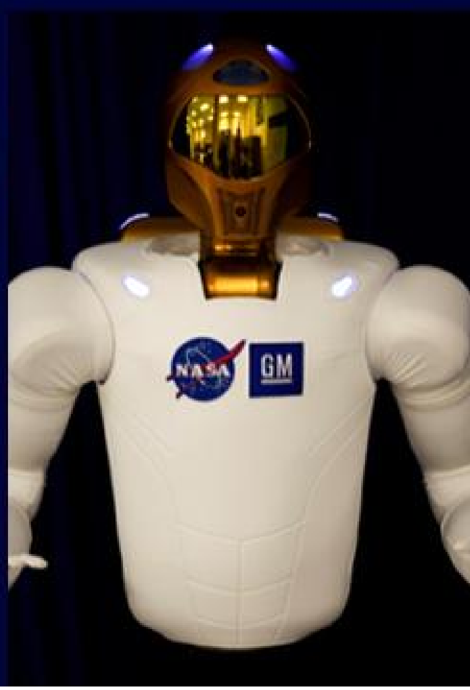
Traction batteries: automotive requirements, current status, and challenges ahead

4th Symposium on Energy Storage: Beyond Lithium Ion
Pacific Northwest National Laboratory, Richland, Washington

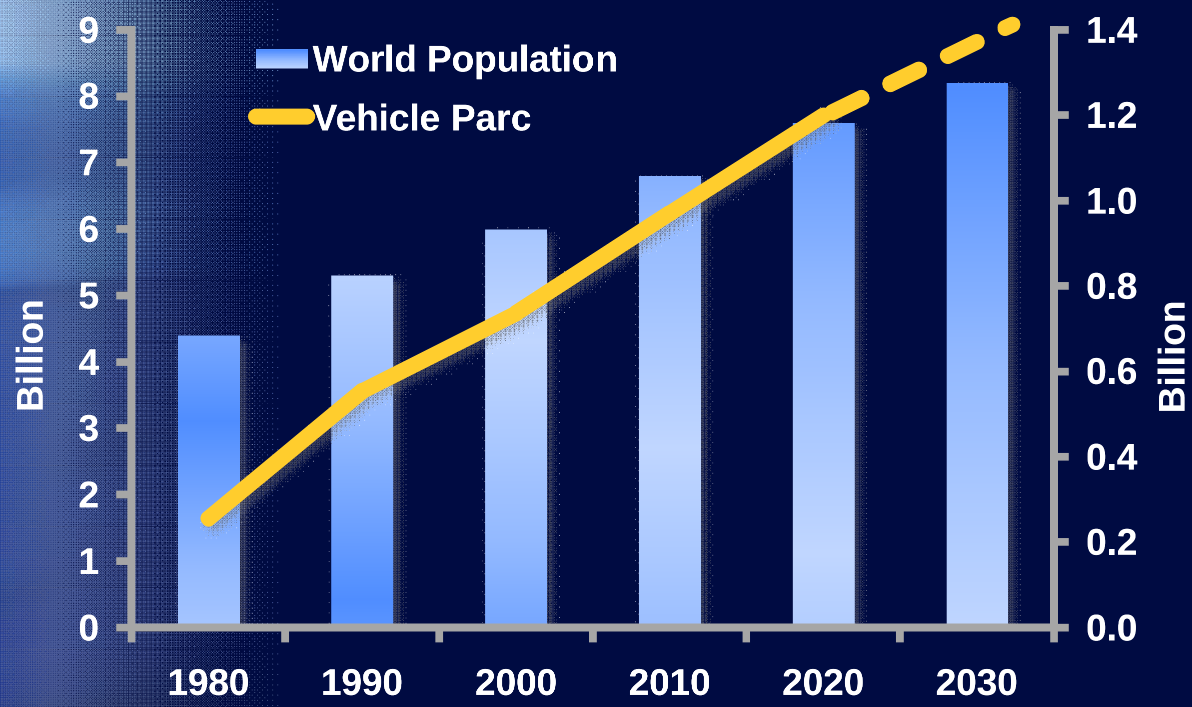
Mark Verbrugge, **Director, Chemical Sciences and Materials Systems Lab**
General Motors Research & Development


Outline

- ❑ **Automotive drivers**
  - Societal drivers
  - Automotive challenges
  - GM electrification strategy
- ❑ **Beyond lithium ion…a couple thoughts**
- ❑ **Progress and challenges for lithium ion**
  - How do lithium ion cells degrade?
  - Some potential approaches to solving degradation challenges
- ❑ **Summary**

PERSONAL MOBILITY MUST BE REINVENTED FOR THE 21st CENTURY



Sustainability Challenges

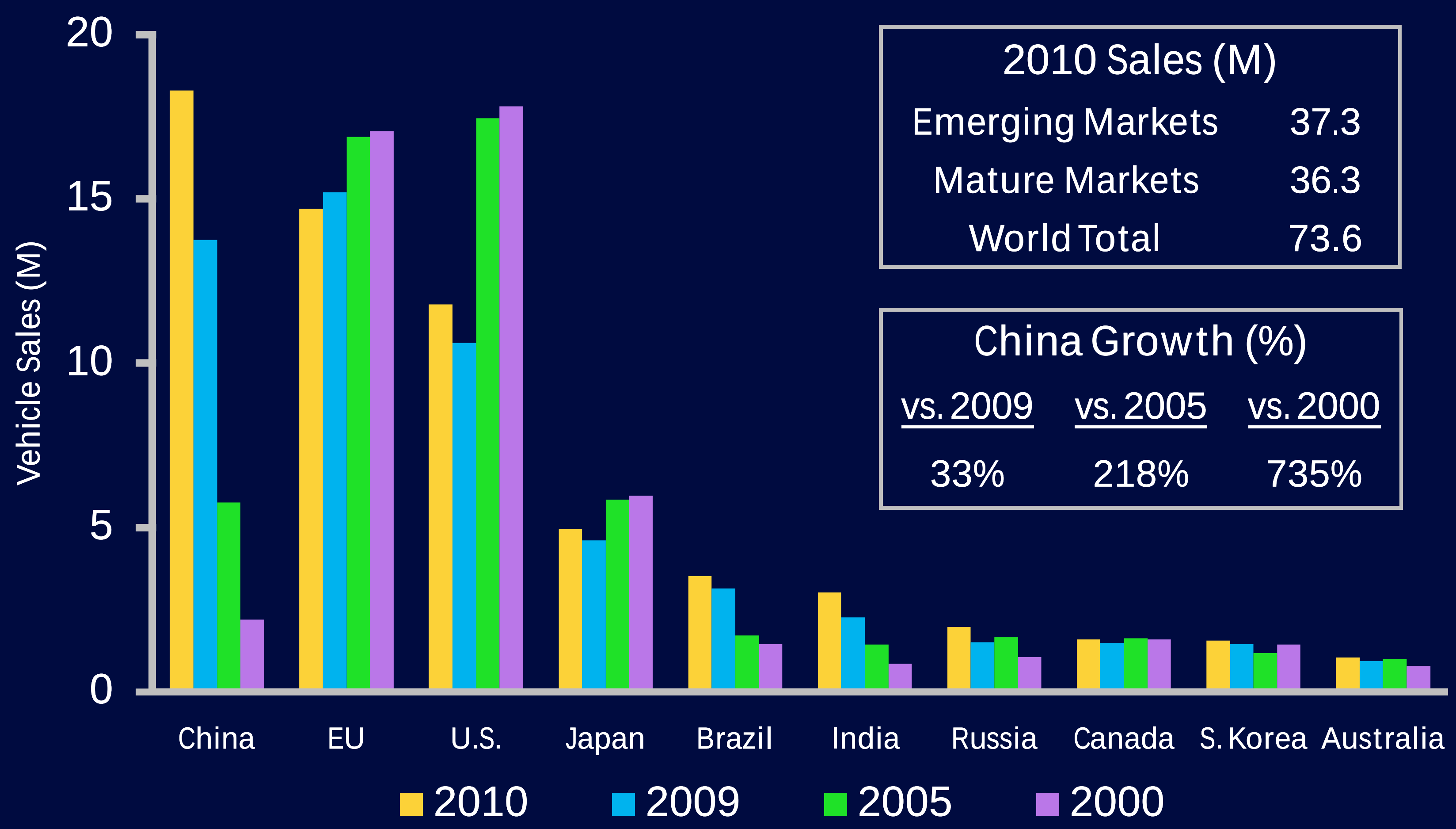
- Energy +
- Emissions +
- Safety NA
- Megacity NA
  - Congestion
  - Parking
- Affordability –

Data from U.S. Census Bureau and GM Global Market & Industry Analysis

EMERGING VS. MATURE MARKETS – GLOBAL COMPARISON: 2010

Source: GM Economics & Trade; IMF; U.S. Census Bureau/Haver Analytics

TOP 10 MARKETS BY NEW VEHICLE SALES IN 2010



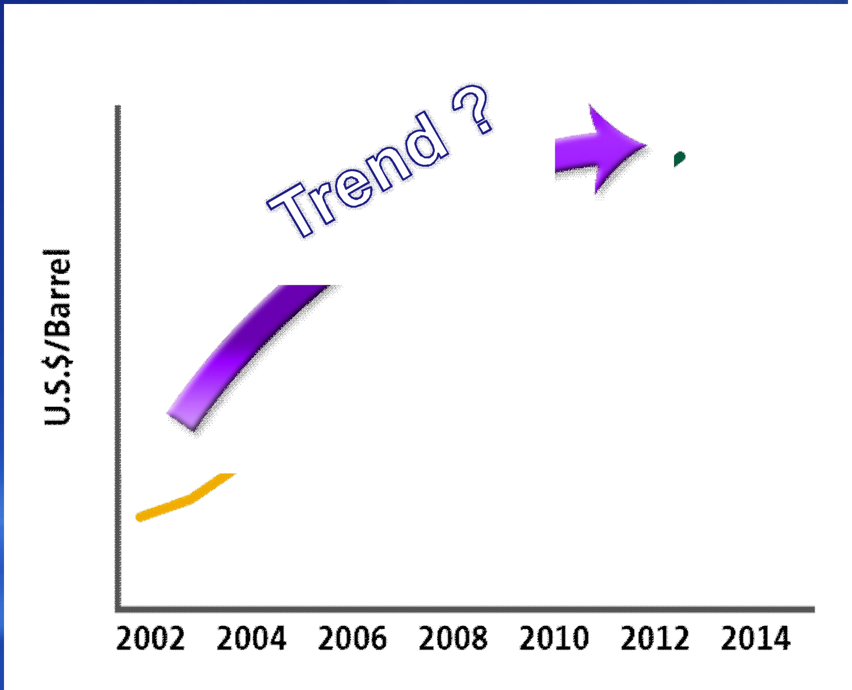
2010 Sales (M)	
Emerging Markets	37.3
Mature Markets	36.3
World Total	73.6

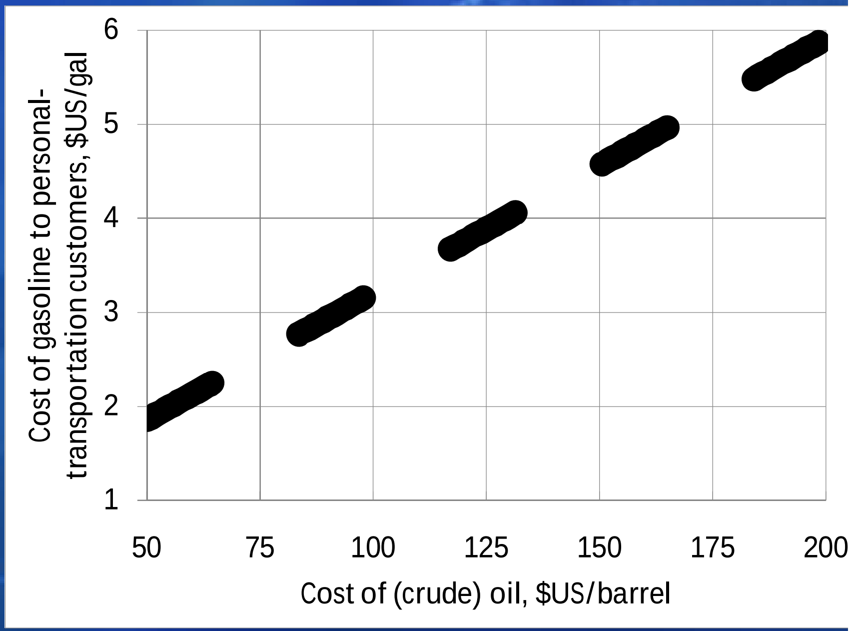
China Growth (%)

vs. 2009	vs. 2005	vs. 2000
33%	218%	735%

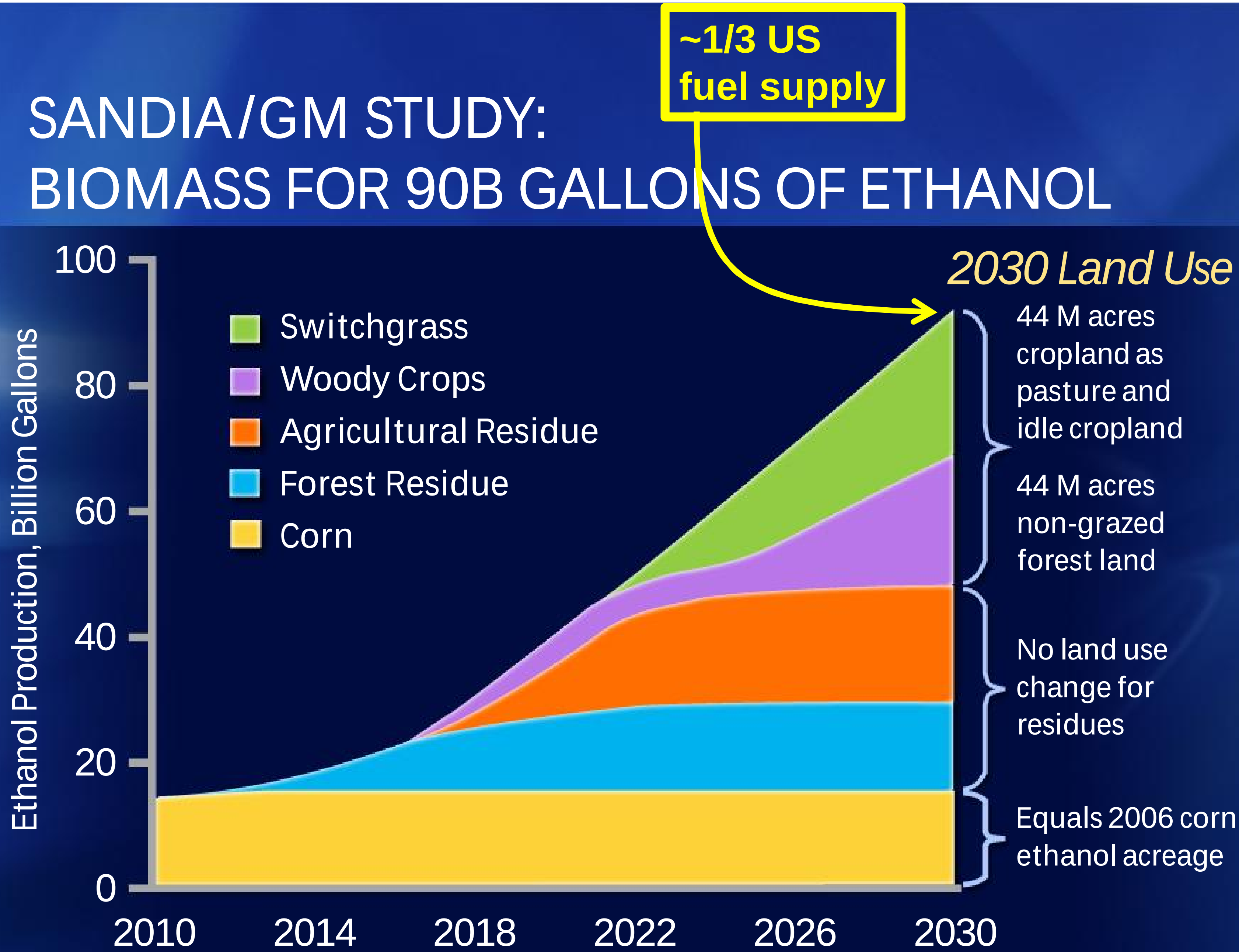
Really BIG questions

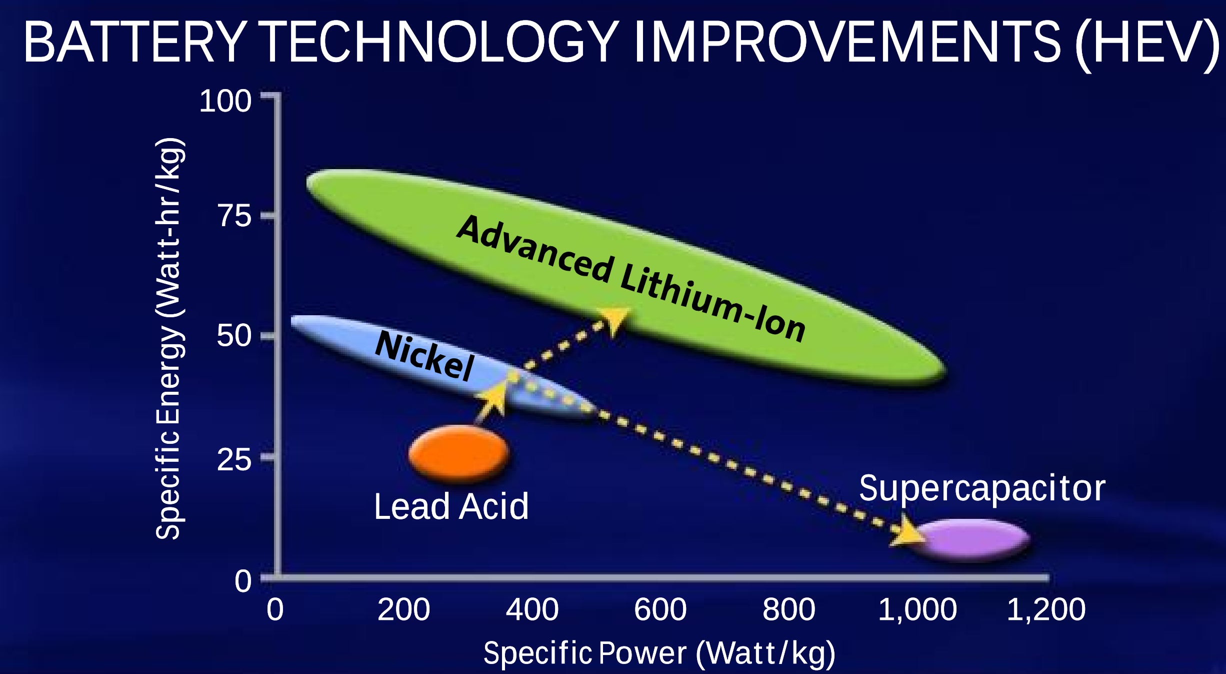
- Liquid fuels
  - Future price & availability of oil?
  - Efficacy of bio-derived fuels?
- Importance of zero on-vehicle "regulated emissions" vs. CO_2 emissions & energy security?
  - Fuel cells offer
    1. Range
    2. Short re-charge times
    3. Zero emissions
    4. Technical efficacy now
  - What else can do this?
- FCEVs vs. BEVs with fast charge vs. EREVs with bio-derived fuels?

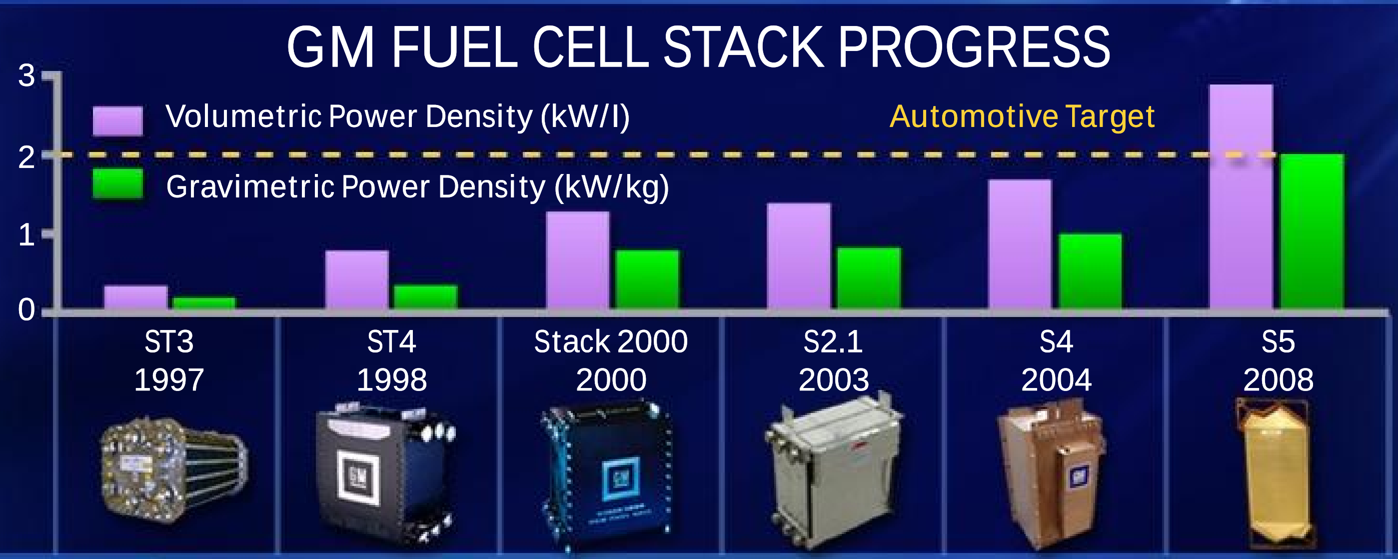


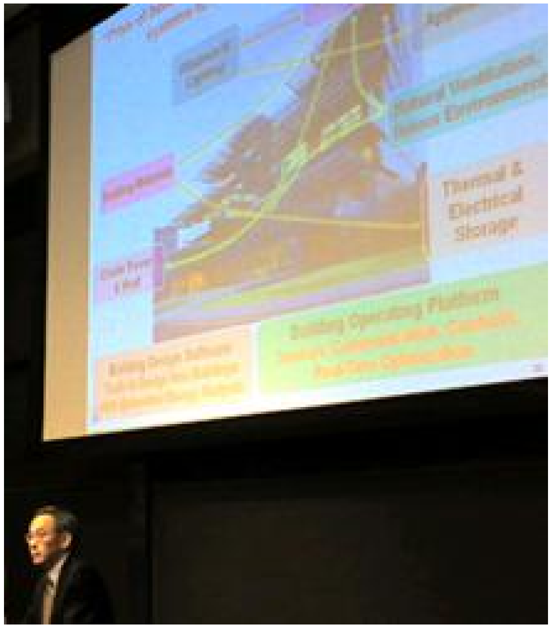


SANDIA/GM STUDY: BIOMASS FOR 90B GALLONS OF ETHANOL

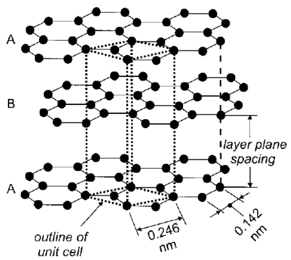



BATTERY TECHNOLOGY IMPROVEMENTS (HEV)
Specific Energy (Watt-hr/kg)
100
75
50
25
0
Advanced Lithium-Ion
Nickel
Lead Acid
Supercapacitor
0
200
400
600
800
1,000
1,200
Specific Power (Watt/kg)


GM FUEL CELL STACK PROGRESS
3
2
1
0
Volumetric Power Density (kW/l)
Automotive Target
Gravimetric Power Density (kW/kg)
ST3
1997
ST4
1998
Stack 2000
2000
S2.1
2003
S4
2004
S5
2008

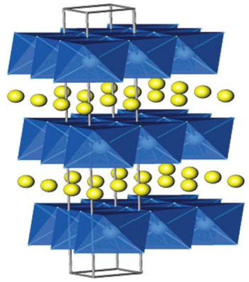


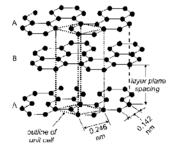
- ❑ In the interview (Technology Review 2009), Chu said that there are four "miracles" that need to happen before hydrogen fuel cells can be practical. Basically, he says, we need better ways to produce, distribute, and store hydrogen, and we need better, cheaper fuel cells. "If you need four miracles, that's unlikely: saints only need three miracles," he said.
- ➢ Underscores the importance of the scientific method…**make things work first at the cell level**.



Li^+ ⇄

EC+DEC

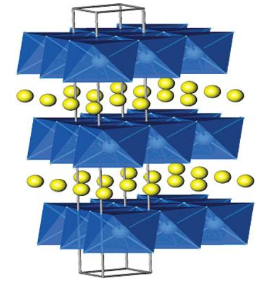




or Li^0

Li^+ ⇄

Ceramic electrolyte



1. Conventional lithium ion

+ Specific power and energy
+ Life (cycle and calendar)
– Abuse tolerance

- Martin Winter, Jürgen O. Besenhard, Michael E. Spahr, and Petr Novák, Adv. Mater. 1998.
- M. Stanley Whittingham, Chem. Rev. 2004.

2. Solid state lithium ion

- Boone B. Owens, J. Power Sources, 2000.
- Danilov, Niessen, and Notten, J. Electrochem. Soc., 2011

+ Abuse tolerance
+ Specific energy
– Specific power (particularly at low temperatures)
– Vibration resistance

Li^0

Li^+ ⇄

- Ceramic electrolyte over Li
- Organic solvent or membrane over cathode

Fuel cell air cathode

3. Li-air batteries

+ Specific energy (note gain in cell mass with discharge)
– Life
– Specific power
– Complexity

- Kowalczk, Read, and Salomon, J. Pure Appl. Chem., 2007.
- 1Danilov, Niessen, and Notten, J. Electrochem. Soc., 2011
- Na|Air cell: Peled, Golodnitsky, Mazora, Goora, Avshalomova. J. Power Sources, 2010.

USABC

UNITED STATES ADVANCED BATTERY CONSORTIUM

FreedomCAR & Fuel Partnership

USABC Requirements of End of Life Energy Storage Systems for PHEVs

Characteristics at EOL (End of Life)		**High Power/Energy**	**High Energy/Power**
Reference Equivalent Electric Range	miles	10	40
Peak Pulse Discharge Power (10 sec)	kW	45	38
Peak Regen Pulse Power (10 sec)	kW	30	25
Available Energy for CD (Charge Depleting) Mode, 10 kW Rate	kWh	3.4	11.6
Available Energy for CS (Charge Sustaining) Mode	kWh	0.5	0.3
Minimum Round-trip Energy Efficiency (USABC HEV Cycle)	%	90	90
Cold cranking power at -30°C, 2 sec - 3 Pulses	kW	7	7
CD Life / Discharge Throughput	Cycles/MWh	5,000 / 17	5,000 / 58
CS HEV Cycle Life, 50 Wh Profile	Cycles	300,000	300,000
Calendar Life, 40°C	year	15	15
Maximum System Weight	kg	60	120
Maximum System Volume	Liter	40	80
Maximum Operating Voltage	Vdc	400	400
Minimum Operating Voltage	Vdc	>0.55 x Vmax	>0.55 x Vmax
Maximum Self-discharge	Wh/day	50	50
System Recharge Rate at 30°C	kW	1.4 (120V/15A)	1.4 (120V/15A)
Unassisted Operating & Charging Temperature Range	°C	-30 to +52	-30 to +52
Survival Temperature Range	°C	-46 to +66	-46 to +66
Maximum System Production Price @ 100k units/yr	$	$1,700	$3,400

More battery requirements:
www.uscar.org

P/E, 1/hr	13	3.3

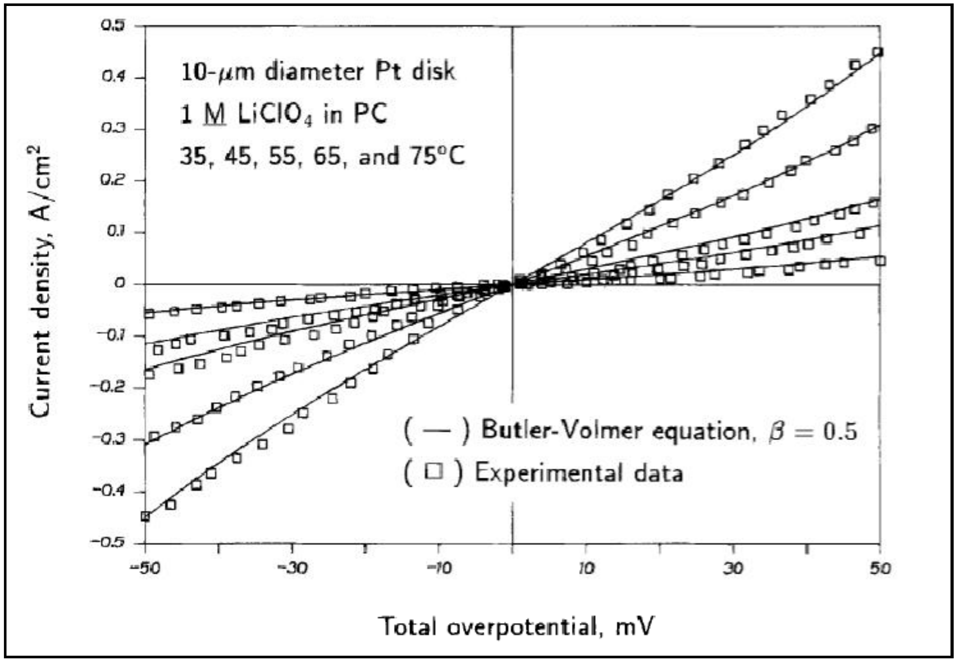
P/E, 1/hr, EFlex/Volt: ~8

Microelectrode Study of the Lithium/Propylene Carbonate Interface: Temperature and Concentration Dependence of Physicochemical Parameters

Mark W. Verbrugge* and Brian J. Koch
Physical Chemistry Department, General Motors Research and Development Center, Warren, Michigan 48090-9055

J. Electrochem. Soc., Vol. 141, No. 11, November 1994 © The Electrochemical Society, Inc

β = 0.5 and i_0 = 300 mA/cm^2 at 75^{o}C



Conclusion: *Li metal anodes in conventional aprotic solvents are initially impressive but are not stable.*

Microdisk electrodes
- Very high current densities
- High sensitivity to interfacial phenomena

Microelectrode investigation of ultrahigh-rate lithium deposition and stripping

Mark W. Verbrugge and Brian J. Koch
Physical Chemistry Department, General Motors Research and Development, Warren, MI 48090-9055 (USA)

Journal of Electroanalytical Chemistry, 367 (1994) 123–129

electrochemical reaction	$Li^+ + e^- \rightleftharpoons Li$
chemical reaction	Li + solvent $\rightarrow$ degradation product

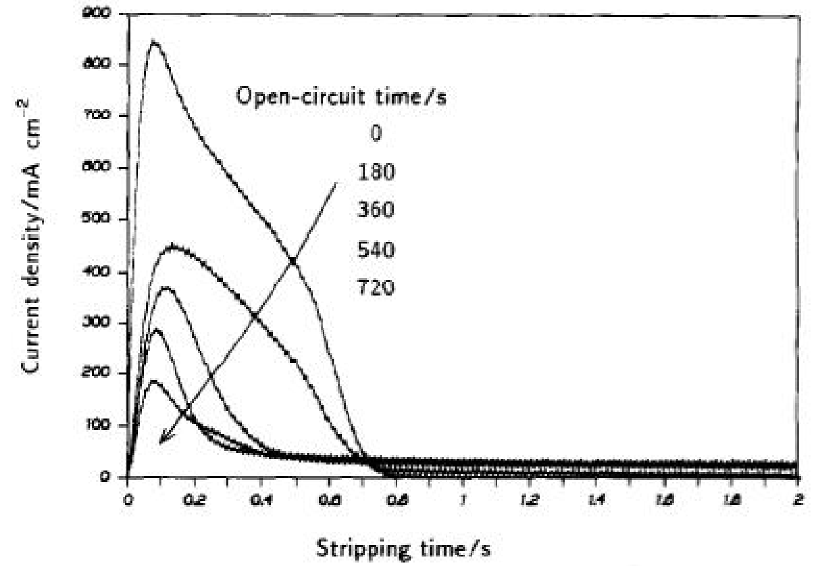


Fig. 6. Effect of open-circuit standing on lithium stripping. The trace with the highest current density corresponds to immediate stripping after deposition. Open-circuit standing for longer times after deposition are shown to yield reduced stripping currents. Pt disk of diameter 10 μm; 1 s deposition at −200 mV; 200 mV stripping potential.

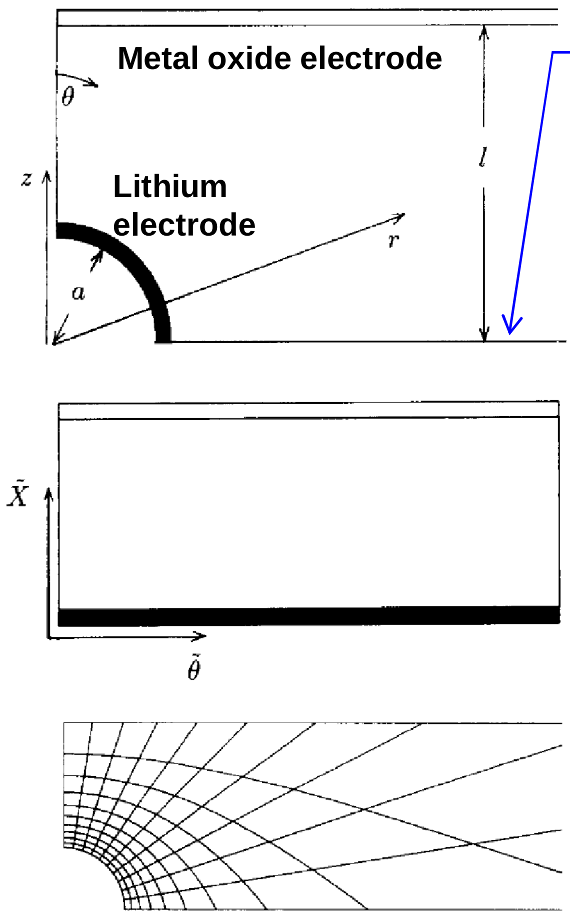
Journal of Crystal Growth 155 (1995) 81–92

Reaction distribution over a nodule in a thin-film battery

Mark W. Verbrugge [a,*], Donn W. Glander [b], Daniel R. Baker [b]

Secondary current distribution with linear charge-transfer kinetics

$$\tan(j_1) = (\alpha_{a,1} + \alpha_{c,1}) f i_{0,1} a / \kappa$$



Examine active and passive surrounding anode…which is preferred?

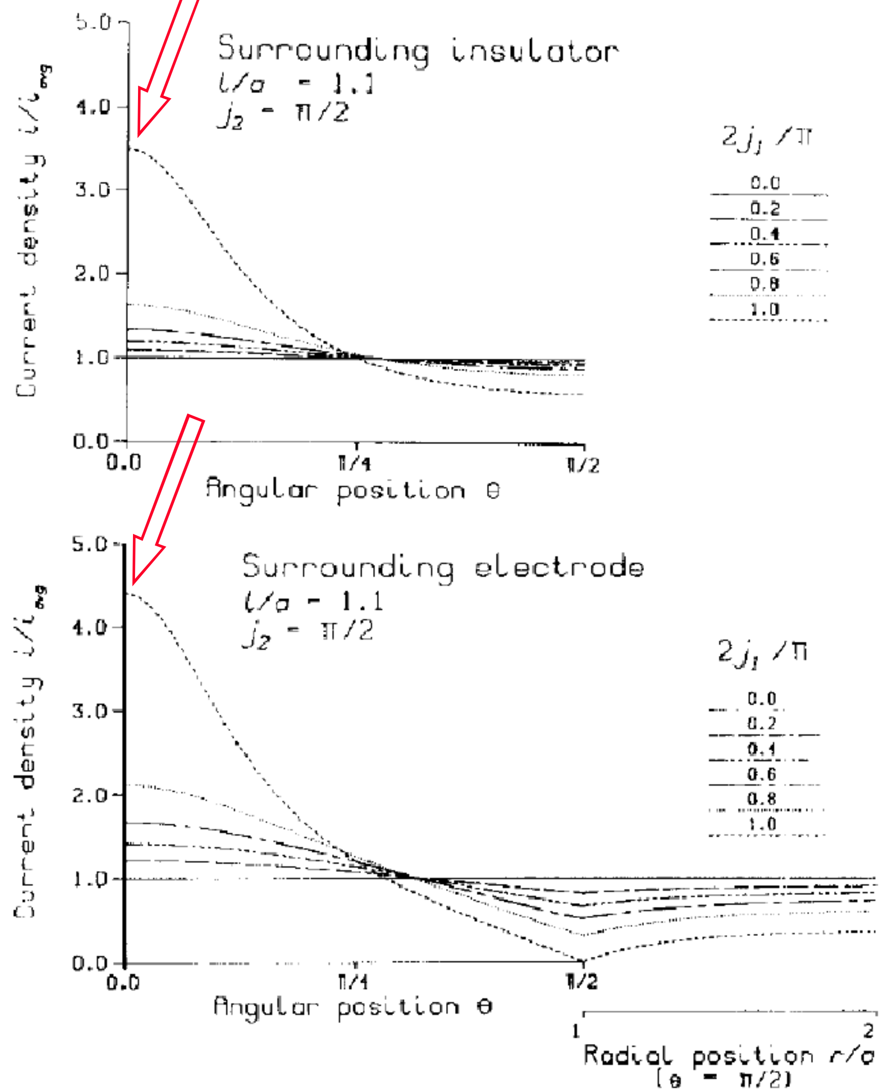


Fig. 4. Current distributions for an equipotential counter-electrode.

- **Surrounding electrode:**
  - More nonuniform current distribution
  - But lower average (nodule) current

⇒ Metal electrodes are problematic

J. Electrochem. Soc., Vol. 143, No. 1, January 1996 © The Electrochemical Society, Inc.

Lithium Intercalation of Carbon-Fiber Microelectrodes

Mark W. Verbrugge* and Brian J. Koch*

General Motors Research and Development Center, Physical Chemistry Department, Warren, Michigan 48090-9055, USA

$$Li^{+} + e^{-} + S_j \underset{k_a}{\overset{k_c}{\rightleftharpoons}} [Li^{\chi} - S_j^{-\chi}]$$

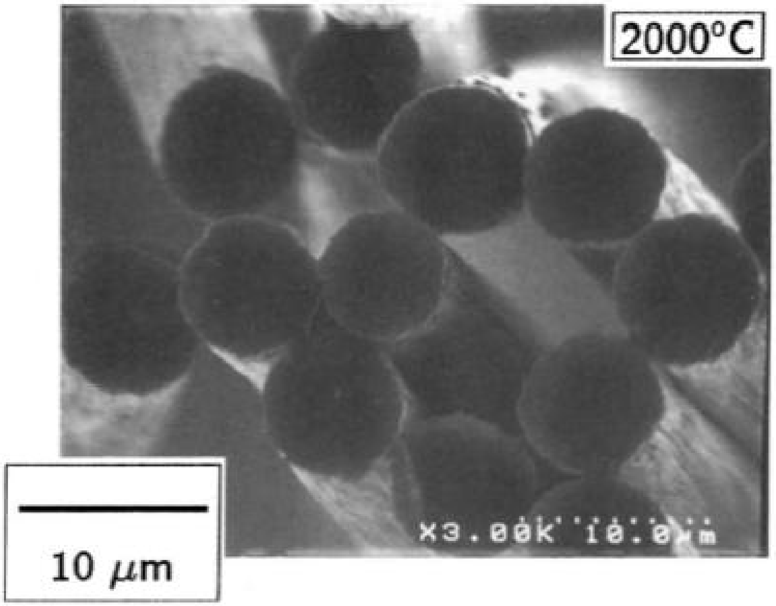


Fig. 2. Micrograph of fibers heat-treated for 4 h at 2000°C.

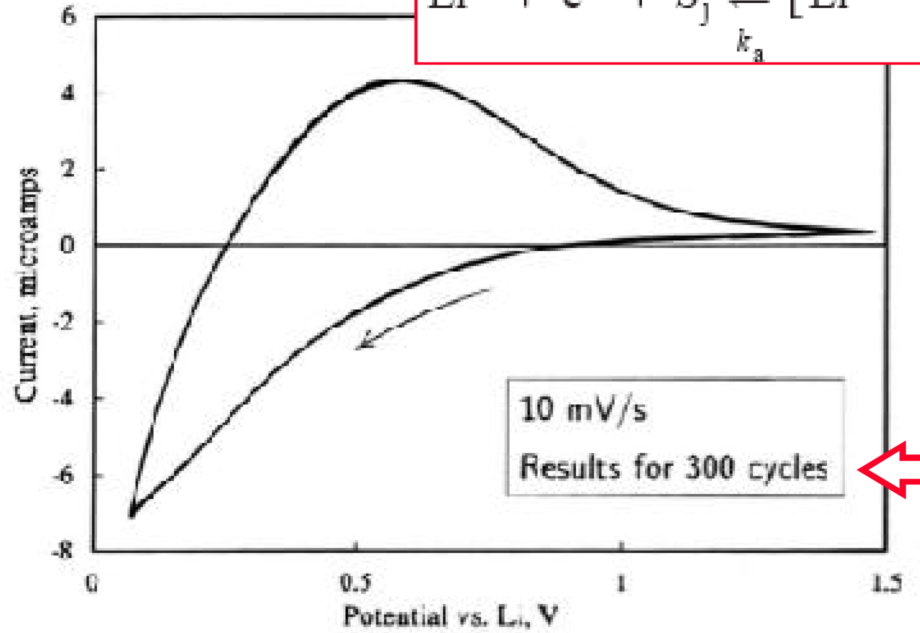
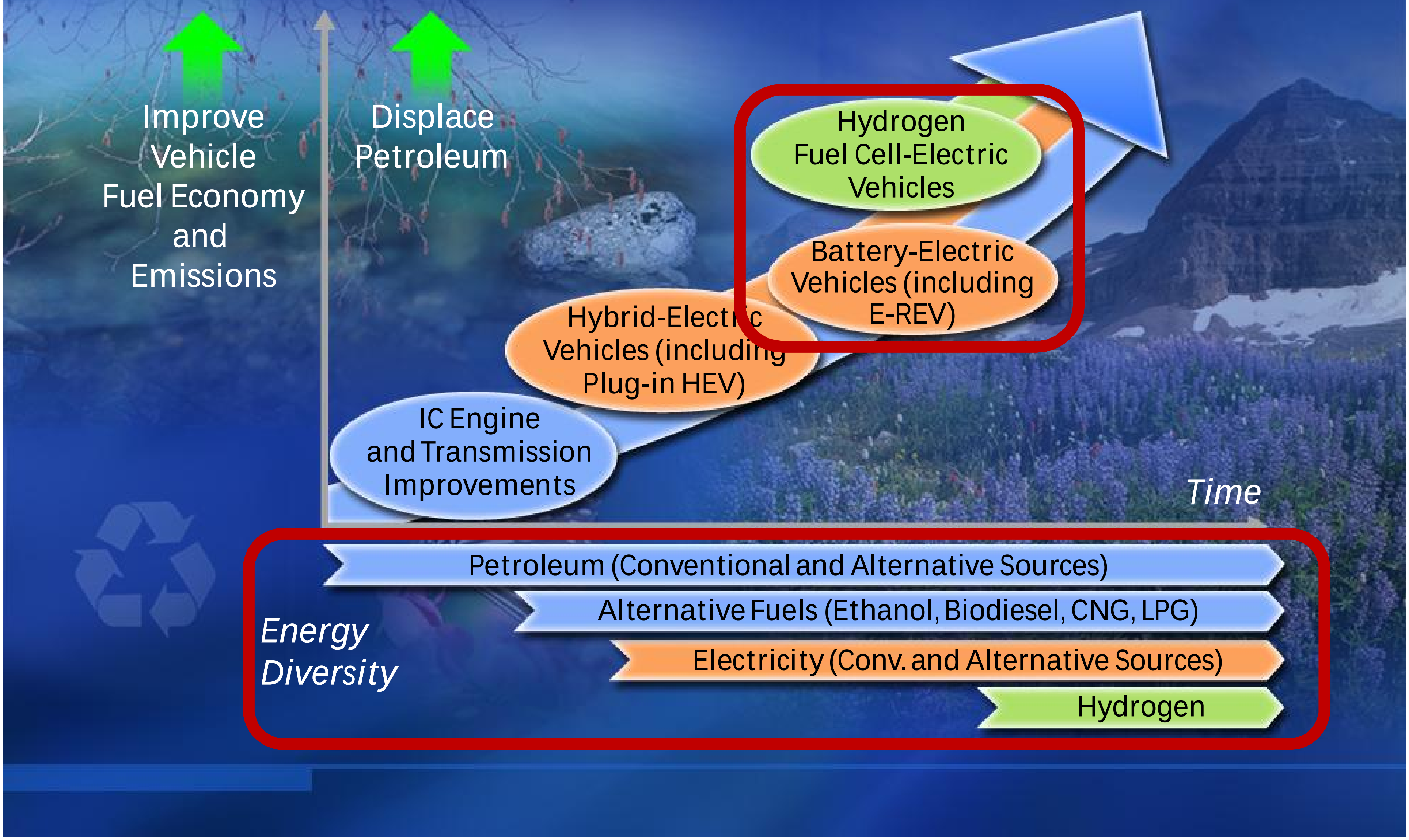


Fig. 3. Characteristic cyclic voltammogram. Data for 300 cycles are plotted.

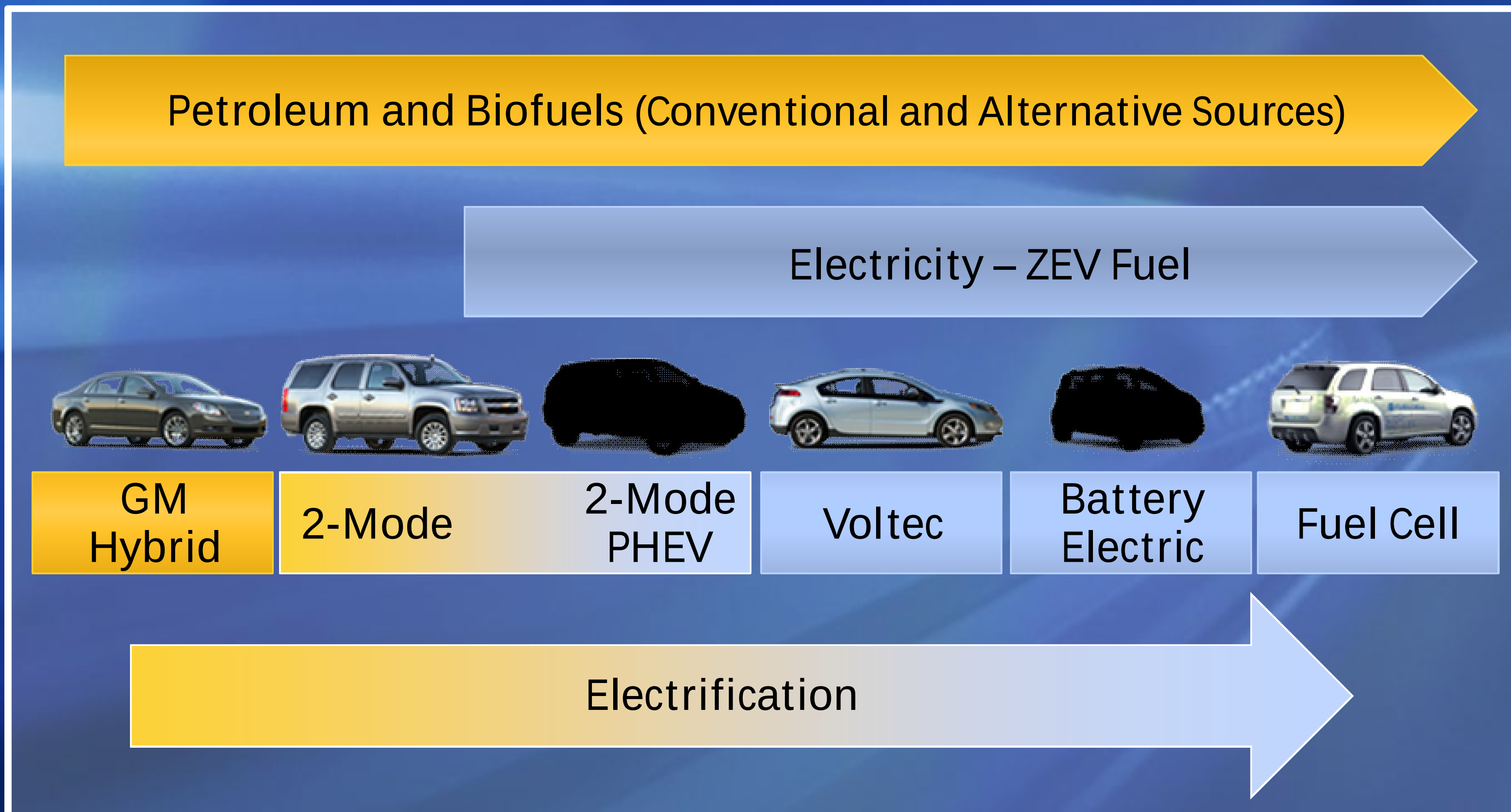
- ❑ Ability of lamellar compounds of carbon to insert various species was well known by the later half of the 1800s (Schauffaütl, 1841…Sony, 1992)
- ❑ Aprotic solvents with high dielectric constants: W.S. Harris, Ph.D. Thesis, University of CA, Berkeley, 1958.
- ❑ Single fiber electrode: phenomena associated with the fabrication of a porous electrode do not obfuscate the subsequent characterization…use the Scientific Method to isolate critical characteristics
- ❑ Extremely stable lithiated carbon anode <u>and</u> Li reference (there is *still* confusion around the stability of carbon lithiation!)

ADVANCED PROPULSION TECHNOLOGY STRATEGY



GM VEHICLE ELECTRIFICATION STRATEGY

Portfolio of solutions for full range of vehicles that provide customer choice



GM'S PATH TO ELECTRIFICATION

	Conventional Powertrain	Mid Hybrid	Full Hybrid	Plug-in Hybrid	Extended Range Electric Vehicle	Battery Electric Vehicle & Fuel Cell
FUNCTIONALITY	Baseline	15-20%	30% RWD 50% FWD	FWD: ~100% for (20) Miles, 50% After	40 Miles Pure EV	30 Miles Pure EV
DRIVE SYSTEM	Mechanical	Mechanical with Electric Assist			Electric with Mechanical Assist	All Electric

INCREASING LEVELS OF ELECTRIFICATION AND EFFICIENCY

VOLT

PROJECT DRIVEWAY

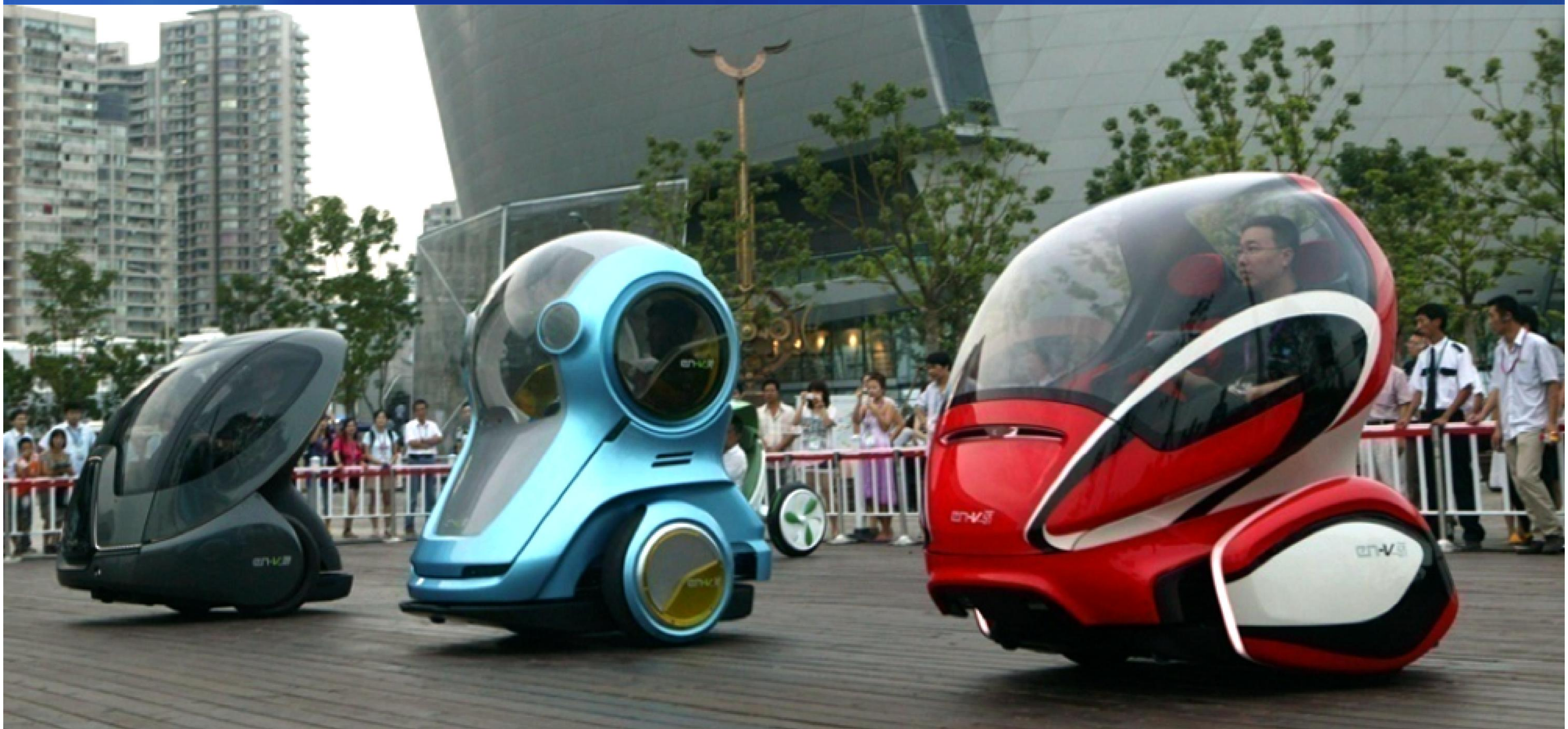
25-45 MILES
GAS-FREE

1,850,000
MILES LOGGED

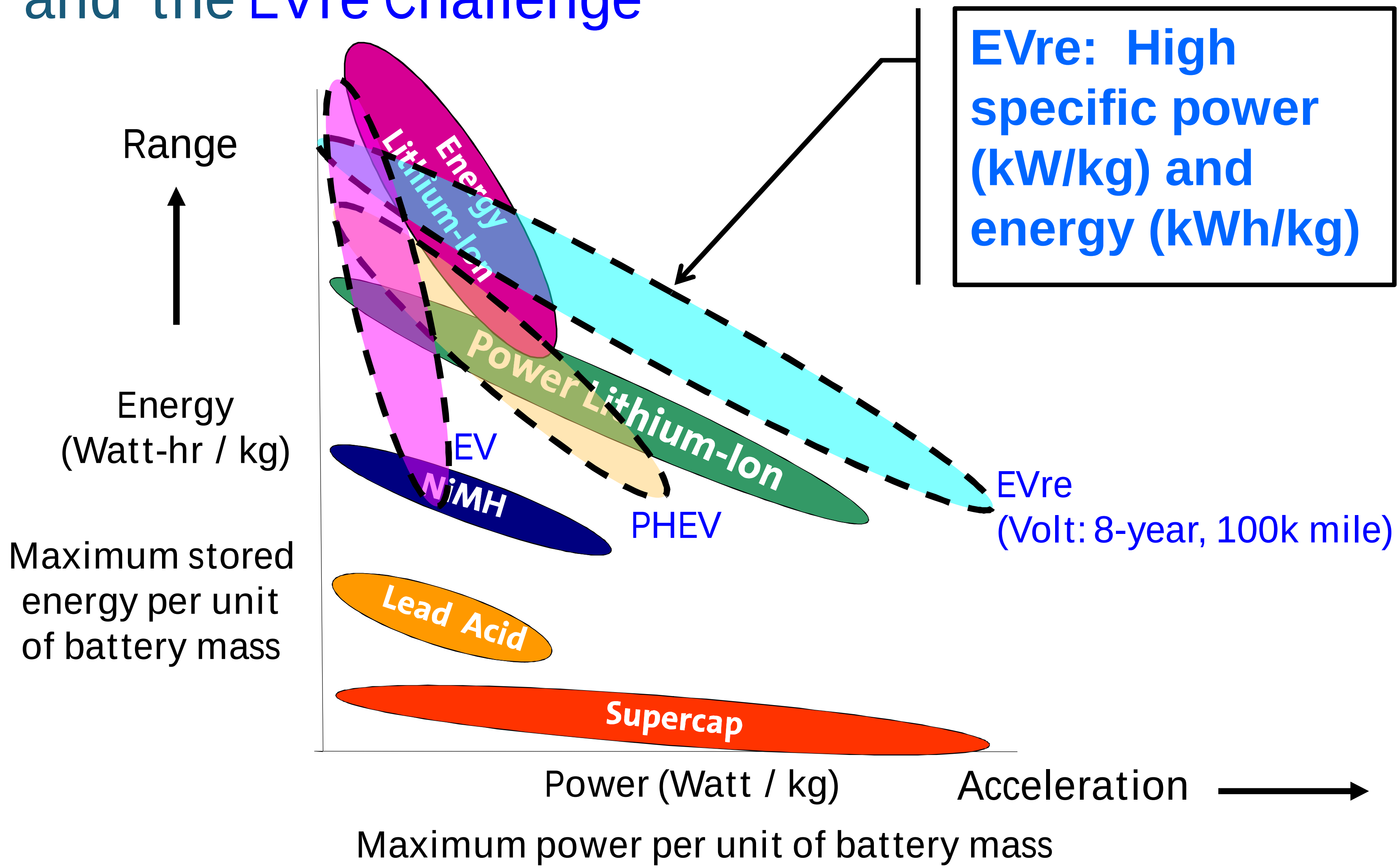
INVENTION 1900s

REINVENTION TODAY

REINVENTING PERSONAL URBAN MOBILITY: EN-V (ELECTRIC, NETWORKED VEHICLE)



Battery Technology Improvements and the EVre Challenge

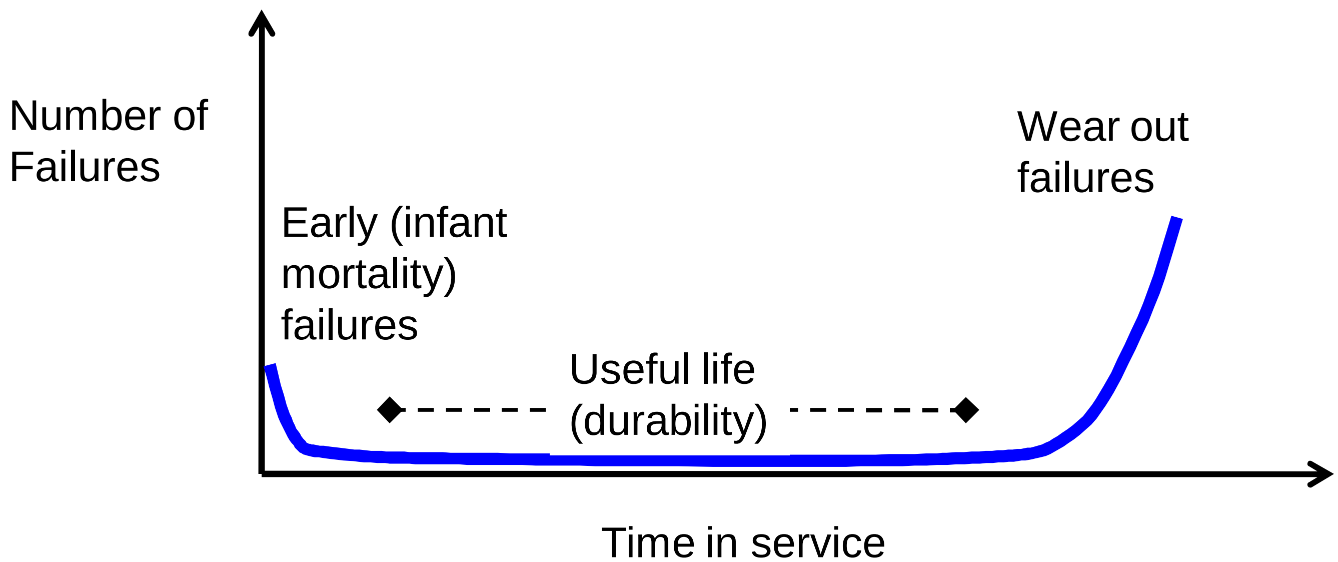


Lithium ion challenges

- **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?

Durability…terminologies, bathtub curves

- **Chemical degradation**
  - Critical role of SEI (solid electrolyte interface) to impede deleterious degradation reactions within lithium ion cells
  - Calendar life determined by chemical degradation
- **Mechanical degradation**
  - Cyclic expansion and contraction of insertion or alloy materials leads to fatigue, cracking, and structural changes
  - Cyclic life issues are affected by mechanical degradation and chemical degradation



ELSEVIER

Journal of Power Sources 72 (1998) 66–70

JOURNAL OF POWER SOURCES

Composition analysis of the passive film on the carbon electrode of a lithium-ion battery with an EC-based electrolyte

C.R. Yang, Y.Y. Wang *, C.C. Wan

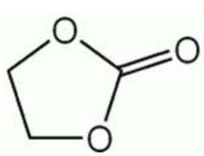
Department of Chemical Engineering, National Tsing-Hua University, Hsinchu, 30043, Taiwan

Received 17 March 1997; accepted 31 March 1997

Abstract

This work examines the formation of a passive film on the carbon electrode of lithium-ion batteries. With a single solvent of EC (ethylene carbonate), the structure of the passive film is found to be $(CH_2OCOOLi)_2$. In a DEC (diethyl carbonate) or DMC (dimethyl carbonate) system, $C_2H_5OCOOLi$ and Li_2CO_3 are formed on the surface of the carbon electrode. According to results from mass spectra, CO_2 gas is the main product when EC is decomposed. By contrast, DEC is decomposed into CO and C_2H_6, and DMC into CO and CH_4. These findings suggest that the composition of the passive film depends on the chosen solvent. In a binary solvent system which contains EC, the passive film contains chiefly $(CH_2OCOOLi)_2$, which is identical to a single EC solvent system.

Keywords: Lithium battery; Passive film; Organic electrolyte

$2\boxed{Li} + 2$ 

$\longrightarrow (CH_2OCO_2Li)_2 + H_2C{=}CH_2 + 2\boxed{}$

Mathematical modeling of high-power-density insertion electrodes for lithium ion batteries

Mark W. Verbrugge[a,*], Daniel R. Baker[b], Brian J. Koch[c]

[a]General Motors Research and Development Center, Warren, MI 48090-9055, USA
[b]General Motors Fuel Cell Propulsion Center, Warren, MI 48090-9055, USA
[c]General Motors Advanced Technology Vehicles, 1996 Technology Drive, Troy, MI 48007-7083, USA

Journal of Power Sources 110 (2002) 295–309

$$\mathrm{Li}^+ + \mathrm{e}^- + S_\mathrm{j} \underset{k_\mathrm{a}}{\overset{k_\mathrm{c}}{\rightleftharpoons}} [\mathrm{Li}^\chi - S_\mathrm{j}^{-\chi}]$$

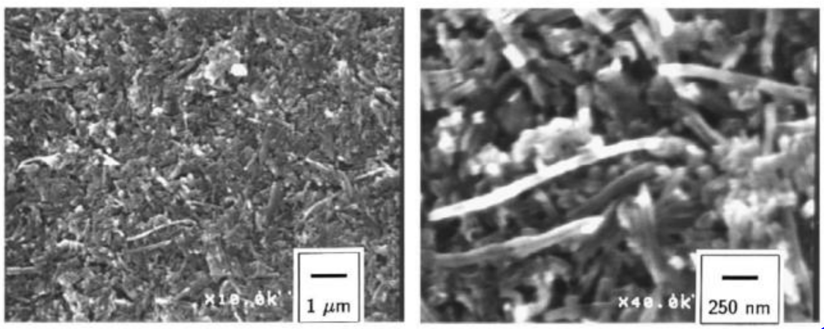
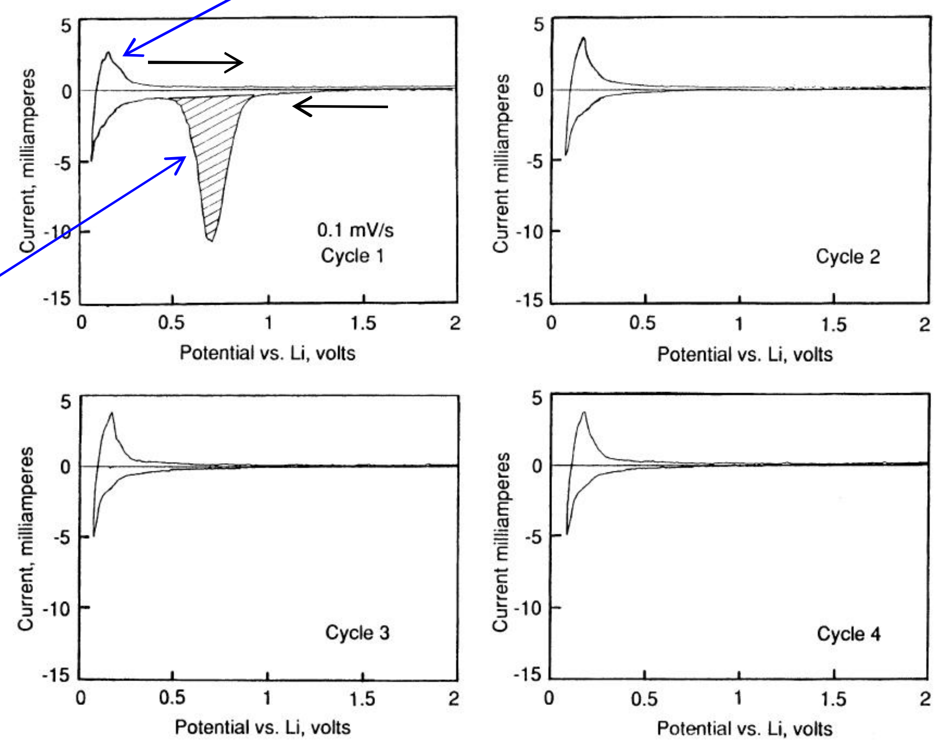
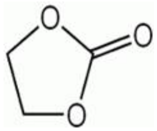


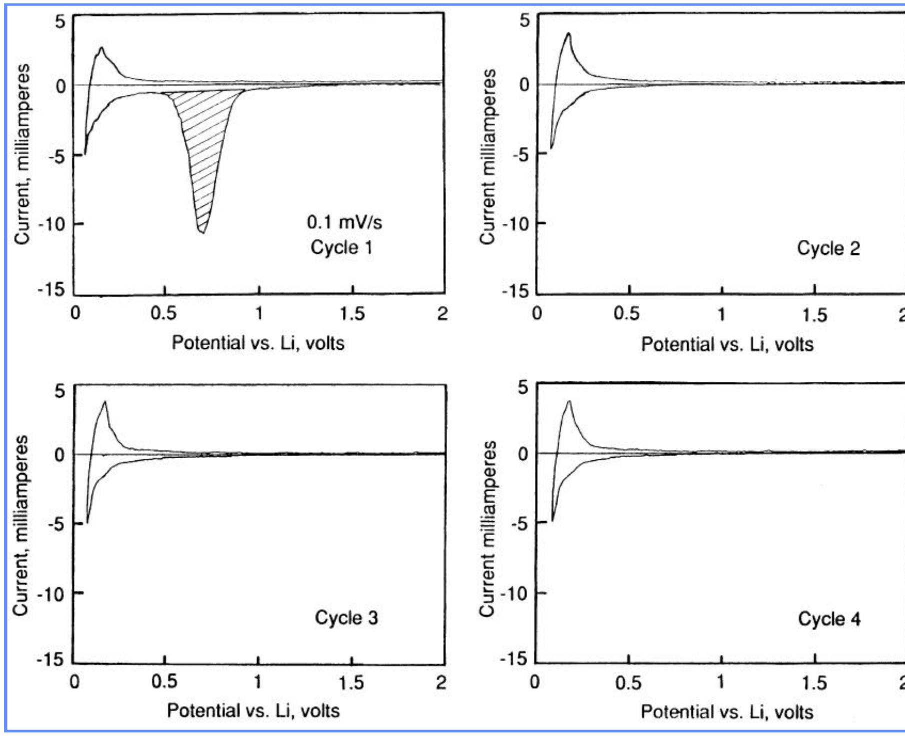
Fig. 3. High-magnification electrode micrographs.



- Solvent reduction at ~0.8V vs Li on first cycle
- Then ~100% Coulombic efficiency
- Next slide for more detail

On the importance of Coulombic efficiency η_I

$Li^+ + e^- + \frac{1}{2}$  $\longrightarrow \frac{1}{2} LiCH_2CH_2OCO_2Li$



Cycle	Capacity
1	$(Ah_0)\eta_I$
2	$[(Ah_0)\ \eta_I]\eta_I$
3	$[(Ah_0)\ \eta_I\ \eta_I]\eta_I$
⋮	
N	$(Ah_0)(\eta_I)^N$

1

For N = 5000 cycles and a 12/16 or 75% capacity retention, the current efficiency per cycle must be such that

$[Ah_0(\eta_I)^N]/Ah_0 > 0.75$, or $\eta_I > (0.75)^{(1/5000)}$, hence $\eta_I >$ **0.99994**.

- This is why very low rates of lithium-consuming reactions can lead to premature cell failure. The rates can be so low that they are not measureable in terms of seeing current maxima associated with solvent reduction.
- Note: high capacity negatives (Si, Sn based)…large challenge!

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0013-4651/2010/157(4)/A499/9/$28.00 © The Electrochemical Society

Aging Mechanisms of $LiFePO_4$ Batteries Deduced by Electrochemical and Structural Analyses

Ping Liu,[a,*,z] John Wang,[a] Jocelyn Hicks-Garner,[a,*] Elena Sherman,[a] Souren Soukiazian,[a] Mark Verbrugge,[b,*] Harshad Tataria,[b,*] James Musser,[c] and Peter Finamore[c]

[a]*HRL Laboratories, LLC, Malibu, California 90265, USA*
[b]*General Motors Corporation, Warren, Michigan 48092, USA*
[c]*John Deere Southeast Engineering Center, Charlotte, North Carolina 28241, USA*

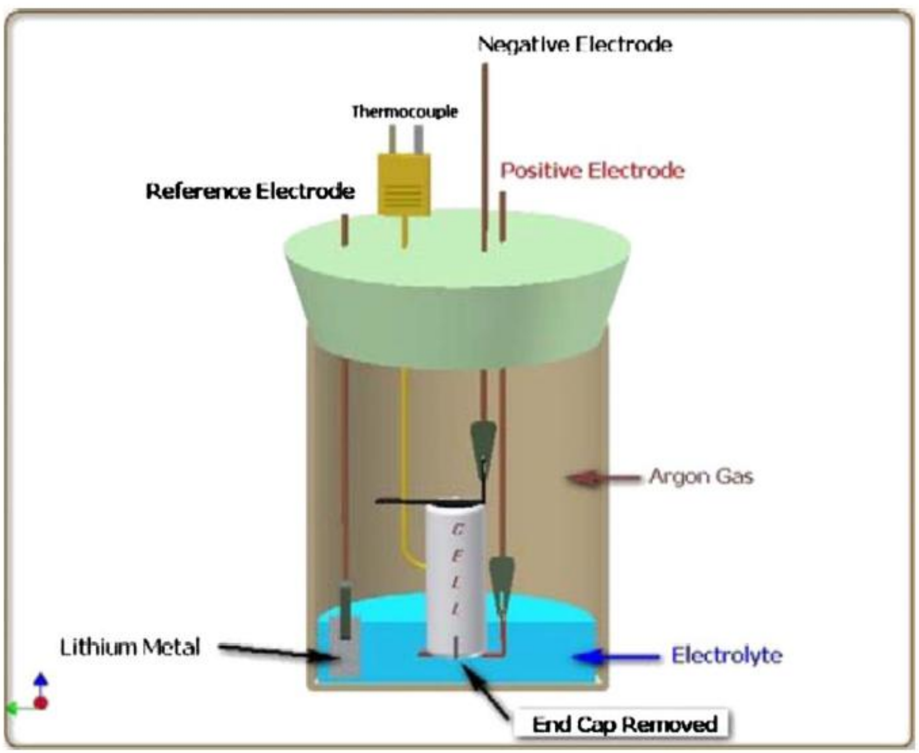
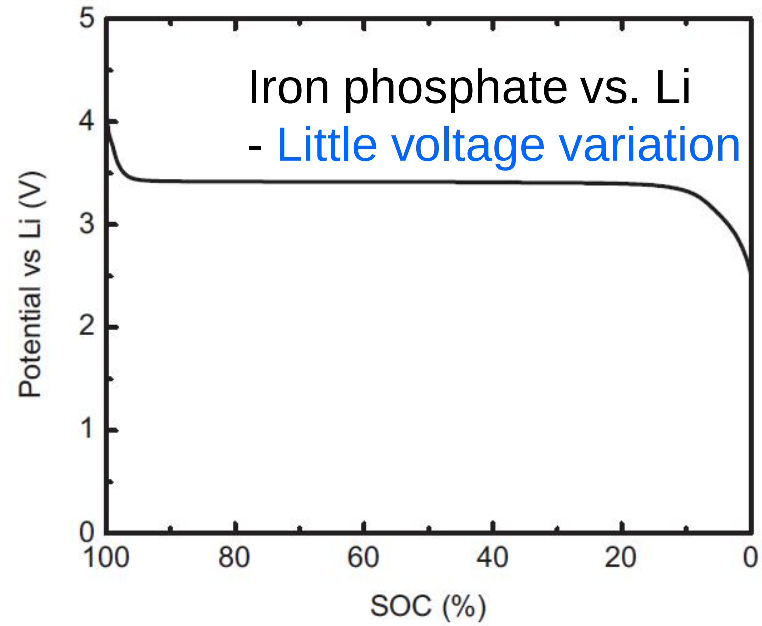


Figure 1. (Color online) Schematic of an in situ reference electrode measurement setup. The end cap of the cylindrical cell was removed. The cell is immersed in a liquid electrode, and a lithium reference electrode is located next to the cell. During constant current charge and discharge, the potential of the carbon negative can be recorded.



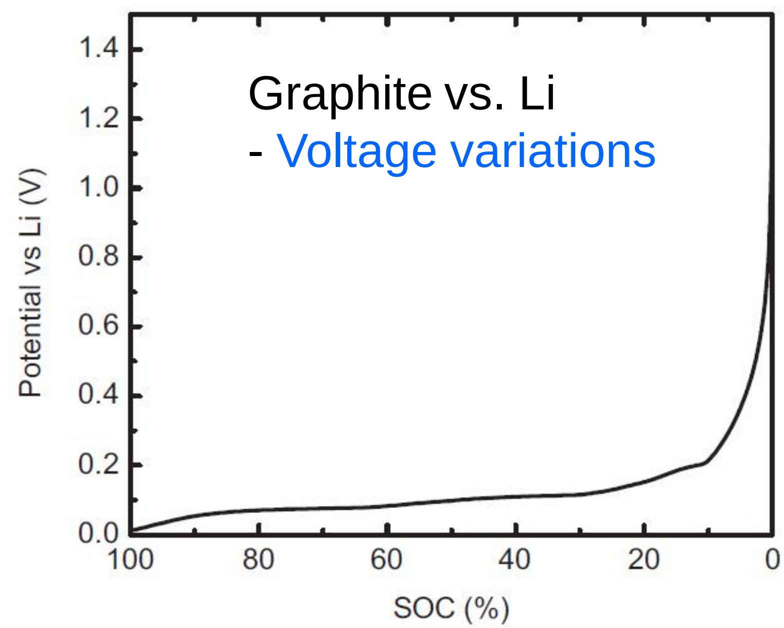
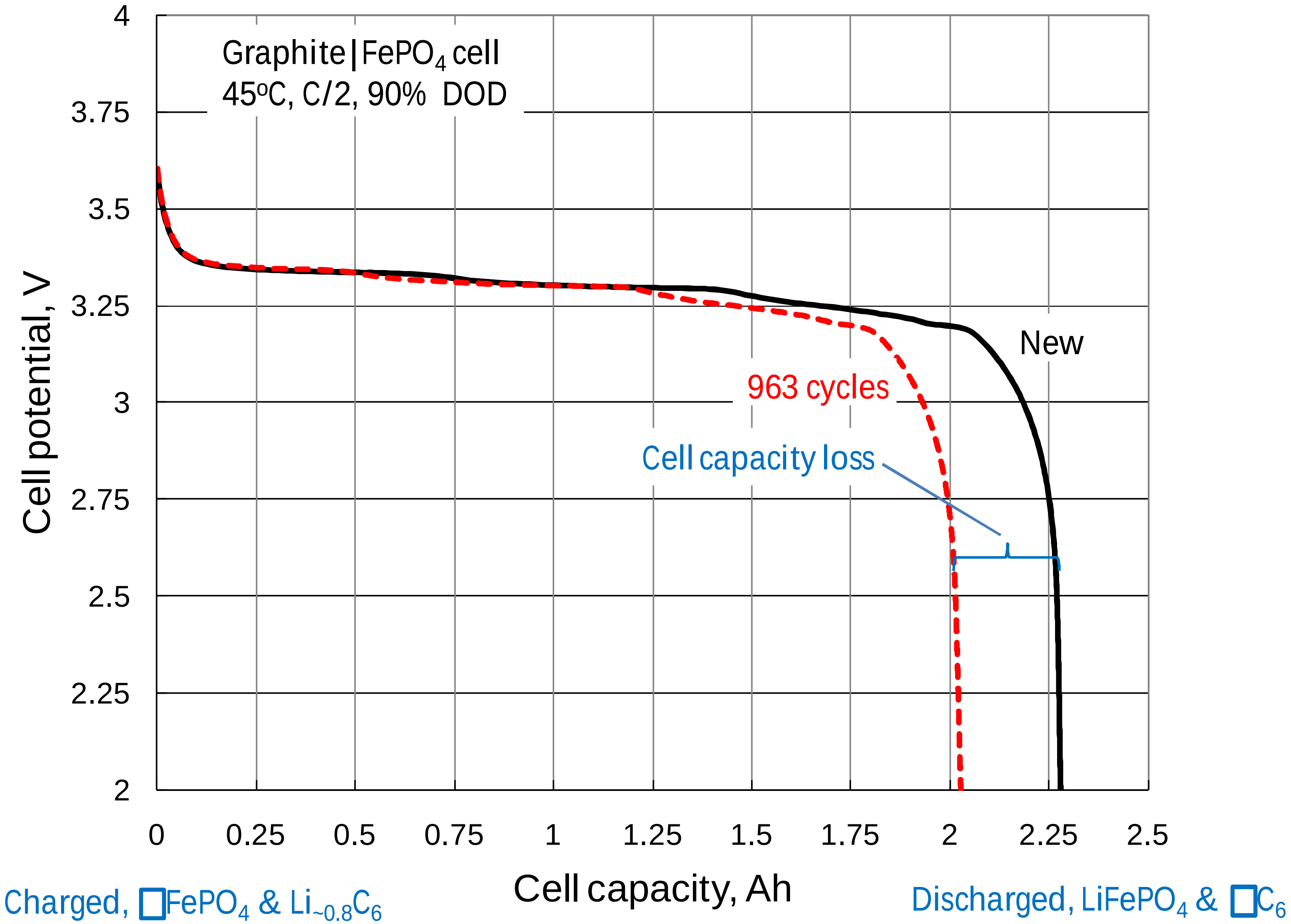
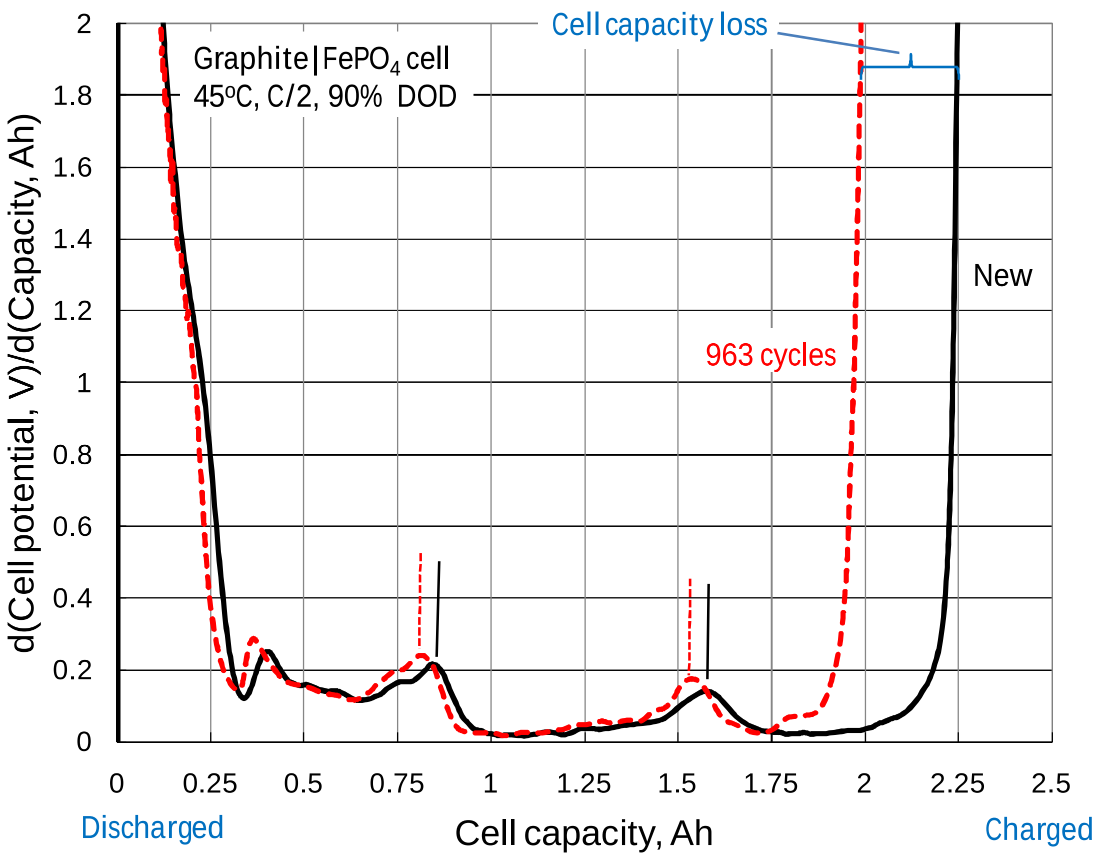


Figure 5. C/20 discharge curves for $LiFePO_4$ (top) and graphitic carbon (bottom) when measured against metal lithium.

Graphite|iron-phosphate cell…excellent power density, life, and potential for low cost. Challenged on energy density.



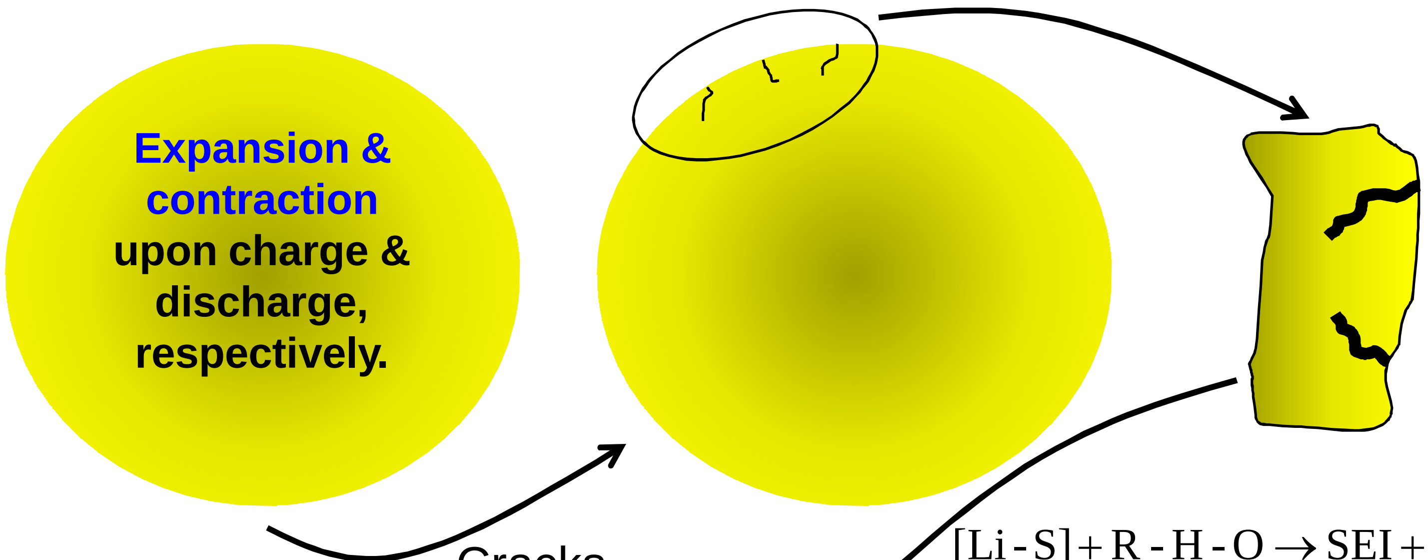
Utility of dV/dQ vs Q, uniform shifting of peaks for graphite/$FePO_4$ cells



- **Same as previous plot with the exception that origin now is at the fully discharged state…clear that distance between graphite peaks is nearly constant**
- **Conclusion: lithium consumption (at the negative electrode surface) is leading to capacity decline**

2

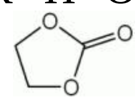
Chemical-mechanical degradation at the negative electrode



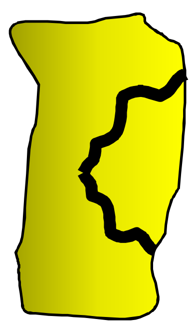
Cracks
via cycling

SEI forms on newly exposed surfaces (cracks)

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

$2[Li\text{-}S] +$  $\rightarrow 2S + Li_2CO_3 \downarrow + H_2C = CH_2 \uparrow$

Increased disorder and cracking
- Consistent with loss of active lithium



Electrode isolation and loss of active material when cracks join
- Consistent with additional loss of negative capacity

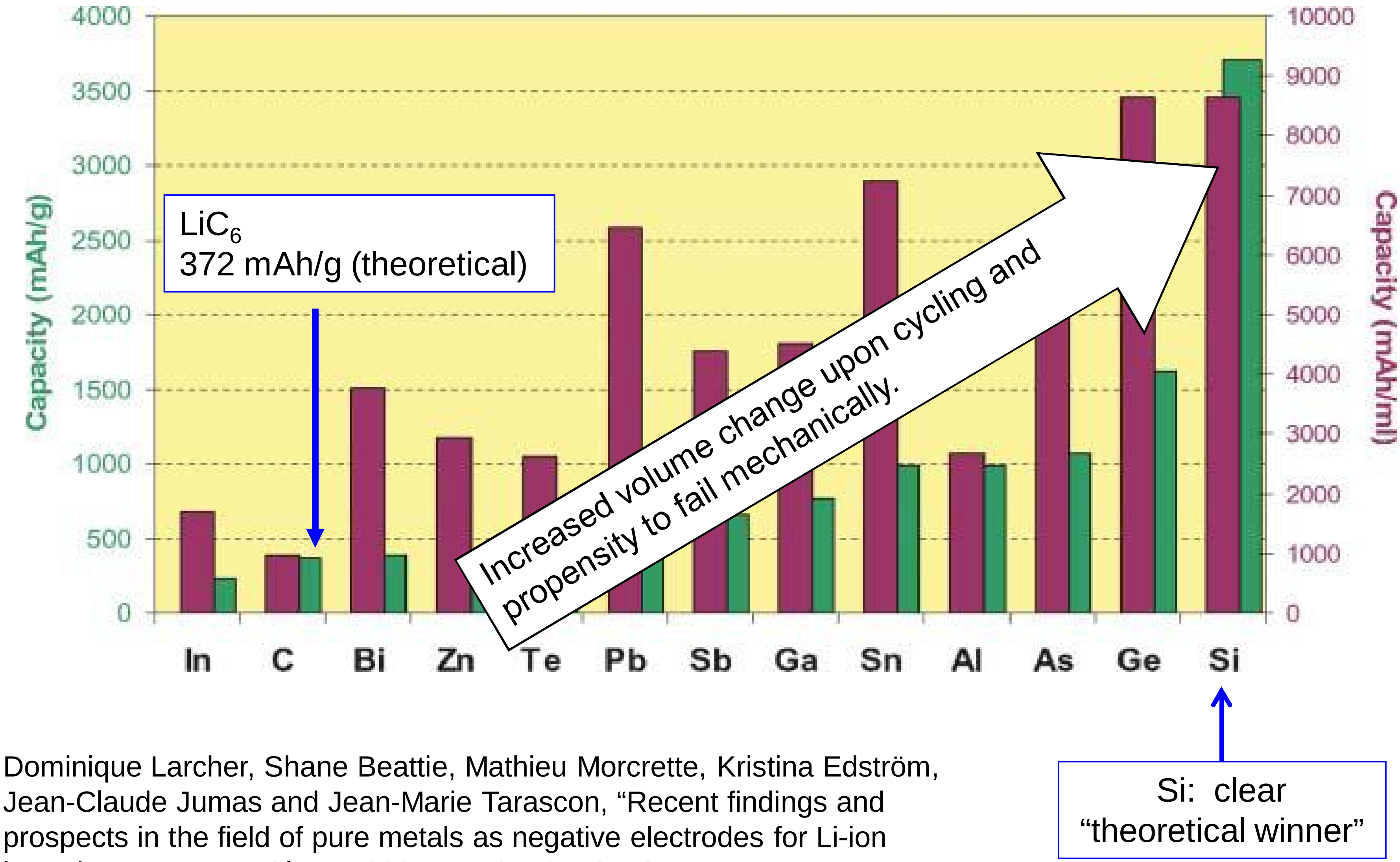
THIS IS A LARGE CHALLENGE FOR HIGH CAPACITY ELECTRODE MATERIALS

- Current efficiency must be 0.9999 to reach 1000 cycles with 80% of initial capacity.
- A current efficiency of 0.99 yields 23 cycles!

3

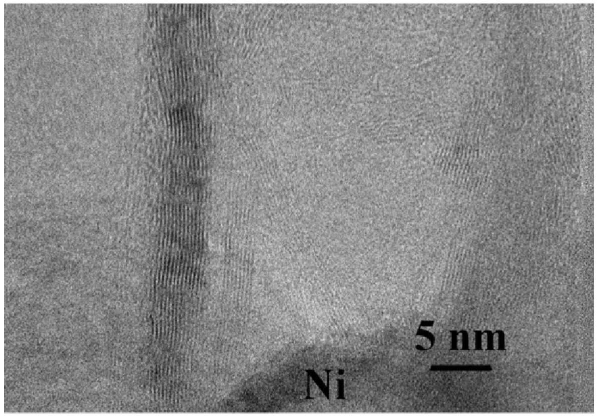
M. W. Verbrugge and Y-T. Cheng, “Stress and Strain-Energy Distributions within Diffusion-Controlled Insertion-Electrode Particles Subjected to Periodic Potential Excitations,” *J. Electrochem. Soc.*, 156(2009)A927.

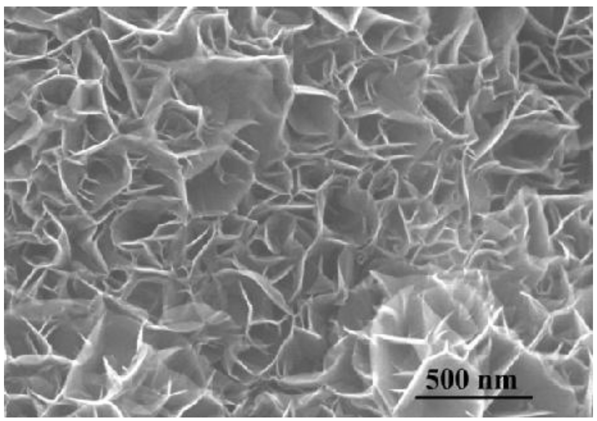
Current and next generation negative electrodes

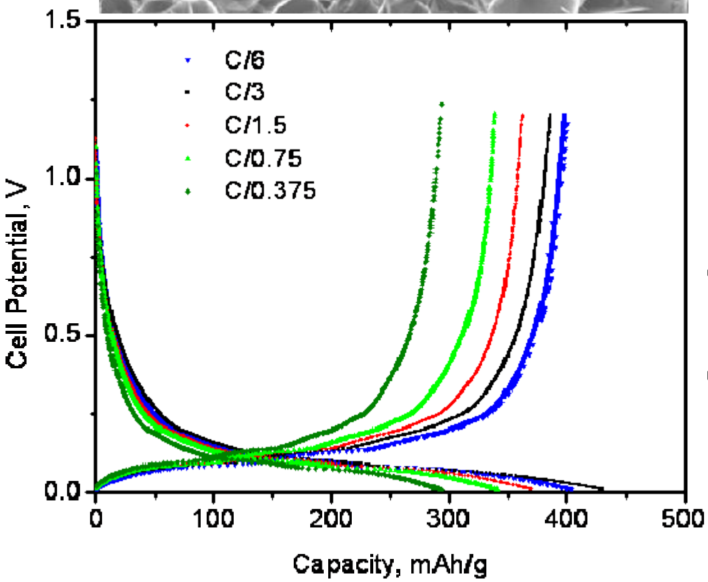


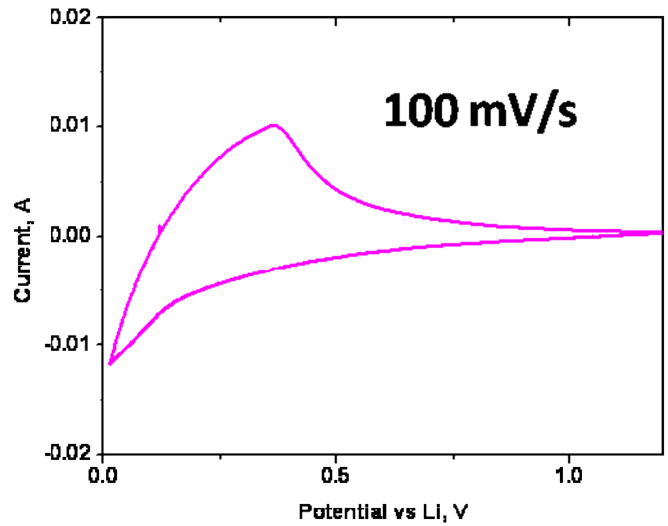
Dominique Larcher, Shane Beattie, Mathieu Morcrette, Kristina Edström, Jean-Claude Jumas and Jean-Marie Tarascon, "Recent findings and prospects in the field of pure metals as negative electrodes for Li-ion batteries," *J. Mater. Chem.*, 2007, 17, 3759 – 3772

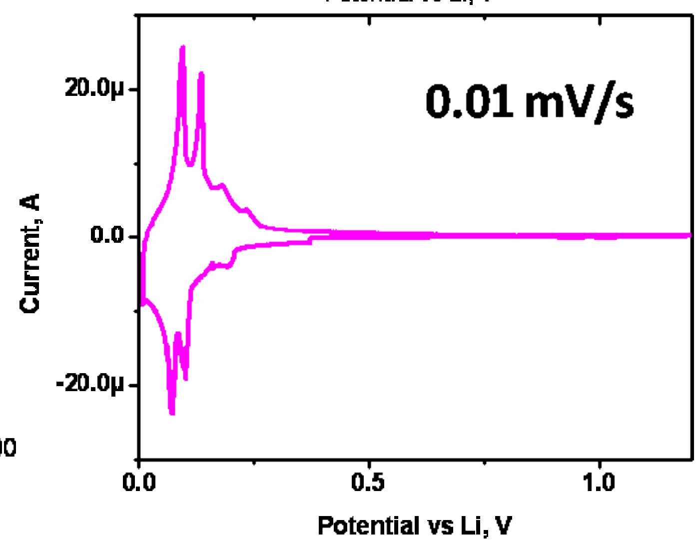
X. Xiao, P. Liu, J. S. Wang, M. W. Verbrugge, and M. P. Balogh, "Vertically Aligned Graphene Electrode for Lithium Ion Battery with High Rate Capability," *Electrochemistry Communications*, 13 (2011) 209–212.



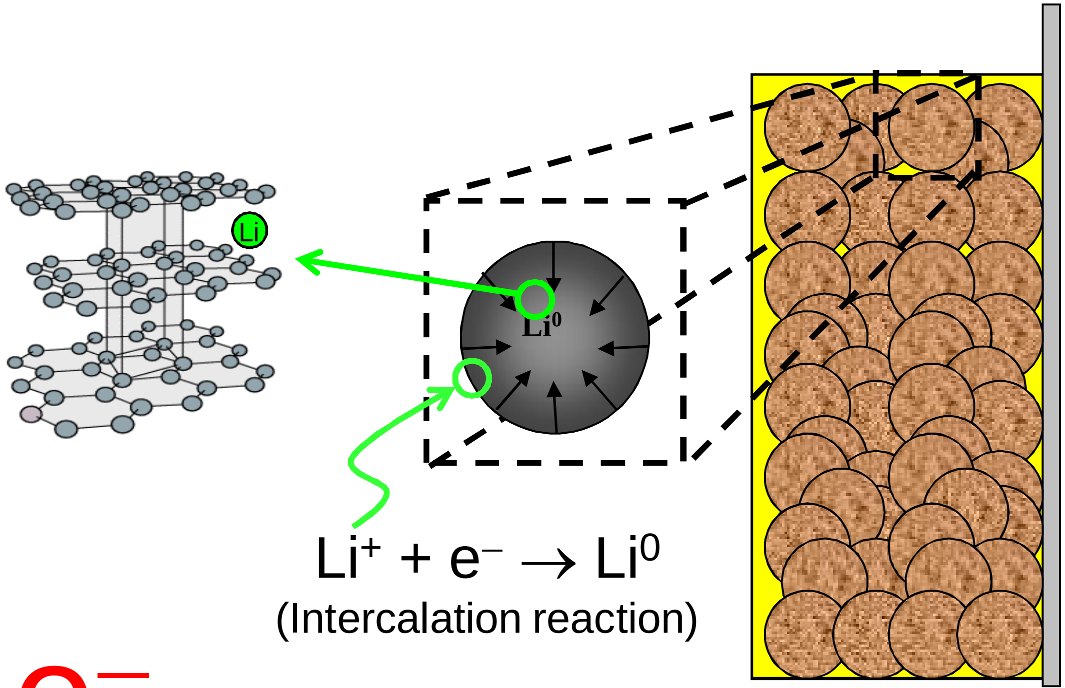






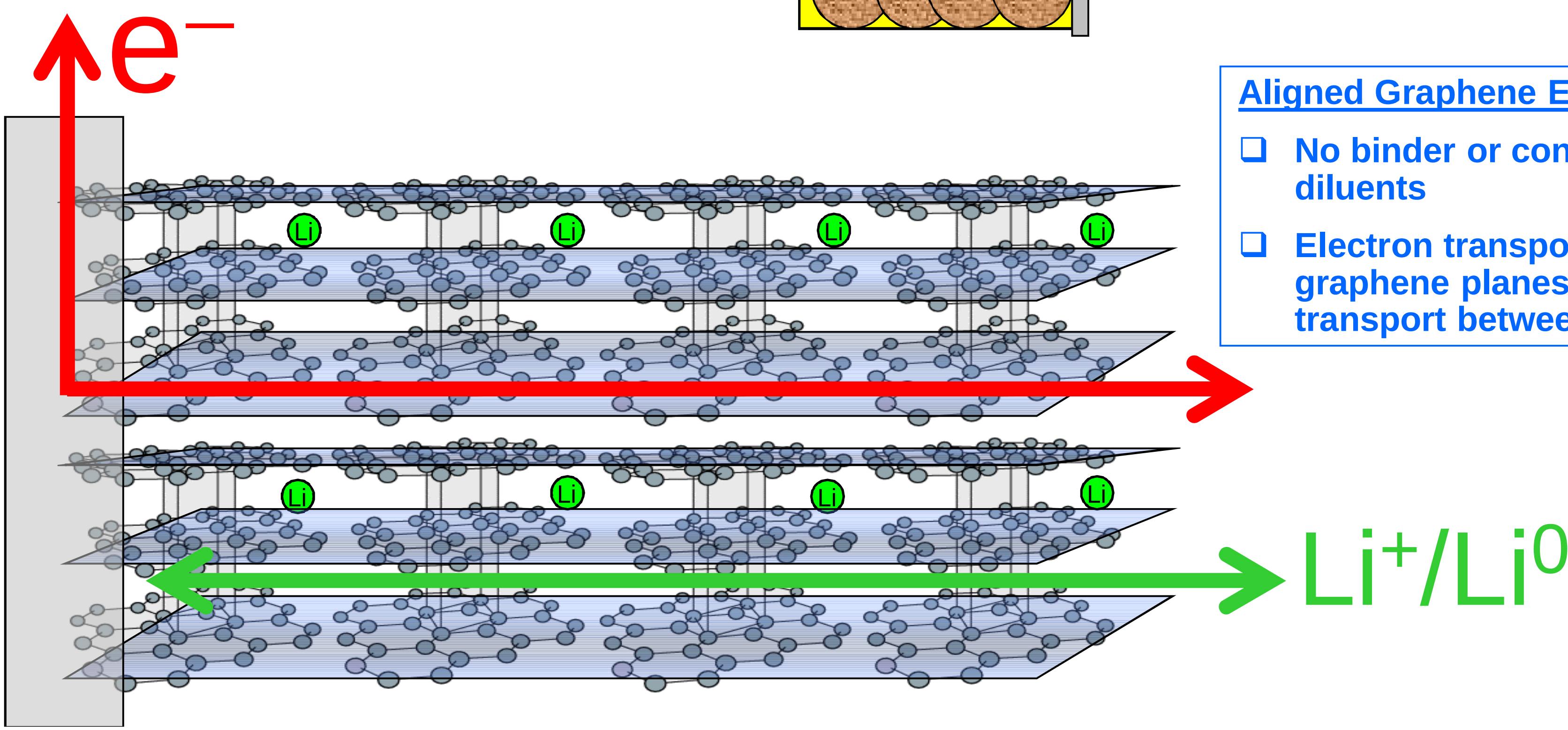


- ❑ **Nano-stabilization: thin films, small particles…surface forces for stabilization**
- ❑ **Nanometer thick aligned graphene films show excellent stability**
- ❑ **Should be helpful for characterization of the graphite-electrolyte interface**
- ❑ **Perhaps useful for very high specific power applications**
  - (Low energy due to thin film approach as presented)



Conventional graphite anode.
M. W. Verbrugge and B. J. Koch, "Electrochemical Analysis of Lithiated Graphite Anodes," *J. Electrochem. Soc.*, 150(2003)A374.

- Graphite, ~80 to 90% by mass
- Binder, ~5 to 10%
- Electronically conductive diluents, ~0 to 10%

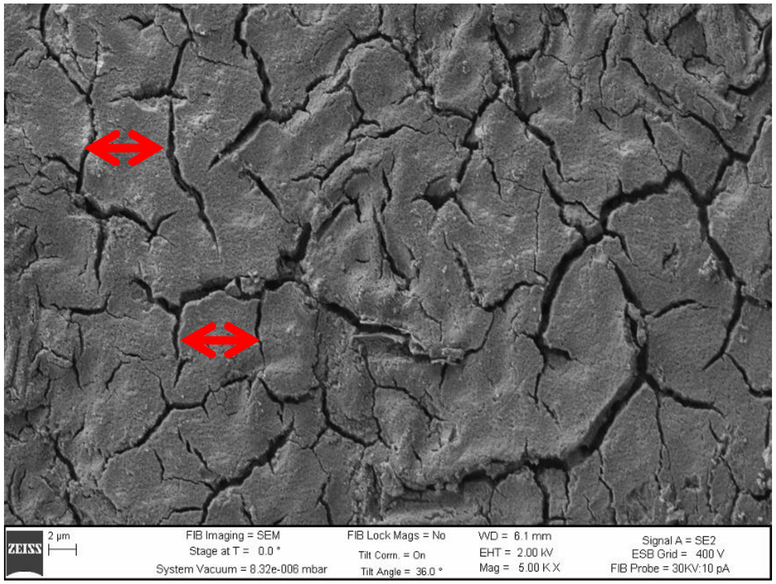


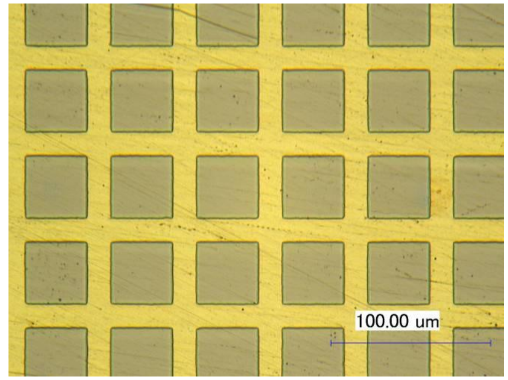
Aligned Graphene Electrode

- ❑ **No binder or conductive diluents**
- ❑ **Electron transport along graphene planes; Li transport between planes.**

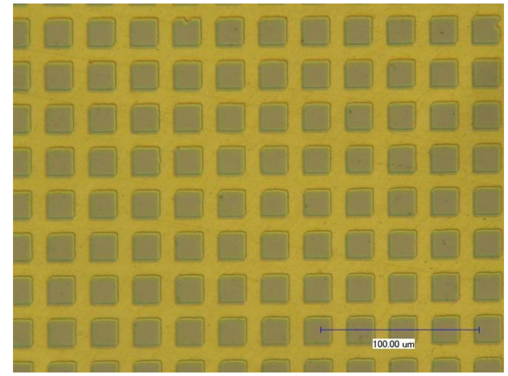
Si Patterns

X. Xiao, P. Liu, M. W. Verbrugge, H. Haftbaradaran, and H. Gao, *Journal of Power Sources* , 196 (2011) 1409–1416



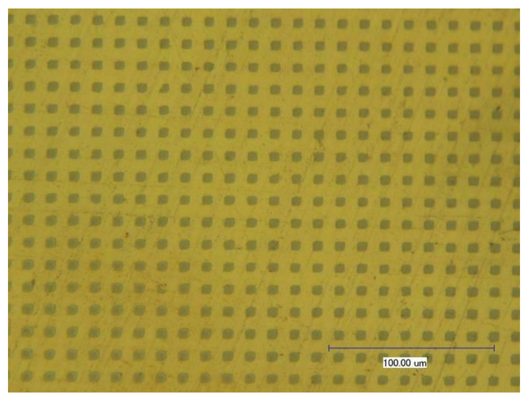


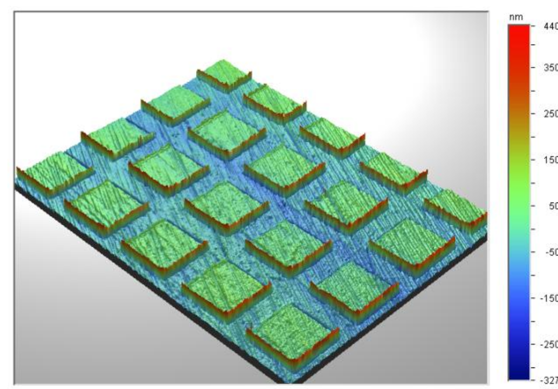
Pattern size 40 x 40 μm^2
Gap: 15 µm



Pattern size 17 x 17 μm^2
Gap: 10 µm

The crack spacing is around 5 to 10 microns, comparable to the pattern with 2000 mesh size.





Pattern size 7 x 7 μm^2
Gap: 7 µm

- Can the gaps provide necessary stress relaxation?
- How large of a pad size can be accommodated?

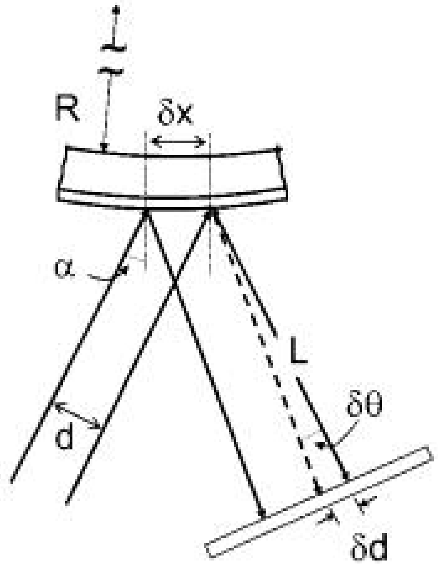
L.Y. Beaulieu, K.W. Eberman, R.L. Turner, L.J. Krause, J.R. Dahn, Electrochem. Solid-State Lett. 4 (2001) A137.

Y. Tian, A. Timmons, J.R. Dahn, J. Electrochem. Soc. 156 (2009) A187.

Related Si island works

In-situ Stress Measurement with MOSS system

(Multibeam Optical Stress Sensors)



Wafer curvature

$$\frac{1}{R} = \left(\frac{d - d_0}{d_0} \right) \frac{\cos \alpha}{2L}$$

Stoney Equation

$$\sigma_f h_f = \frac{1}{6} M_s H_s^2 R$$

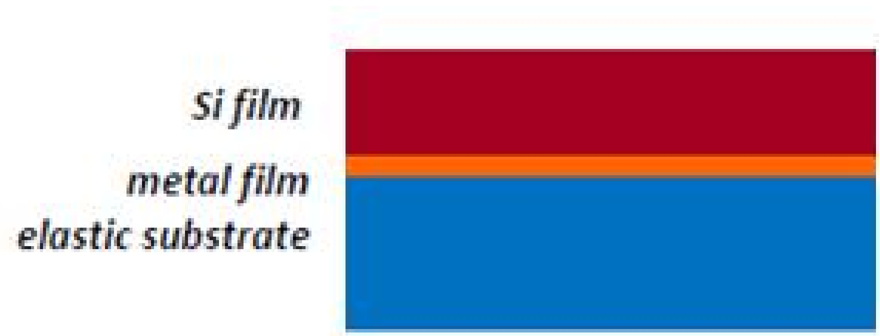
σ_f in-plane film stress

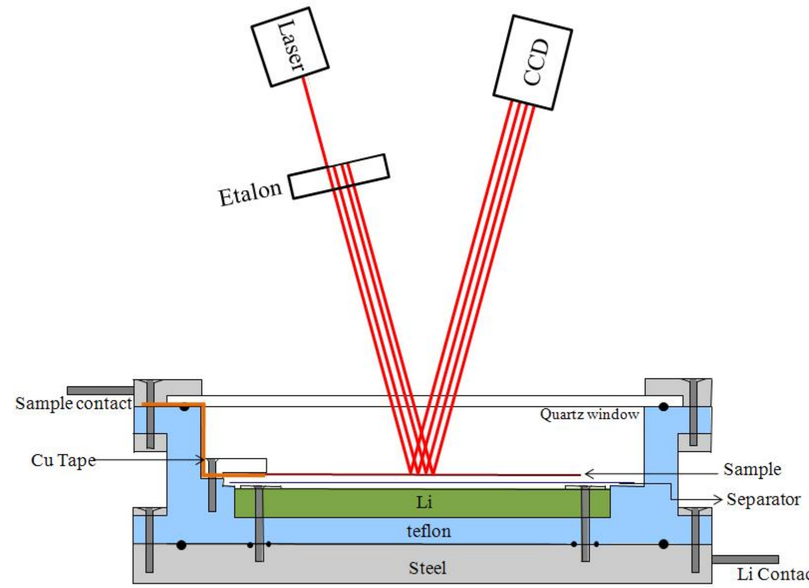
h_f film thickness

M_s substrate biaxial modulus

H_s substrate thickness

R substrate radius of curvature

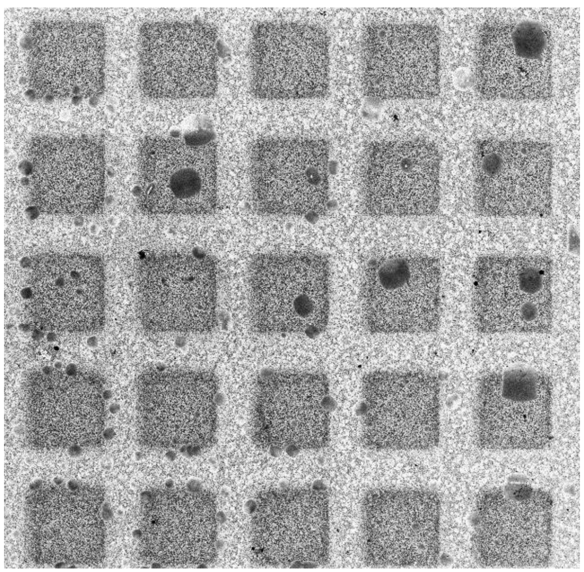




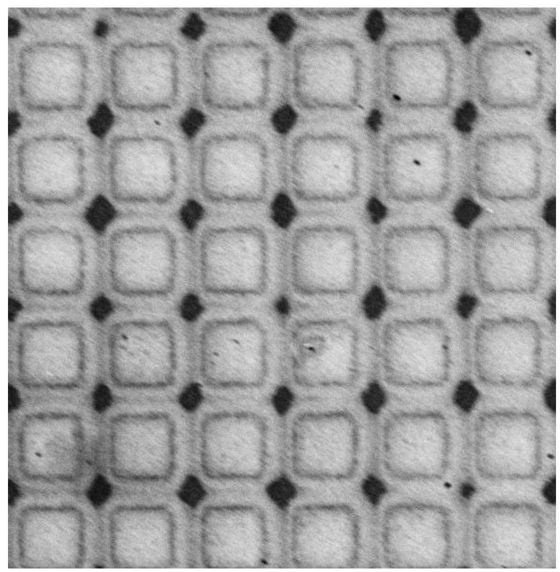
See Janssen et al., "Celebrating the 100th anniversary of the Stoney equation for film stress: Developments from polycrystalline steel strips to single crystal silicon wafers," *Thin Solid Films* 517 (2009) 1858–1867.

Preparation of Si patches

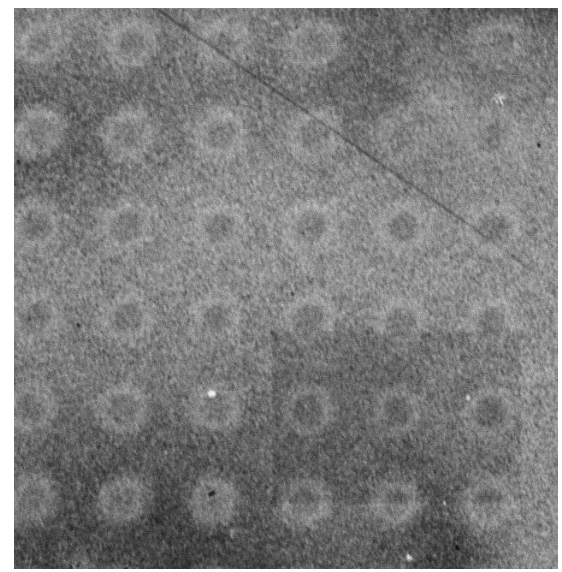
41 x 41 μm^2, 10 μm gap



17 x 17 μm^2, 7 μm gap



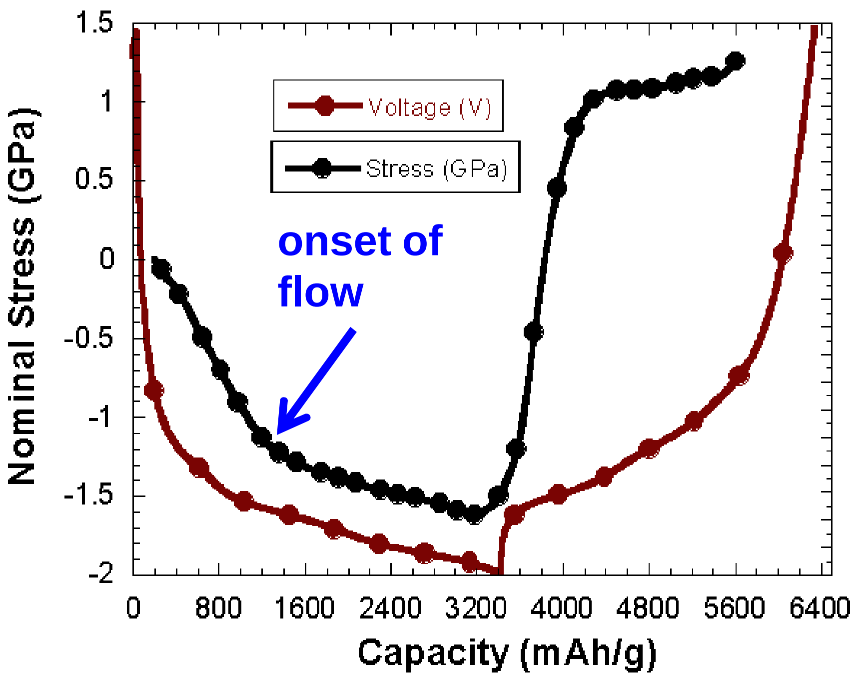
7 x 7 μm^2, 6 μm gap



SEM images of through-mask, sputtered, patterned Si film

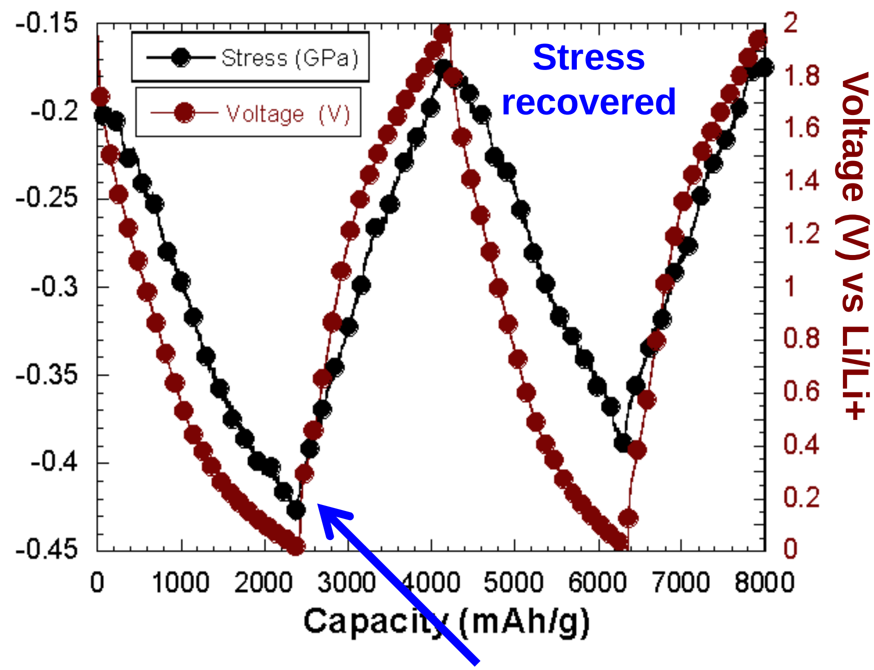
Comparison of 50 nm thick Si samples: continuous film vs. 7x7 μm^2 pattern

Continuous Film



Patterned Sample

2nd & 3rd Cycle



Note stress ordinate scales differ

No evidence of flow

See also Sumit K. Soni, Brian W. Sheldon, Xingcheng Xiao and Anton Tokranov, “Thickness effects on the lithiation of amorphous silicon thin films,” *Scripta Materialia* 64 (2011) 307–310.

Solid mechanics

We seek the minimum crack spacing L_{cr} that does not allow an extra crack to be formed in between the existing cracks.

Below this minimum crack spacing, the stress in the lithiated Si film can not reach its plastic yield stress and therefore no strain localization in the film can take place to form an additional crack.

$$\tau_{cr}^{int} = \min(\tau_Y^{Cu}, \tau_f^{int})$$

$$\tau_Y^{Cu} = 40\,\text{MPa}$$

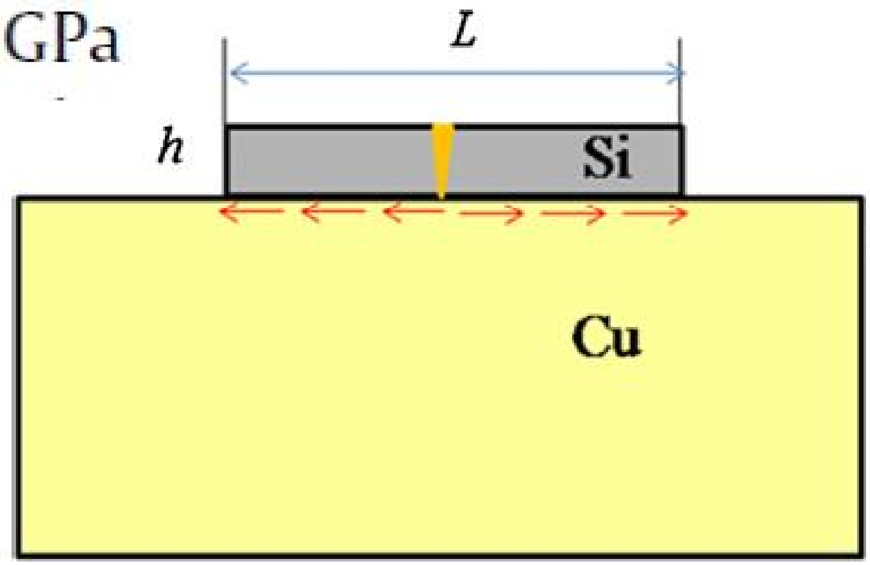
$$\tau_f^{int} = 40\,\text{MPa}$$

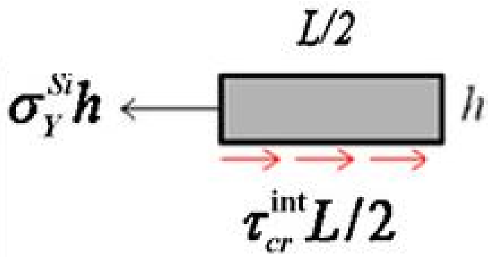
Q. Li, K.-S. Kim, Proc. R. Soc. A 464 (2008) 1319.

$$\boxed{L_{cr} = \frac{2\sigma_Y^{Si}}{\tau_{cr}^{int}} h \sim 5.1 - 8.9\,\mu\text{m}}\ !!$$

$$\sigma_Y^{Si} = 1 - 1.75\,\text{GPa}$$

$$h = 0.1\,\mu\text{m}$$

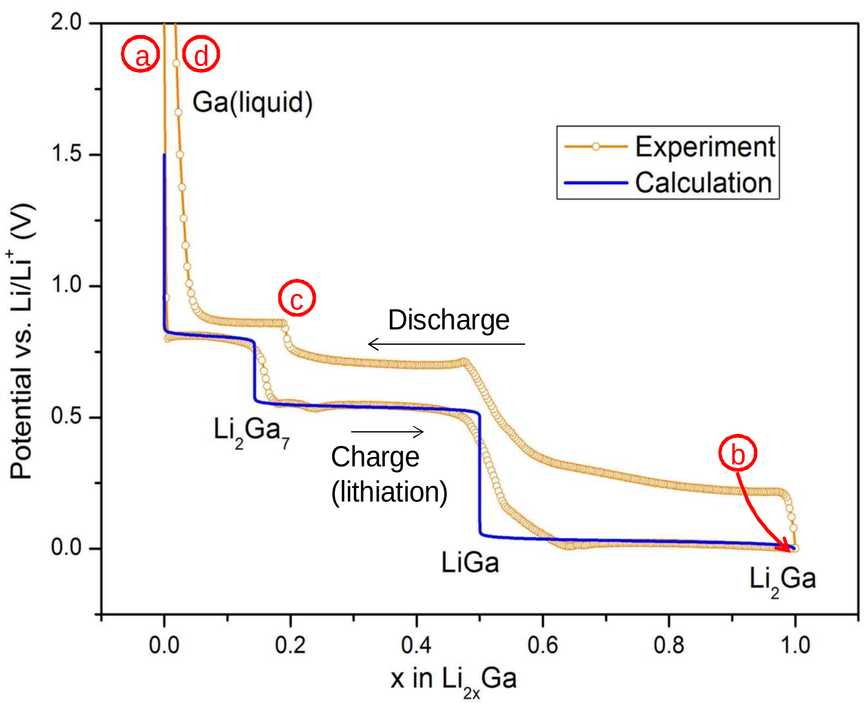




$$\sigma_Y^{Si} h = \tau_{cr}^{int} L/2$$

M. W. Verbrugge,[1] R. D. Deshpande,[2] J. Li,[2] and Y-T. Cheng,[2] "The search for high cycle life, high capacity, **self healing** negative electrodes for lithium ion batteries and a potential solution based on lithiated gallium," 2011 MRS Spring Meeting Symposium M Paper Number 1029460.

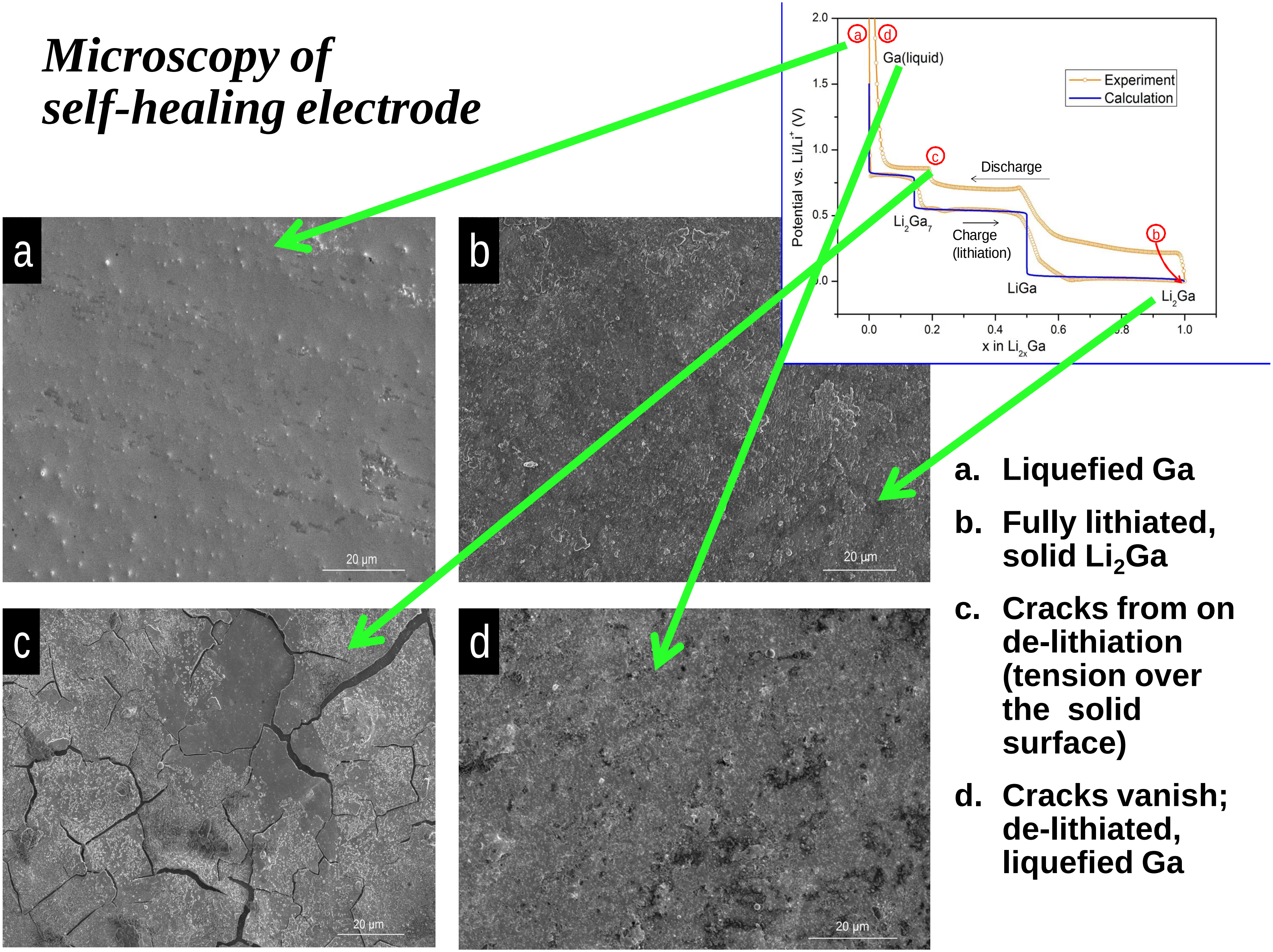
[1]Chemical Sciences and Materials Systems Laboratory, General Motors Research and Development Center, Warren, MI 48090, USA
[2]Department of Chemical and Materials Engineering, University of Kentucky, Lexington, Kentucky 40506, USA



❑ Related works

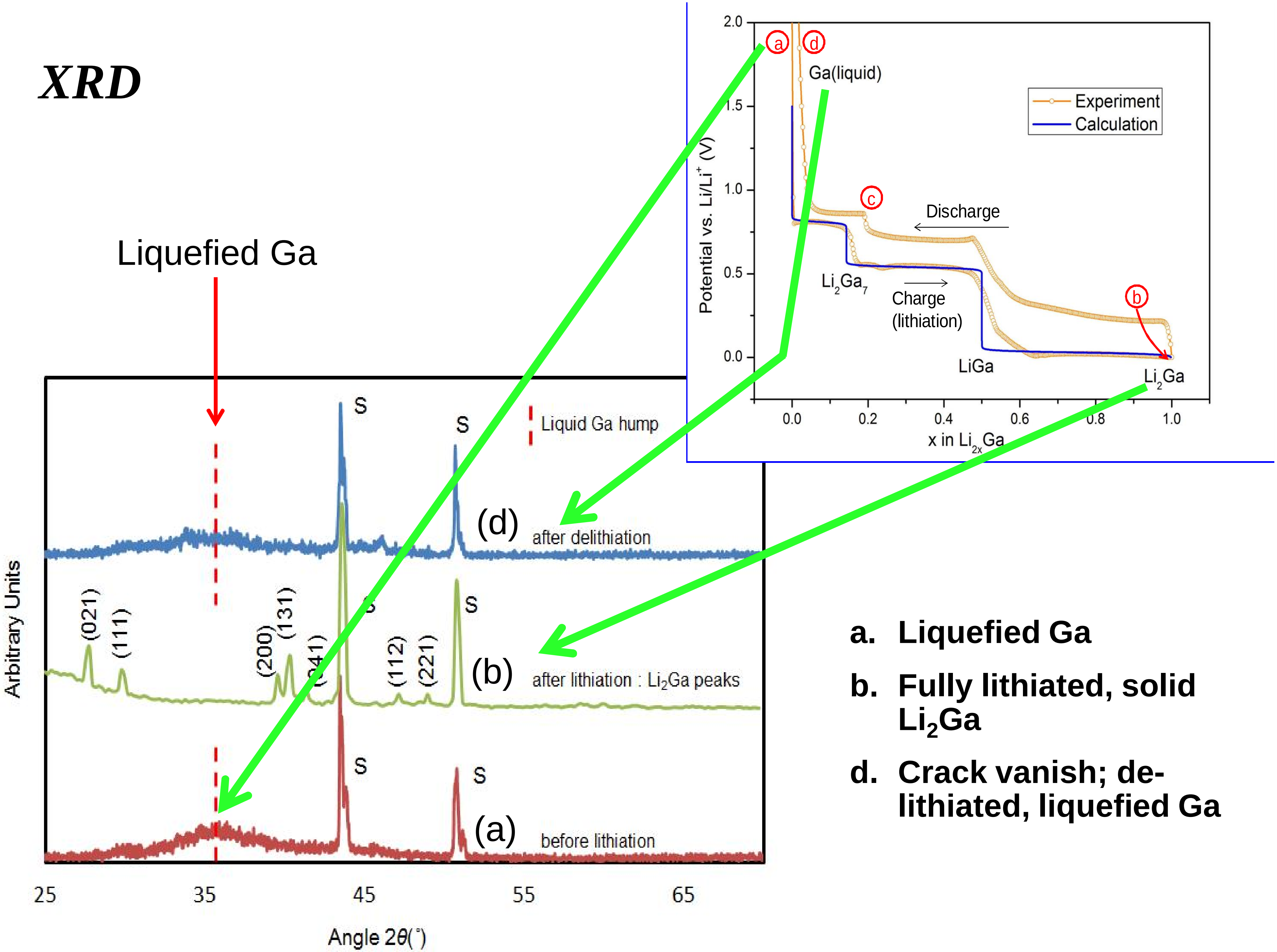
- Wen, C.J. and Huggins, R.A., "Electrochemical Investigation of the Lithium-Gallium System," *J. Electrochem. Soc.*, 128 (8): 1636-1641 (1981).
- Saint, J., Morcrette, M., Larcher, D., and Tarascon, J.M., "Exploring the Li-Ga Room Temperature Phase Diagram and the Electrochemical Performances of the Li_xGa_y Alloys vs. Li," *Solid State Ion.*, 176 (1-2): 189-197 (2005).

Microscopy of self-healing electrode



a. **Liquefied Ga**
b. **Fully lithiated, solid Li_2Ga**
c. **Cracks from on de-lithiation (tension over the solid surface)**
d. **Cracks vanish; de-lithiated, liquefied Ga**

XRD

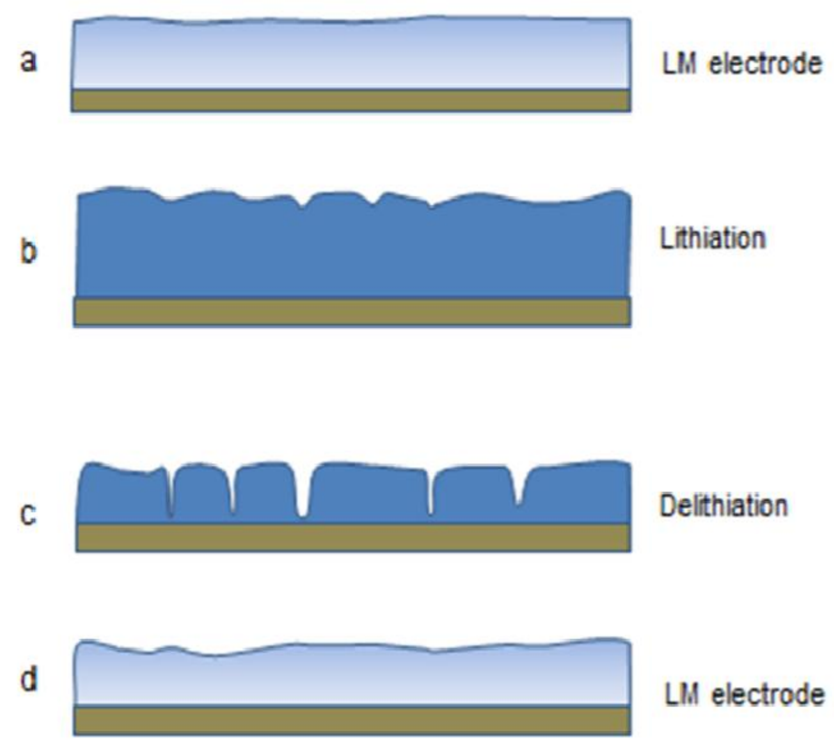


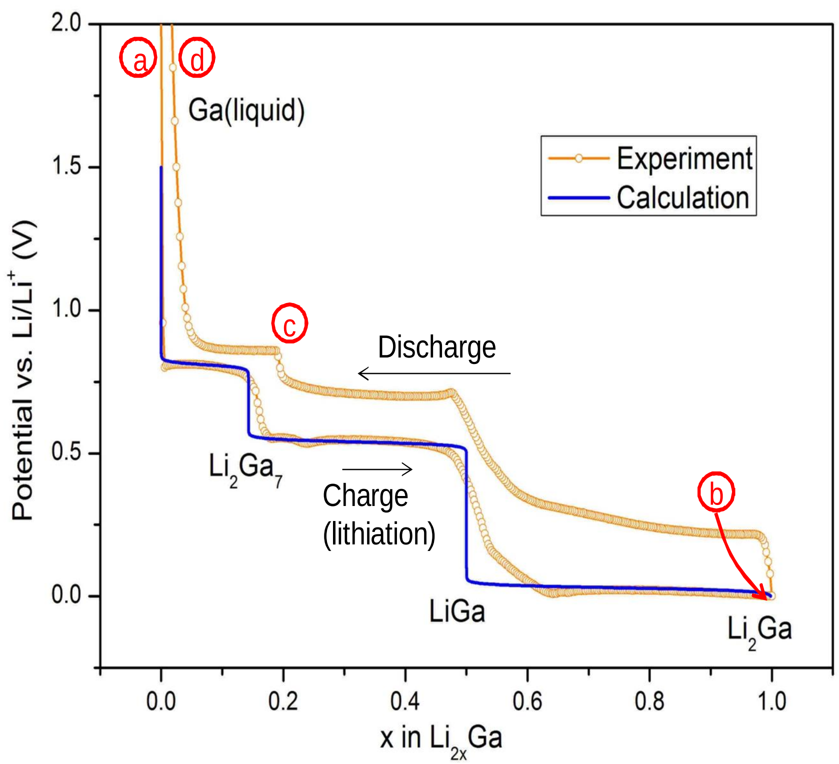
a. **Liquefied Ga**
b. **Fully lithiated, solid Li_2Ga**
d. **Crack vanish; de-lithiated, liquefied Ga**

Mechanistic summary

$Li_{2x}Ga$ system ($0 < x < 1$) at 40^oC

LM: Liquid Metal





- ❑ **Cracks are self-healed by the solid-to-liquid phase transformation upon discharge of the negative $Li_{2x}Ga$ electrode**


GM