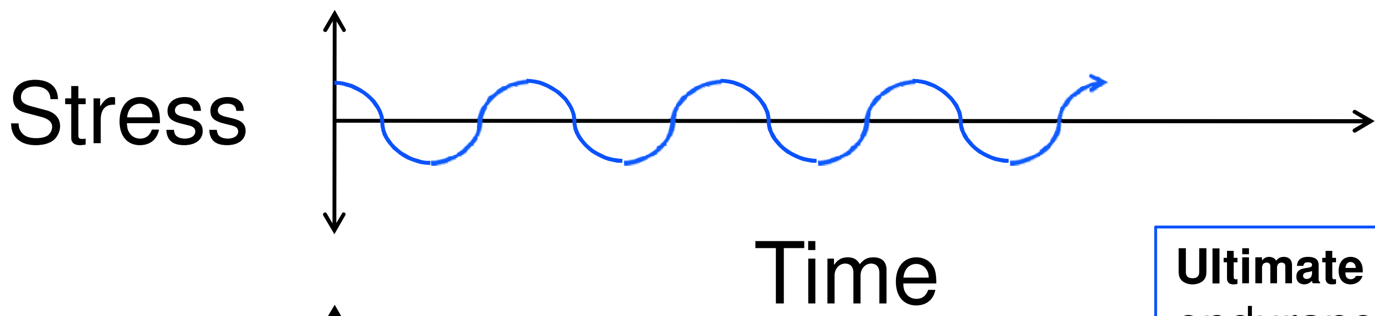
$LiFePO_4$ possesses an olivine structure with three-dimensional network. The lattice constants of $LiFePO_4$ are a = 10.33 Å, b = 6.01 Å, c = 4.69 Å, V = 291.2 Å^3 and the lattice constants of $FePO_4$ are a = 9.81 Å, b = 5.79 Å, c = 4.78 Å, V = 271.5 Å, respectively [11]. The volume change of this phase transformation is 6.77 %. The volume change is



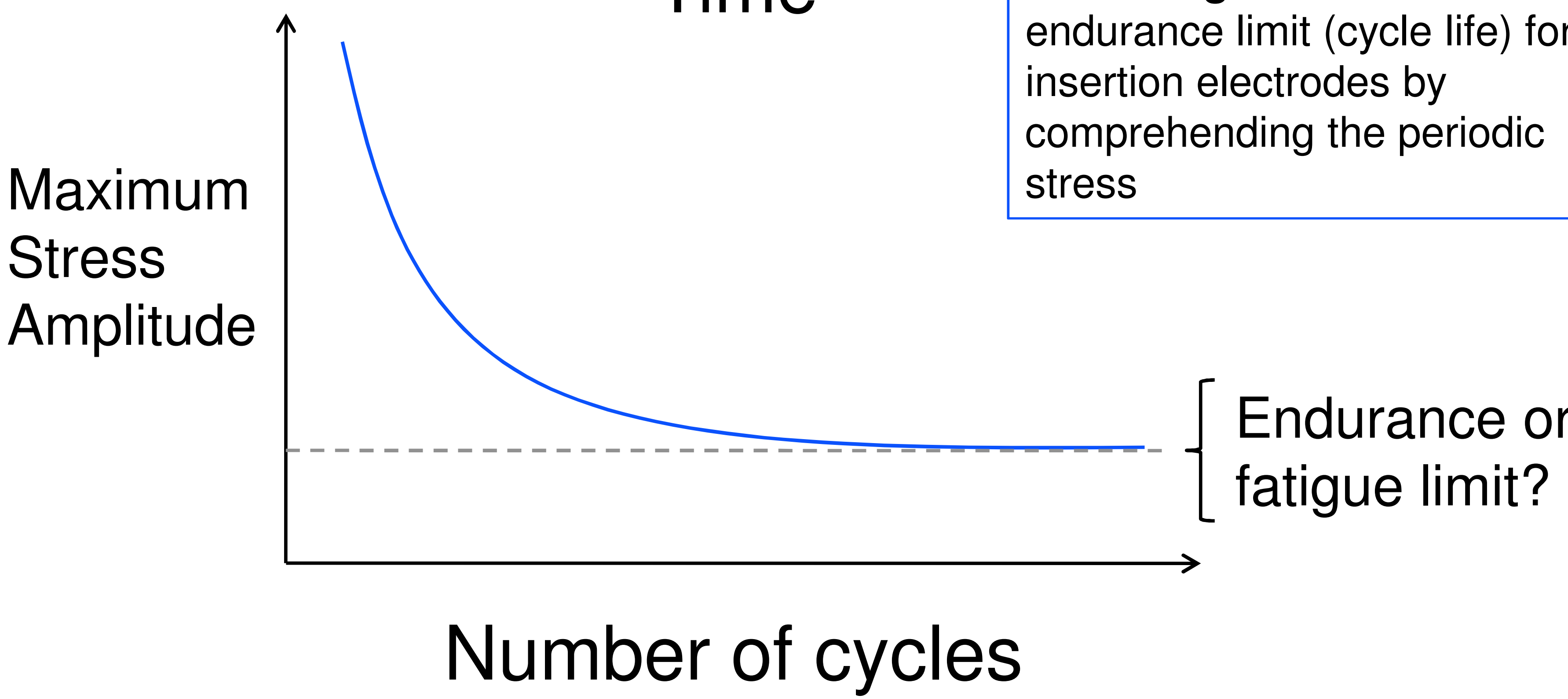
Li-extraction/insertion. The formation of cracks will lead to increased polarization of electrode and poor electric contact between active particles and conductive additives or aluminum foil current collector. This should be one of the

Wöhler S-N curve

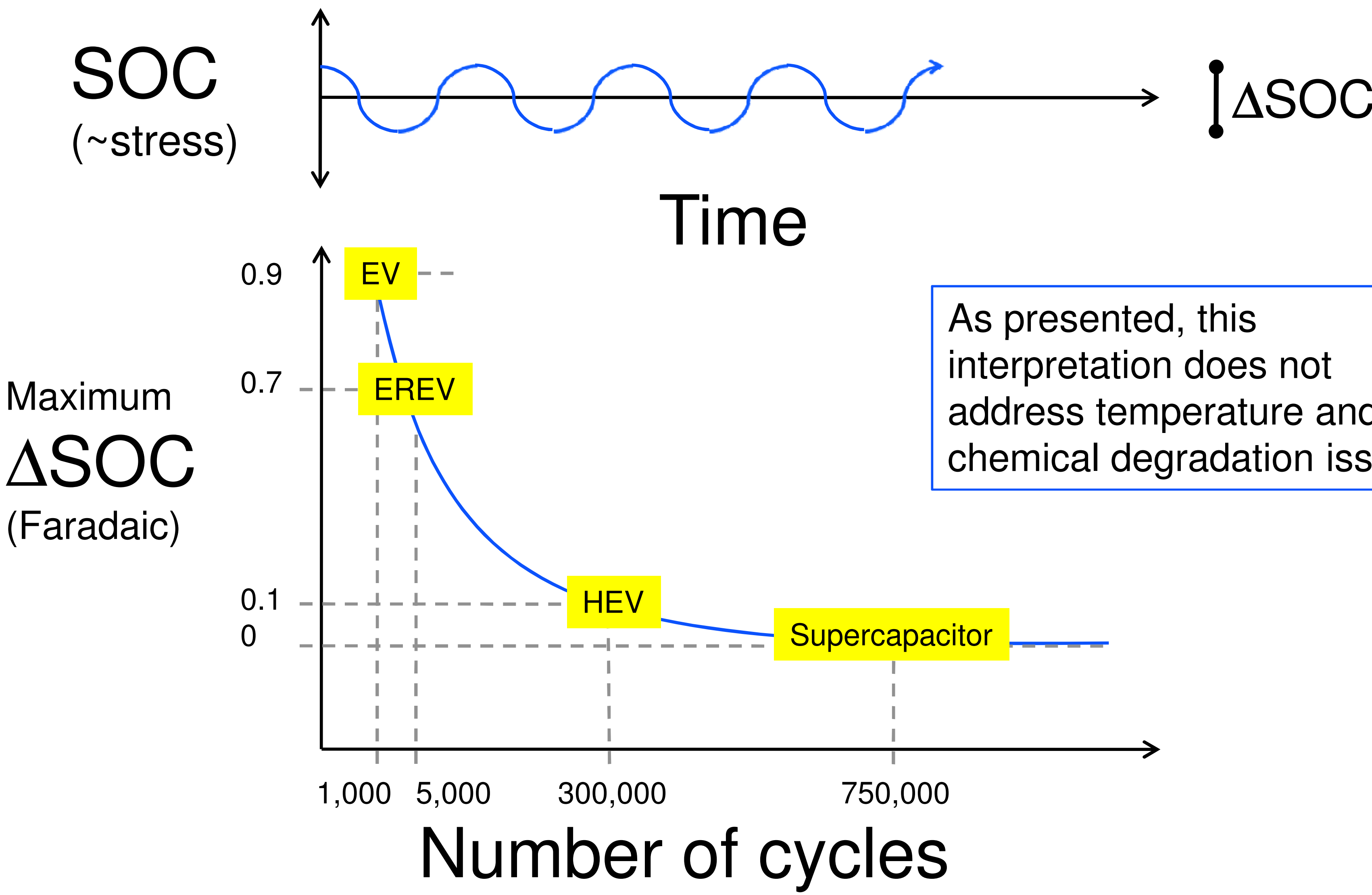
(1870…railroad axles)



Ultimate goal: Determine the endurance limit (cycle life) for insertion electrodes by comprehending the periodic stress



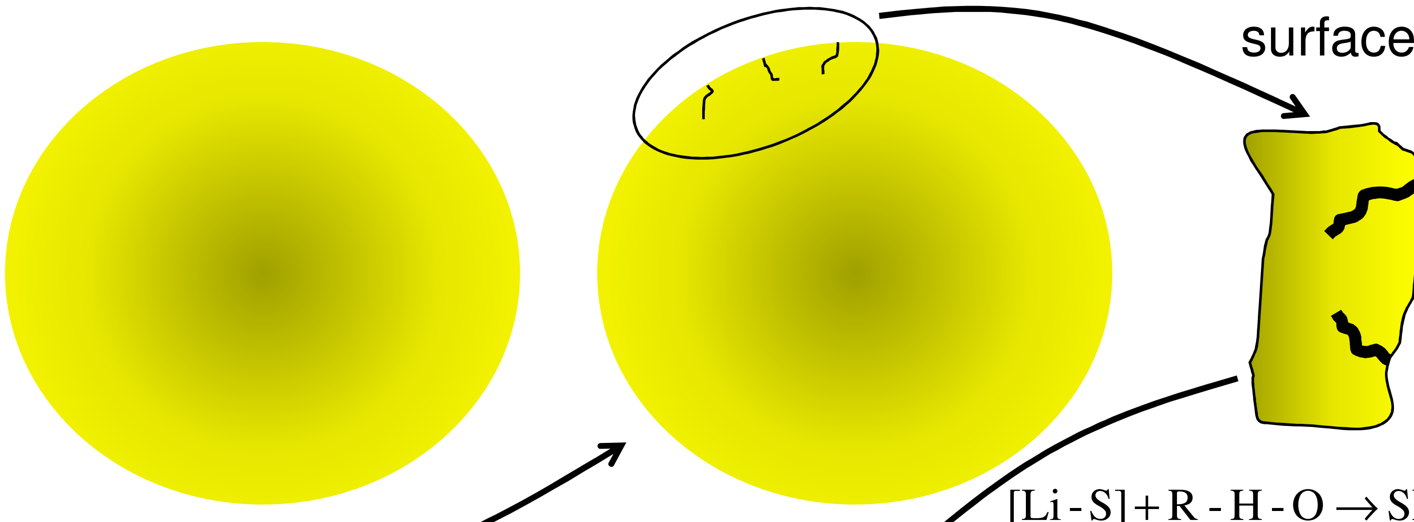
S-N curves as ΔSOC-N curves

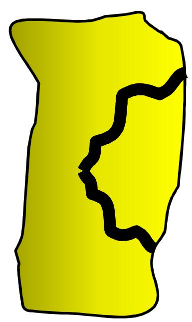


As presented, this interpretation does not address temperature and chemical degradation issues.

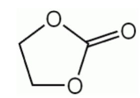
What's wrong with cracks?

Overall qualitative degradation model…Li-carbon





$$[Li - S] + R - H - O \rightarrow SEI + gasses + \ldots$$

$[Li - S] +$  $\rightarrow S + LiCO_3 \downarrow + H_2C = CH_2 \uparrow$

Increased disorder. d_{002} peak-width at half max amplitude increases with time for lithiated carbon

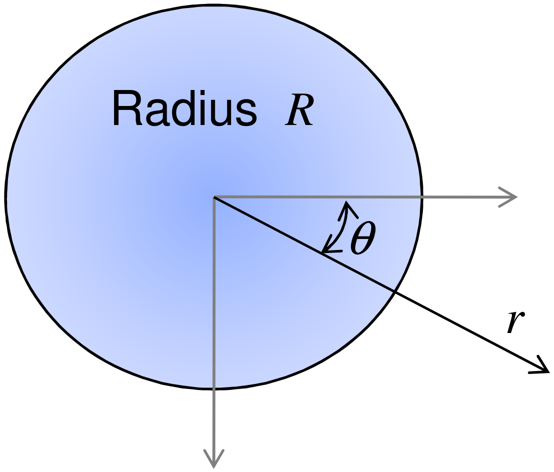
1. Loss of Li: SEI formation and loss of Li seen in full cell experiments

2. Electrode isolation and loss of active material when cracks join

No firm experimental confirmation to date, but consistent with observations

Mathematical details

Potential step, $\Theta_0 \rightarrow \Theta_R$



$$S_1 = \frac{1 - \dfrac{(1+\nu)}{E}\dfrac{K^s}{R}}{1 + \dfrac{(1-2\nu)}{E}\dfrac{2K^s}{R}} \quad , \quad S_2 = -\frac{2\dfrac{\tau^0}{R}}{1 + \dfrac{(1-2\nu)}{E}\dfrac{2K^s}{R}}$$

Surface modulus K^s Surface stress τ^0

- ❑ **Influence of both terms vanish as $R \rightarrow \infty$**
- ❑ **Results now consistent with nano-particle and thin film electrodes yielding enhanced cycle life**

$$\frac{3(1-\nu)}{E\Omega C_S}\sigma_r(t,r) = \frac{2}{3}\Theta_R(S_1 - 1) - 4(\Theta_R - \Theta_0)\sum_{n=1}^{\infty}\left[\frac{S_1}{(n\pi)^2} + (-1)^n \frac{\sin(n\pi x) - n\pi x\cos(n\pi x)}{(n\pi x)^3}\right]e^{-n^2\pi^2\tau} + \frac{3(1-\nu)}{E\Omega C_S}S_2$$

$$\frac{3(1-\nu)}{E\Omega C_S}\sigma_\theta(t,r) = \frac{2}{3}\Theta_R(S_1 - 1) - 2(\Theta_R - \Theta_0)\sum_{n=1}^{\infty}e^{-n^2\pi^2\tau}\left[\frac{2S_1}{(n\pi)^2} - (-1)^n \frac{(\sin n\pi x - n\pi x\cos n\pi x)}{(n\pi x)^3} + (-1)^n \frac{\sin(n\pi x)}{n\pi x}\right] + \frac{3(1-\nu)}{E\Omega C_S}S_2$$

❑ **For the stress functions, the transient terms are proportional to ΔSOC (ΔSOC ∝ stress)**

On surface energy and surface stress

J. Willard Gibbs, H. A. Bumstead, W. R. Longley, R. G. Van Name, *The Collected Works of J. Willard Gibbs,* Longmans, Green and Co., 1928.

- Pioneering work on surface thermodynamics

R. Shuttleworth, *Proc. Phys. Soc. London, Ser. A*, 63 (1950)444.

- Relates surface stress to the work of formation of an elastically strained surface

J. C. Eriksson, *Surf. Sci.*, 14(1969)221.

- Gibbs-Eriksson equation…generalized surface thermodynamics

B.M. Grafov, G. Paasch, W. Plieth, A. Bund, *Electrochim. Acta*, 48(2003) 581.

- Unifying treatment for Shuttleworth equation for the elastic spherical electrode with the Laplace formula and the Gibbs adsorption equation

P. Sharma, S. Ganti, and N. Bhate, Appl. Phys. Lett., 82(2003)535, 89(2006)049901.

- Boundary condition used in this work, $\sigma_\theta^{surf} = \sigma_\phi^{surf} = \tau^0 + K^s \varepsilon_\theta$

Helpful related texts

D. Maugis, *Contact, Adhesion, and Rupture of Elastic Solids*, Springer, 1999.

J. Newman and K. E. Thomas-Alyea, *Electrochemical Systems*, 3rd ed., Wiley, 2004.

Next steps on life modeling

- **Crack initiation and propagation within a particle**
  - A difficult problem even in the absence of electrochemical phenomena
  - Flaw distributions within electrode particles?
  - Primary particles, potentially with grains, and secondary particles (agglomerates)
  - Incorporate the influence of chemical degradation processes
  - How does temperature come into play?
    - Mechanical deformation within particles is not substantially affected by the limited temperature fluctuations
    - Chemical reactions rates are thermally activated
- **Last, scale up from individual particles to porous electrodes**

2

Details

- Model equations
- Plots of intercalate and stress distributions

Surface Mechanics. $\sigma_\theta^{surf} \equiv \sigma_{\theta\theta}^{surf} = \sigma_{\phi\phi}^{surf} = \tau^0 + 2(\mu^s + \lambda^s)\varepsilon_{\theta\theta} \equiv \tau^0 + K^s \varepsilon_\theta$,
where $K^s = 2(\mu^s + \lambda^s)$ is known as the "surface modulus." For mechanical equilibrium,

$$\sigma_r(r \to R) = -\frac{2\sigma_\theta^{surf}}{R}$$

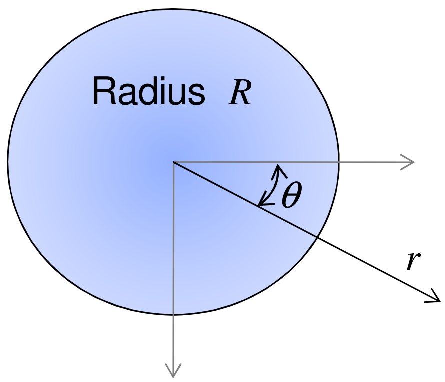
Solid Mechanics

$$\varepsilon_r = \frac{1}{E}(\sigma_r - 2\nu\sigma_\theta) + \frac{1}{3}\Omega C$$

$$\varepsilon_\theta = \frac{1}{E}[(1-\nu)\sigma_\theta - \nu\sigma_r] + \frac{1}{3}\Omega C$$

$$\varepsilon_r = \frac{du}{dr} \text{ and } \varepsilon_\theta = \frac{u}{r}.$$

$$\frac{d\sigma_r}{dr} + 2\frac{\sigma_r - \sigma_\theta}{r} = 0$$



$$\frac{d^2u}{dr^2} + \frac{2}{r}\frac{du}{dr} - \frac{2u}{r^2} = \left(\frac{1+\nu}{1-\nu}\right)\frac{\Omega}{3}\frac{dC}{dr}$$

$$u(0) = 0$$

Intercalate (lithium) transport

$$\tau = \frac{Dt}{R^2}, \quad x = \frac{r}{R}, \text{ and } \quad y = \frac{C(t,r) - C_0}{C_R - C_0} = \frac{\Theta(t,r) - \Theta_0}{\Theta_R - \Theta_0}$$

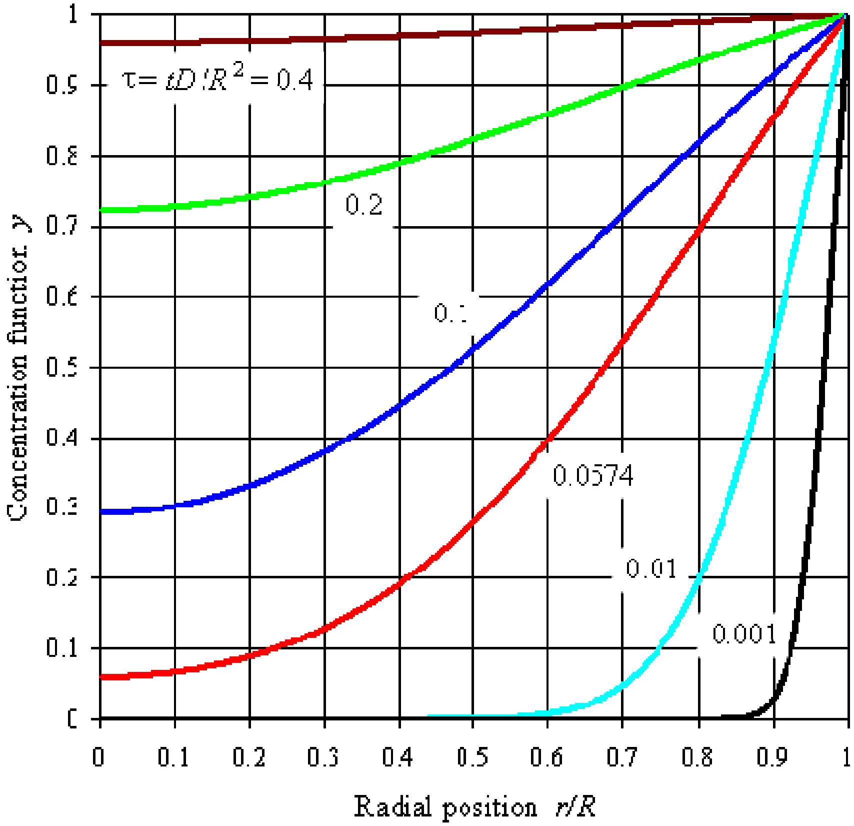
$$\frac{\partial y}{\partial \tau} = \frac{\partial^2 y}{\partial x^2} + \frac{2}{x}\frac{\partial y}{\partial x}$$

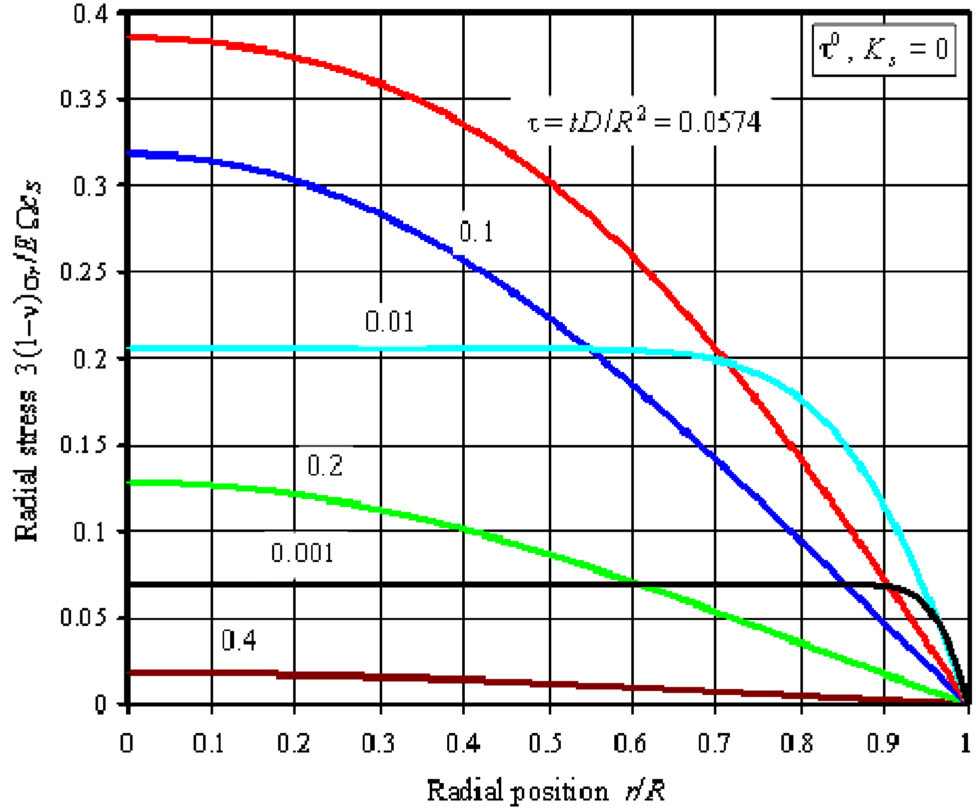
$$y(0,x) = 0$$

$$y(t,1) = 1$$

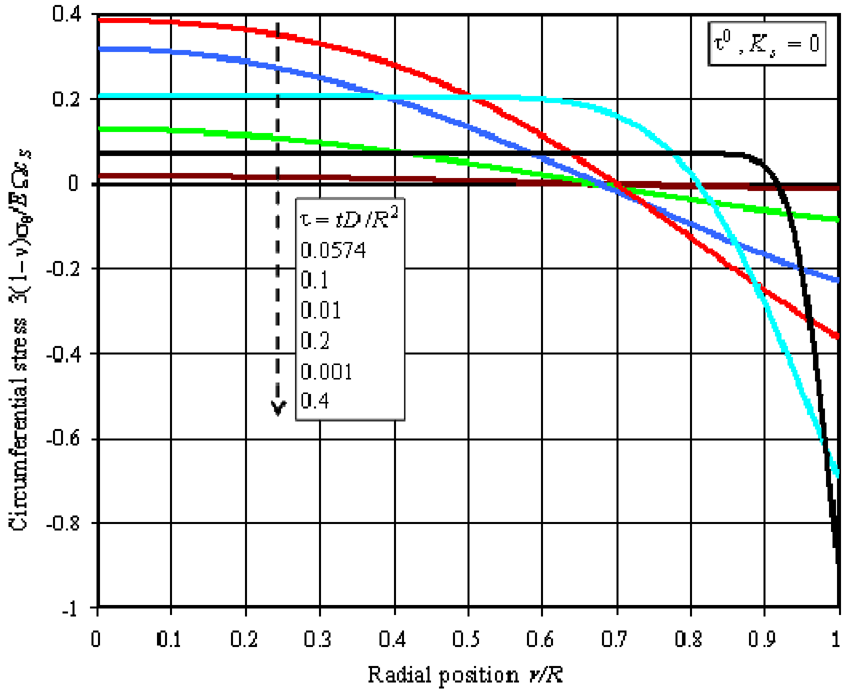
$$\left.\frac{\partial y}{\partial x}\right|_{x=0} = 0$$

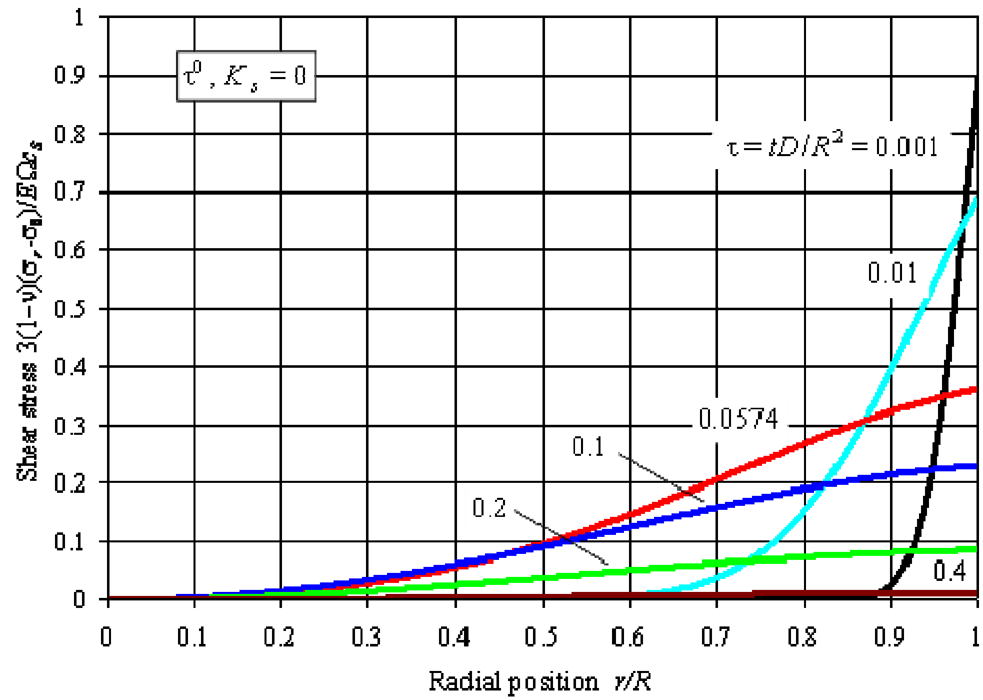
These coupled equations can be solved analytically.



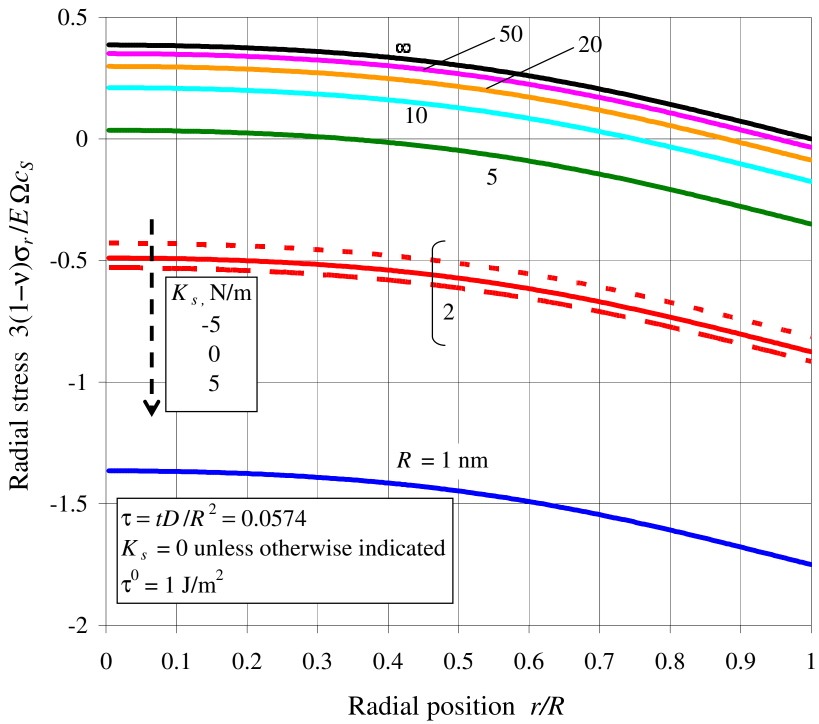


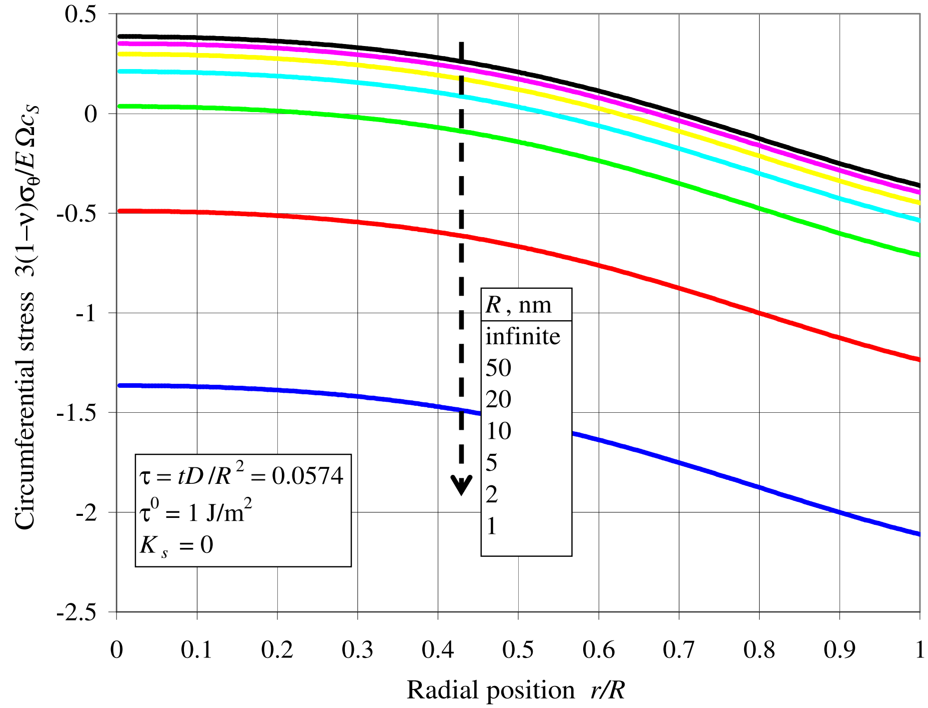
- ❑ **Positive stress: tension. Negative stress: compresion.**
- ❑ **Charge (lithiation) of negative (carbon) electrode**
- ❑ **Conventional surface conditions**
- ❑ **Maximum tensile (radial) stress at the particle center at $\tau = 0.0574$**
  - No concentration gradients initially and at end of charge





- ❑ Charge (lithiation) of negative (carbon) electrode
- ❑ Conventional surface conditions
- ❑ **Max (hydrostatic) tensile stress at the particle center**
- ❑ **Max shear stress and circumferential compressive stress at the surface initially**





- ❑ **Charge (lithiation) of negative (carbon) electrode**
- ❑ **Influence of surface mechanics are quite significant**
  - Radial stress transformed from tensile to compressive
  - Similar influence on tangential (circumferential) stess
- ❑ **Note: it is more challenging to make electrodes with smaller particles…enhanced stability comes with a cost**

Summary

- Automotive trends and technology drivers
- GM HEV (hybrid electric vehicle) and EREV (extended-range electric vehicle) roll-out plan
  - Eflex/Volt Rechargeable Energy Storage System for extended range electric vehicles
- A look towards understand battery life degradation issues