Symposium on Scalable Energy Storage Beyond Li-Ion: Materials Perspectives

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Developing Li-S Chemistry for High Energy Rechargeable Batteries

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SION POWER

The Rechargeable Battery Company™

Outline of Presentation

- **Li-S Basics and Current Status**
  - Why Develop Li-S?
  - The Li-S Discharge Characteristic.
  - The Polysulfid Shuttle.
  - Li-S Capacity Limitations and Primary Failure Mechanisms.
    - Cell Capacity is Primarily a Function of the Cathode.
    - Cycle Life is Primarily a Function of the Anode.
  - Commercial Status of Li-S.
- **Anode Protection Strategies**
  - Releasable Substrate/Carrier Substrate.
  - Anode Current Collector Externally.
  - Multi-Layer Anode Stabilization Laminates (ASL).
  - Gel Separator.
  - Dual Phase Electrolyte.
  - Applied Uniaxial Pressure.
- **Future Li-S EV Cell Design and Projected 2013 Performance**

Why Choose Lithium and Sulfur?

For high specific energy and volumetric energy density.

$$S_8 + 16e^- + 16Li^+ \rightarrow 8Li_2S$$

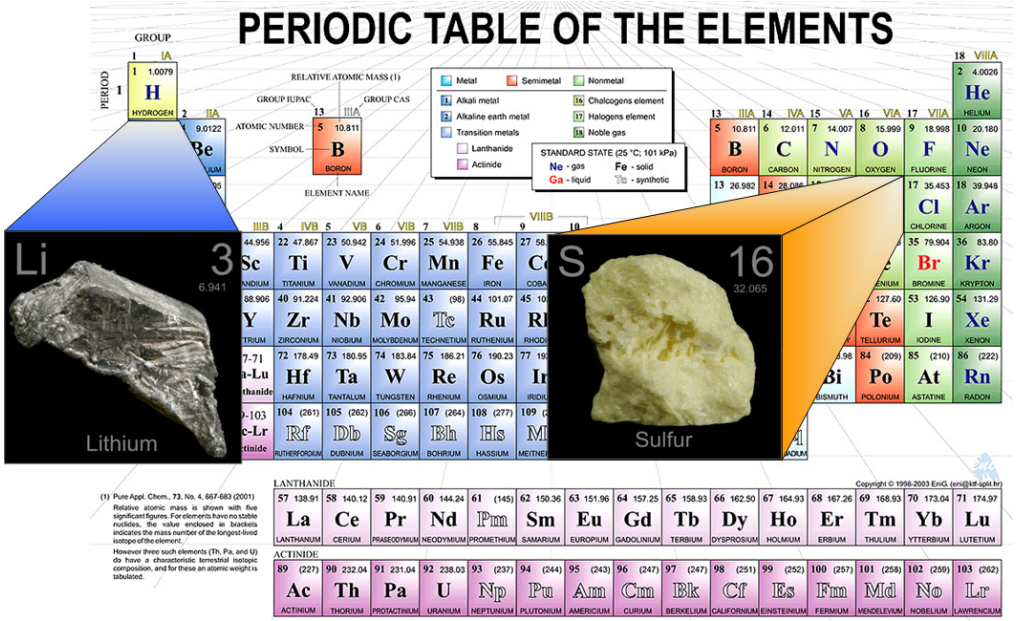
$$\Delta G \sim -422 \text{ kJ/mol}$$

The Li-S couple has the highest *theoretical* specific energy and energy density of any pair of solid elements.

Li-S:	**<OCV> ~2.18 V**
Theoretical	**~2,835 Wh/L**
Theoretical	**~2,572 Wh/kg**

Compare With Li-ion Theoreticals:

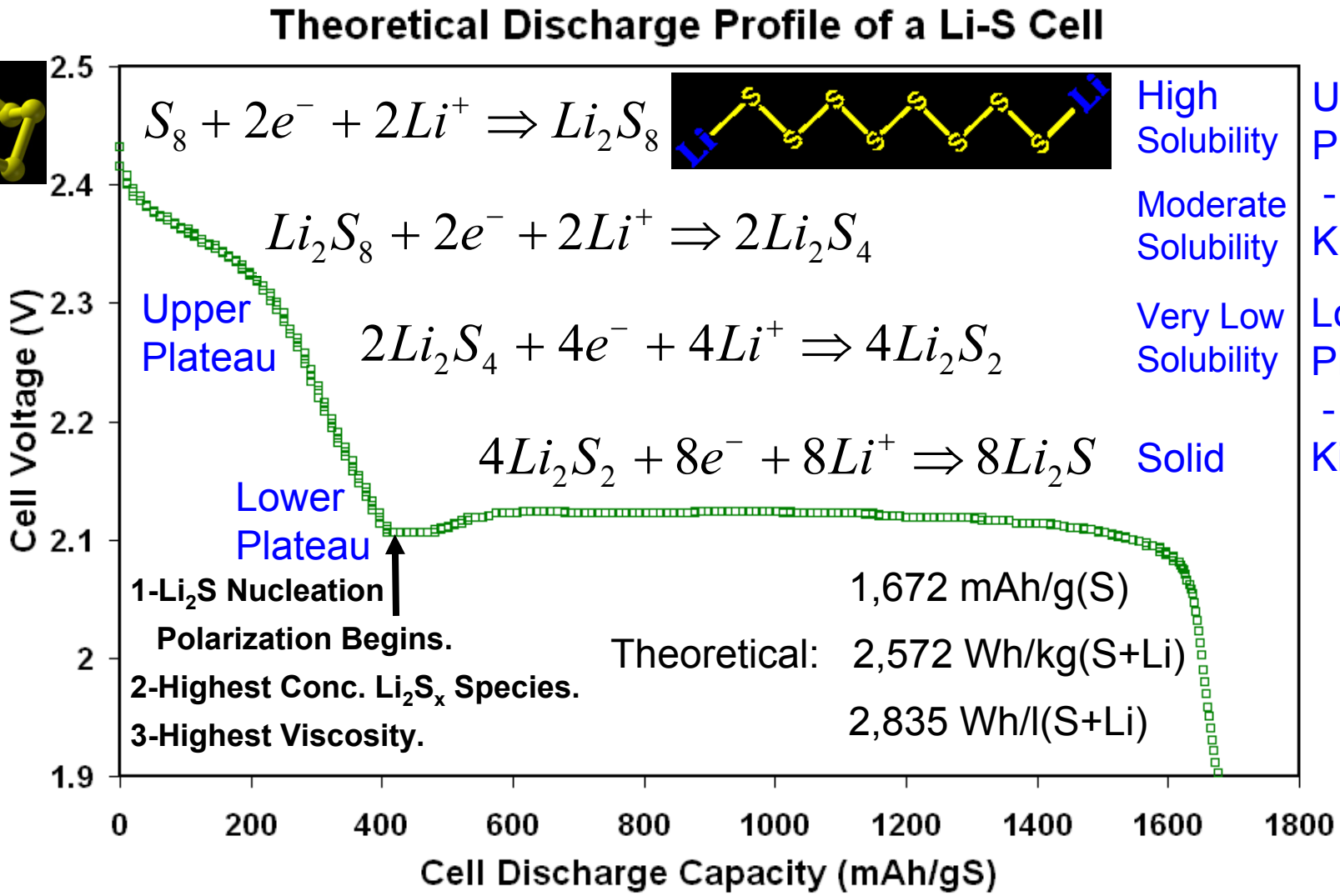
~600 Wh/kg; ~1,800 Wh/l



Current Li-ion chemistries at, or near, practical limit of ~40% of theoretical specific energy.

At 350 Wh/kg, Sion's baseline Li-S cell is only at 14% of theoretical specific energy.

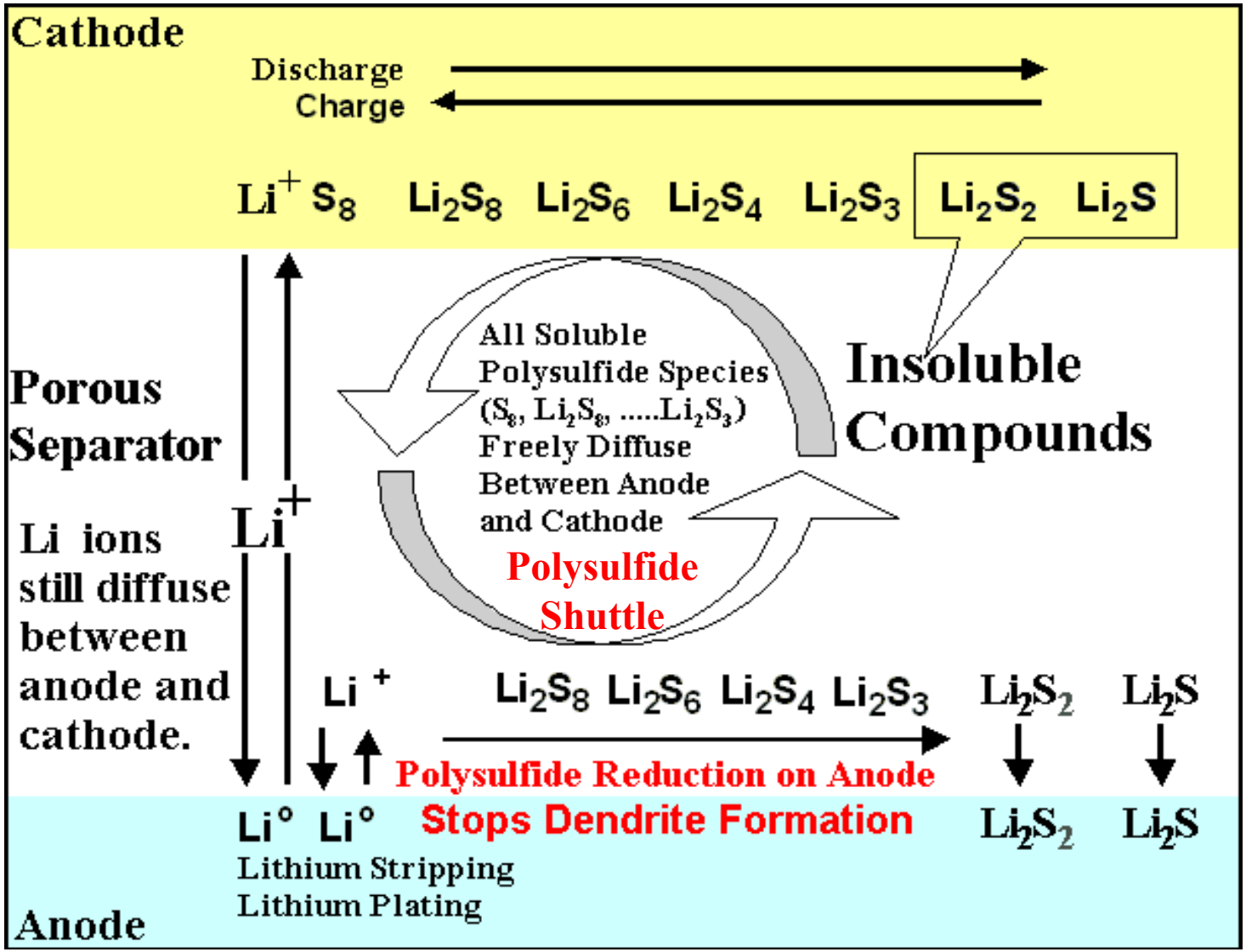
Li-S Discharge Characteristics Tell Much, but not all of the Story



- The Li-S discharge curve looks great.
- But…..What are the real world problems?

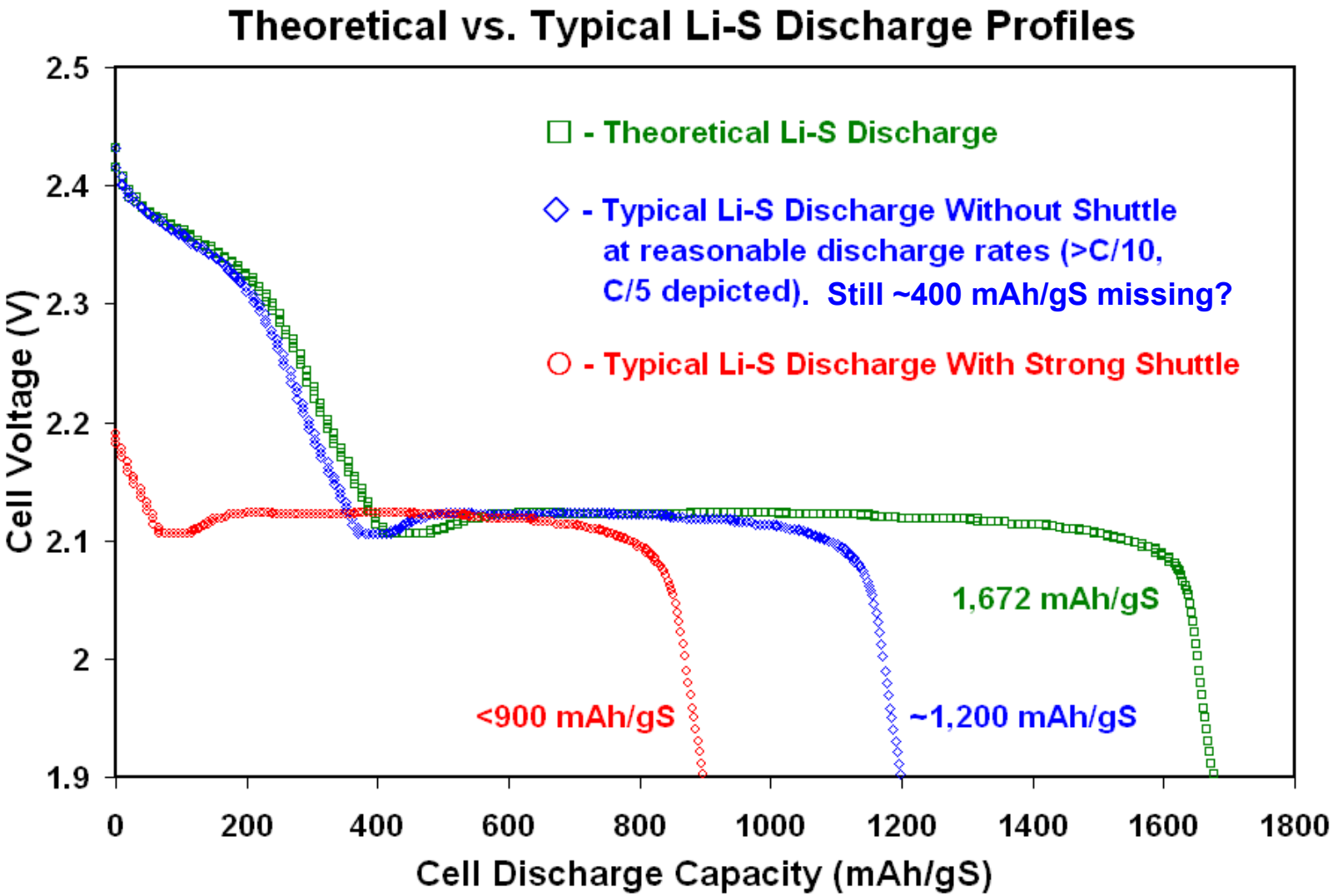
- The high solubility and fast kinetics of the Upper Plateau species leads to the Polysulfide Shuttle that results in loss of ~400 mAh/gS from the Upper Plateau.

The Polysulfide Shuttle Causes Massive Self-Discharge of Li-S Cells



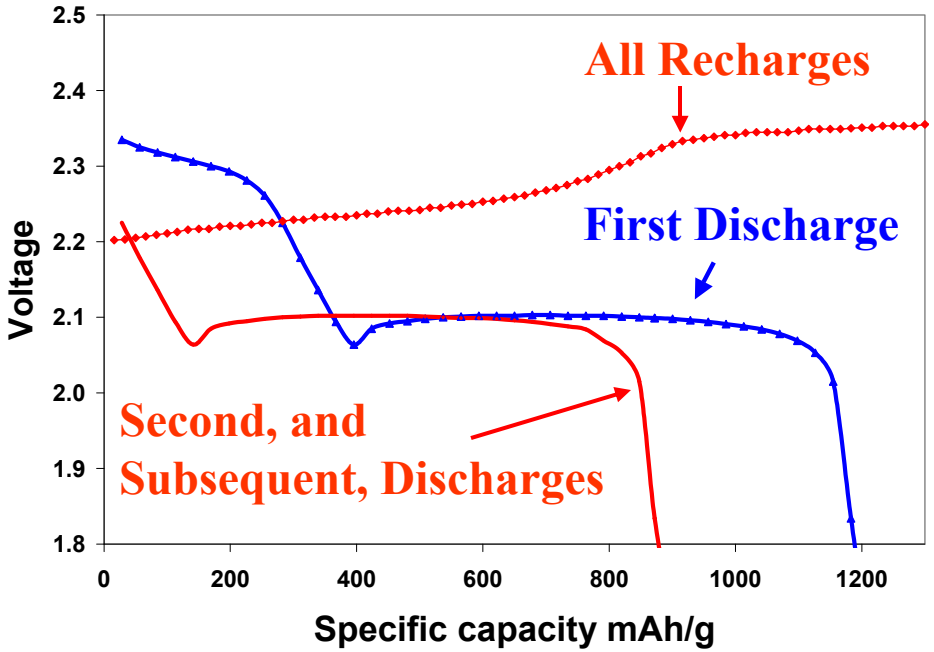
- Soluble Li_2S_x species on the Upper Plateau diffuse to the anode where they are reduced to Li_2S.
- This results in Rapid Self-Discharge and loss of the Upper Plateau capacity, ~400 mAh/gS.

The Polysulfide Shuttle Causes Loss of ¼ of Li-S Cell Discharge Capacity

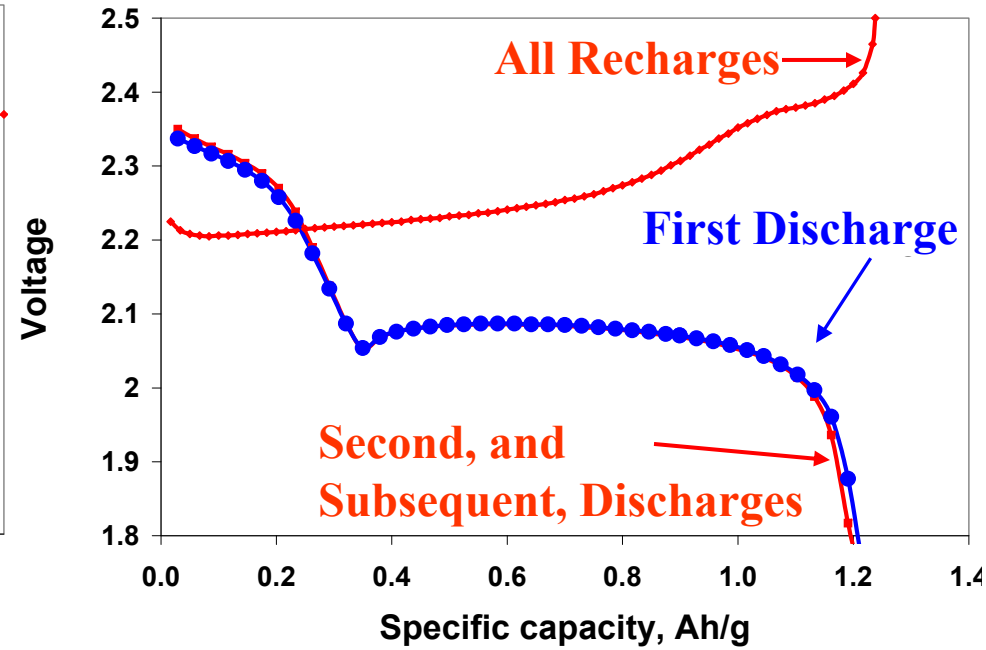


NO_X Compounds, and Physical Barriers, Will Suppress the Shuttle, Restore Li-S Cell Capacity and Allow Charge Control

Typical charge (C/8) and discharge (C/5) profiles with strong shuttle.



Typical charge (C/8) and discharge (C/5) for cells containing Nitrate.



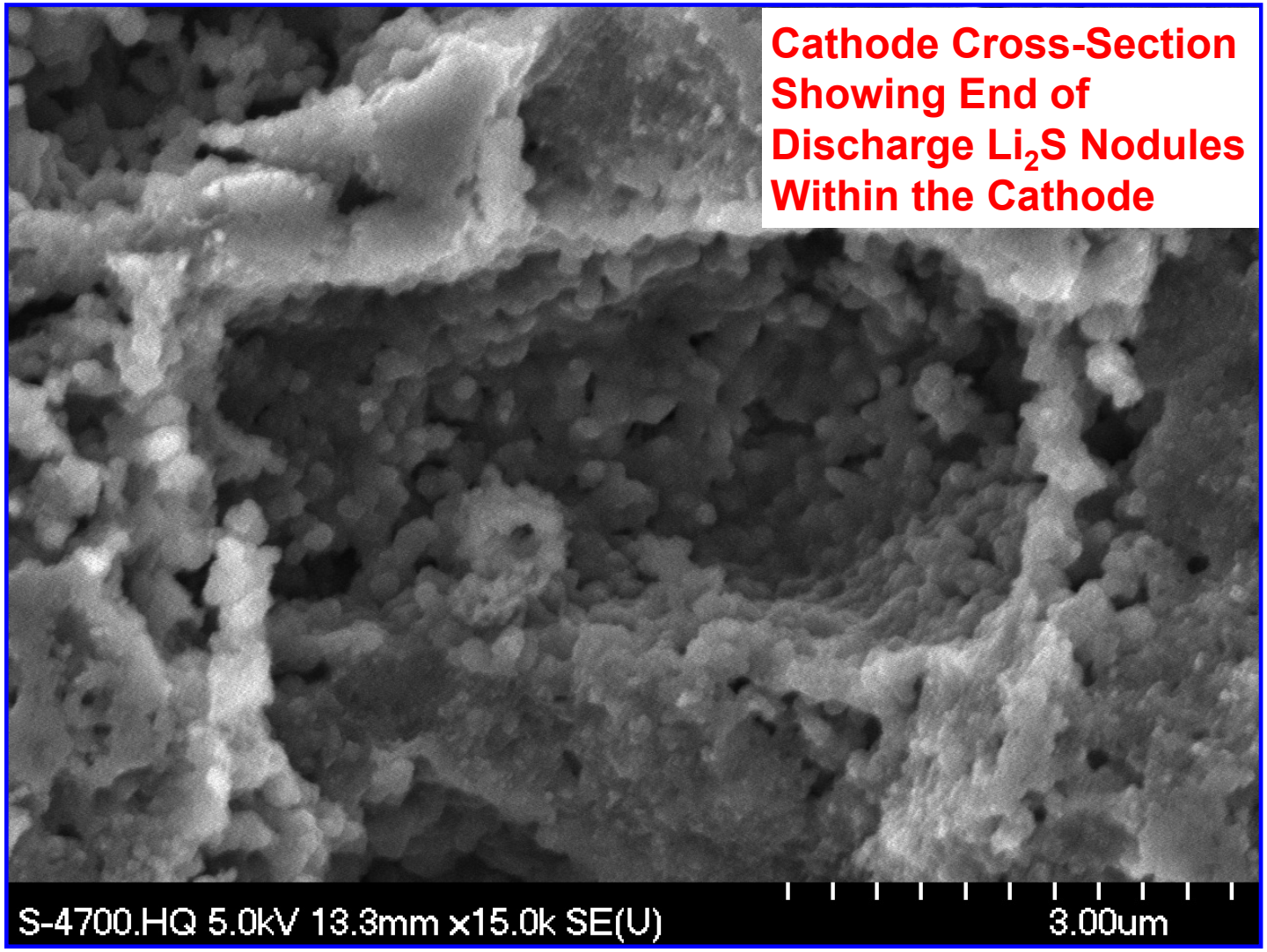
Sion's shuttle inhibitors permit near 100% utilization of the high voltage plateau sulfur and 350 – 450 Wh/kg with the current baseline cell design.

The shuttle can be suppressed by a *physical barrier* over the Li, or by various classes of NO_X compounds, like nitrates and nitrites.

Data circa 2005.

- The low solubility and slow kinetics of the Lower Plateau species, and clogging susceptible cathode structures, result in polarization that is responsible for loss of ~400 mAh/gS from the Lower Plateau.
  - The effect becomes larger as rate is increased and/or solvent depletes.

Cathode Diffusion Limitations and Li_2S Precipitation Limit Li-S Cell Capacity

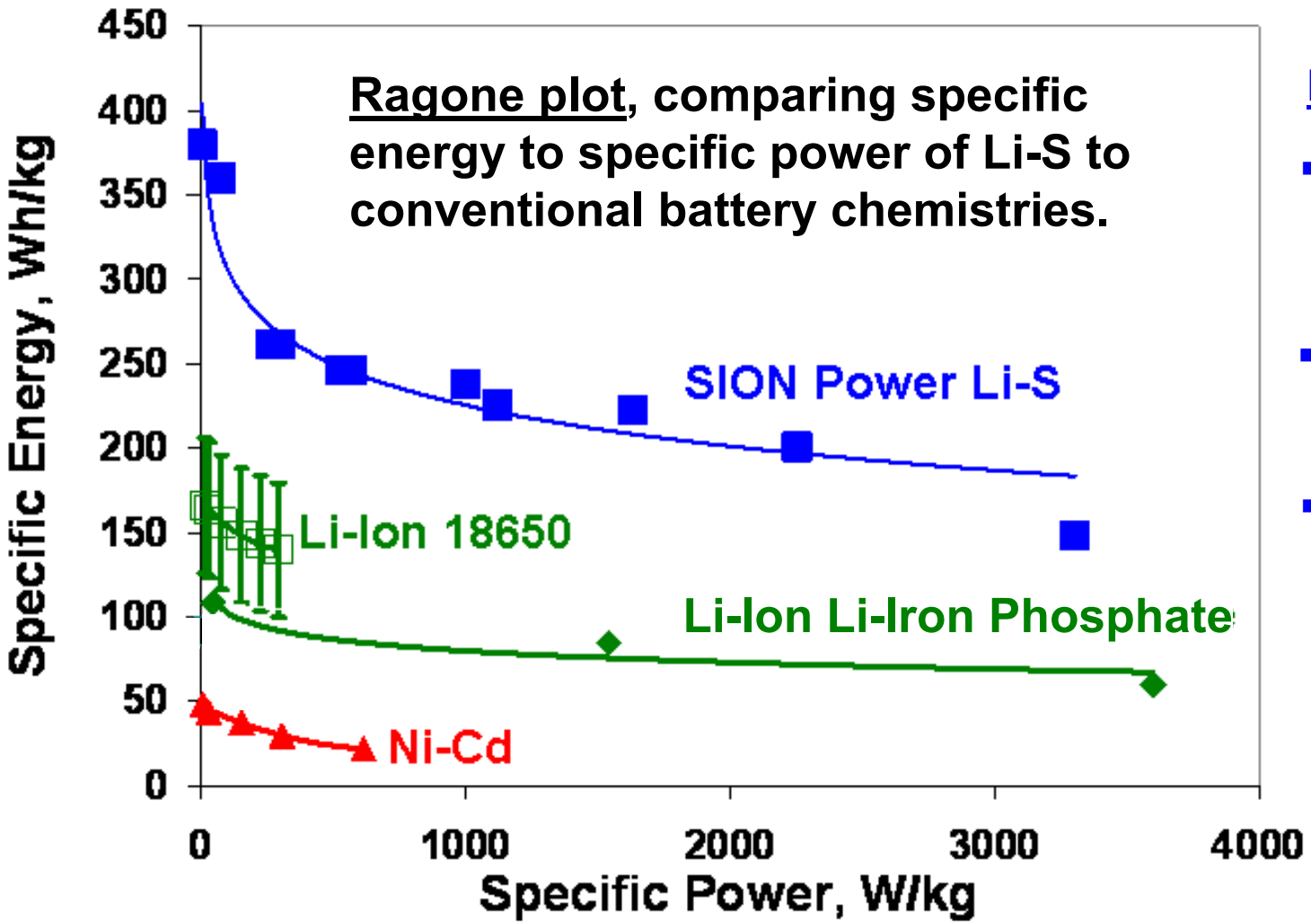


Li_2S deposits block cathode porosity, limiting capacity to <1,200 mAh/gS, in current high energy-high rate baseline cell designs.

Without anode protection, solvent is lost on each cycle. This leads to increased Li_2S precipitation, polarization and loss of capacity on each cycle, and eventually end of life.

Data circa 2005.

Still, for 25-80 Cycles Depending on Cell Design, Baseline 350 Wh/kg Li-S Cells are Capable of Delivering High Power



Li-S Parameters

- **Continuous discharge up to 2 kW/kg.**
- **30 A pulses up to 3.3 kW/kg.**
- **ASR = 26 Ω•cm² (Cell area specific resistance)**

Li DoD ~50%

Data circa 2005.

Baseline Li-S Cell Data Sheet

Lithium Sulfur Rechargeable Battery Data Sheet

Lithium sulfur has the highest theoretical specific and volumetric energy densities of any rechargeable battery chemistry (2550 Wh/kg and 2862 Wh/l theoretically). SION Power has learned how to unlock this potential and has created a unique rechargeable battery system. This patented technology is enabling new applications for rechargeable batteries and replacing existing primary and rechargeable batteries in applications where weight is a critical factor.

Typical applications include:

- Unmanned Vehicle Systems
- Weight sensitive electronic applications
- Military communication systems
- Sensors

Electrical Specifications:

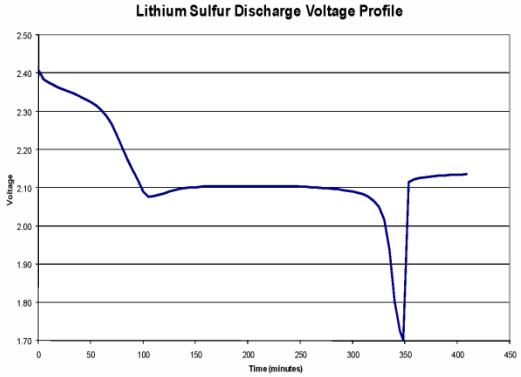
Nominal Voltage:	2.15V
Maximum Charge Voltage:	2.5V
Minimum Voltage on Discharge:	1.7V
Nominal Capacity @ 25°C:	2.5 Ah @ C/5
Maximum continuous discharge rate:	2C
Maximum charge rate:	C/5
Specific Energy:	350 Wh/kg
Energy Density:	320 Wh/l
Cell Impedance:	25 mΩ

Mechanical Specifications:

Configuration:	Prismatic
Length:	55 mm (top flanged folded)
Width:	37 mm
Thickness:	11.5 mm
Weight:	~16 g

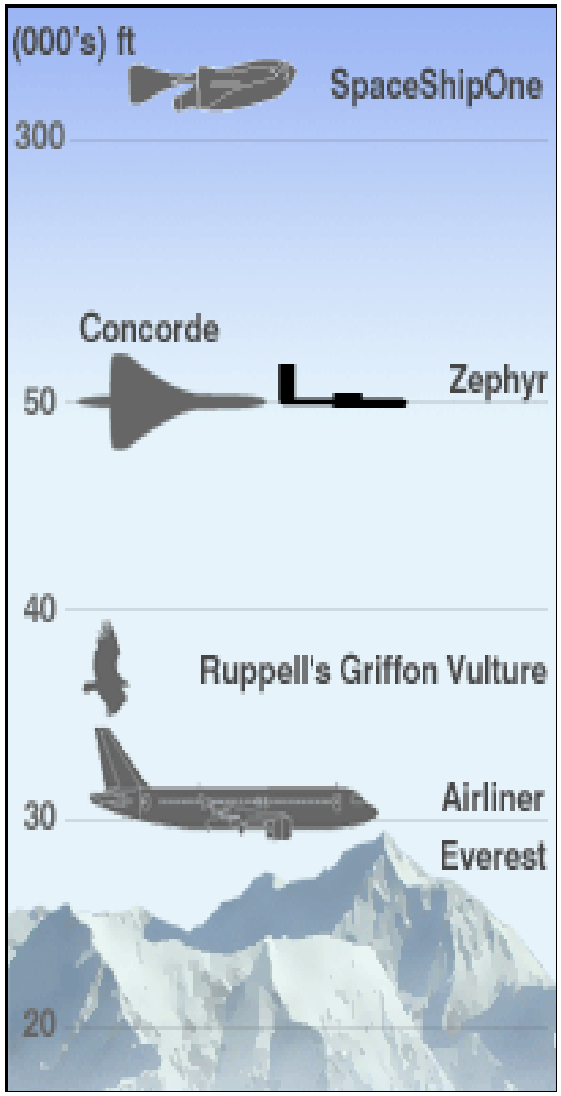
Environmental Specifications:

Discharge Temperature:	-20°C to +45°C
Charge Temperature:	-20°C to +45°C
Storage Temperature:	-40°C to +50°C



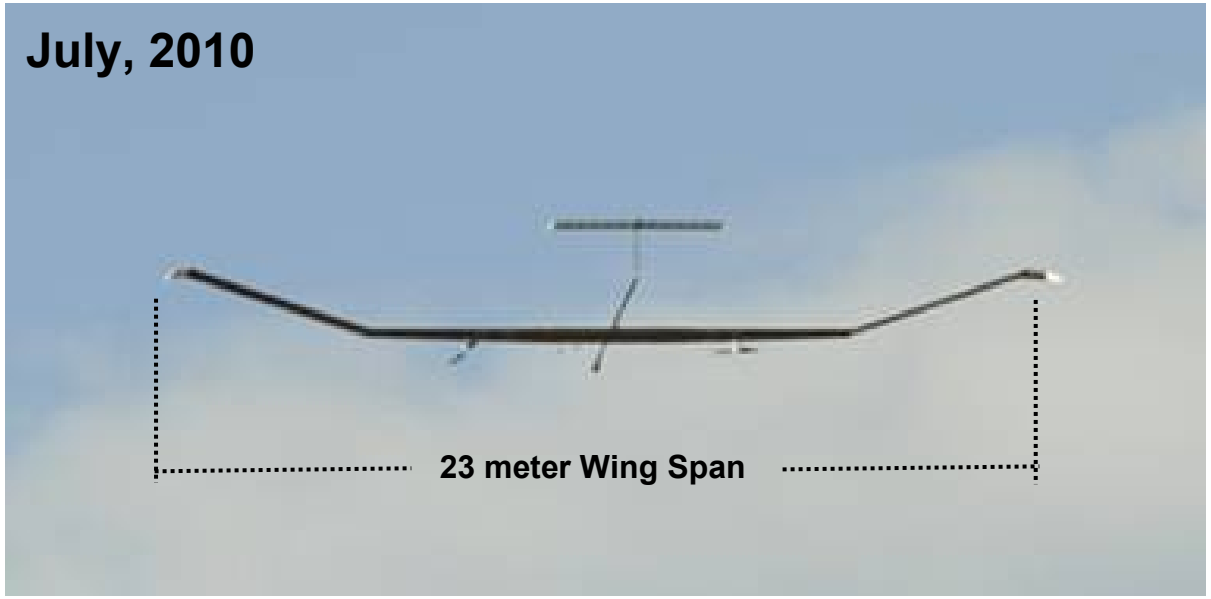
- Sion's current high energy baseline Li-S cells utilize:
  - ***Un-protected*** Li-foil anodes;
  - Slurry coated carbon-sulfur cathodes; and
  - A wound prismatic design.
- Capacity is limited by Li_2S precipitation/cathode structure.
- Cycle life is limited by Li-solvent reactions increasing Li_2S_x concentration, which increase Li_2S precipitation & cathode clogging problems.
  - Cycle life is *not* limited by the polysulfide shuttle when nitrate is used.

First Commercial Li-S Application is Unmanned Aerial Vehicles - UAVs



"QinetiQ's Zephyr 7 UAV Exceeds Official World Record for Longest Duration Unmanned Flight."

- **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.**
- **Pending world record: >14 days of continuous flight.**



Summary of Cycle Life, Safety and Capacity issues with Present Generation Li-S Cells

- Cycle life is limited by solvent depletion due to the metallic Li anode reacting with the electrolyte solvent.
- Safety is limited by metallic Li reacting with sulfur species.
- The capacity is limited by Upper Plateau self-discharge, through the Polysulfide Shuttle mechanism, and by Lower Plateau precipitation of Li_2S and cathode clogging.
  - The shuttle can be suppressed by Sion's NO_x additives, or by physical membranes protecting the anode.
    - NO_x additives do not stop solvent depletion.
  - The Li_2S precipitation requires more Li_2S_x aggressive solvents and a cathode microstructure that doesn't clog and improves overall conduction through the cathode.

- How can the Li-S capacity and cycle life issues be overcome?
- What are Sion's approaches?

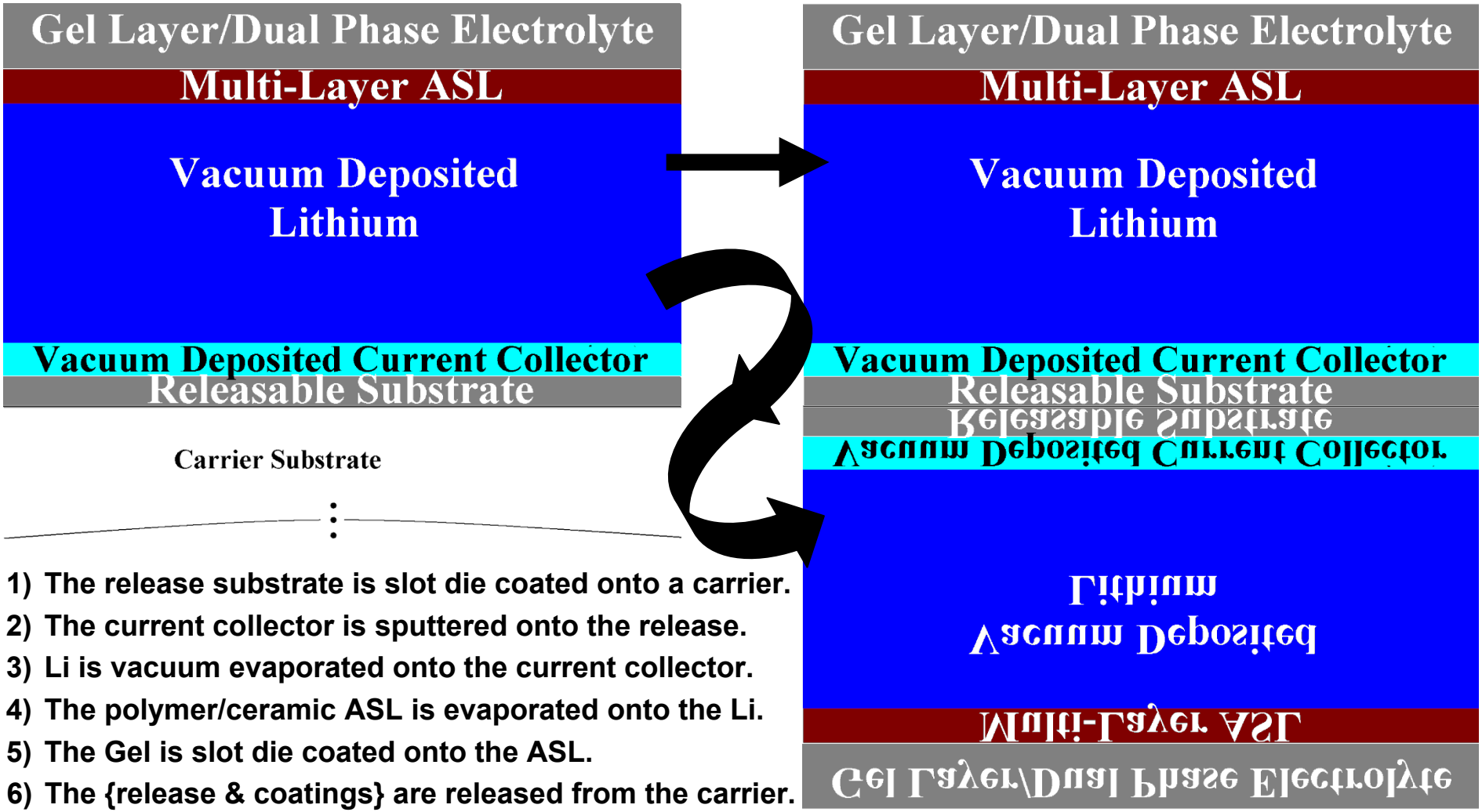
Increasing Li-S Cycle Life

- The key to increasing cycle life is stopping the Li anode from reacting with *solvents*, and controlling Li morphology.
  - Sion's Approach – ***Protect the Metallic Lithium Anode and Decouple the Anode and Cathode Chemistries***:
    - A thin release substrate;
    - A vacuum deposited current collector;
    - Vacuum Deposited Li (VDLi);
    - ***Anode Stabilization Laminates (ASLs);***
      - ***comprising multi-layer ceramic/polymer protective coatings;***
    - Semi-compliant polymer gel coated separator;
    - A dual phase solvent system; and
    - Externally applied uniaxial pressure.
- *Cathode issues are secondary with respect to cycle life*.

The Purpose of the Dual Phase Solvent

- When employing a dual phase solvent system:
  - A relatively Li benign solvent, that excludes polysulfides, migrates to the gel on the anode side of the cell – protecting the anode from the cathode solvent and polysulfides should there be any pinholes in the ASL; and
  - A more polysulfide aggressive solvent migrates to the cathode to increase sulfur utilization, capacity and rate capability.

Schematic Procedure for Fabricating Protected Li Anode Assemblies



1) The release substrate is slot die coated onto a carrier.
2) The current collector is sputtered onto the release.
3) Li is vacuum evaporated onto the current collector.
4) The polymer/ceramic ASL is evaporated onto the Li.
5) The Gel is slot die coated onto the ASL.
6) The {release & coatings} are released from the carrier.
7) Two {release/CC/anode/ASL/Gel} laminates are laminated back-to-back & used as the anode in the cell.

Improving Li-S Safety

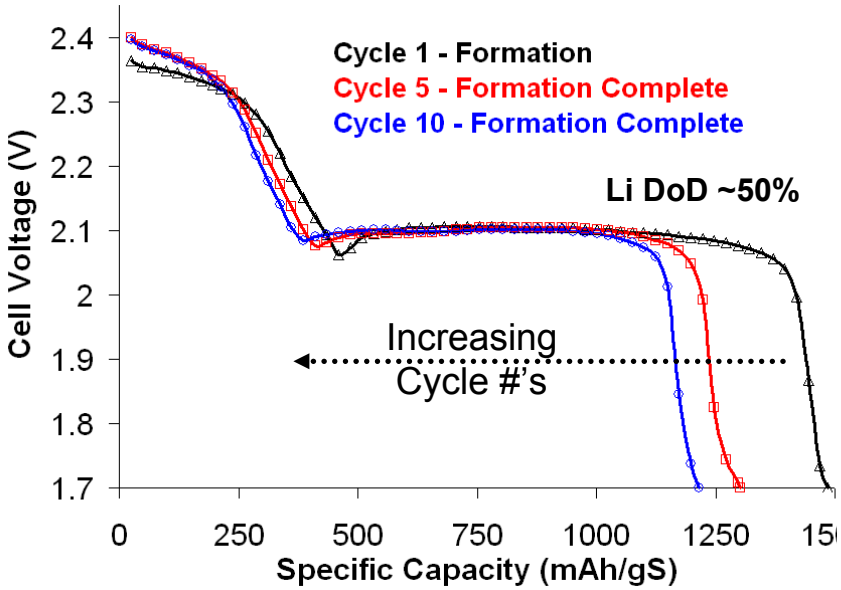
- The key to improving safety is stopping the Li anode from reacting with <u>*sulfur*</u>, and controlling Li morphology.
  - Sion's Approach – ***Protect the Metallic Lithium Anode and Decouple the Anode and Cathode Chemistries*** (*the same as for increasing cycle life*):
    - A thin release substrate;
    - A vacuum deposited current collector;
    - Vacuum Deposited Li (VDLi);
    - ***Anode Stabilization Laminates (ASLs);***
      - ***comprising multi-layer ceramic/polymer protective coatings;***
    - Semi-compliant polymer gel coated separator;
    - A dual phase solvent system; and
    - Externally applied uniaxial pressure.

Increasing Li-S Capacity

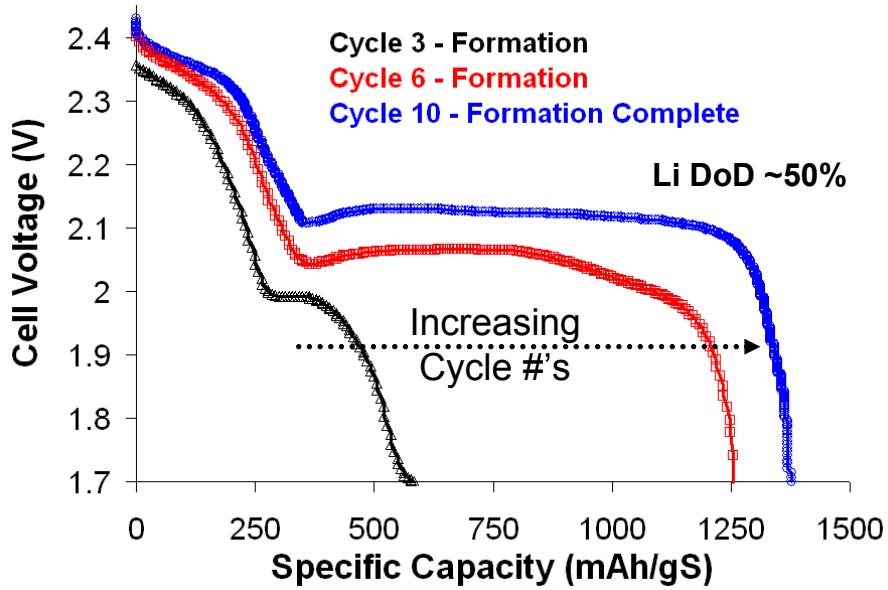
- The key to increasing Li-S capacity is increasing sulfur loading while maintaining/increasing sulfur utilization.
  - Sion's Approaches:
    - Employing all previous *anode protection* methods to reduce solvent loss in order to maintain cathode function/capacity over many cycles;
    - With the anode protected, and employing the *dual phase electrolyte* methodology, use more cathode aggressive solvents on the cathode side of the cell; and
    - Optimize *cathode structure and porosity* to limit pore blocking and increase conduction through the cathode.
      - The last two bullets above improve cathode function/sulfur utilization, resulting in secondary cycle life increases, but the cells still fail due to solvent depletion without anode protection.

Cathode Performance as a Function of Structure

Current Commercial Cathode Structure



Enhanced, Future, Cathode Structure

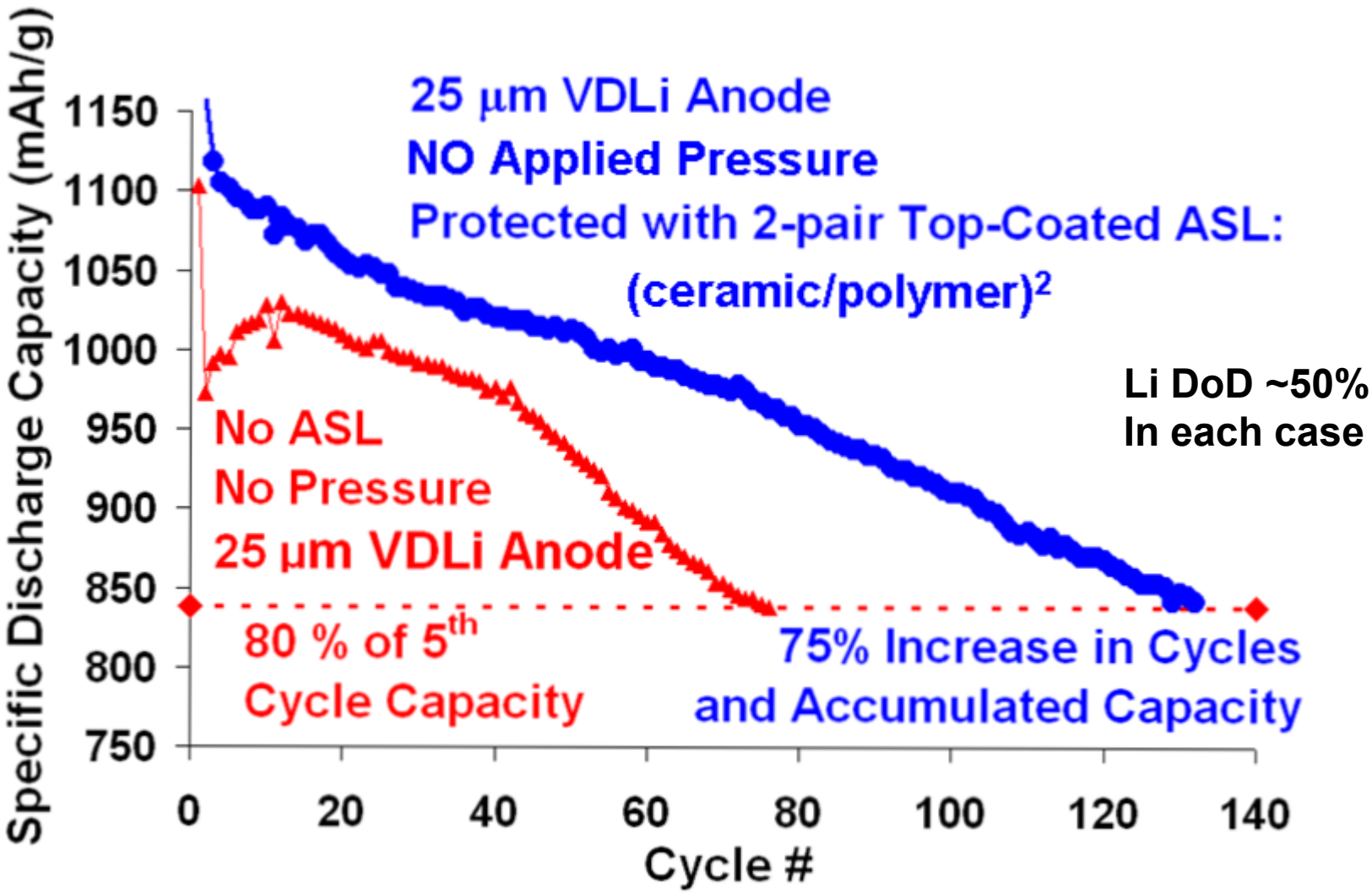


- With current cathode structure:
  - The pores plug with cycling.
    - Cell reaches polarization induced voltage cut-off at lower capacity with each cycle.
- With enhanced cathode structure:
  - Pores don't plug with cycling.
    - Cathode polarization is reduced and capacity stays higher longer, even as solvent depletes.

Data circa 2009.

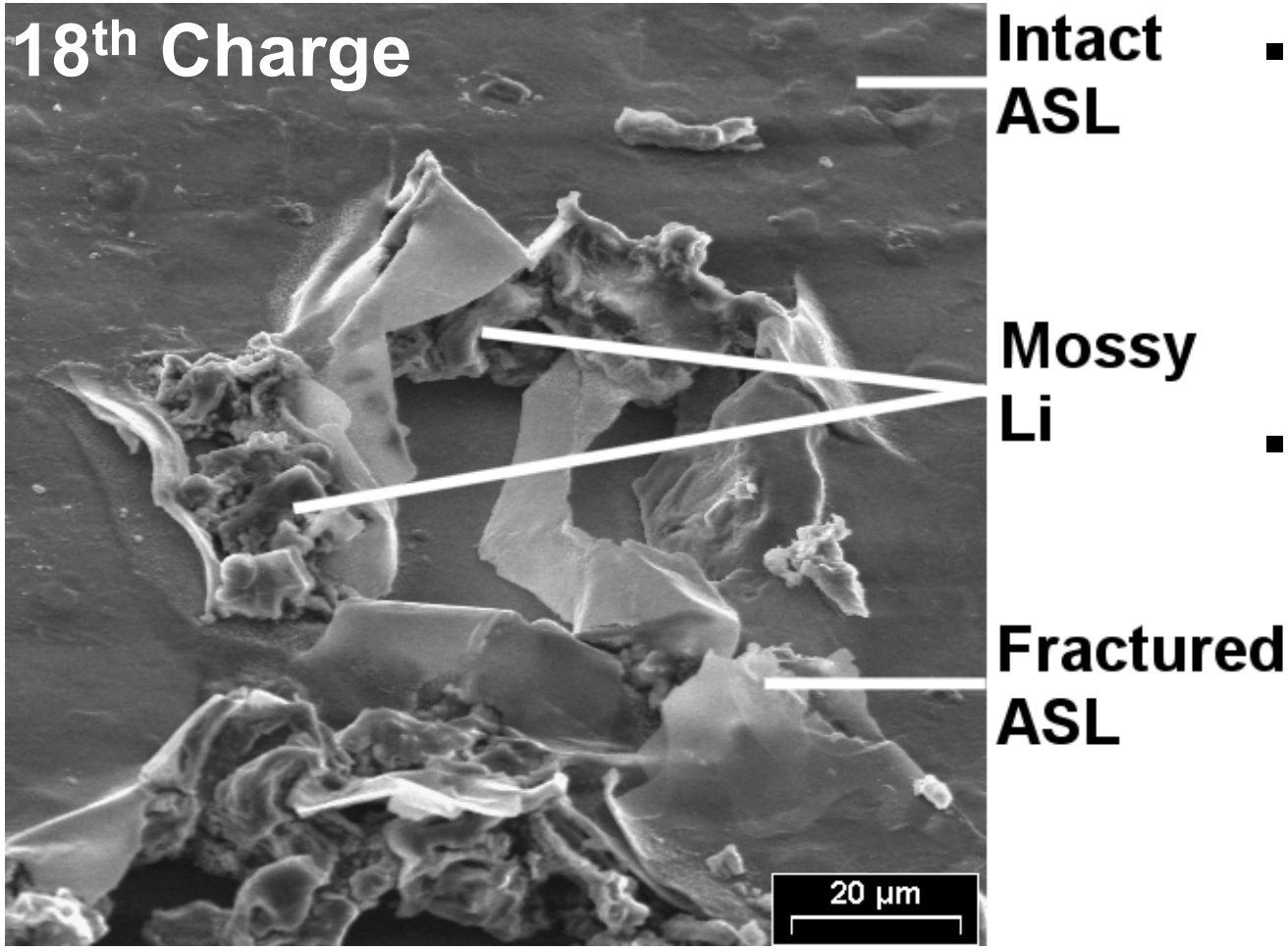
- The most important component in the anode protection strategy is the ASL.
- The ASL will decouple the anode chemistry from the cathode chemistry if the ASL remains intact.

Multiple Ceramic/Polymer Anode Stabilization Laminates (ASLs) Alone Can Increase Cycle Life and Accumulated Capacity by more than 75%



Data circa 2008.

In the Absence of Applied Pressure, Cycle Life With ASL Coatings Is Limited by Mossy Li Morphology Fracturing the ASL, Leading to Li-Solvent Reactions



- Mossy Li is a by-product of cycling, even without exposure to solvent.
- Mossy morphology eventually fractures thin ASL layers and lithium-solvent reactions begin, leading to end of life.

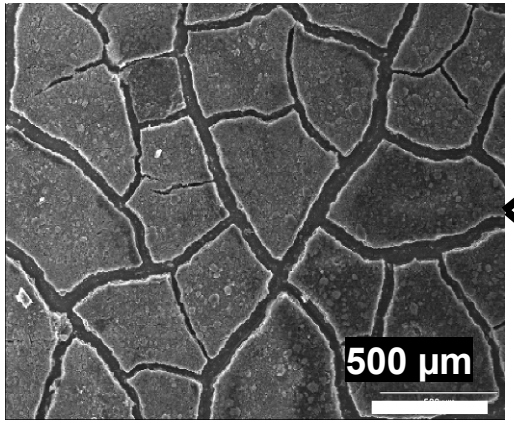
12.5 µm Li layer doubles in thickness by cycle 18, Li DoD ~50%.

Data circa 2008.

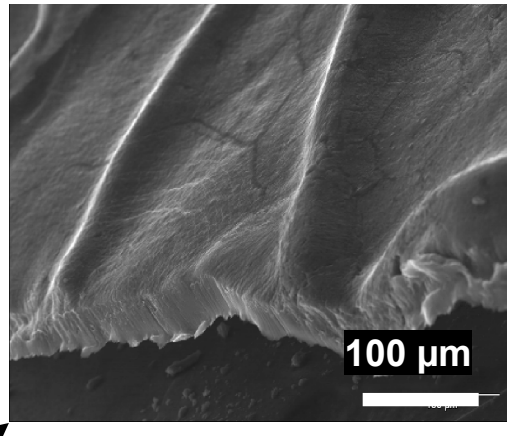
- Under pressure, the soft Li anode takes on the surface topography of whatever is pressed against it.
- A compliant gel pad pressing against the anode distributes the forces, keeps the Li smooth and stabilizes the ASL protective coating over the Li.

Metallic Li Anode Morphology is Stabilized by Uniaxial Pressure

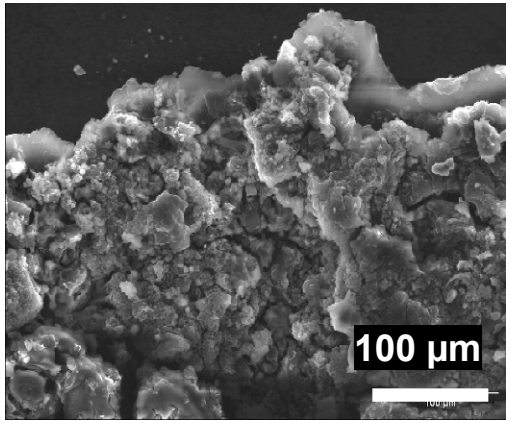
A poorly coated cathode.



Very smooth plateaus separated by large mud-cracks



Two anodes, each initially 50 µm thick, cycled from each side, after 50 cycles. ***Li DoD ~50%.***



Top: Anode, cycled under pressure:

- Remains dense Li metal;
- Retains original 50 µm thickness; and
- Is very smooth except for extrusion into cathode mud-cracks.

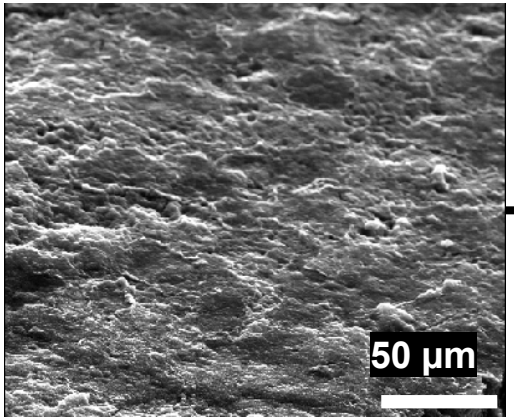
Bottom: Anode, cycled without pressure:

- Becomes highly mossy;
- Is over 200 µm thick; and
- Is very rough on all scales and surfaces.

Data circa 2008.

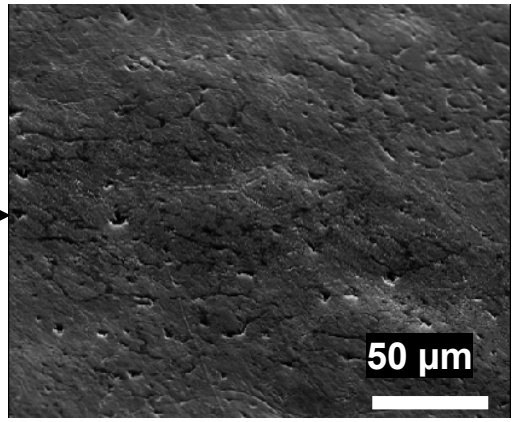
Under Pressure, Anode Surfaces Mimic Cathode Surfaces and Cathode Imprints are Muted by a Gel Layer

A better coated cathode.



Relatively smooth, without mud-cracks and with relatively small features.

A single anode.



Initially 50 µm thick, cycled from each side, after 450 cycles - with a semi-compliant gel layer between anode and cathode. ***Li DoD ~50%.***

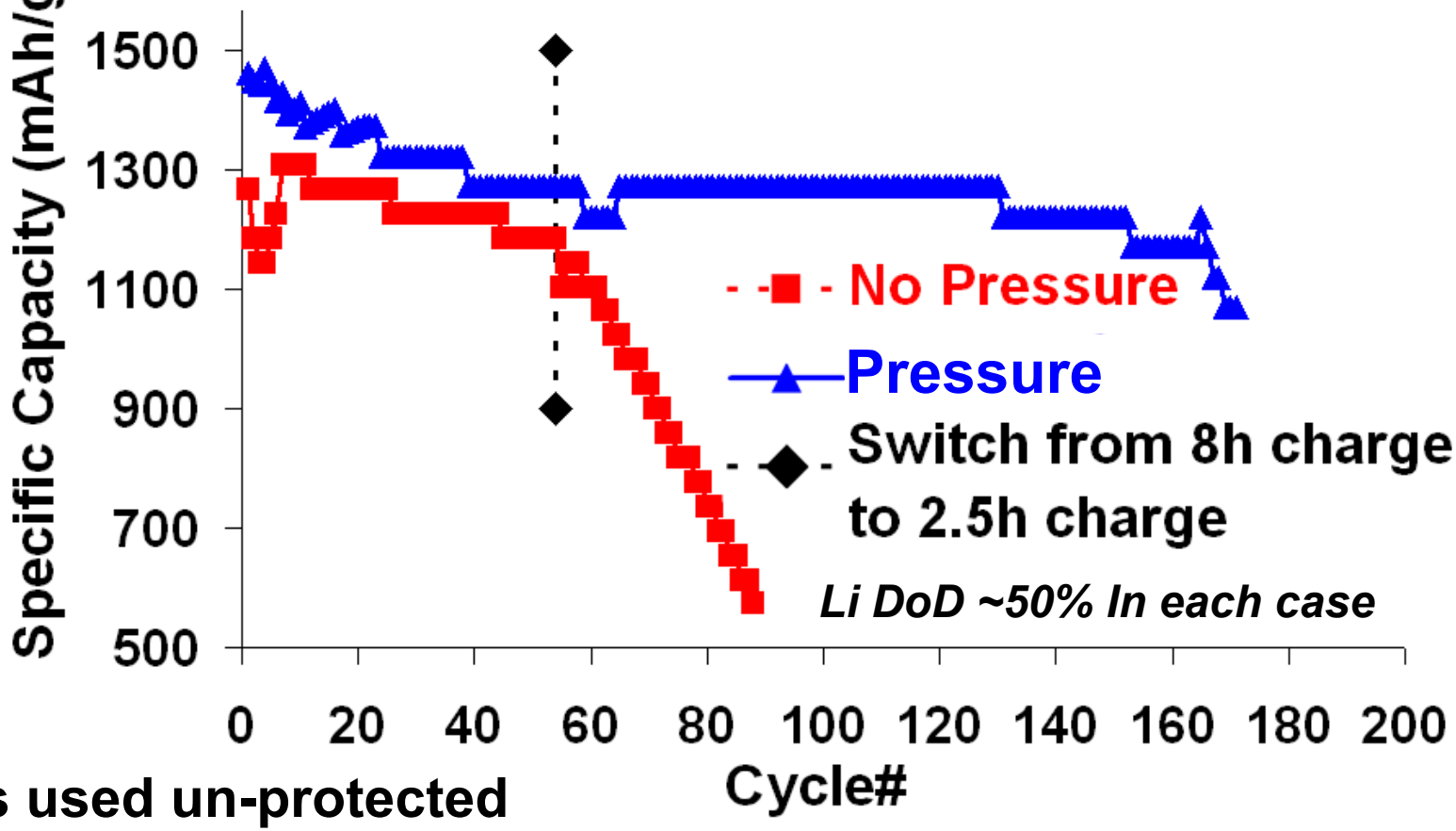
Anode cycled under pressure:

- Remains dense Li metal;
- Retains original 50 µm thickness;
- Is very smooth and approximately mimics the cathode surface; and
- Cathode features are muted on anode surface due to intervening gel layer.

Data circa 2008.

Pressure Improved Li Morphology Allows Increased Re-Charge Rates too

Under Pressure, Without an ASL, 2.5h Re-Charge Rates Have no Effect on Capacity or Cycle Life



Cells used un-protected Li-foil anodes.

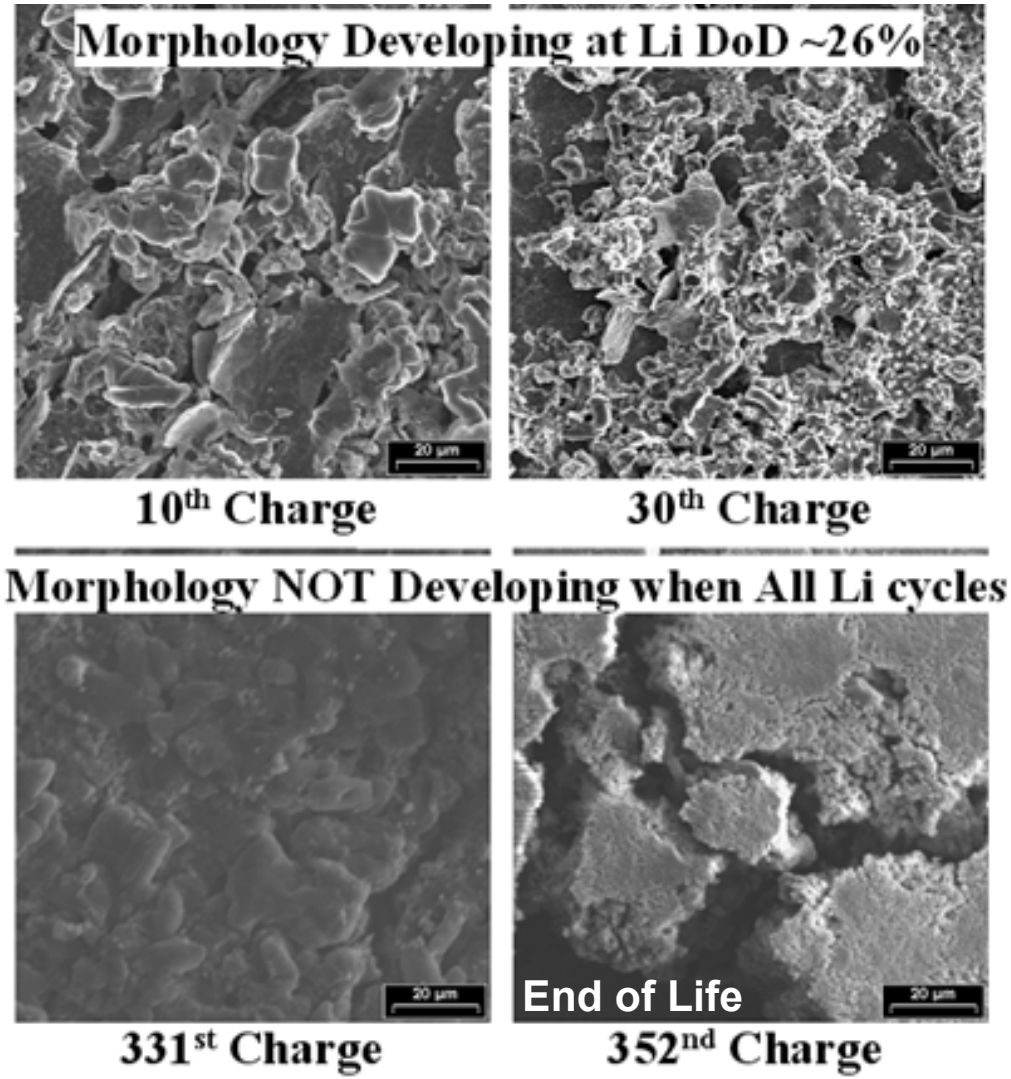
Data circa 2008.

Current Collectors also Help to Improve Li Morphology and Increase Cycle Life

Mossy Li morphology rapidly develops for cells at 26% Li DoD (depth of discharge) even at 10th cycle (Top).

For Li cycling at 100% DoD (Bottom), the Li remains dense for over 300 cycles – without pressure or protective coatings.

pg 37.6, 2nd Edition Handbook of Batteries, D. Linden, Cites 100% Zn cycling, with a current collector, improves performance due to very smooth re-plating.

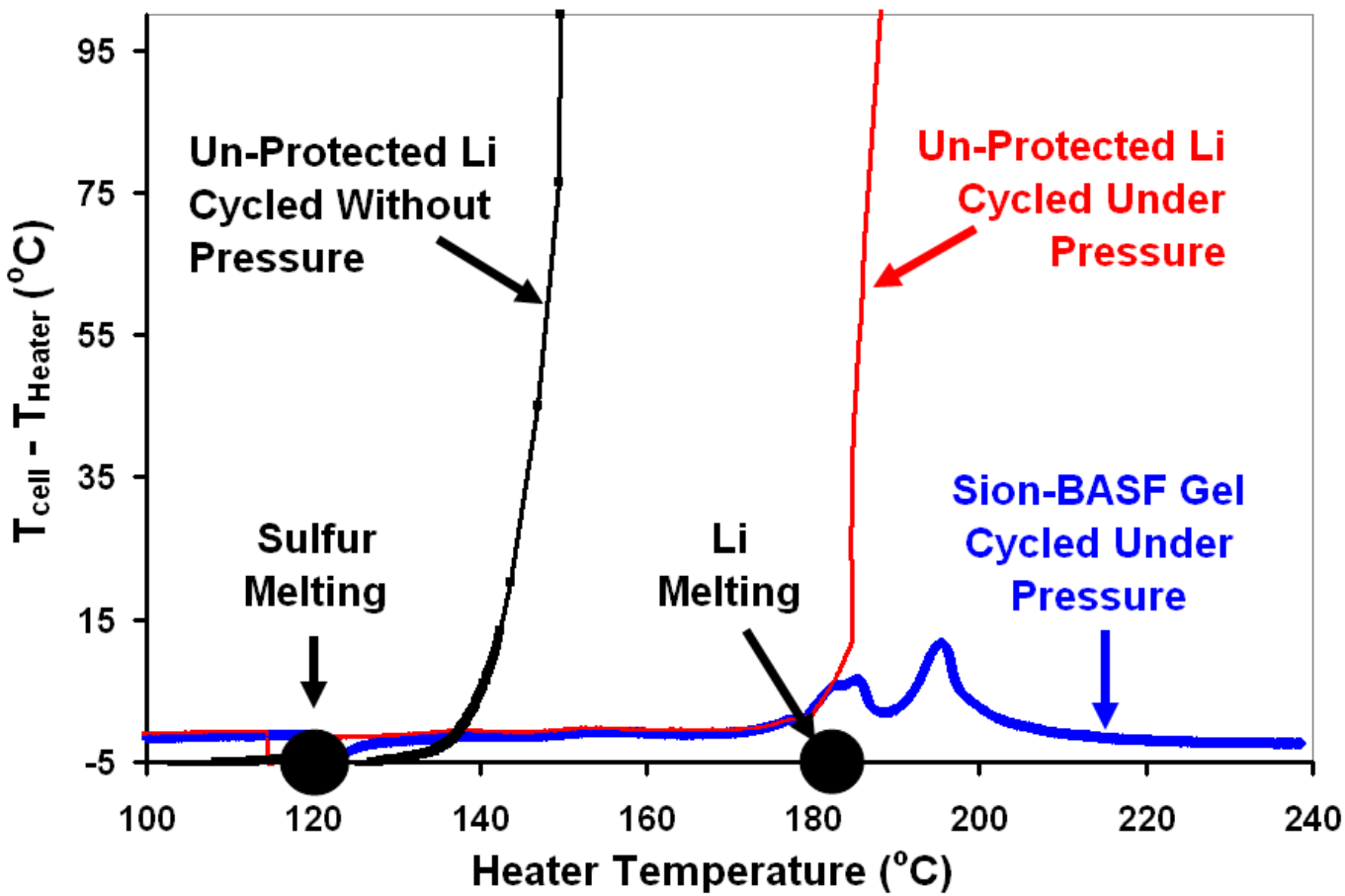


Data circa 2005.

- Sion's Li-S current baseline cells already fail gracefully under electrical abuse, puncture tests and other UN and DOT tests – except Thermal Runaway.
- The compliant gel improves Li-S cell safety by preventing thermal runaway - even when the Li melts.

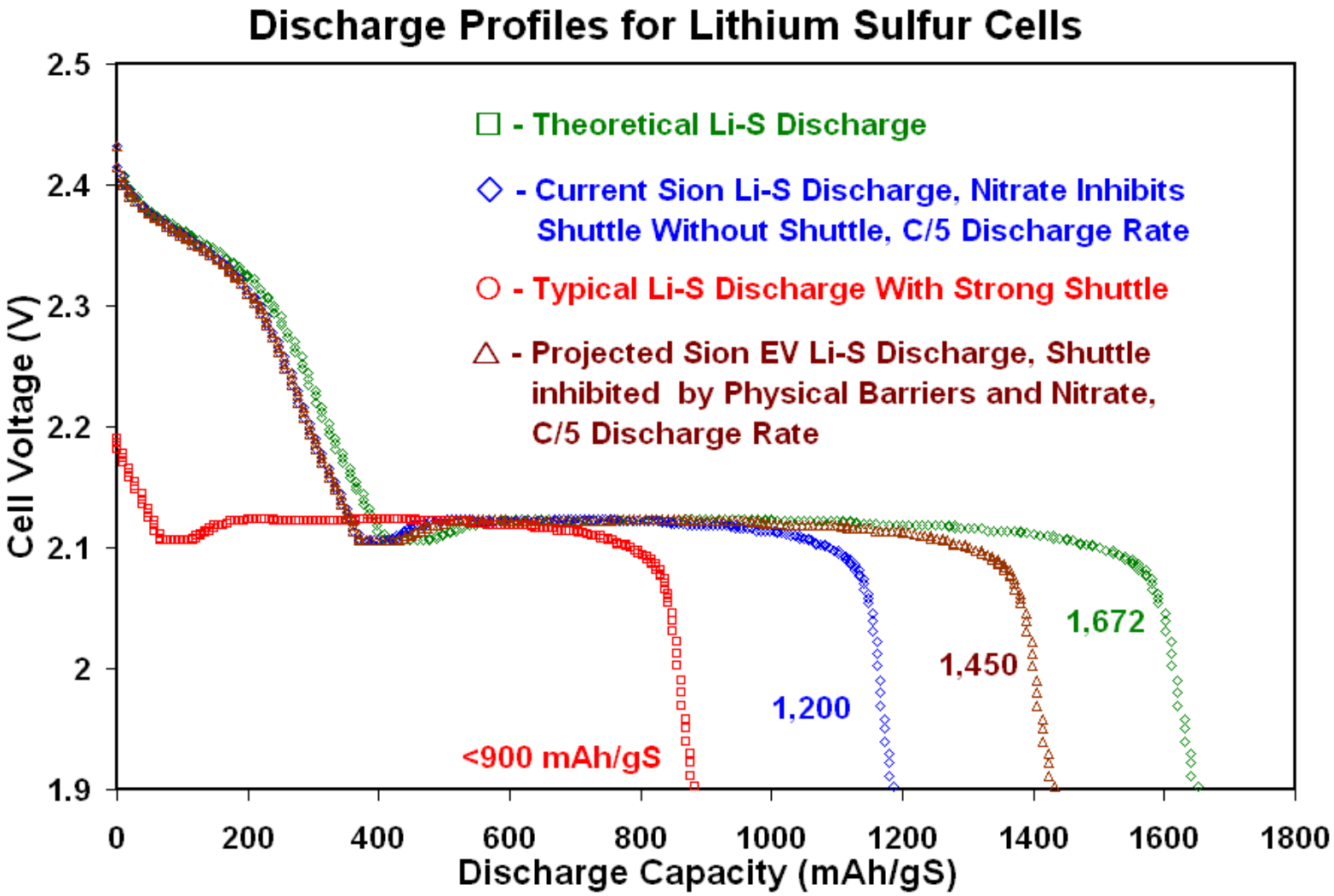
Safety Improved by Sion-BASF Compliant Gel Layer when Cycling Under Pressure

Thermal Ramp Test: Fully charged Li-S cells ramped at 5 °C/min after 20 cycles, ***Li DoD ~50%.***

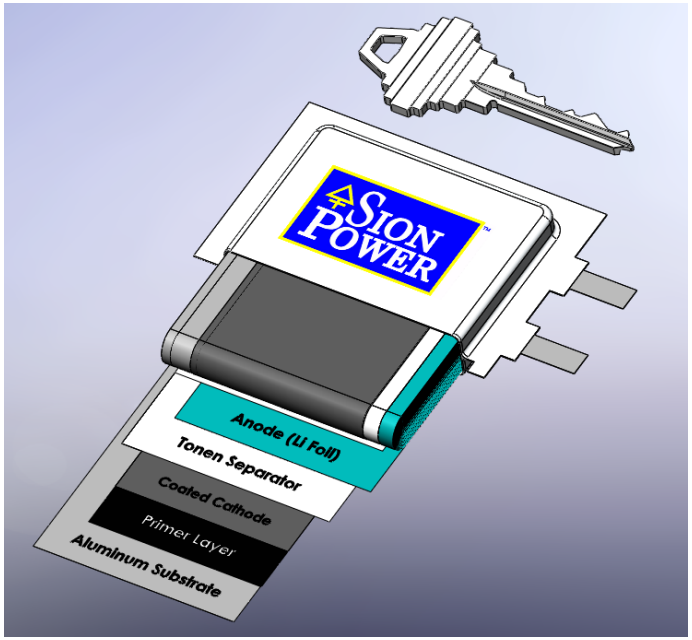


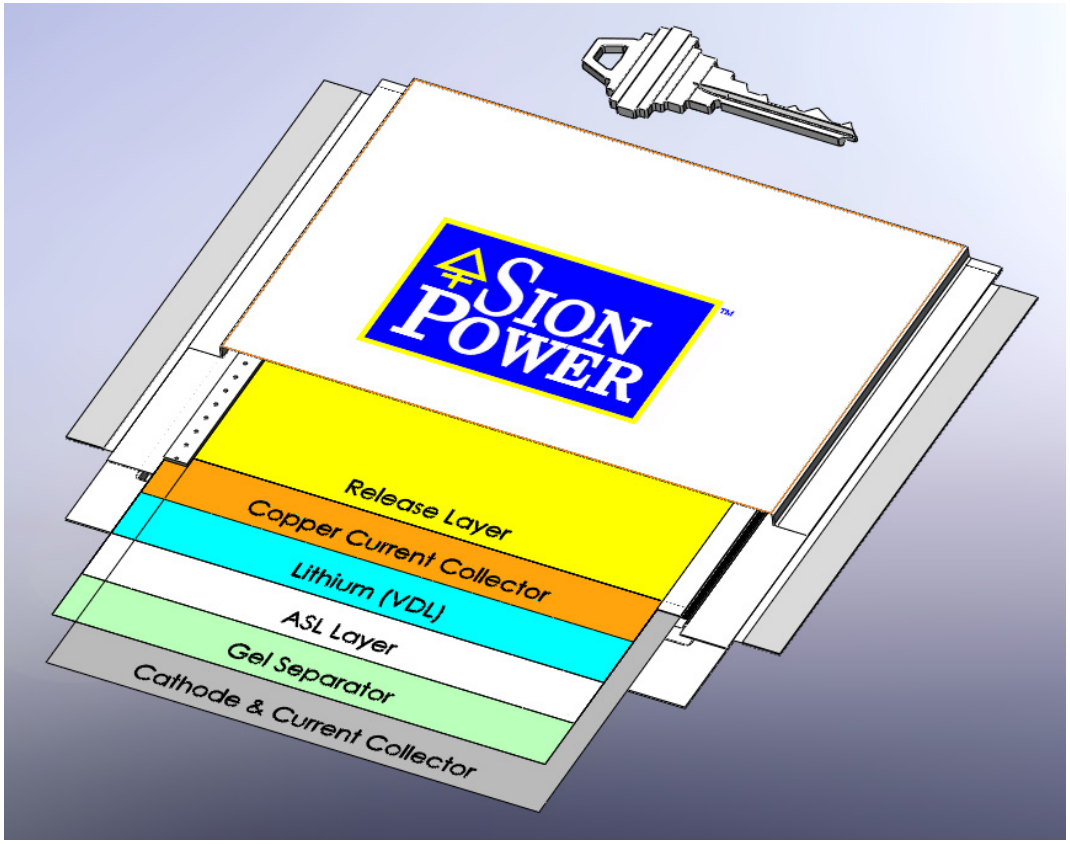
Data circa 2009.

Projected Discharge Capacity of Sion EV Cell by the End of 2013



Comparison of Performance Parameters of Current and Projected 2013 Li-S Cells





Current Sion Li-S Cell

- 63 mm x 43 mm x 11.5 mm
- 2.8 Ah, 350 Wh/kg, 320 Wh/l, 25-80 cycles
- Wound Prismatic Design

Projected Sion Li-S Cell in 2013

- 121 mm x 106 mm x 8.5 mm
- 25 Ah, 500 Wh/kg, ~575 Wh/l, >500 cycles
- Stacked Plate Design

Some of the Sion Team and One of the Vacuum Web Coaters

Thank You.

Any Questions?