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

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Portable Energy Sources (Batteries) are Critical…
Introduction to Batteries

• Batteries are controlled electrochemical reactors
• Oxidation $Li^0 \rightarrow Li^+ + e^-$ at the anode
• Reduction $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$ at the cathode
• Overall reaction:
  
  - $2Li^0 + 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

\[
\text{Energy} = V \cdot C \quad 1J = 1\text{Volt} \cdot 1\text{Coulomb}
\]

- $Li^0 \rightarrow Li^+ + e^- \quad V^o = +3.04$ Volts
- $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad V^o = -0.54$ Volts
- $2Li^0 + 1/2O_2 + H_2O \rightarrow 2LiOH \quad \Delta V^o = +3.58 \text{ V}$

\[
\Delta G^o (T, P) = -n\mathcal{G}\Delta V^o = -2\cdot96,485 \text{ C/mole} \cdot 3.58 \text{ V} = -690,832 \text{ J/mole}
\]
### Table 15.1 Standard electrode potentials at 298 K, 1 atm (standard state is 1 molal)

<table>
<thead>
<tr>
<th>Electrode reaction</th>
<th>( \mathcal{E}^\circ, \text{volts} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid solutions</td>
<td></td>
</tr>
<tr>
<td>( \text{F}_2 + 2e^- = 2\text{F}^- )</td>
<td>2.65</td>
</tr>
<tr>
<td>( \text{S}_2\text{O}_4^{2-} + 2e^- = 2\text{SO}_4^{2-} )</td>
<td>1.98</td>
</tr>
<tr>
<td>( \text{Co}^{3+} + e^- = \text{Co}^{2+} )</td>
<td>1.82</td>
</tr>
<tr>
<td>( \text{Ce}^{4+} + e^- = \text{Ce}^{3+} )</td>
<td>1.61</td>
</tr>
<tr>
<td>( \frac{1}{2} \text{Cl}_2 + e^- = \text{Cl}^- )</td>
<td>1.3595</td>
</tr>
<tr>
<td>( \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + e^- = 2\text{Cr}^{3+} + 7\text{H}_2\text{O} )</td>
<td>1.33</td>
</tr>
<tr>
<td>( \text{MnO}_2 + 4\text{H}^+ + 2e^- = \text{Mn}^{2+} + 2\text{H}_2\text{O} )</td>
<td>1.23</td>
</tr>
<tr>
<td>( \text{Br}_2(l) + 2e^- = 2\text{Br}^- )</td>
<td>1.0652</td>
</tr>
<tr>
<td>( 2\text{Hg}^{2+} + 2e^- = \text{Hg}_2^2+ )</td>
<td>0.92</td>
</tr>
<tr>
<td>( \text{Hg}^{2+} + 2e^- = \text{Hg} )</td>
<td>0.854</td>
</tr>
<tr>
<td>( \text{Ag}^+ + e^- = \text{Ag} )</td>
<td>0.7991</td>
</tr>
<tr>
<td>( \text{Fe}^{3+} + e^- = \text{Fe}^{2+} )</td>
<td>0.771</td>
</tr>
<tr>
<td>( \text{I}_2 + 2e^- = 2\text{I}^- )</td>
<td>0.5555</td>
</tr>
<tr>
<td>( \text{Fe(CN)}_6^{3-} + e^- = \text{Fe(CN)}_6^{4-} )</td>
<td>0.36</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + 2e^- = \text{Cu} )</td>
<td>0.337</td>
</tr>
<tr>
<td>( \text{S}_2\text{O}_6^{2-} + 2e^- = 2\text{S}_2\text{O}_4^{3-} )</td>
<td>0.17</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + e^- = \text{Cu}^+ )</td>
<td>0.153</td>
</tr>
<tr>
<td>( \text{Sn}^{4+} + 2e^- = \text{Sn}^{2+} )</td>
<td>0.15</td>
</tr>
<tr>
<td>( \text{S} + 2\text{H}^+ + e^- = \text{H}_2\text{S} )</td>
<td>0.141</td>
</tr>
<tr>
<td>( 2\text{H}^+ + e^- = \text{H}_2 )</td>
<td>0.000</td>
</tr>
<tr>
<td>( \text{Mg}^{2+} + 2e^- = \text{Mg} )</td>
<td>-2.37</td>
</tr>
<tr>
<td>( \text{Na}^+ + e^- = \text{Na} )</td>
<td>-2.714</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + 2e^- = \text{Cu} )</td>
<td>-2.87</td>
</tr>
<tr>
<td>( \text{Ba}^{2+} + 2e^- = \text{Ba} )</td>
<td>-2.90</td>
</tr>
<tr>
<td>( \text{Cs}^+ + e^- = \text{Cs} )</td>
<td>-2.923</td>
</tr>
<tr>
<td>( \text{K}^+ + e^- = \text{K} )</td>
<td>-2.925</td>
</tr>
<tr>
<td>( \text{Li}^+ + e^- = \text{Li} )</td>
<td>-3.045</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Anode</th>
<th>Cathode</th>
<th>Anode</th>
<th>Cathode</th>
<th>Anode</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td></td>
<td>Li</td>
<td></td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Li_{x}M</td>
<td></td>
</tr>
</tbody>
</table>

- **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

\[
\text{Anode: } \text{Li}_1\text{C}_6 \rightarrow \text{Li}^+ + e^- + \text{C}_6
\]

\[
\text{Cathode: } \text{Li}_1\text{CoO}_2 + \text{Li}^+ + e^- \rightarrow \text{LiCoO}_2
\]
Capacity Calculations of Anode Materials

- The composition of lithiated graphite is Li$_1$C$_6$
- Recall Faraday’s constant 96,485 C/mole e$^-$
- 1 mole C$_6$ = 72 gr C/mole = 1 mole Li$^+$ = 1 mole e$^-$ transferred
  \[
  \left( \frac{96,485 \text{ C/mole Li}^+}{72 \text{ gr/mole C}_6} \right) = 1,340 \text{ C/mole C}_6
  \]
  1 mAh = 3.6 C
  C$_6$ = 372 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\textsubscript{2} a common cathode material? A.W. Co = 58.93 gr/mole
• 295 mAh/gram
• What is the capacity of Li\textsubscript{2}S? A.W. S = 32.06 gr/mole
• 1,675 mAhr/gr
• What is the capacity of Li\textsubscript{2}O?
• 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)

- $\text{Li}_x\text{C}_n \leftrightarrow x\text{Li}^+ x\text{e}^- + \text{C}_n$
- $x \sim 1, n \sim 6$
- C has high e-conductivity
- Cheap
- Plentiful
- Good voltage, near 0V
- Relatively low capacity, small x

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

Where we are…

Where we want to go…

Just for comparison…

Where we are…

Where we can go…

10 fold increase in energy density!
So… Why does the Chevy Volt only go 40 miles between charges….

• Because today’s Li batteries use Li$_1$C$_6$ as the Anode
• And the Cathode, Li$_1$CoO$_2$, is equally less energy dense
• Comparison….
• Gasoline: C$_8$H$_{18}$ + 12 ½ O$_2$ $\rightarrow$ 8CO$_2$ + 9H$_2$O + Energy
• 44,400 J/g C$_8$H$_{18}$
• 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

Lithium Dendrite Formation in Li-Ion Batteries

- Cell short circuits, leading to overheating and fires
All Solid State Lithium Batteries

- Replace flammable liquid electrolyte with highly conducting glassy solid electrolyte
No Cathode to match Li metal energy density

- Recall our Voltage – Capacity graph.

Matching Cathodes?

4,000 mAhr/gram Cathodes?

- Must change the paradigm…
- \( \text{Li}_nX_1 \ n = 1, 2, 3, 4 \ldots \) instead of \( \text{Li}_{0.5}\text{CoO}_2 = \text{Li}_1X_6 \),
- Must have \( \text{Li}^+ \) in the oxidized form, like rust, sand, rocks…
- What is the corresponding simple oxide of Li?
- \( \text{Li}_2\text{O} \) and consider…
- \( 2\text{Li} + \frac{1}{2} \text{O}_2 \rightarrow \text{Li}_2\text{O} \)
- \( \sim 3,350 \text{ mAhr/g O} \), very similar to Li
- And… you don’t have to carry the \( \text{O}_2 \) around!
- Air-breathing batteries…Lithium-Air batteries
- Note the similarity to gasoline, except no \( \text{CO}_2 \) and only \( \text{O}_2 \) 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?
  - $10 \times 365 = 3,650$?
- 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 $\rightarrow$ 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$_5$

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

<table>
<thead>
<tr>
<th>Compound and crystal structure</th>
<th>Unit cell volume ($\text{Å}^3$)</th>
<th>Volume per silicon atom ($\text{Å}^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon cubic</td>
<td>160.2</td>
<td>20.0</td>
</tr>
<tr>
<td>Li$_{12}$Si$<em>7$, (Li$</em>{1.71}$Si) orthorhombic</td>
<td>243.6</td>
<td>58.0</td>
</tr>
<tr>
<td>Li$_{14}$Si$<em>6$, (Li$</em>{1.71}$Si) rhombohedral</td>
<td>308.9</td>
<td>51.5</td>
</tr>
<tr>
<td>Li$_{13}$Si$<em>4$, (Li$</em>{3.25}$Si) orthorhombic</td>
<td>538.4</td>
<td>67.3</td>
</tr>
<tr>
<td>Li$_{22}$Si$<em>5$, (Li$</em>{4.4}$Si) cubic</td>
<td>659.2</td>
<td>82.4</td>
</tr>
</tbody>
</table>

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

![Graph showing 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 LiPF₆ in ethylene carbonate (EC)–diethyl carbonate (DEC) (1:1) [22].]

1 mAhr/g = 1 Ahr/kg

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, \(10^{-3} \ (\Omega \text{cm})^{-1}\) at 25\(^\circ\)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
  - $\text{Li}_2\text{O} + \text{P}_2\text{O}_5$ has $\sigma_{RT} \sim 10^{-9}$ (Ωcm)$^{-1}$
  - $\text{Li}_2\text{S} + \text{P}_2\text{S}_5$ has $\sigma_{RT} \sim 10^{-3}$ (Ωcm)$^{-1}$
  - 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
- \( \text{SnO(P}_2\text{O}_5) + (x+2)\text{Li} \rightarrow \text{Li}_x\text{Sn} + \text{Li}_2\text{O} \)

Fig. 4. First charge-discharge curves for the cells using the \( x\text{SnO} \cdot (100 - x)\text{P}_2\text{O}_5 \), \( 30 \leq \text{SnO (mol\%)} \leq 70 \), glasses as a working electrode. A constant current density of \( 1.0 \text{ mA cm}^{-2} \) was used. A mixture of \( 1 \text{ M LiPF}_6/\text{EC + DEC} \) 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·33P2O5 (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·50B2O3 (mol%) and 67SnO·33BPO4 (mol%) glasses [7] is also shown for comparison.
Inorganic Glasses as Hosts for Active Materials

- SnS + P$_2$S$_5$ Glasses
- Two step insertion process
  - SnS(P$_2$S$_5$) + (x+2)Li $\rightarrow$ Li$_x$Sn + Li$_2$S
- Mechano-chemical milling to produce amorphous materials
  - Cheap, easy direct method to produce high surface area powders

Fig. 1. XRD patterns of the 80SnS-20P$_2$S$_5$ (mol%) samples prepared by mechanical milling for several hours. The numbers in the figure denote the milling periods. The pattern of SnS milled for 20h is also shown in this figure.

Tatsumisago et al. J Power Sources, 146(2005)496
SnS + P$_2$S$_5$ Glasses as Hosts for Active Materials

Fig. 3. Charge–discharge curves of all-solid-state cells Li–In/80SnS–20P$_2$S$_5$ and Li–In/SnS at the 1st cycle. The 80Li$_2$S–20P$_2$S$_5$ 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–20P$_2$S$_5$ and SnS electrodes.
Comparative behavior of pure Ge

Cell potential (V) (vs. Li⁺/Li)
Capacity (mAh/g)

Intensity (a.u.)

Comparative behavior of GeO$_2$ Glass

![Graph of capacity vs. potential](image)

GeS$_2$ Glass Li anodes

Cell Potential (Volts vs Li$^+/\text{Li}$)

Capacity (mAh/g)

Discharge Cycles

Charge Cycles

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.

Mechanism of Glassy Anodes

• Reaction steps:
  1. $\frac{x}{2} \text{GeS}_2 + 2x\text{Li} \rightarrow x\text{Li}_2\text{S} + \frac{x}{2}\text{Ge}$
  2. $\text{Ge} + n\text{Li} \rightarrow \text{Li}_n\text{Ge}, n \sim 4$
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...