Ion Conducting Glasses for Use in Batteries: 1
Introduction – Anodes and Cathodes

Steve W. Martin

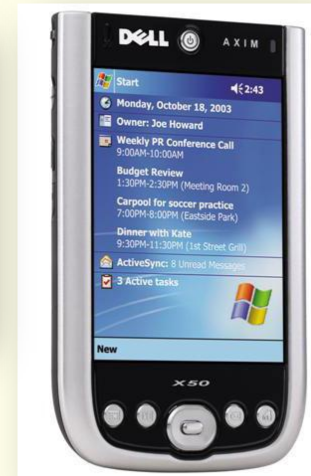
Anson Marston Distinguished Professor of Engineering

University Professor

Department of Materials Science & Engineering

Iowa State University

Portable Energy Sources (Batteries) are Critical…



Introduction to Batteries

- Batteries are controlled electrochemical reactors
- Oxidation $Li^o \rightarrow Li^+ + e^-$ at the anode
- Reduction $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$ at the cathode
- Overall reaction:
  – $2Li^o + 1/2O_2 + H_2O \rightarrow 2LiOH$ + energy
  – Energy is the product of the net Voltage of the electrochemical reaction and the charge transferred as a result of the chemical reaction

$$Energy = V \cdot C \qquad 1J = 1Volt \cdot 1Coulomb$$

  – $Li^o \rightarrow Li^+ + e^-$ $V^o = +3.04$ Volts
  – $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$ $V^o = -0.54$ Volts
  – $2Li^o + 1/2O_2 + H_2O \rightarrow 2LiOH$ $\Delta V^o = +3.58$ V

$$\Delta \bar{G}^o(T,P) = -n\Im\Delta V^o = -2 \cdot 96,485C/mole \cdot +3.58V = -690,832J/mole$$

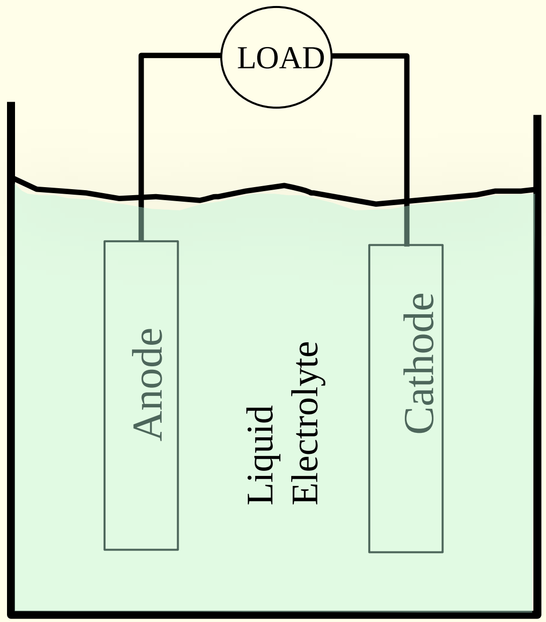
Standard Potentials

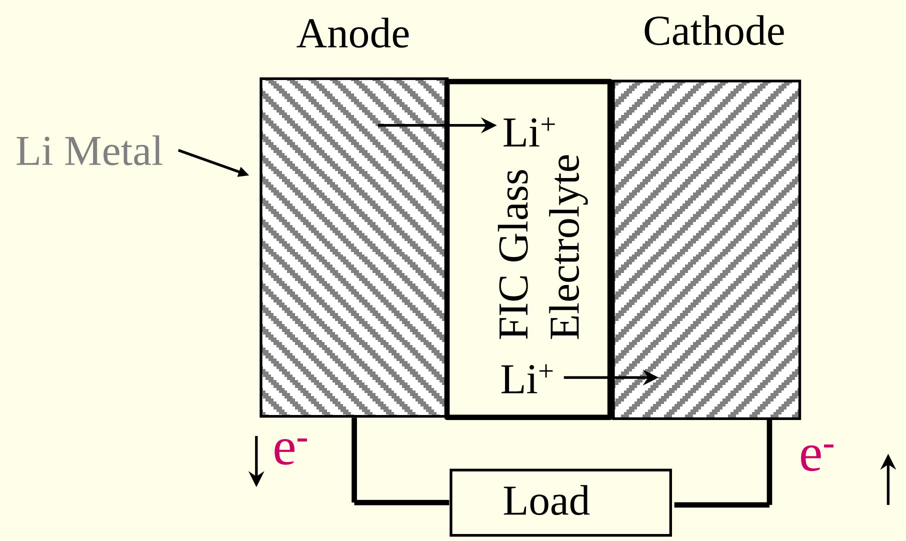
Table 15.1 Standard electrode potentials at 298 K, 1 atm (standard state is 1 molal)

Electrode reaction	$\mathscr{E}^{\circ x}$, volts
Acid solutions	
$F_2 + 2e^- = 2F^-$	2.65
$S_2O_8^{2-} + 2e^- = 2SO_4^{2-}$	1.98
$Co^{3+} + e^- = Co^{2+}$	1.82
$Ce^{4+} + e^- = Ce^{3+}$	1.61
$\frac{1}{2}Cl_2 + e^- = Cl^-$	1.3595
$Cr_2O_7^{2-} + 14H^+ + e^- = 2Cr^{3+} + 7H_2O$	1.33
$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	1.23
$Br_2(l) + 2e^- = 2Br^-$	1.0652
$2Hg^{2+} + 2e^- = Hg_2^{2+}$	0.92
$Hg^{2+} + 2e^- = Hg$	0.854
$Ag^+ + e^- = Ag$	0.7991
$Fe^{3+} + e^- = Fe^{2+}$	0.771
$I_2 + 2e^- = 2I^-$	0.5355
$Fe(CN)_6^{3-} + e^- = Fe(CN)_6^{4-}$	0.36
$Cu^{2+} + 2e^- = Cu$	0.337
$S_4O_6^{2-} + 2e^- = 2S_2O_3^{2-}$	0.17
$Cu^{2+} + e^- = Cu^+$	0.153
$Sn^{4+} + 2e^- = Sn^{2+}$	0.15
$S + 2H^+ + e^- = H_2S$	0.141
$2H^+ + e^- = H_2$	0.000
$Mg^{2+} + 2e^- = Mg$	−2.37
$Na^+ + e^- = Na$	−2.714
$Ca^{2+} + 2e^- = Ca$	−2.87
$Ba^{2+} + 2e^- = Ba$	−2.90
$Cs^+ + e^- = Cs$	−2.923
$K^+ + e^- = K$	−2.925
$Li^+ + e^- = Li$	−3.045

Introduction to Batteries

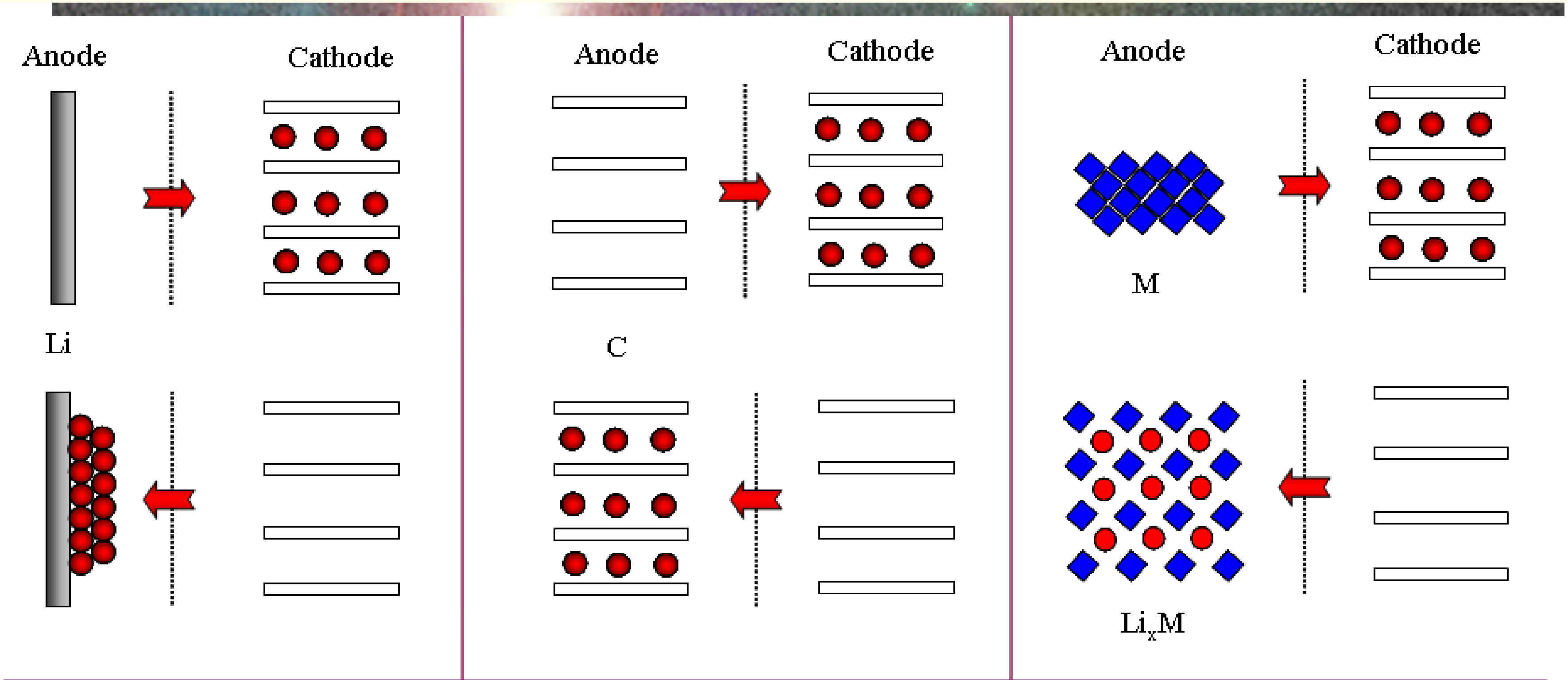
- Liquid State Batteries vs. Solid State Batteries





- Liquid electrolyte surrounds and separates the anode and cathode
- Solid electrolyte separates the anode and the cathode

Different Types of Lithium Batteries – Solid or Liquid Electrolyte



Li metal battery | Li-ion battery | Li metal alloy battery

Now the Details of a Li-ion Battery…

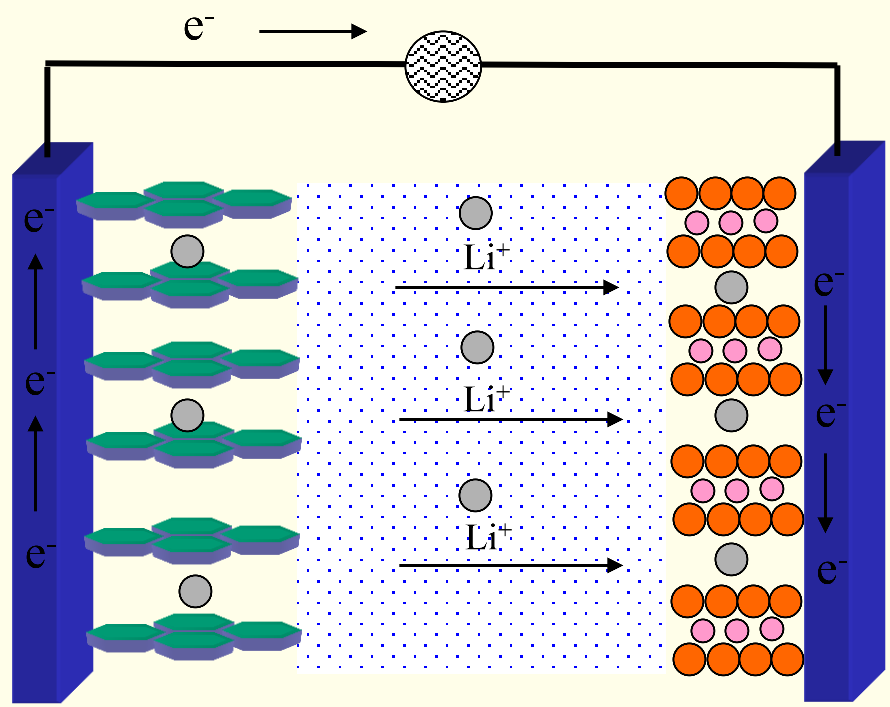
C_6 (graphite) is a common anode material for Li-ion batteries

The composition is Li_1C_6

That is it takes 6 C atoms to store 1 Li atom

This gives good cycle-life

But, low capacity, short battery life before recharging is necessary



Li_1C_6 | Li^+ conducting Liquid electrolyte | Li_1CoO_2

Anode: $Li_1C_6 \longrightarrow Li^+ + e^- + C_6$

Cathode: $Li_1CoO_2 + Li^+ + e^- \longrightarrow LiCoO_2$

Capacity Calculations of Anode Materials

- The composition of lithiated graphite is Li_1C_6
- Recall Faraday's constant 96,485 C/mole e^-
- 1 mole C_6 = 72 gr C/mole = 1 mole Li^+ = 1 mole e^- transferred

$$\left(96,485\ \text{C/mole Li}^+\right)/\ 72\text{gr/mole C}_6 = 1,340\ \text{C/mole C}_6$$

$$1\ \text{mAh} = 3.6\ \text{C}$$

$$C_6 = 372\ \text{mAh/gr}$$

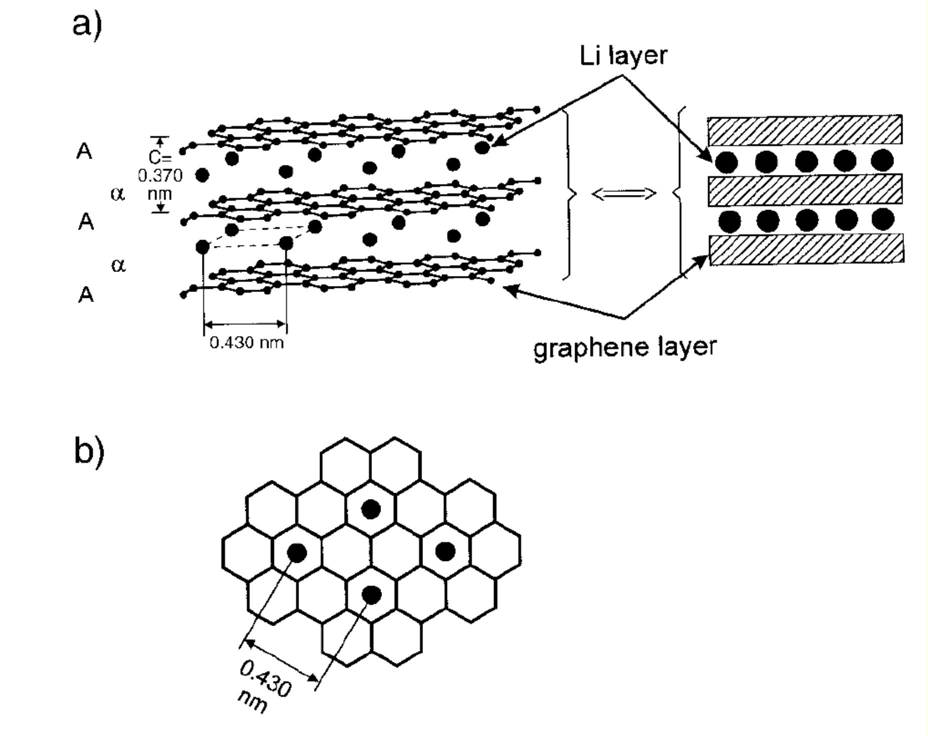
- Now, what is the capacity of pure Li metal? A.W. Li is 6.94 gr/mole
- 3,862 mAh/gr
- What is the capacity of $Li_{22}Si_5$? A.W. Si = 29.06 gr/mole
- 4,058 mAh/gr
- More charge storage than pure Li!
- And Si is one of the most abundant of all elements!

Capacity Calculations of Cathode Materials

- Now, what is the capacity of $LiCoO_2$ a common cathode material? A.W. Co = 58.93 gr/mole
- 295 mAh/gram
- What is the capacity of Li_2S? A.W. S = 32.06 gr/mole
- 1,675 mAhr/gr
- What is the capacity of Li_2O?
- 3,350 mAhr/gr
- Notice that one gram of Li is about equally matched to 1 gram of O

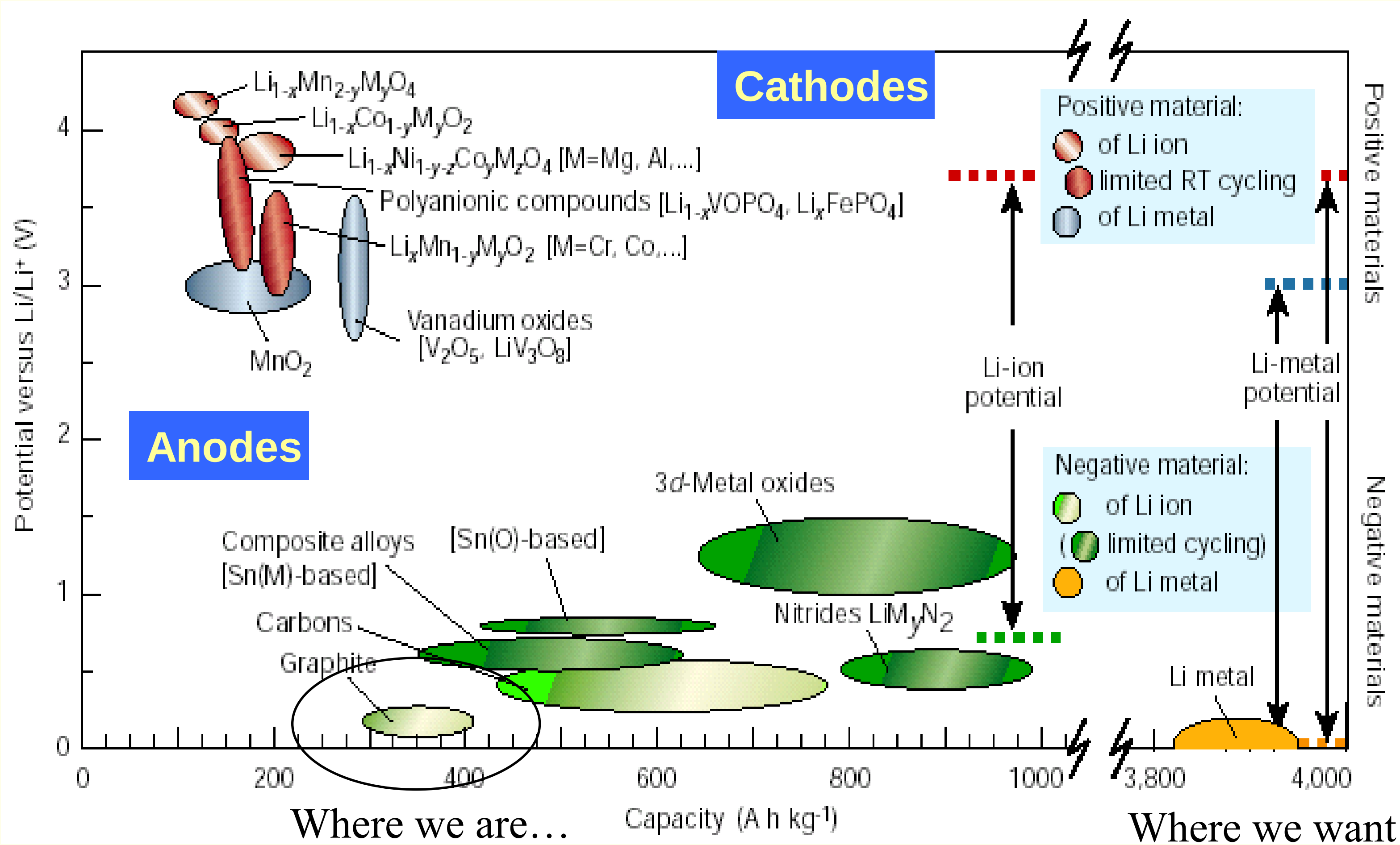
Carbons as Negative Insertion Electrodes (anodes)

- $Li_xC_n \leftrightarrow xLi^+ \; xe^- + C_n$
- $x \sim 1$, $n \sim 6$
- C has high e-conductivity
- Cheap
- Plentiful
- Good voltage, near 0V
- Relatively low capacity, small x



M. Winter, J. Besenhard, M. Spahr, P. Novak, Adv. Mater. 10(1998) 10

Anode and Cathode Combinations Determine the Voltage and Energy Density of Lithium Batteries



Where we are…

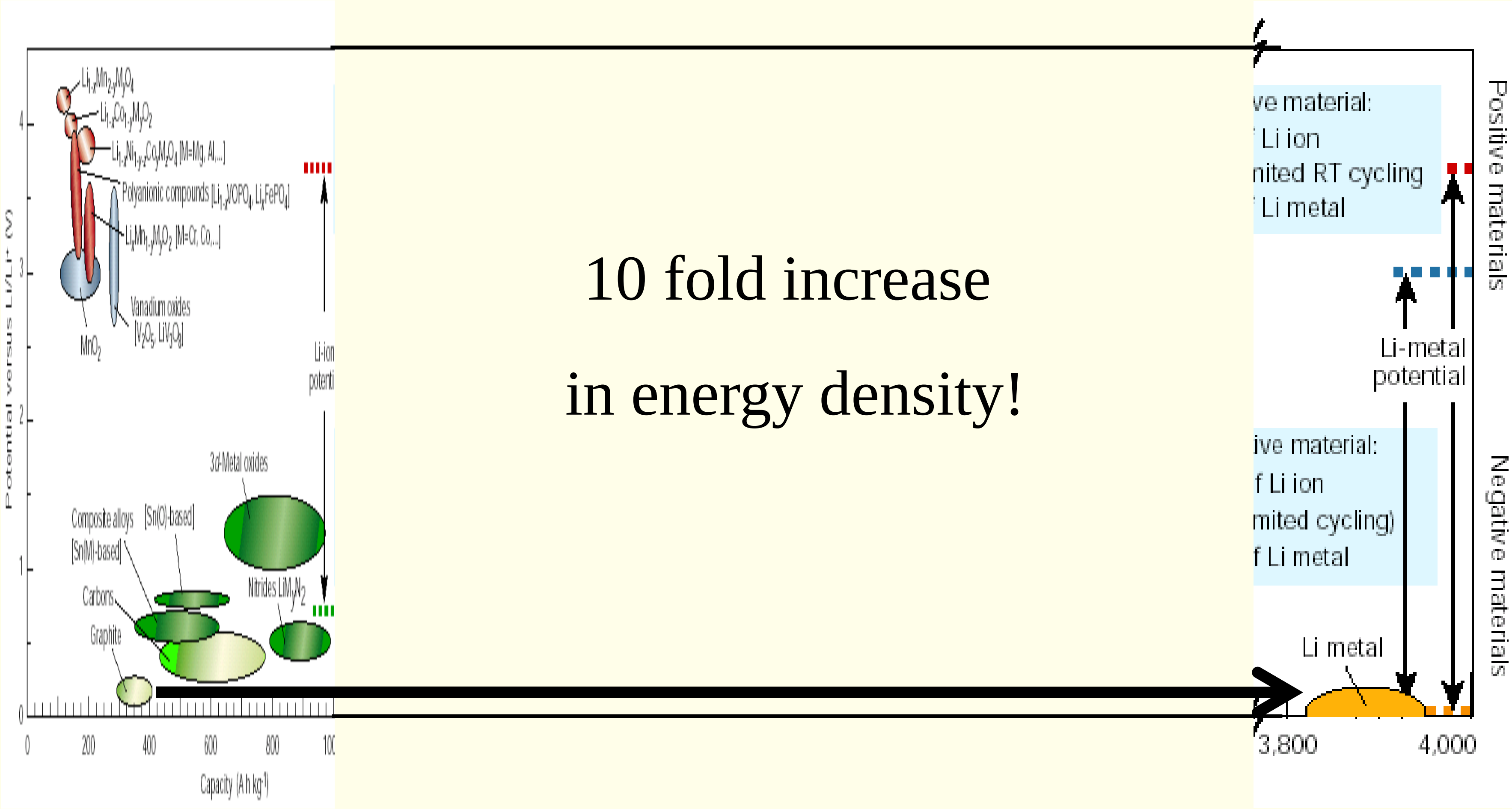
Where we want to go…

J.M. Tarascon, M. Armand, Nature, 414, 15 (2001) 359

Just for comparison…

Where we are…

Where we can go…



So… Why does the Chevy Volt only go 40 miles between charges….

- Because today's Li batteries use Li_1C_6 as the Anode
- And the Cathode, Li_1CoO_2, is equally less energy dense
- Comparison….
- Gasoline: $C_8H_{18} + 12\frac{1}{2} O_2 \rightarrow 8CO_2 + 9H_2O$ + Energy
- 44,400 J/g C_8H_{18}
- Graphite: ~ 400 mAhr/g x 3,600 sec/hr x ~ 4 V = 5,760 J/g
- Li: ~4,000 mAhr/g x 3,600 sec/hr x ~4 V = 57,600 J/g Li
- *Gasoline and Li are comparably energy dense*

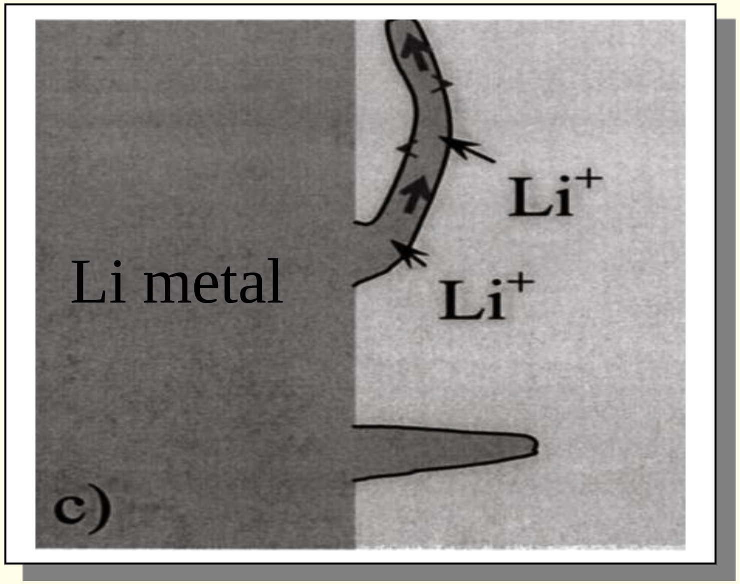
Therefore, consider a Li – Air battery…

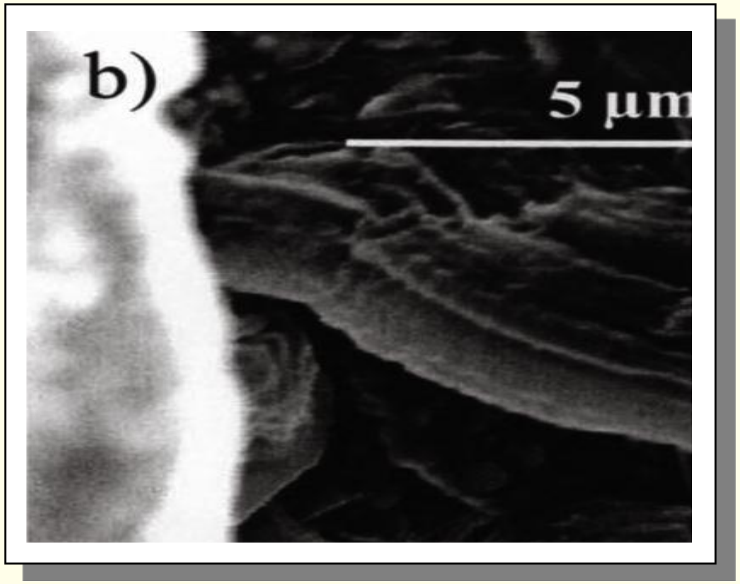
- At ~4,000 mAhr/gr anode material
- ~100 kg battery ~ 10 kg anode (only 10% active mass)
- ~40,000 Ahr at 35V (10 3.5 V cells)
- ~1,400 kWhr
- ~50 kW to power a car at 60 MPH
- > 1,000 miles..?

So…Why don't we use Li metal batteries….?

- Safety…
- No available cathode to match Li metal energy density
- Remember, electrons must be balanced on both sides of the battery…

Safety….Lithium Dendrites in Li ion Batteries





Non-epitaxial deposition of lithium after each cycle leads to the growth of uneven "fingers" or dendrites of lithium

Internal dendrites can cause short circuits of the battery

M. Dolle et al. Electrochemical and Solid-State Letters, 5(12) (2002)A286

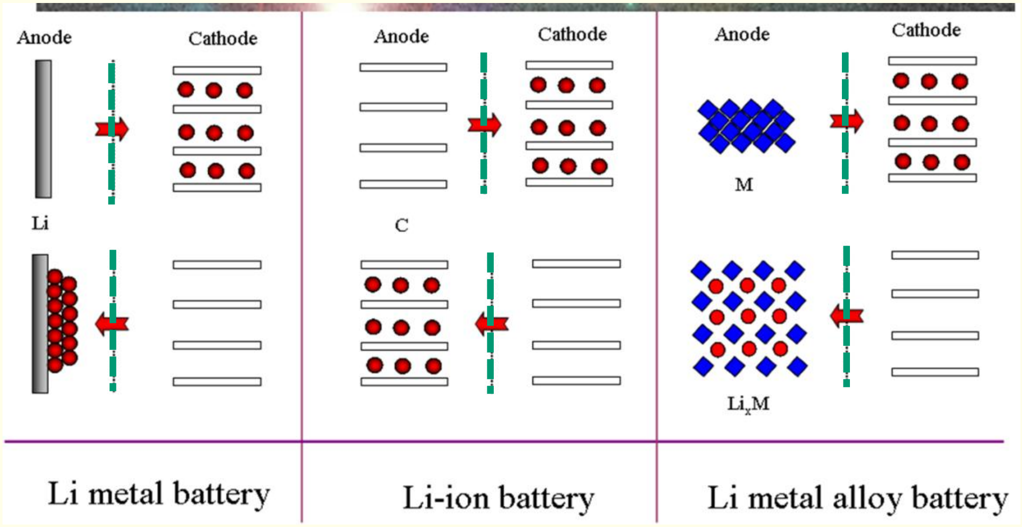
Lithium Dendrite Formation in Li-Ion Batteries

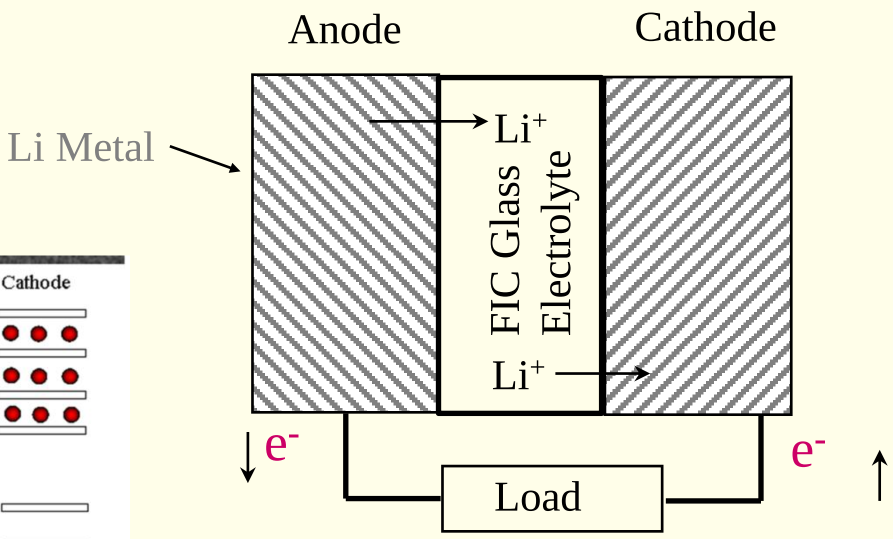
- Cell short circuits, leading to over heating and fires

All Solid State Lithium Batteries

- Replace flammable liquid electrolyte with highly conducting glassy solid electrolyte

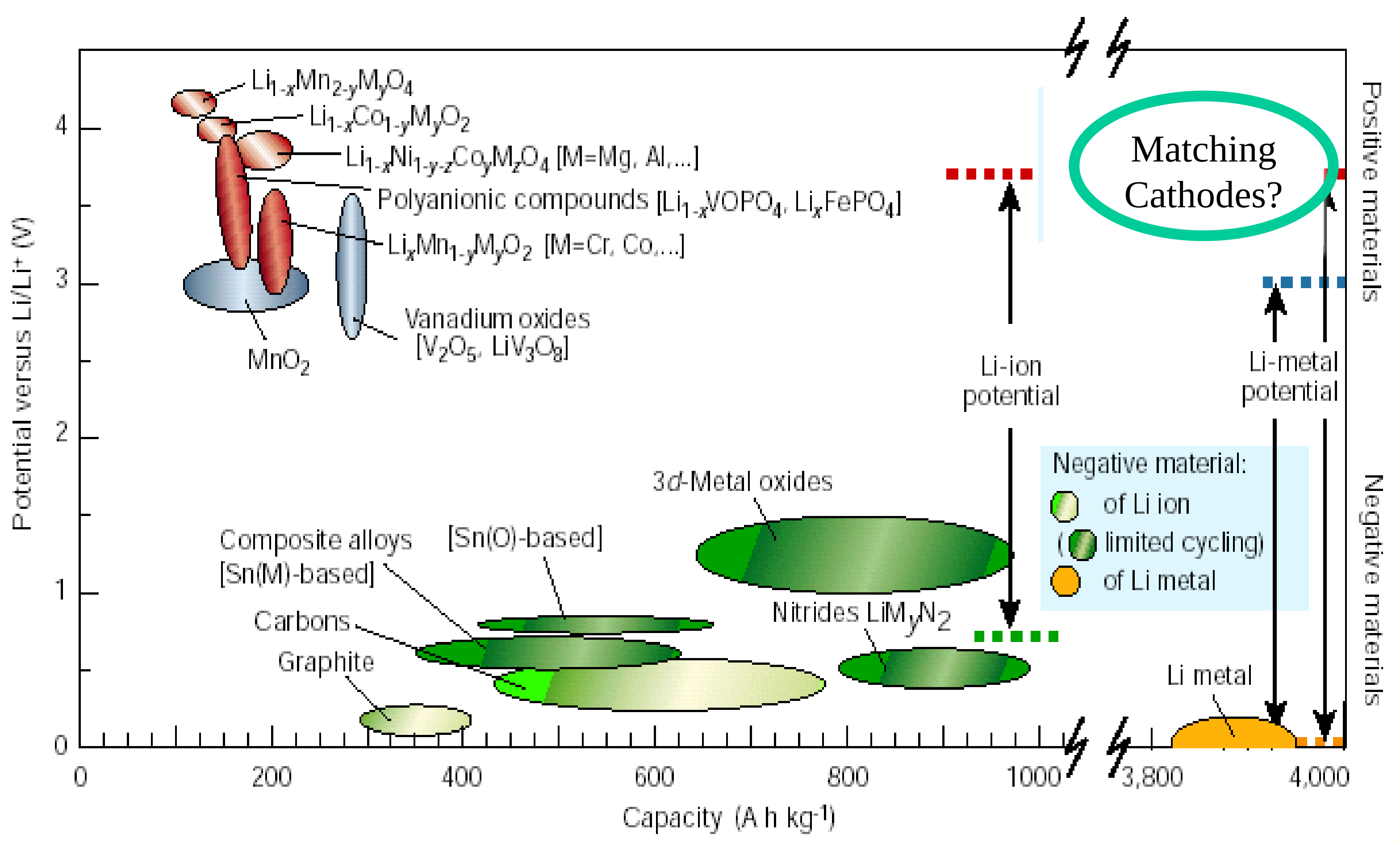
Glassy solid electrolytes





No Cathode to match Li metal energy density

- Recall our Voltage – Capacity graph….



J.M. Tarascon, M. Armand, Nature, 414, 15 (2001) 359

4,000 mAhr/gram Cathodes?

- Must change the paradigm…
- Li_nX_1 n = 1, 2, 3, 4…. instead of $Li_{0.5}CoO_2 = Li_1X_6$,
- Must have Li^+ in the oxidized form, like rust, sand, rocks…
- What is the corresponding simple oxide of Li?
- Li_2O and consider…
- $2Li + \frac{1}{2} O_2 \rightarrow Li_2O$
- ~3,350 mAhr/g O, very similar to Li
- And… you don't have to carry the O_2 around!
- Air-breathing batteries…Lithium-Air batteries
- Note the similarity to gasoline, except no CO_2 and only O_2 given back off when the battery is recharged at night in your garage…

So… Back to the Lithium Battery Problem – The Anode (Electrolyte we will consider next time….)

- Consider the problem… your cell phone lasts ~ 2 years, how many charges and discharges?
- 700?
- What capacity loss can you tolerate so that your battery still has some capacity left after 2 years of operation?
- 25%?
- Now, what capacity retention must you have at each cycle so that you can still have 25% of your battery capacity at your last charge?
- $0.25 = (\text{Capacity retention})^{700}$
- Cycle retention = 99.80% at each cycle

Cycle Retention…

- Now consider the automobile battery…
- How long do you want your plug-in electric car battery to last?
- 10 years?
- Now, how many charge/discharge cycles will this be for the battery?
- 10*365 = 3,650?
- Now, how much capacity do you want your car battery to have at the end of 10 years?
- At least 50%?
- OK, what is the Cycle retention required at the end of 10 years so that the battery still has this much capacity?
- $0.50 = (\text{Capacity retention})^{3,650}$
- 99.981%
- Meaning the battery must recharge back to within 0.019% of it original state one each charge

New Lithium Battery Designs - Anode

- Metallic alloy anodes
- Metal + xLi → MLi_x
- x can be very large
- $Li_{22}Si_5$, for example
- However, large capacity fade
- Associated with large volume change
- +400% from Si to $Li_{22}Si_5$

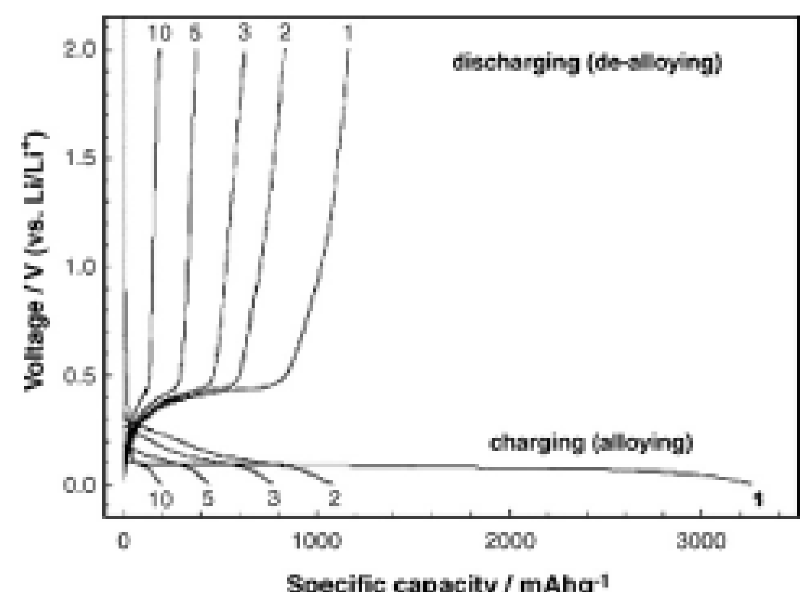


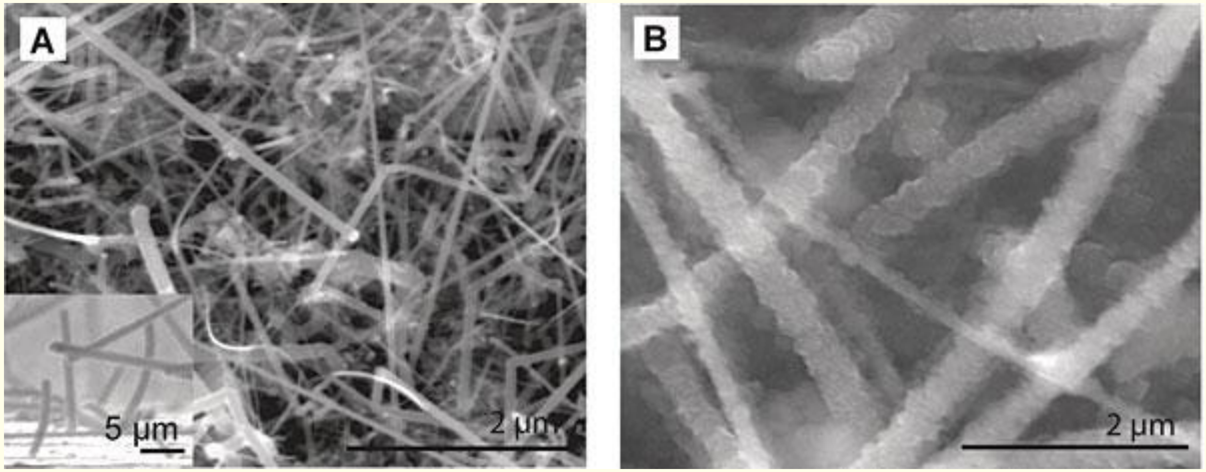
Table 1
Crystal structure, unit cell volume and volume per Si atom for the Li–Si system [10]

Compound and crystal structure	Unit cell volume (Å^3)	Volume per silicon atom (Å^3)
Silicon cubic	160.2	20.0
$Li_{12}Si_7$, ($Li_{1.71}Si$) orthorhombic	243.6	58.0
$Li_{14}Si_6$, ($Li_{1.71}Si$) rhombohedral	308.9	51.5
$Li_{13}Si_4$, ($Li_{3.25}Si$) orthorhombic	538.4	67.3
$Li_{22}Si_5$, ($Li_{4.4}Si$) cubic	659.2	82.4

A.J. Appleby, et al. J Power Sources 163(2007)1003

New Lithium Battery Designs - Anode

- Nano-Structured Si
- To increase surface area
- Increase reaction rate
- Decrease volume change on intercalation



Y. Cui et al., Nature Nanotechnology 2007

Nano-Structured Si Anode

- Nano-Structured Si improves cyclability
- Cycle fade still strong
- 4000 cycles is a design goal

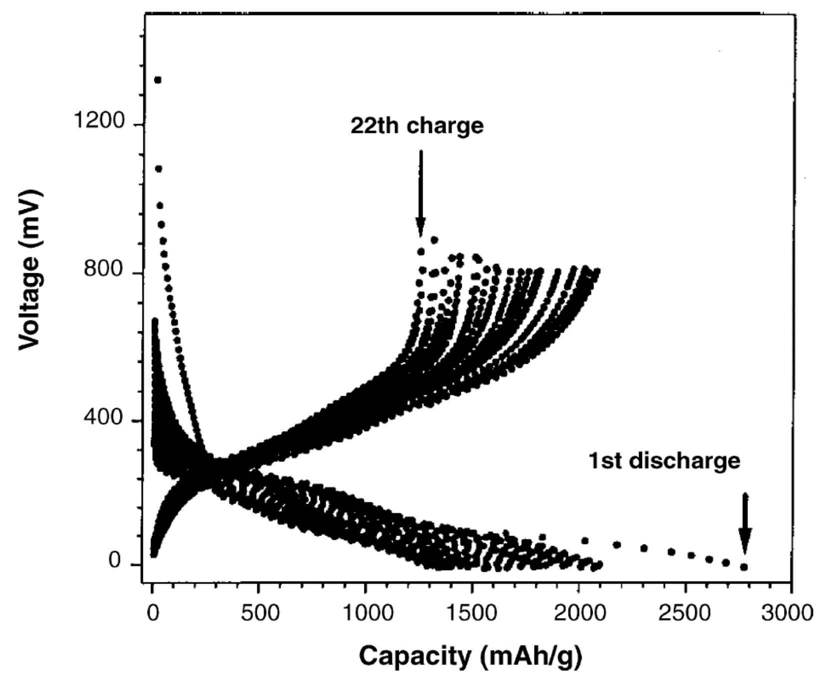


Fig. 5. §§Charge–discharge curves between 0.0 and 0.8 V at 0.1 mA cm^{-2} for nano-Si anode with 4:4:2 weight ratio of nano-Si, carbon black and PVDF binder. Electrolyte: 1 M $LiPF_6$ in ethylene carbonate (EC)–diethyl carbonate (DEC) (1:1) [22].

1 mAhr/g = 1Ahr/kg

A.J. Appleby, et al. J Power Sources 163(2007)1003

New Anodes for Lithium Batteries

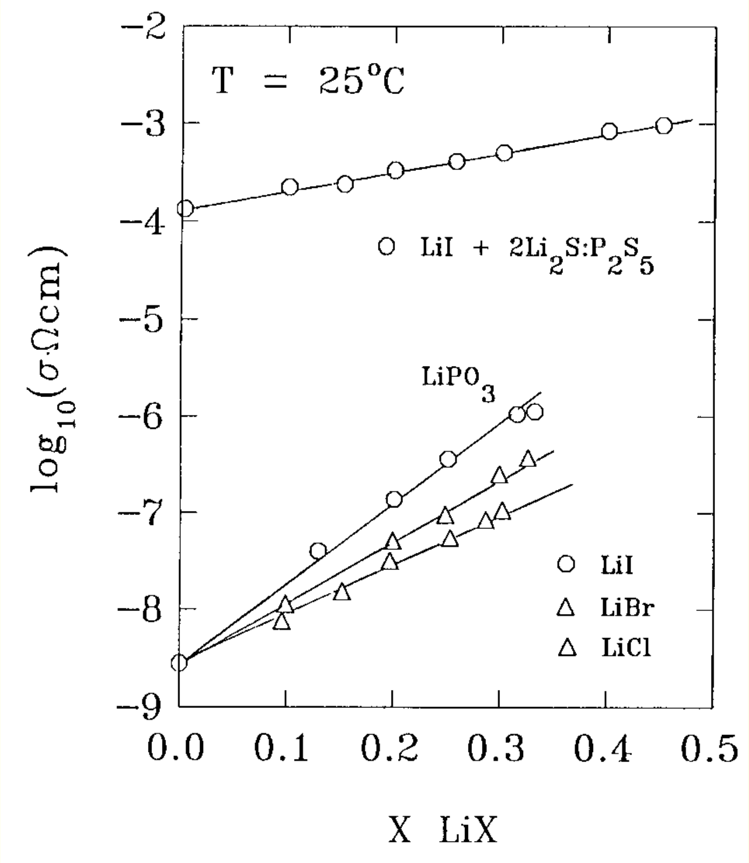
- How can we store more Li near unit activity, but safely, reversibly, and cheaply?
- Li readily alloys with many metals
  - Li-Si, Li-Ge, Li-Al
  - However, large volume changes often occur (> 100 %) with these alloy reactions
  - Anode cracks and crumbles after only a few cycles
- Can we create these Li-alloys inside a buffering material that will accommodate the volume changes leading to improved cyclability, but maintain high Lithium activity and capacity?

Chalcogenide Glasses as High Capacity, High Voltage, High Cyclability, Safe Lithium Battery Anodes

- Idea: Li^+ ion conducting chalcogenide glass anodes
  - Chalcogenide glasses are among the highest of all Li^+ ion conductors known, 10^{-3} $(\Omega cm)^{-1}$ at 25°C
  - Chalcogenide glasses can be readily made using Si and Ge over a continuous range of compositions, ~50 at% to ~ 10 at%
  - Chalcogenide glasses are significantly "softer" than oxide glasses, MPa moduli versus GPa, for example
  - Sulfide glasses while commonly unstable under oxidizing (cathode) conditions can be quite stable under reducing (anode) conditions
  - Due to their ease of preparation, glasses can be inexpensively prepared, especially in powder form, using mechanical milling where no melting is required

Inorganic Glasses as Hosts for Active Materials

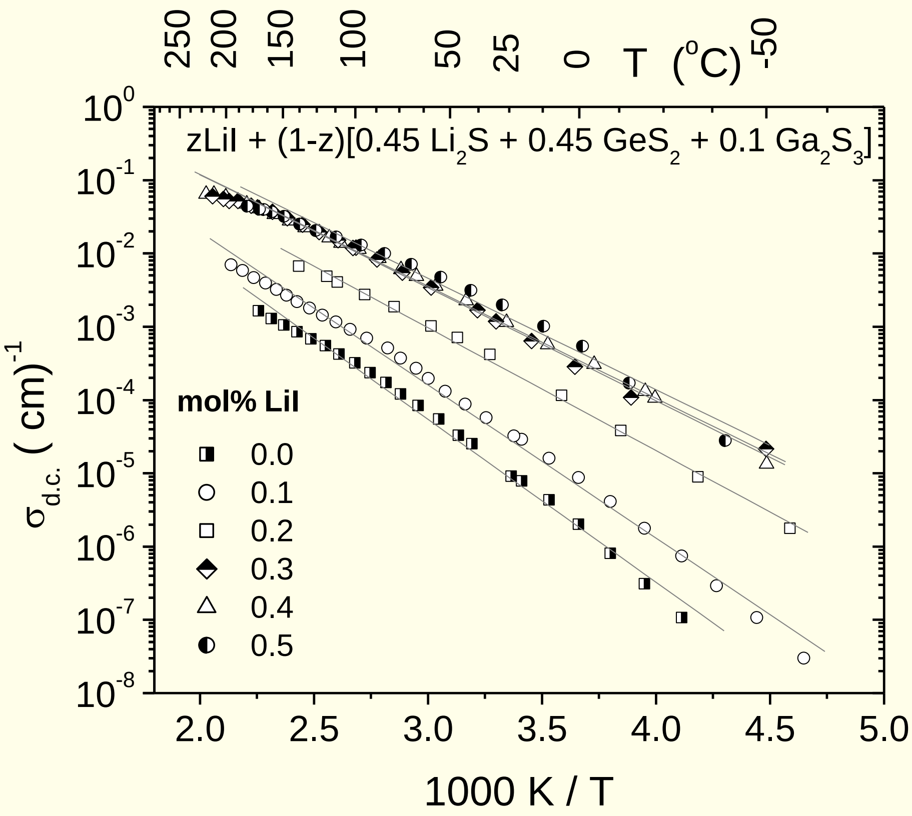
- Sulfide glasses show significantly higher Li^+ ion conductivity over their oxide counterparts
  - $Li_2O + P_2O_5$ has $\sigma_{RT} \sim 10^{-9}$ $(\Omega cm)^{-1}$
  - $Li_2S + P_2S_5$ has $\sigma_{RT} \sim 10^{-3}$ $(\Omega cm)^{-1}$
  - Perhaps sulfide glasses might serve as high capacity anodes?

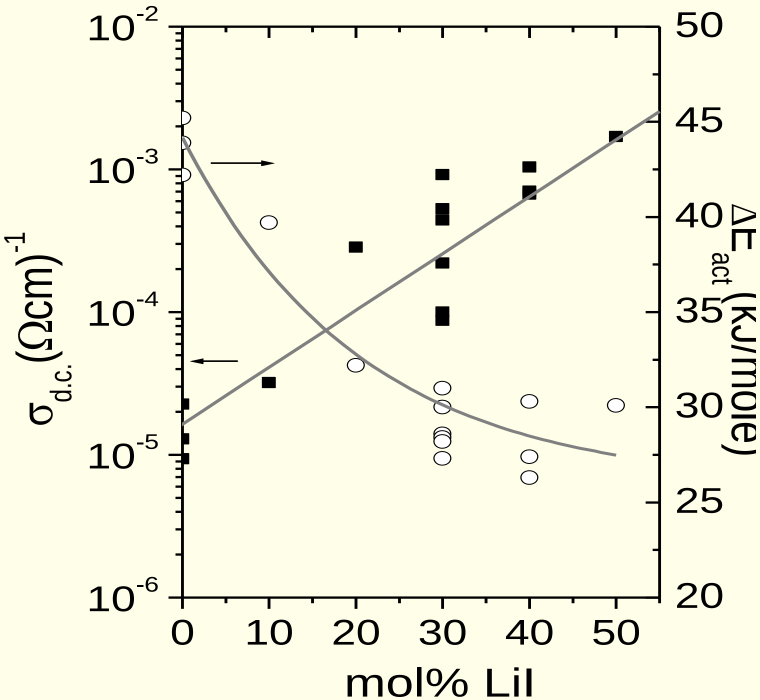


S.W. Martin JACerS 74(1991)1767

Fast Ion Conducting Chalcogenide Glasses

- Research has been active for many years developing new chalcogenide glasses as fast ion conductors, primarily as solid electrolyte materials





Saienga & Martin, JNCS, 354 (2008) 1475 – 1486

New Lithium Battery Designs - Anode

- Inorganic glasses as hosts for active materials
- Active material is still metal/metalloid
- $SnO(P_2O_5) + (x+2)Li \rightarrow Li_xSn + Li_2O$

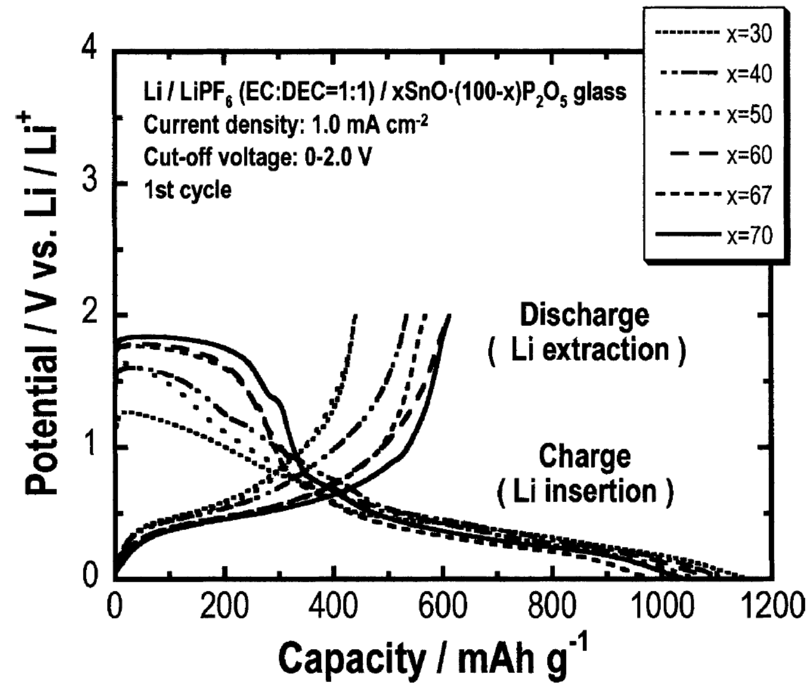


Fig. 4. First charge–discharge curves for the cells using the xSnO·(100 − x)P_2O_5, 30 ≦ SnO (mol%) ≦ 70, glasses as a working electrode. A constant current density of 1.0 mA cm^{-2} was used. A mixture of 1 M $LiPF_6$/EC + DEC was used as an electrolyte.

Tatsumisago et al. JNCS 345/346(2004)478

Inorganic Glasses as Hosts for Active Materials

- Capacity shows modest gain over Carbon
- Cycle fade is still large ~.5%/cycle
- ~200 cycle lifetime
- < ~ 0.1% required for ~ 1,000 cycle life
- < ~ 0.02% required for ~ 4000 cycle life

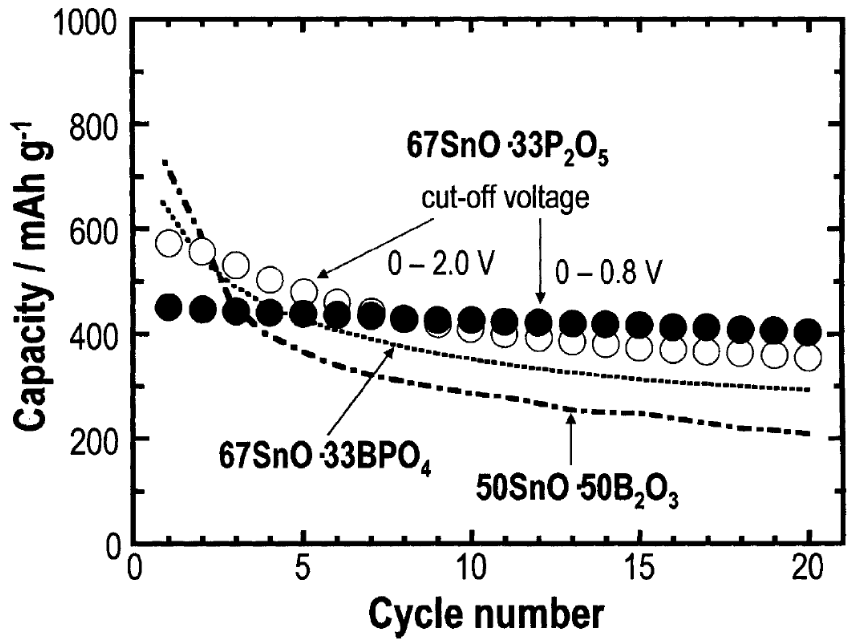


Fig. 5. Cycle performance for the cells using the $67SnO \cdot 33P_2O_5$ (mol%) glass under the two different cut-off voltage conditions of 0–2.0 and 0–0.8 V. Cyclability for the cells with $50SnO \cdot 50B_2O_3$ (mol%) and $67SnO \cdot 33BPO_4$ (mol%) glasses [7] is also shown for comparison.

Tatsumisago et al. JNCS 345/346(2004)478

Inorganic Glasses as Hosts for Active Materials

- $SnS + P_2S_5$ Glasses
- Two step insertion process
  - $SnS(P_2S_5) + (x+2)Li \rightarrow Li_xSn + Li_2S$
- Mechano-chemical milling to produce amorphous materials
  - Cheap, easy direct method to produce high surface area powders

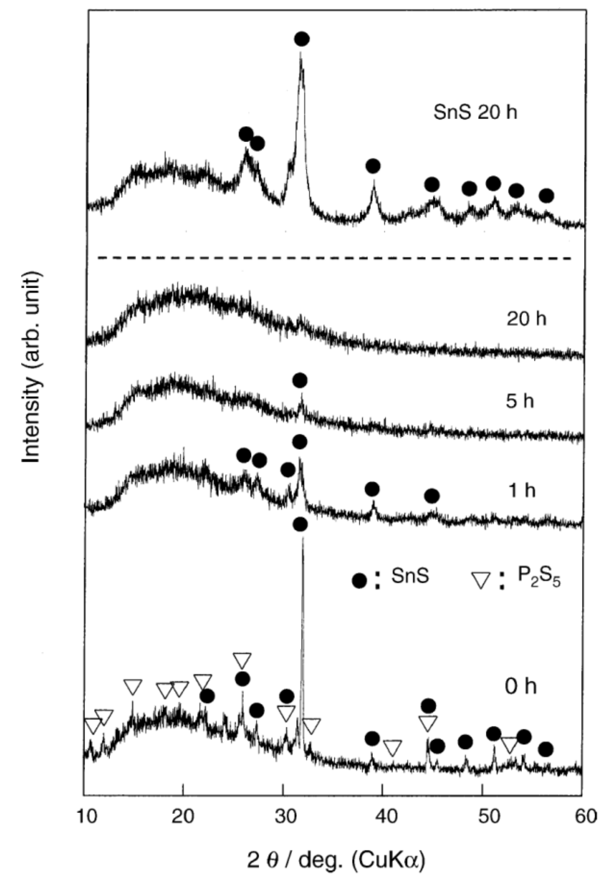


Fig. 1. XRD patterns of the $80SnS{\cdot}20P_2S_5$ (mol%) samples prepared by mechanical milling for several hours. The numbers in the figure denote the milling periods. The pattern of SnS milled for 20 h is also shown in this figure.

Tatsumisago et al. J Power Sources, 146(2005)496

$SnS + P_2S_5$ Glasses as Hosts for Active Materials

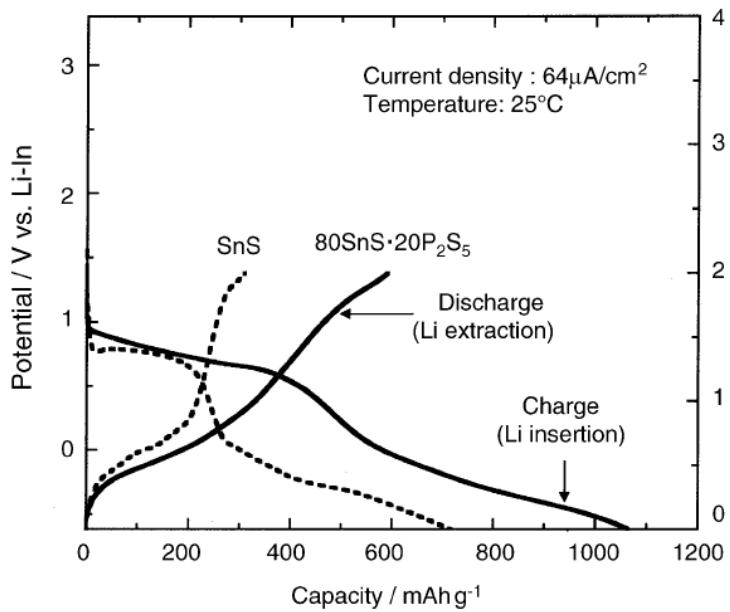


Fig. 3. Charge–discharge curves of all-solid-state cells Li–In/$80SnS \cdot 20P_2S_5$ and Li–In/SnS at the 1st cycle. The $80Li_2S \cdot 20P_2S_5$ glass-ceramic solid electrolyte with high conductivity was used in these cells. The charge–discharge measurements were carried out at a current density of 64 μA cm^{-2} at 25 °C.

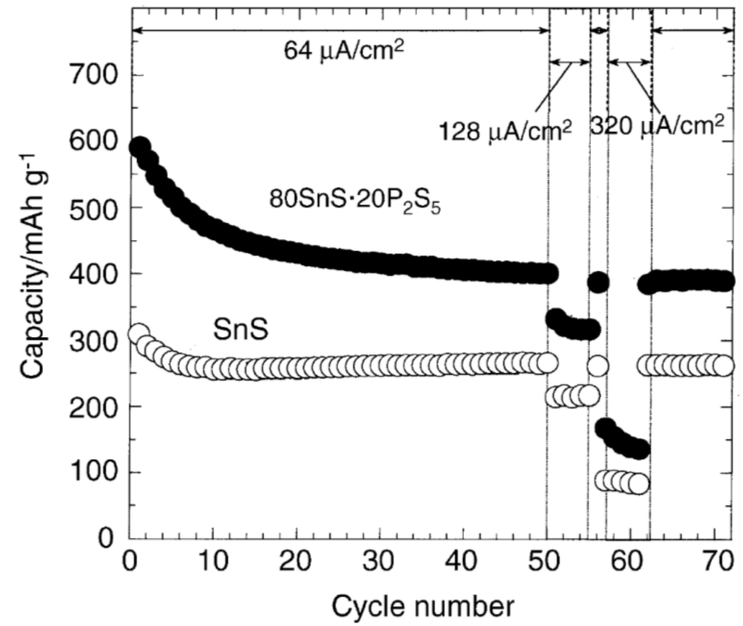
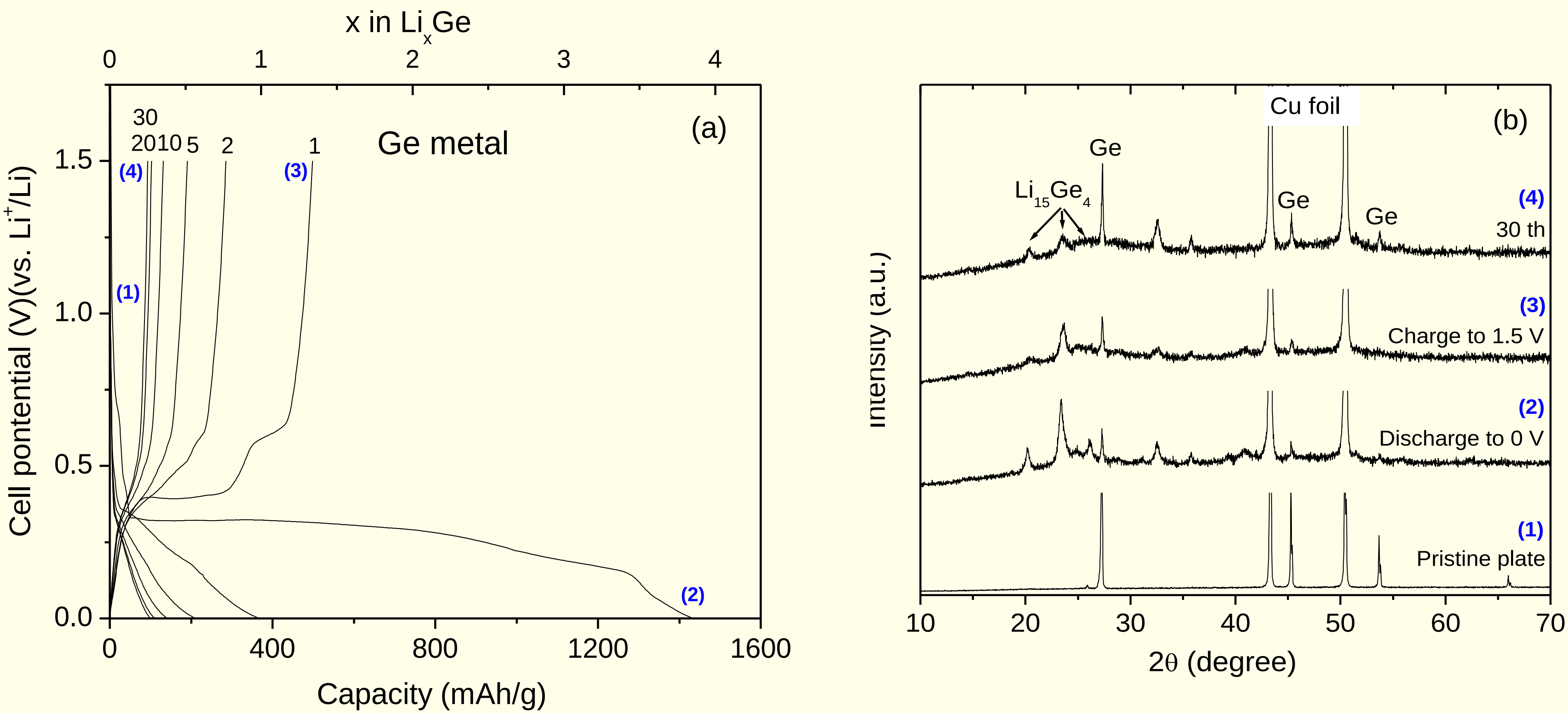


Fig. 4. Cycling performance on discharge capacity for the all-solid-state cells using the $80SnS \cdot 20P_2S_5$ and SnS electrodes.

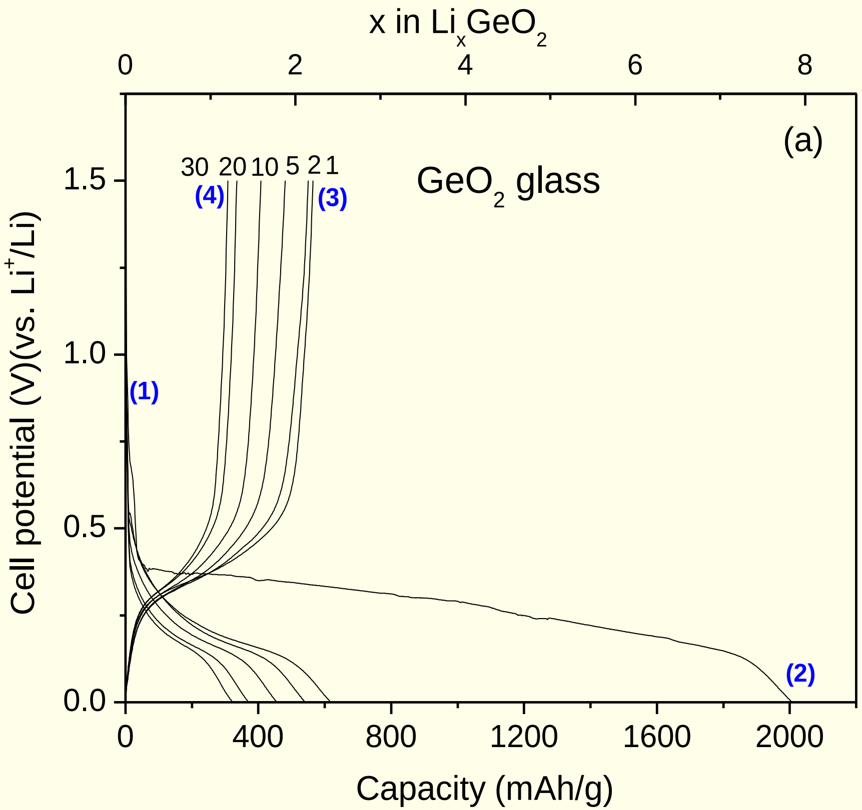
Tatsumisago et al. J Power Sources, 146(2005)496

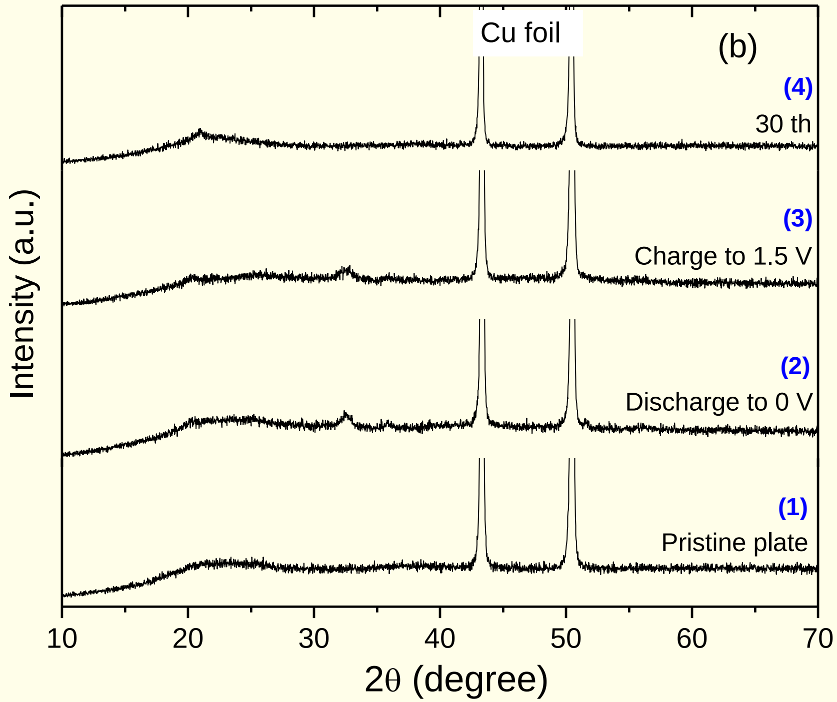
Comparative behavior of pure Ge



Kim and Martin et al. Electrochimica Acta 53(2008) 5058

Comparative behavior of GeO_2 Glass





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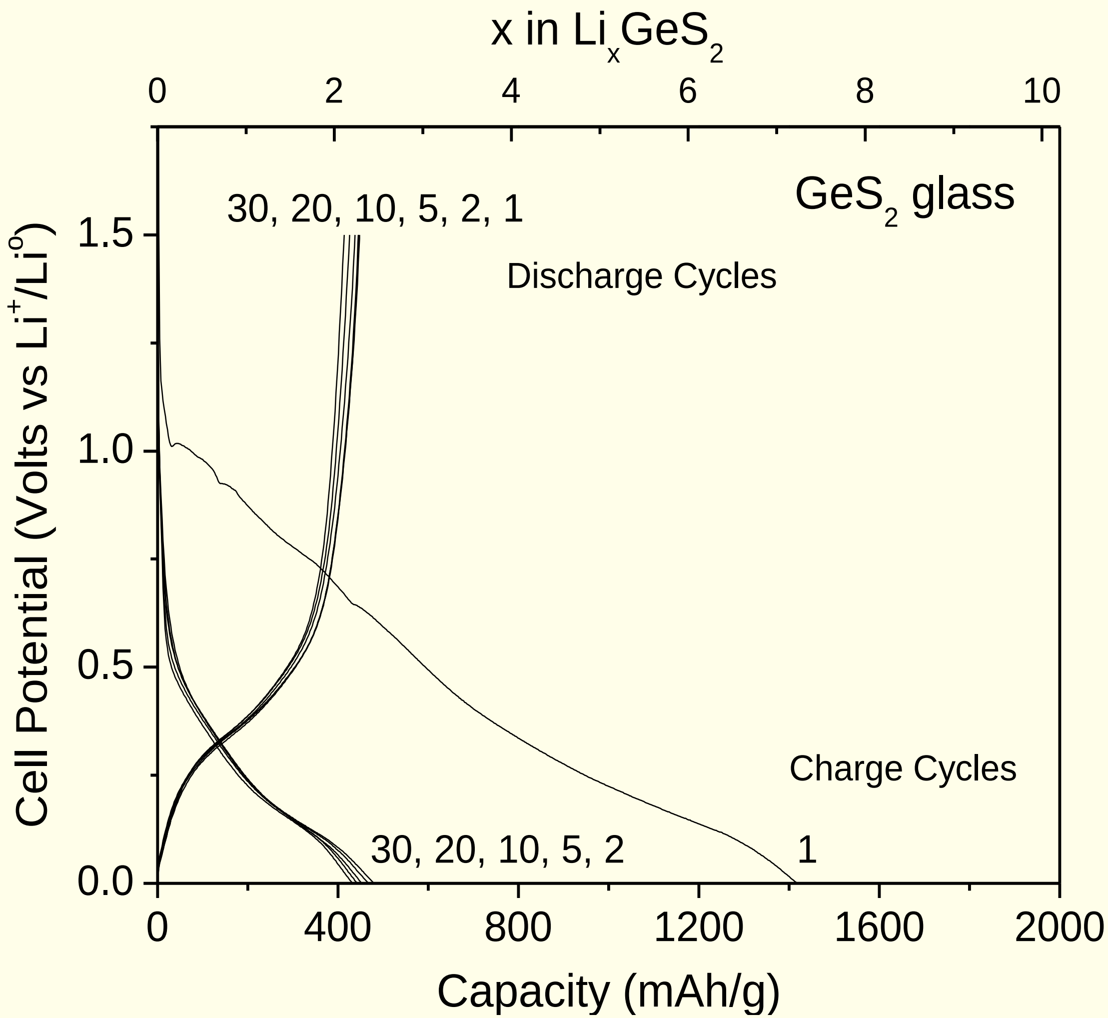
GeS_2 Glass Li anodes



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Ge-based Active Material Anodes

- GeS_2 glass based anode has best reversibility

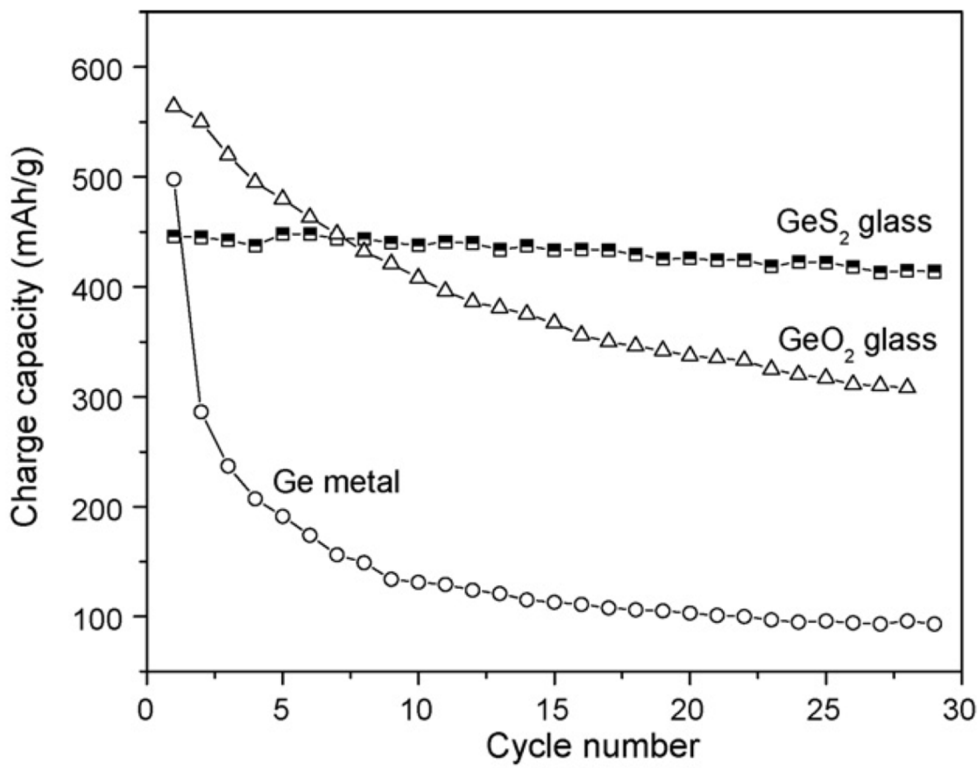

Fig. 5. Cycle-life performance of Ge metal, GeO_2 glass, and GeS_2 glass, respectively. They are operated between 1.5 and 0 V at the rate of 0.1 C.

Kim and Martin et al. Electrochimica Acta 53(2008) 5058

Mechanism of Glassy Anodes

- Reaction steps:
  1. $x/2GeS_2 + 2xLi \rightarrow xLi_2S + x/2Ge$

  2. $Ge + nLi \rightarrow Li_nGe$, $n \sim 4$

Summary and Conclusions

- Progress has been made in advancing the anode capacity of Lithium batteries
- Fast Ion Conducting Chalcogenide Glasses offer another attractive material for Lithium anodes
- Modest increases over the capacity of carbon achieved in the first chalcogenide glass explored, GeS_2
- Other glasses will be explored in the future
- Need to improve first cycle irreversibility
- Decrease formation of lithium sulfide, for example

Concluding comment…..

It's all we've got …(for now)…..let's take good care of it…