Lithium Rechargeable Solid Electrolyte Battery Market 2017

Ver. 1

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The Need to Renew Lithium Rechargeable Battery Technology

- Present Li-ion technology (150-272 Wh/kg, 400-775 Wh/l – (4.45v cells in mass production) - not satisfy the power needed by E-Mobility and other applications.

- Improvement in Energy Density, cost reduction, safety enhancement, higher charging/discharging rates and cycle life required!!!
The Potential Technologies for Energy Storage Break Through

- Lithium Sulfur
- Lithium Metal
- Li-Ion with Silicon Nano-structure anode
- High voltage lithium rechargeable (4.35-5v)
- Lithium Air
- Solid Electrolyte batteries
What are Solid Electrolyte Cells?

- Lithium rechargeable using a dry polymer/ceramics electrolyte in a solid state cell in which a dry polymer electrolyte is sandwiched between a lithium metal film and a metal film.

- By dissolving lithium, not into a liquid electrolyte but into a really thin dry polymer (plastic), a high-power battery is realized that is light, and yet durable.
What are the difference versus Li-Polymer Cells

- Gel polymer electrolyte – still flammable, poor mechanical property – reasonable conductivity \((10^3 \text{ S/cm @ RT})\)

- Include small sort of liquid/humidity – Not totally dry!!

- Some pouch “Li-Po” cells also include liquid electrolyte – Not even gel.

1998 – Sony first commercial Li-Po cells
Solid Electrolyte Cells

- The laminate construction of such cells offer flexibility of shape and size, which is advantageous for portable power source applications.

- However, at the present time, the conductivity of these batteries is very low at room temperature, compared with those of liquid electrolytes: these batteries are normally operated in the 60-120°C range.

1. The solid-polymer, Li-ion battery—with its excellent combination of safe operation, more flexible packaging, and high performance—is the next step in the evolution of mobile power.

Current Packaging
Solid Electrolyte Types?

- Dry polymer electrolyte – Low ionic conductivity ($10^5$-$10^4$ S/cm @ RT)
- Inorganic or ceramic solid electrolyte
Solid Electrolyte Batteries
Advantages

- Higher energy density than Li-ion
- Safety – no flammable electrolyte (Ceramic, Dry Polymer)
- No electrolyte leakages
- Can fit any casing shape (soft packaging)
- Cells can be made as thin as 0.1 mm or about one-tenth the thickness of the thinnest prismatic liquid Li-ion cells
- Low potentially manufacturing cost
- Excellent cycling stability
- Excellent shelf life
Solid Electrolyte Batteries
Limitations

- Power limited by electrolyte low ionic conductivity
- High temperature working operating temperatures
- High interfacial resistance
- As with other Li-ion batteries, require individual cell monitoring
- Costly manufacturing process when using vapor deposition process

More research is needed!!!
Solid Electrolyte Batteries
Development Status?

- Research is being aimed at increasing conductivity through the use of plasticizers and new polymers.

- The development of "Polymer-In-Salt" materials, in which super ionic glass electrolytes are mixed with small quantities of the polymers, has been suggested.

- Dissolution of the polymer into these melt-glass-electrolytes produces a rubbery version of a glassy electrolyte with a thousand-fold increase in lithium ion mobility.
Solid State Batteries for Implants

Solid state enables new applications

1. Open Circuit Voltage: 2.8 Volt
2. Control Circuit minimal voltage: 2.2 Volt
3. Control Circuit current drain: 10 \( \mu \text{A} \)
4. EOL battery resistance: 10 \( \text{k Ohms} \)
5. \( C_{\text{hold}} \): 10 \( \mu \text{F} \)
6. Oscillator frequency: 167 Hz
7. Duty Cycle; 16.7 %
8. Ah rating: 2 Ah (typical rating)
9. Reliability: 99.6% probability of survival beyond 8 years
10. Failure Rate: 0.005 % failures/month

Lithium iodine battery for cardiac pacemaker
Apple Invents Charging Techniques for Solid State Batteries

Apple's invention provides a system that manages use of a solid-state battery in portable electronic devices. During operation, the system monitors a temperature of the solid-state battery during use of the solid-state battery with the portable electronic device. Next, the system modifies a charging technique for the solid-state battery based on the monitored temperature to increase a capacity or a cycle life of the solid-state battery. To modify the charging technique based on the monitored temperature, the system may increase a charge rate of the solid-state battery if the temperature exceeds a first temperature threshold (e.g., 25. degree. Celsius). On the other hand, the system may maintain the charge rate of the solid-state battery if the temperature does not exceed the first temperature threshold. In some embodiments, the system further increases the charge rate of the solid-state battery if the temperature exceeds a second temperature threshold such as 45. degree. Celsius. In some embodiments, increasing the charge rate of the solid-state battery involves at least one of increasing a charge current of the solid-state battery, and increasing a charge voltage of the solid-state battery. Apple states that the new solid state batteries will apply to such devices as the iPhone, iPad, iPod, MacBooks and more. This would be ideal for bendable and/or wearable computers.
The LMP Battery

- Based on extruded films
  - All solid design
  - No liquid electrolyte
- High discharge power
- Environment friendly:
  - No solvent
  - Highly recycle or reuse
- Operating temperatures -20 to 60 C
  - Internal temperature 60-80 C
Samsung SDI Flexible Solid Electrolyte Pouch Cells

- Presented at Interbatt Korea, Seoul 10/2013
- Higher energy Density than Li-Po
- Safer – No leaks – No flammable electrolyte
- Expected commercially on 2015
Samsung SDI Flexible Solid Electrolyte Pouch Cells
Cymbet EnerChip™ thin film rechargeable solid-state smart batteries (SSB)

Packaged as a Surface Mount Technology (SMT) component, the EnerChip provides energy storage in a convenient form factor.

Cymbet's EnerChip SSBs are well suited for applications where battery backup power is needed to maintain the settings of microcontroller memories, real-time-clocks and SRAM during power loss or power failures.
Infinite Power Solutions

Thin Film Batteries, Supercaps and Coin Cells

TFB = Best of Both
- High Drive Current
- High Energy Density
  - 50 X SuperCap
- Lowest Leakage
  - 4,000 X < SuperCap
- Rechargeable/Long Life
- Superior Lifetime Energy
By using ionic liquids and thin films -- two cutting edge materials technologies, SolidEnergy reduces the limitations of lithium-polymer cells. [Image Source: MIT]
ATL – Solid State Batteries

ATL Solid State Battery—High Capacity

ATL’s solid-state battery can be cycled normally after being cut.

Solid state battery can “self-healed” after repeated nail tests.

- **Nail Test**

Cell with liquid electrolyte after hot-box test.

- **Hot Box Test**

Solid-state cell after hot-box test.
Solid polymer electrolyte battery introduction

Merits
- High ED
- High security

Demerits
- Narrow electrochemical window
- Low ionic conductivity

Voltage (V)
- PEO
- LFP
- NCA
- LCO

Ionic conductivity (S/cm)

Obvious oxidation above 4V

Roll-to-roll manufacturing

Flexibility

A: Cathode; B: Over-coated cathode; A': Anode; B': Over-coated anode; C: Cell sheet; D: UV system; E: Electrolyte coater

http://www.cnkoslight.com/
Coslight work on polymer solid-state battery

LFP/SPE/Li pouch sample cell

- Design capacity: 480 mAh
- Predicted life: 80%@500 cycles
- Nail test: No fire, no explosion

Cycling testing at 60 °C, 0.5C/0.5C

- Capacity ratio
- Coulombic Efficiency

Nail test

Solid battery

Liquid LIB
Strategies to improve the performance

- Cathode coating
- Passive film on lithium
- Add frame substrate in SPE
- Thinner Lithium
- Thinner SPE layer
- Thicker cathode electrode
- New polymer electrolyte

Improvement

- Lower interface impedance
- Lithium dendrite inhibition
- Higher mechanical strength
- Higher energy density
- Wider electrochemical window

Cu foil
Lithium + Passive film
SPE + Frame substrate
NCM+SPE
Al foil
The Panasonic Solid Solution technology combines two major battery properties: capacity and safety. This technology provides the customer with a high capacity such as the standard Panasonic Lithium-Ion (Cobalt based) cells and also owns a high safety standard like the LiMn$_2$O$_4$ (Manganese based) Lithium-Ion batteries.*1

**Characteristics of the Panasonic PSS featured Lithium-Ion battery:**
- Thermal stability of cathode materials leads to high safety
- Same energy density as cobalt based Lithium-Ion batteries
- Excellent cycle life
- Less voltage drop at initial discharge than other Lithium-Ion batteries

**COMPARISON BETWEEN CAPACITY AND SAFETY OF CATHODE MATERIALS**
Prologium

PLG Power Solutions

**Wearable**

- **PLG Solutions**
  - Vest
    - (1). 200Wh
    - (2). 100Wh
    - (3). 50Wh
  - Power Helmet
    - (4). 50Wh
  - Power Belt
    - (5). 7.5Wh

- **Applications**
  - Manpack radio
  - Portable energy system
  - Handheld radio
  - GPS
  - Thermal weapon sight
  - Emergency GPS Belt

- **SAFT**
  - BA684A
    - 08232S, 51Wh
  - BB2800
    - 08034L, 40Wh
  - PES
    - 08258U, 102Wh
  - BB2590
    - 06611S, 51Wh
  - BB2847
    - 06611S, 51Wh
Looking to gather momentum in the electric vehicle field, Toyota’s focus is also on batteries. The Japanese giant has recently unveiled a solid-state LiCoO2 (lithium cobalt oxide) battery that features higher energy density and bears temperatures of up to 100 degrees Celsius. The new cell is made from 4 x 3.6V units, totaling a 14.4 V.

Solid state batteries have the advantage of being able to be used far above the temperatures an organic electrolyte battery would be. When an all-solid-state battery is in an ideal state, the lithium spreads faster than electrolyte, and thus obtains higher power output.
### Some Solid State Battery Developers/Manufacturers

<table>
<thead>
<tr>
<th>Company Name</th>
<th>Battery Type</th>
<th>Cathode</th>
<th>Anode</th>
<th>Electrolyte</th>
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<td>Bathium</td>
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<td>LFP</td>
<td>Lithium Metal</td>
<td>Polymer</td>
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<td>Canada</td>
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<td>Cymbet</td>
<td>Thin Film Solid State</td>
<td>LCO</td>
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<td>Ceramic (LiPON)</td>
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<td>Ceramic (Not LiPON)</td>
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<tr>
<td>Front Edge</td>
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<td>Ceramic (LiPON)</td>
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<tr>
<td>SolidEnergy</td>
<td>Solid State</td>
<td>LCO, NCA</td>
<td>Lithium</td>
<td>Polymer and ionic liquid</td>
<td><a href="http://solidenergysystems.com">http://solidenergysystems.com</a></td>
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<tr>
<td>Toyota</td>
<td>Solid State</td>
<td>LCO</td>
<td>Indium metal</td>
<td>Ceramic (Li10GeP2S12)</td>
<td></td>
<td>Japan</td>
</tr>
</tbody>
</table>

In total we know 21 Developer/Manufacturers and ~ 20 Universities/Institutes working on Solid Electrolyte Technologies!!!
Market Forecast & Trends

• Solid Electrolyte Batteries may provide the break through we are waiting for – farther development needed.

• Technology Status - Still under development – few companies to reach prototype manufacturing level.

• Power capacities are essential for that technology success

• Mass worldwide research efforts will lead to some progress on the coming years that will allow technology commercialization within 10 years time frame.
Information for presentation obtained by:
1. Public web sources.
2. Shmuel De-Leon Battery/Energy Sources DataBase ® (Includes 29000 cell PDF data sheets)  http://www.sdle.co.il/Default.asp?sType=0&Pageld=45580