High Energy Rechargeable Li-S Battery Development at Sion Power and BASF


*Sion Power Corporation, **BASF SE
Outline

- Fundamentals of Li-S electrochemical system.
- Current status of 350 Wh/kg Sion Power cells and their high power and extreme low temperature variations.
- Sion Power and BASF approach for next generation of Li-S technology.
Fundamentals of Li-S electrochemical system
Theoretical Energy Density Comparison

\[ S + 2\text{Li} = \text{Li}_2\text{S} \quad \Delta G \sim -425 \text{ kJ/mol} \]

- OCV \sim 2.2 \text{ V}
- Energy density \sim 2800 \text{ Wh/L}
- Specific Energy \sim 2500 \text{ Wh/kg}

Compare Specific Energy with:
- Li-ion \sim 580 \text{ Wh/kg}
- TNT equivalent \sim 1280 \text{ Wh/kg}
Fundamentals of Li-S electrochemical system

Discharge mechanism

Typical Li-S cell discharge profile at room temperature and rates C/10 - C/2

1. Slightly soluble elemental sulfur reduction to soluble Li$_2$S$_8$

\[ S_8 + e^- + Li^+ \rightarrow Li_2S_8 \]

2. Soluble Li$_2$S$_8$ reduction to soluble Li$_2$S$_4$

\[ Li_2S_8 + e^- + Li^+ \rightarrow Li_2S_4 \]

3. Soluble Li$_2$S$_4$ reduction to solid Li$_2$S and partially Li$_2$S$_2$

\[ Li_2S_4 + e^- + Li^+ \rightarrow Li_2S + Li_2S_2 \]

4. High polarization due to exhaustion of soluble Li$_2$S$_4$ and porosity blocking by solid Li$_2$S

Up to 1500 mAh/g capacity can be gained at rates below C/50
Fundamentals of Li-S electrochemical system

Discharge mechanism

Discharge profilers at low rate and temperatures below –40°C showed multi-step sulfur reduction.

Differential discharge capacity at -50 °C suggests existence of up to 6 intermediate sulfur reduction species.
Fundamentals of Li-S electrochemical system
Polysulfide shuttle mechanism

- Soluble Li$_2$S$_x$ species on the Upper Plateau diffuse to the anode where they are reduced to lower polysulfides.

- This results in Rapid Self-Discharge and loss of the Upper Plateau capacity, ~400 mAh/gS.
NO$_x$ compounds chemically protect Li anode, suppress the shuttle, restore Li-S cell capacity and allow charge control at 99.8% efficiency.

Sion’s shuttle inhibitors permit near 100% utilization of the high voltage plateau sulfur and up to 75% of total sulfur utilization at C/10 - C/5 rates.
Chemical protection of Li from polysulfide shuttle

Cells without protection from shuttle showed significant overcharge and heat generation while charged at upper plateau. Soluble polysulfides were not converted into elemental sulfur.

Cells protected from shuttle can be charged completely and demonstrated endothermic effects at upper plateau when soluble polysulfides were converted into elemental sulfur.
Current status of 350 Wh/kg Sion Power cells with chemically protected Li anode

- Wound Prismatic
- 37mm x 55mm x 11mm
- 17 grams
- 350 Wh/kg
- 320 Wh/l
- -20°C to +45°C operating temp.
- 30 to 60 cycles @ 100% DOD
- 25 mΩ impedance
First Commercial Li-S Application is Unmanned Aerial Vehicles - UAVs

QinetiQ's Zephyr 7 UAV Captures World Record for Longest Duration Flight (unmanned or otherwise).

- Flew to >70,000 ft where temperature is < -60°C.
- Used solar power to fly & recharge batteries by day.
- Flight was powered by Sion Li-S batteries at night.
- New World Record: >14 days of continuous flight.

July, 2010
Current status of 350 Wh/kg Sion Power cells
Low Temperature Modification

Batteries with modified electrolyte delivered:
1) ~160 Wh/kg at -60°C at 1C,
2) ~130 Wh/kg at -70°C at 1C,
3) The battery can be recharged at -60°C.

Work was partially supported by NASA Glenn Research Center.
Contract NNC06CA85C
Current status of 350 Wh/kg Sion Power cells
Cell design and active materials balance modification

![Graph of Specific Energy vs Cycle]

- Standard Cells: 2.8 Ah, 16 g
- Experimental Cells: 4.8 Ah, 27 g

Optimizing active and cell construction materials balance allows prolonged cycle life at high specific energy.

Work was partially supported by NASA Johnson Space Center.
Contract NNJ10JA74P
Current status of 350 Wh/kg Sion Power cells
Cell design modification for high power

Optimized cell designs were able to deliver specific power up to 2000 W/kg at continuous discharge (currents up to 15 A) and over 3000 W/kg for 10 s duration high current pulses for wide range of cell Depth of Discharge (DoD).
Current status of 350 Wh/kg Sion Power cells

Ragone plot, comparing specific energy to specific power of Li-S to conventional battery chemistries.

- Continuous discharge up to 2 kW/kg.
- 30 A pulses up to 3.3 kW/kg.
- ASR = 10-26 Ω•cm² (Cell area specific resistance)
Addressing Remaining Challenges
Keys to the EV Market for Lithium-Sulfur

- Cycle life of Li-S cells with chemically protected Li anode is limited to ~ 100 cycles for 350 Wh/kg and higher specific energies designs.
- Elevated temperature stability/safety is limited to ~ 150 °C

Causes of the problems:
- Development of rough lithium morphology affecting cycle life and safety.
- Lithium/Electrolyte depletion affecting cycle life and capacity through cathode clogging.
- Lithium reaction with sulfur and polysulfides affecting thermal stability/safety.
Lithium/Electrolyte depletion

Specific Energy-Cycle Life relationship for Sion Power experimental cells

With excessive amounts of electrolyte and lithium cycle life can exceed 500 cycles at 150 Wh/kg.

Reduced amounts of electrolyte and Li lead to 500 Wh/kg at the expense of cycle life.

The key for success is stopping electrolyte and Li depletion.
Identified depletion products and their impact on battery performance.

1,2-Dimethoxyethane

- **High amount, highly soluble and highly detrimental for S cathode performance.**
- **Moderate amount, low solubility, neutral.**
- **Small amount, soluble, consumes S.**
- **Traces.**

Identified at Sion Power

1,3-Dioxolane

- **Highly soluble and highly detrimental for S cathode performance.**
- **Increases anode polarization**
- **Traces**

Sion Power approach for next generation Li-S technology

- Suppressing rough Li morphology development through externally applied uniaxial pressure
- Physical protection of lithium with multi-functional membrane assemblies:
  - Multi-layer solid electrolyte ceramic/polymer coating
  - Gel electrolyte
  - Dual-phase electrolyte
- Optimize cathode structure and porosity to limit pore blocking and increase sulfur specific capacity
Suppressing rough Li morphology development through externally applied uniaxial pressure

Proprietary design with applied uniaxial pressure allowed for increased charging rate without developing in Li anode surface roughness.
Sion Power BASF approach for next generation Li-S technology

Physically Protected Li Anode

Work is partially supported by USA Department of Energy. Contract DE-AR0000067

IBA2013, Barcelona, March11-15
Sion Power approach for next generation Li-S technology

“Anode” Liquid 1:
- Immobilized within polymeric gel applied to anode.
- Stable with lithium preventing side reactions and dendrite growth.
- Immiscible with Phase 2 electrolyte and does not dissolve polysulfides.
- Polymeric gel can serve as coated separator.

“Cathode” Liquid 2:
- Tailored to improve high energy Sion Power sulfur cathode performance.
- Immiscible with Phase 1 electrolyte.
- High ion conductivity and lithium polysulfide solubility.

Dual Phase Electrolyte Li-S Battery

<table>
<thead>
<tr>
<th>Li Anode</th>
<th>Li°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel-Polymer</td>
<td>Li⁺</td>
</tr>
<tr>
<td>No Li₂Sₓ Solubility with Liquid 1</td>
<td>Li⁺</td>
</tr>
<tr>
<td>Porous Carbon-Sulfur Cathode with Liquid 2</td>
<td>Li⁺</td>
</tr>
</tbody>
</table>

Charge Discharge

S₈ Li₂S₈ Li₂S₆ Li₂S₄ Li₂S₃ Li₂S₂ Li₂S

Work is partially supported by USA Department of Energy. Contract DE-EE0001997
Safety Improved by Sion-BASF Gel Layer including Dual-Phase Electrolyte and Cycling Under Pressure

Fully charged experimental Li-S cells ramped at 5 °C/min after 10 cycles

There was no thermal runaway for cells surpassing the melting point of metallic lithium. Molten lithium and molten sulfur were kept apart, and Li protected cells experienced only about 3-8 °C temperature rise above ambient.
Progress on cathode structure

Improved pore structure provides cathode functioning under pressure without pores clogging and with increased sulfur utilization.

This development paves the way to increasing specific energy from the current 350 Wh/kg to the 550 Wh/kg needed to achieve a 500 km EV range.
Next Generation Li-S Technology

- Sion Power is moving to the next generation with **new anode and cathode materials** to enable a quantum leap in performance.

- Sion’s breakthrough **anode protection technology** will enable higher energy densities and safety than previously possible.
  - Already demonstrated techniques in the laboratory that extend cycle life while inhibiting thermal runaway in Li-S cells.

- Manufacturing technology utilizes standard methods for cell and battery assembly.

- Volume cost for Sion’s Li-S battery is expected to meet or beat long term cost targets for EV commercialization.
January 12, 2012 – BASF announced that it has invested $50 million to acquire an equity ownership position in privately held Sion Power, the global leader in the development of lithium-sulfur (Li-S) batteries, based in Tucson, Arizona.

This equity partnership expands upon an existing joint development agreement that BASF Future Business GmbH established with Sion Power in 2009 to accelerate the commercialization of Sion’s proprietary Li-S battery technology for electric and plug-in electric vehicles and other high-energy applications over the next decade.
Sion Power Corporation, in collaboration with BASF, is very optimistic that the future of all EV applications will be dominated by Sion Power’s lithium-sulfur technology.