Fundamental Chemistry of Sion Power Li/S Battery

Yuriy Mikhaylik

Sion Power Corporation, 9040 South Rita Road, Tucson, Arizona, 85747, USA

Outline

- Thermodynamics of Li-S
- Discharge-charge mechanism in the organic solvents medium: ambient temperatures and Li-S electrochemistry at temperatures below –40^{o}C.
- Polysulfide electrochemical shuttle and impact on charge efficiency and specific capacity. Specific energy beyond 300 Wh/kg.
- Short-chain polysulfides solubility and impact on sulfur utilization. Specific energy beyond 400 Wh/kg.
- Ragone plots and specific power-energy limitations

Why Lithium Sulfur?

Theoretical Energy Density Comparison

$S + 2Li = Li_2S$ $\Delta G \sim - 425$ kJ/mol

OCV ~ 2.2 V

Energy density ~ 2800 Wh/L

Specific Energy ~ 2500 Wh/kg

Compare Specific Energy with:

Li-ion ~ 580 Wh/kg

TNT equivalent ~ 1280 Wh/kg

Theoretical Volume Changes at Discharge

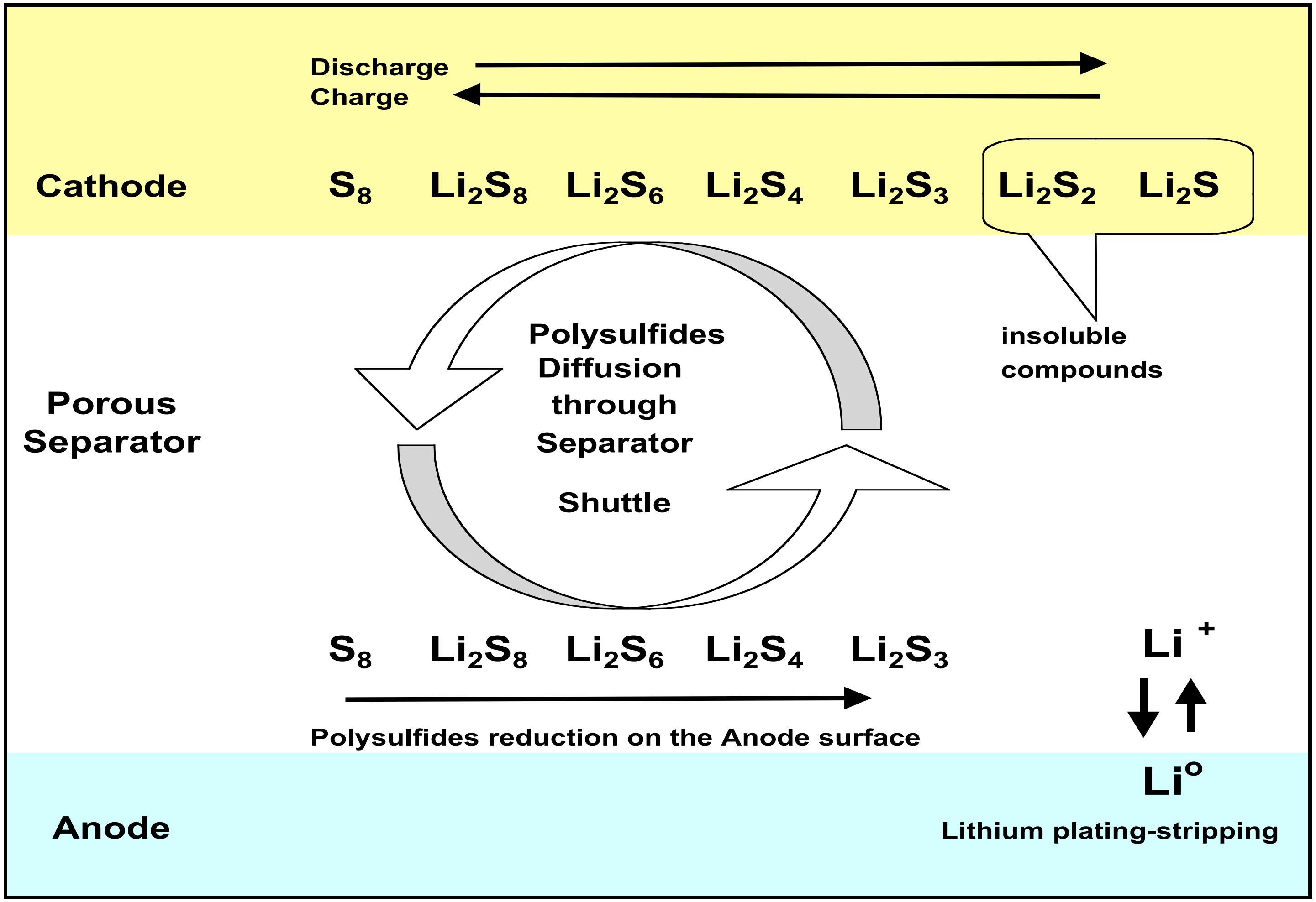
$$S + 2Li = Li_2S$$

	cm^3/Ah	%
Li+S	- 0.258	- 33%
Li	- 0.485	- 100%
S	+ 0.227	+ 79%

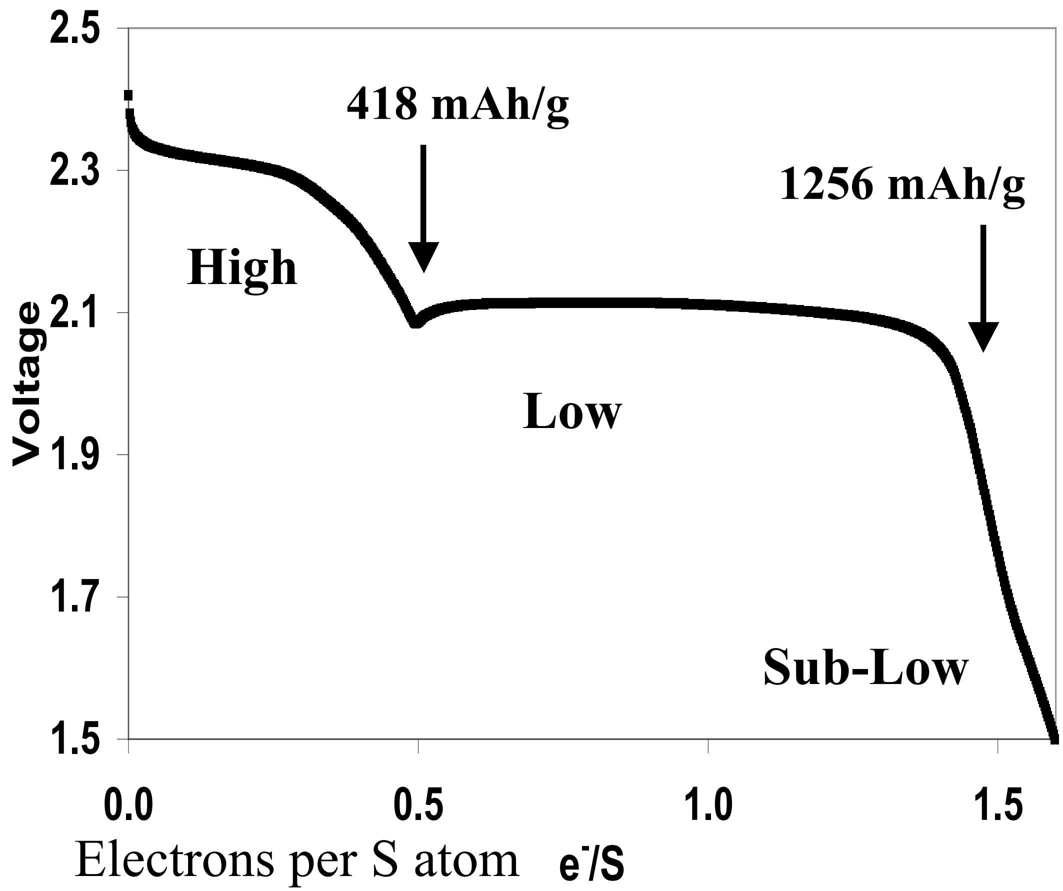
- S cathode has to have high porosity to accommodate bigger volume discharge products – Li_2S
- Cell mechanical design has to sustain volume changes during discharge-charge cycles + - 0.258 cm^3/Ah

How it works?

Active Materials Transformation Diagram



Li-S cell's first discharge at RT



High plateau – fast kinetics

$$S_8^{0} + 4e^{-} = 2S_4^{2-}$$

Low plateau – moderate kinetics

$$S_4^{2-} + 4e^{-} = 2S^{2-} + S_2^{2-}$$

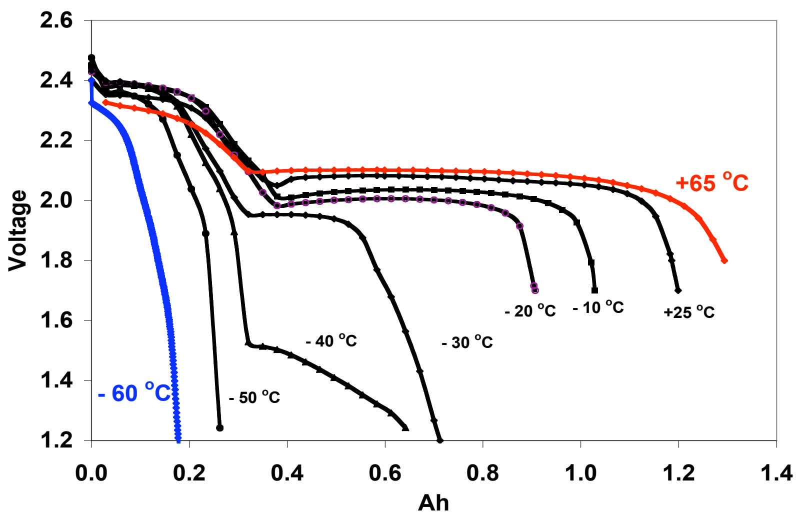
Sub-Low plateau – very slow kinetics

$$S_2^{2-} + 2e^{-} = 2S^{2-}$$

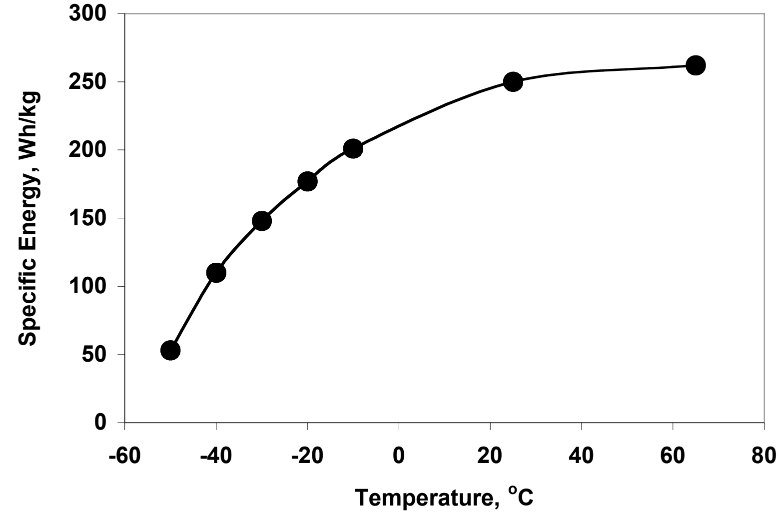
R.D. Rauh, K.M. Abraham, *J. Electrochem Soc*, 1979

E. Peled, H. Yamin, *J. Electrochem Soc*, 1989

Discharge profiles at C/3 rate

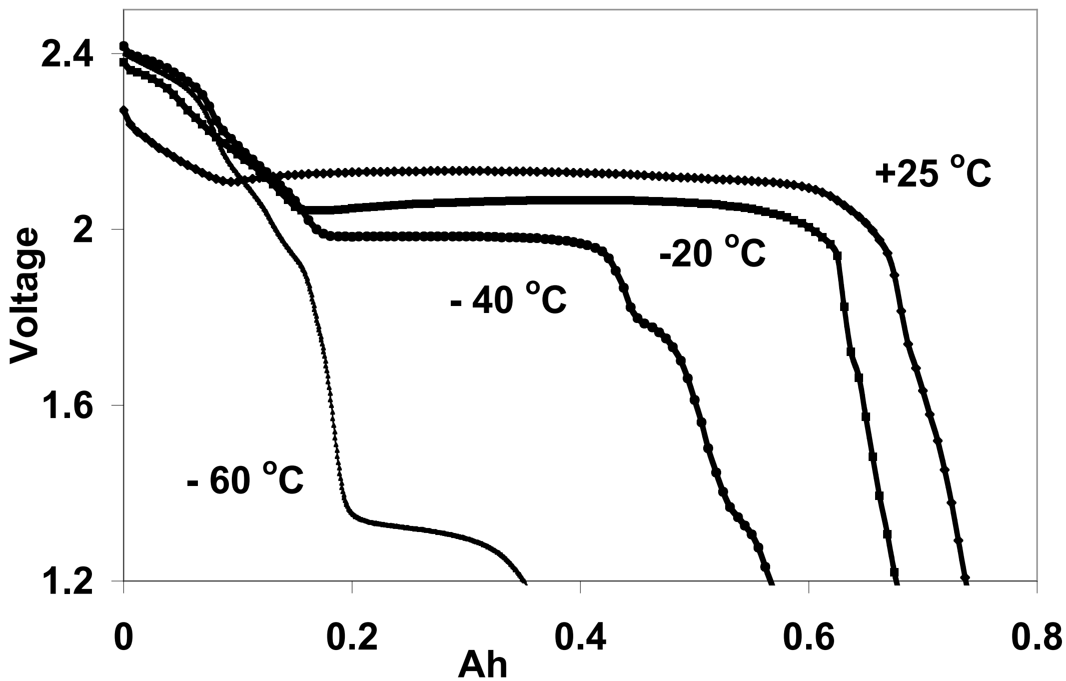


Specific energy at different temperatures C/3 rate

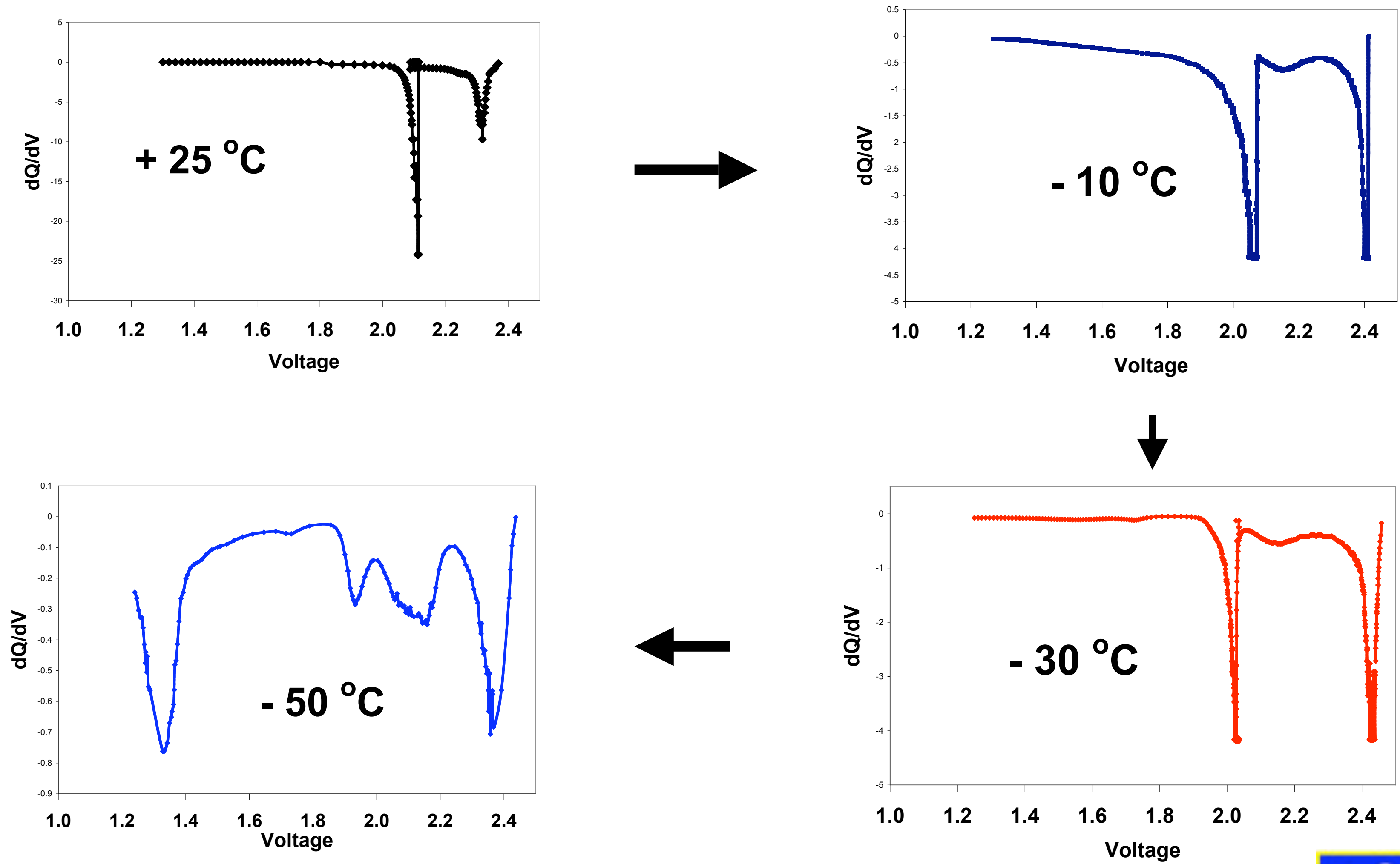


- Only two discharge plateau can be observed at medium or high discharge rates
- High plateau discharge demonstrates very low polarization down to –60°C

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

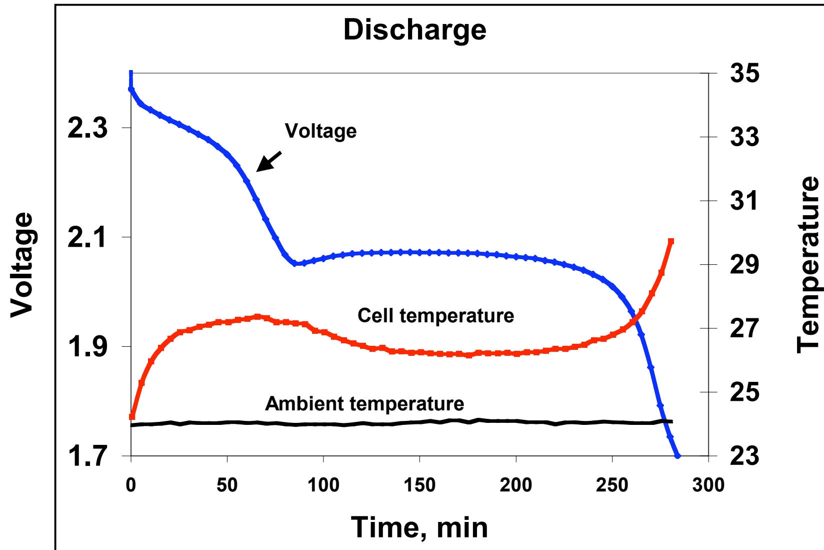


Differential capacity vs Voltage at different temperatures
Evidence of multi-step process

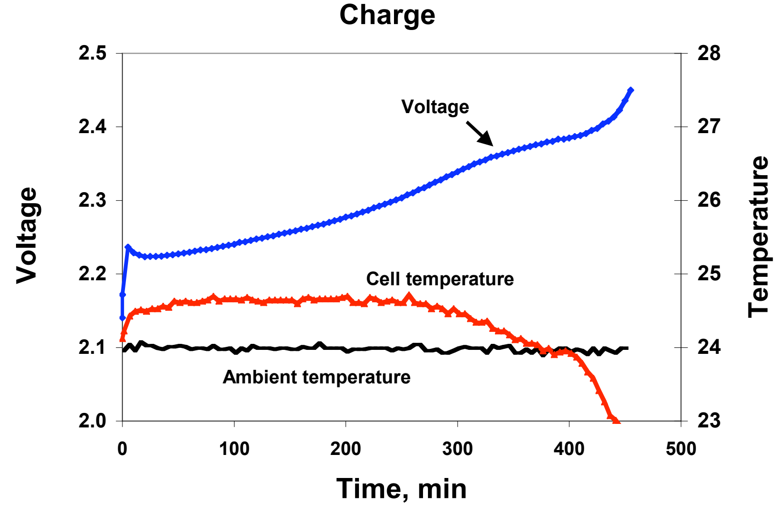


SION POWER

Thermal effects

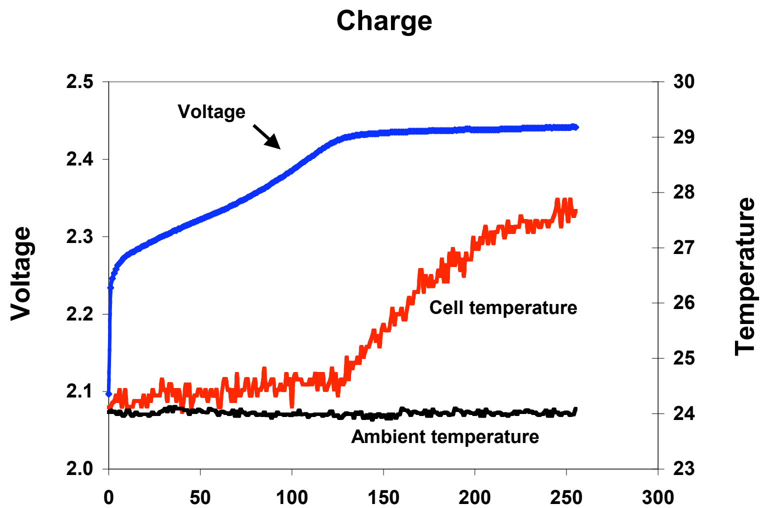


Maximal exothermic effects at transition from high to low plateau and at end of discharge



Inhibited shuttle. No overcharge.

Endothermic effects at high plateau



Charge at strong shuttle.

Significant overcharge.

Exothermic effects at high plateau

Polysulfide Shuttle Understanding and Control

The rate of polysulfide reduction on the Li surface is not limited by diffusion. It is limited by the rate of heterogeneous reaction on the anode surface.

$$\frac{d[S_H]}{dt} = \frac{I}{q_H} - k_s[S_H]$$

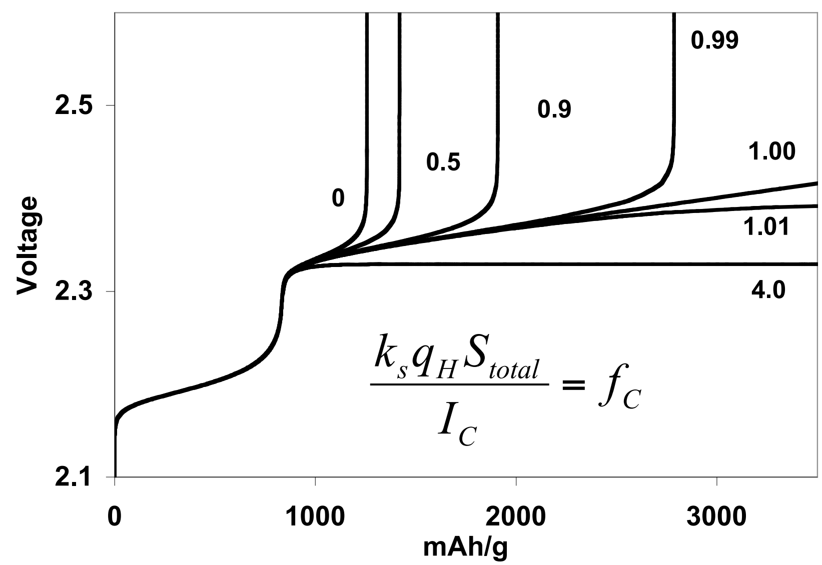
$[S_H]$ – high plateau polysulfide concentrations S_8, Li_2S_8, Li_2S_6.

I – charge current

k_s - the heterogeneous reaction constant or Shuttle constant.

q_H- high plateau specific capacity

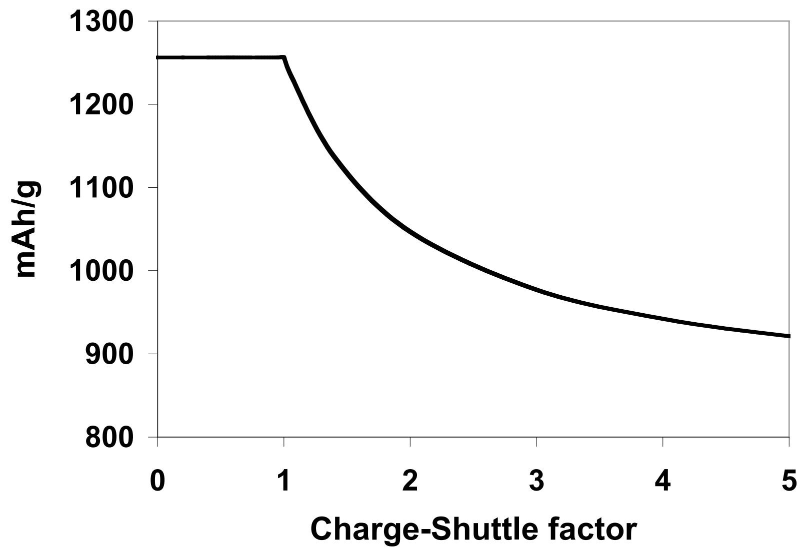
Charge profiles at different Charge-Shuttle factor f_c



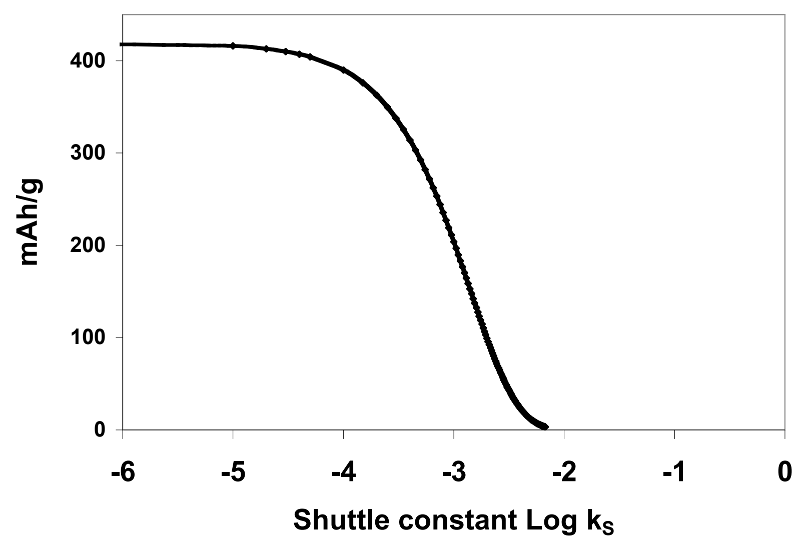
J. Electrochem Soc. 151 A1961-A1976 (2004)

Polysulfide Shuttle Understanding and Control

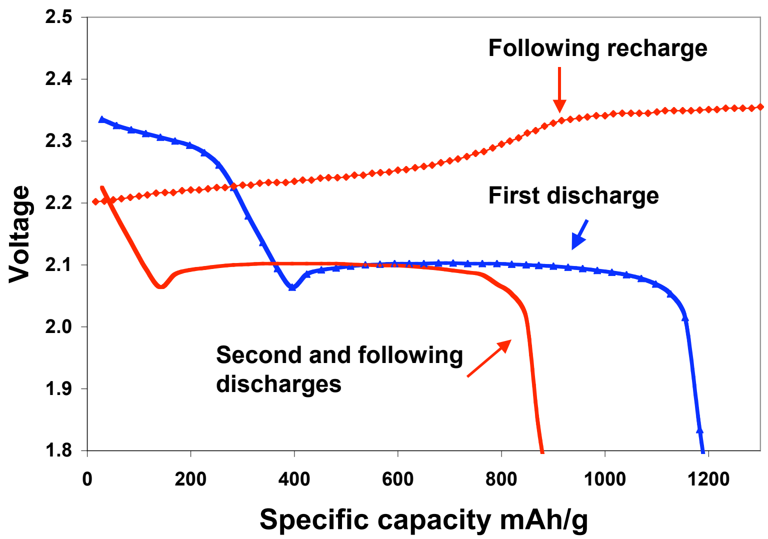
Available S capacity at different Charge-Shuttle factors



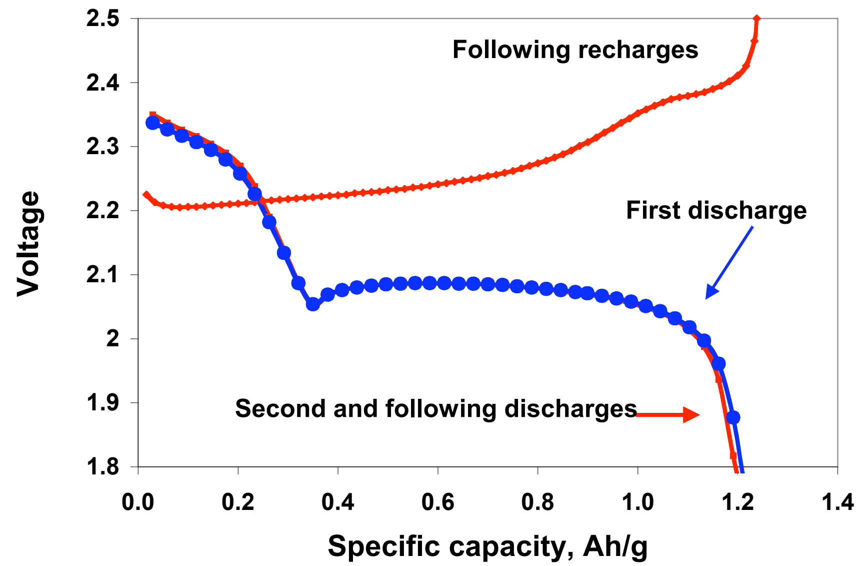
Retained High Plateau capacity after 30 days storage at different shuttle constants ks



Typical experimental discharge and charge profiles with strong shuttle.

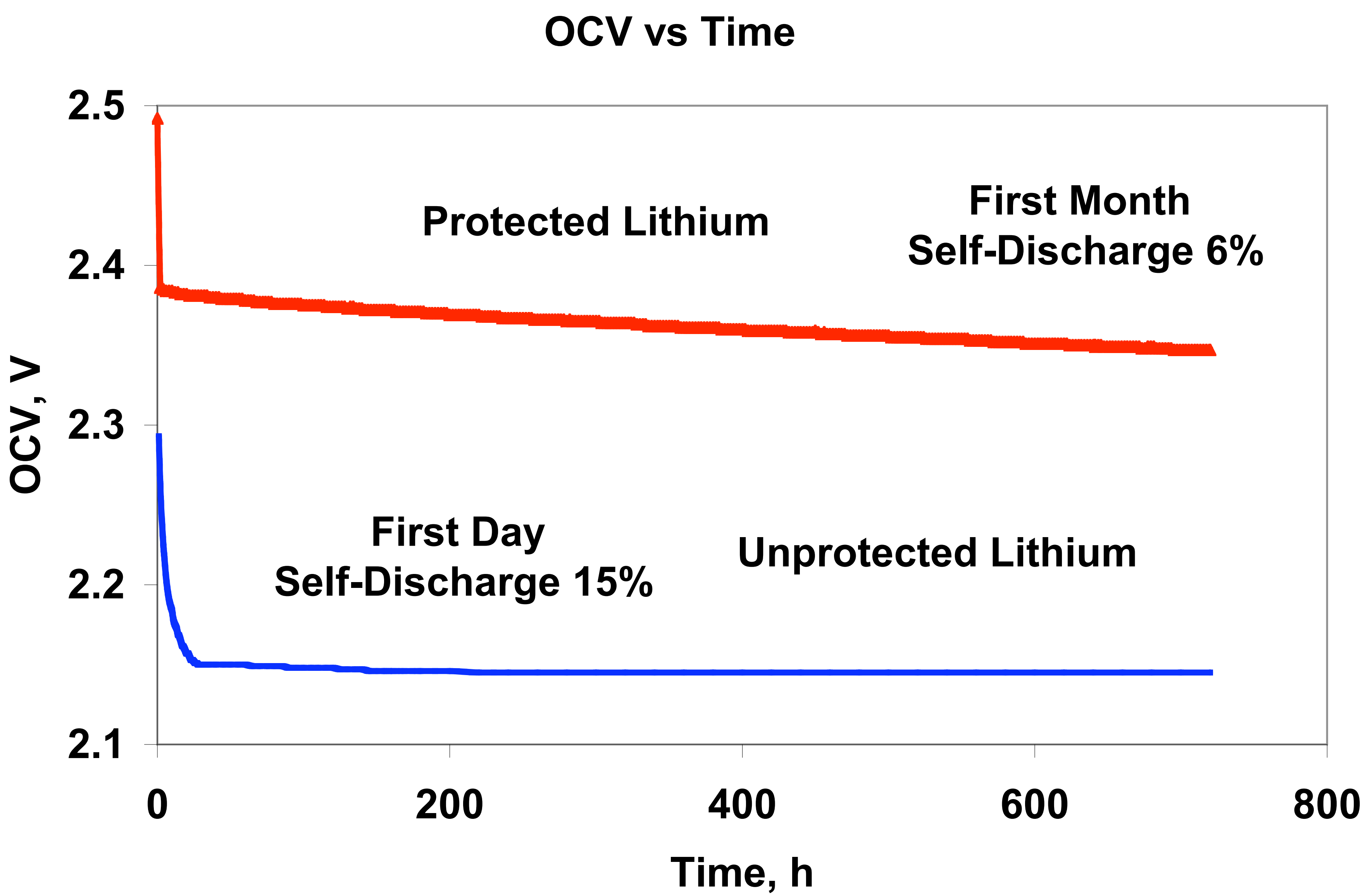


Charge and discharge profiles for cells with strong lithium protection.



Newly discovered shuttle inhibitors allowed us to control shuttle and achieve 100% of high plateau sulfur utilization and 350Wh/kg

SION POWER


OCV vs Time
2.5
2.4
2.3
2.2
2.1
OCV, V
Protected Lithium
First Month
Self-Discharge 6%
First Day
Self-Discharge 15%
Unprotected Lithium
0
200
400
600
800
Time, h

SION POWER

Very strong shuttle.

No charge voltage termination

Partially inhibited shuttle.

Charge voltage termination

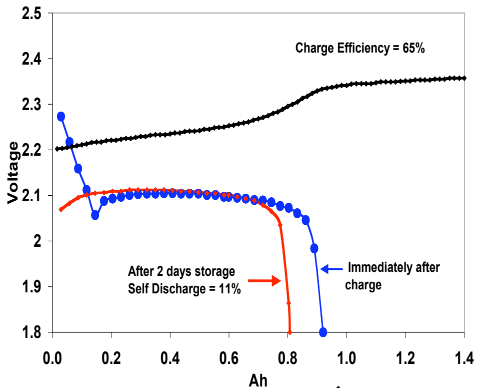
High self-discharge

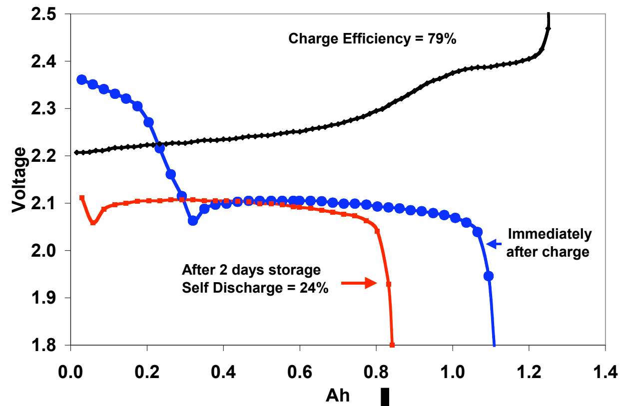
Completely inhibited shuttle.

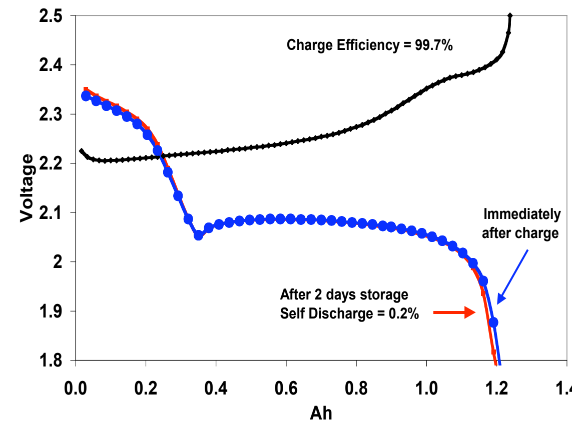
Charge voltage termination

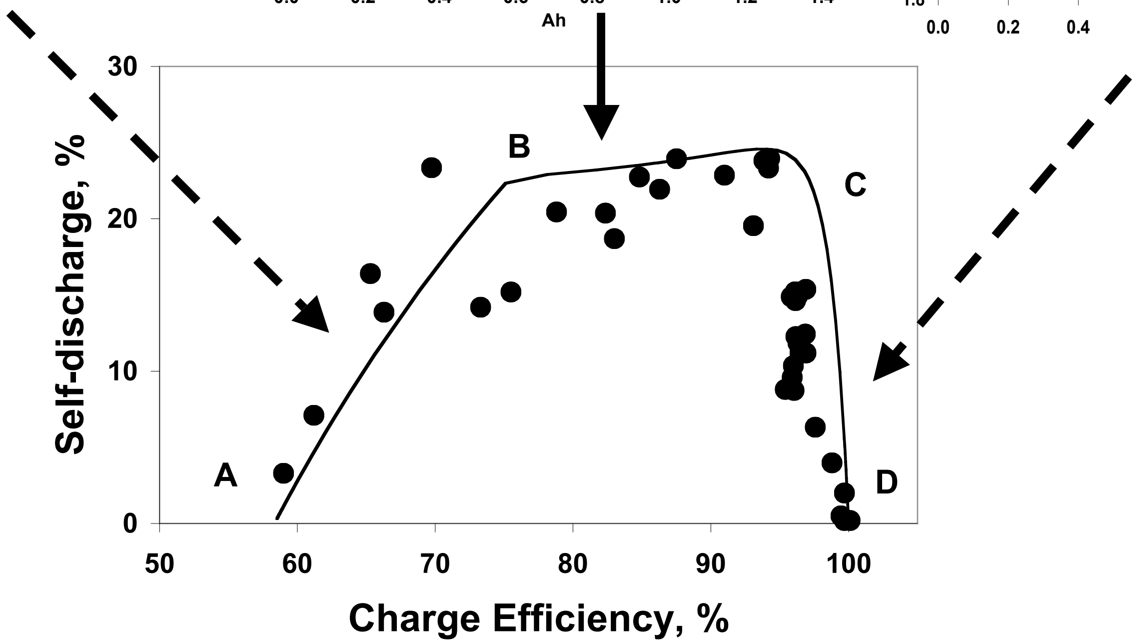
High charge efficiency

Low self-discharge





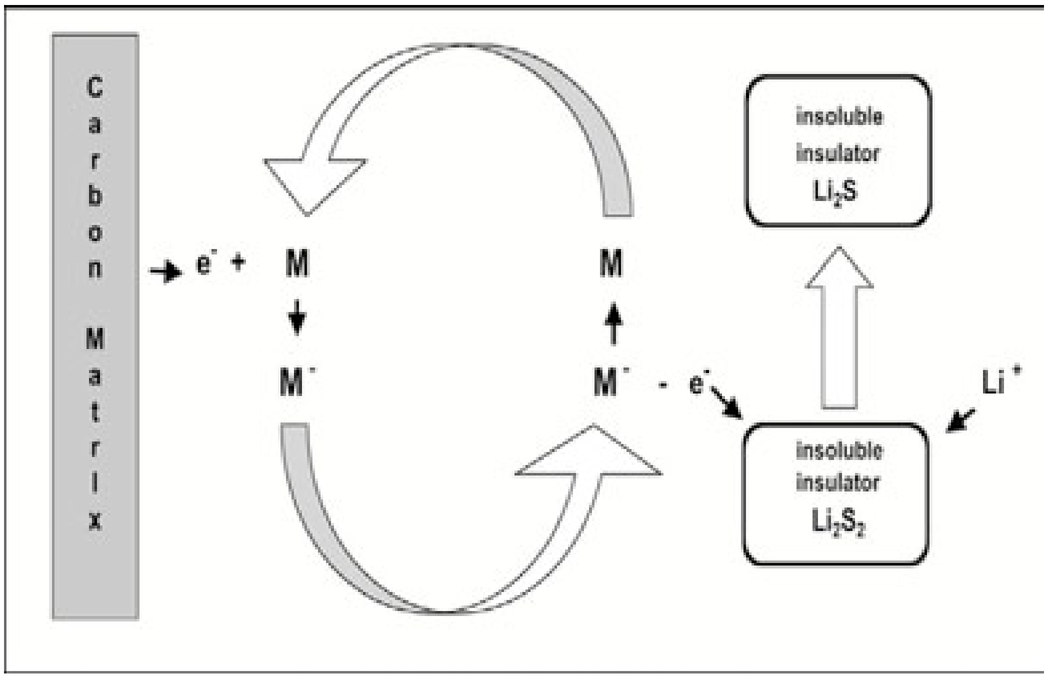




SION POWER

Increasing sulfur utilization at Low discharge plateau

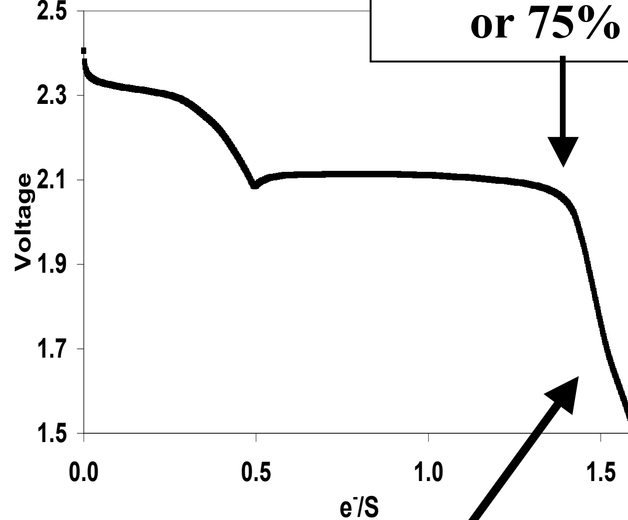
The sulfur cathode internal shuttle mechanism with Red-Ox mediator (M)



$$S_2^{2-} + 2e^- = 2S^{2-}$$

1256 mAh/g

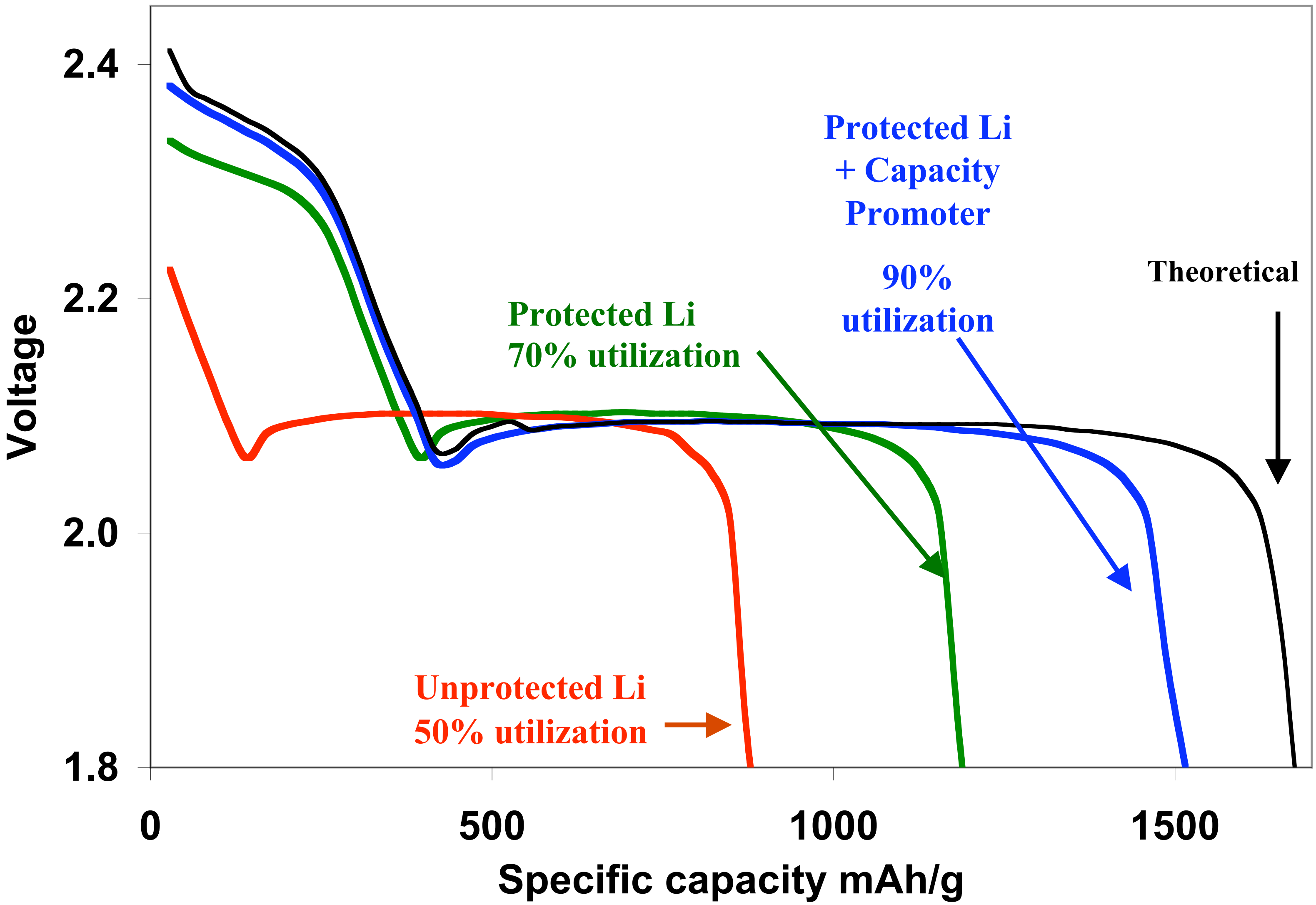
or 75%



Sub-Low plateau – very slow kinetics.

Discharge stops with insoluble Li_2S_2

Sion Power Li/S cells specific capacity evolution



SION POWER

Sion Power Li-S Rechargeable Cells

Weight 14 - 16 g

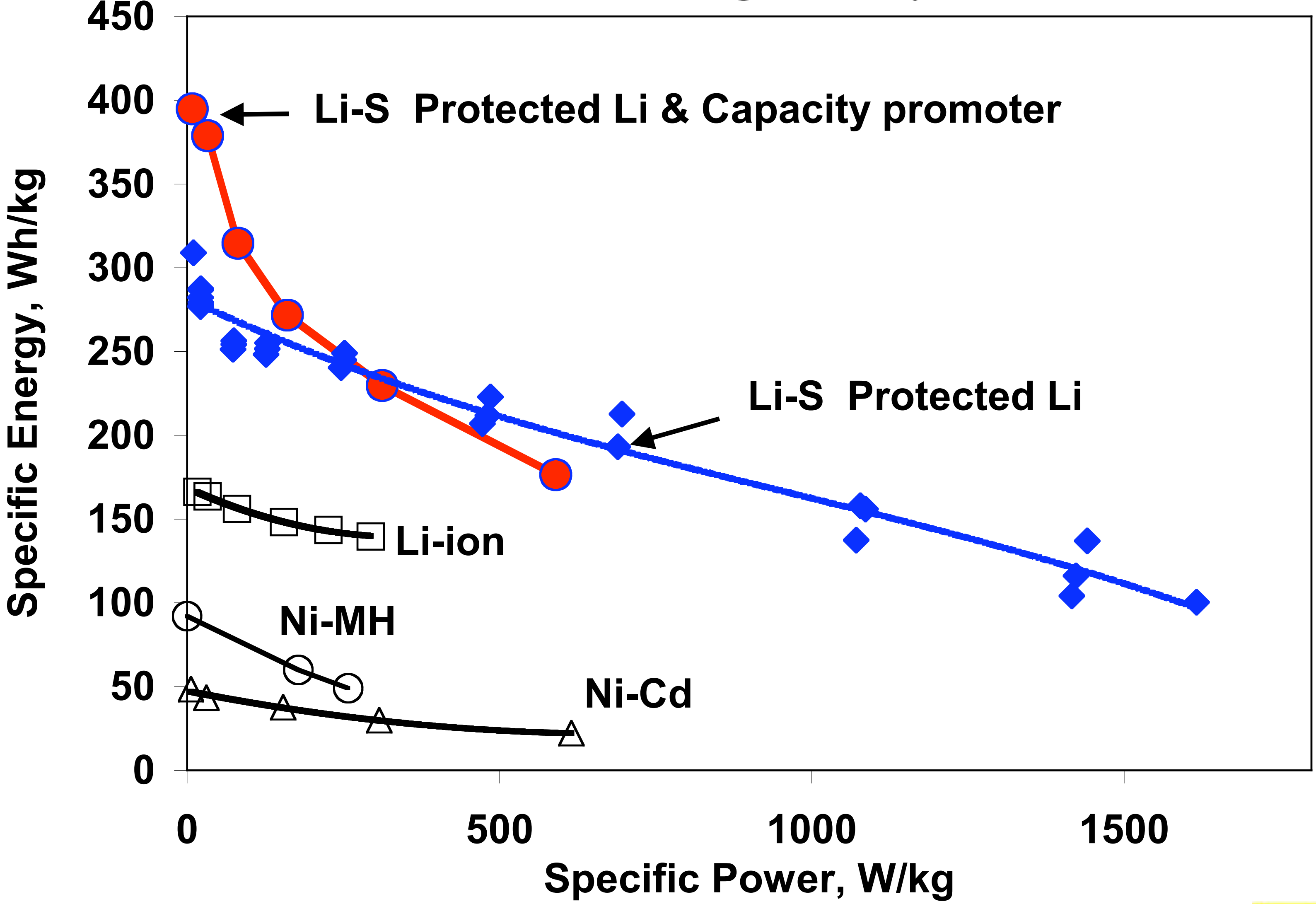
Dimensions 52 x 38 x 10 mm

Capacity 2.4 – 2.8 Ah

Voltage 2.1 V

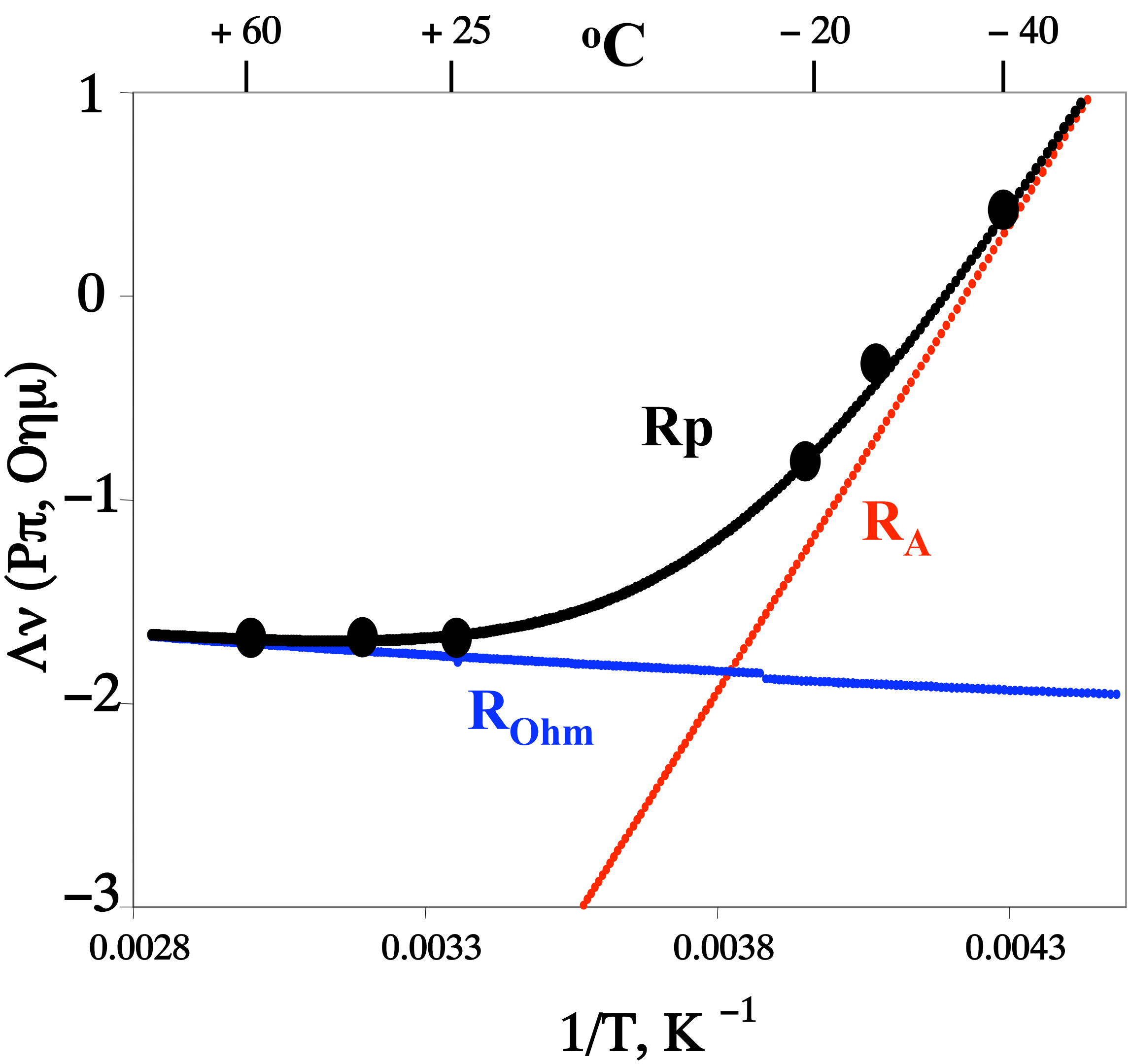
Specific energy 350 - 380 Wh/kg

Ragone plots for different rechargeable systems



SION POWER

Arrhenius plots for cell polarization resistance R_p



$R_p = dV/dI =$

$= R^o_A * \exp(Q/kT) + R_{Ohm}(1+r*T)$

At room temperature the electrochemical processes became so fast that construction materials not chemistry control the polarization resistance.

Conclusion:

•Polysulfide shuttle understanding and control through shuttle inhibitors lead to:

- sulfur utilization 75% and 350 Wh/kg

- charge efficiency ~99.7%

- self-discharge ~ 4-6% per month

•Low plateau discharge limitations understanding and improvement with homogeneous catalysts lead to 85-90% of sulfur utilization and paves the way achieving 450 Wh/kg.

Areas of continuing developing:

•Increase cycle life

•Extend temperature range

•Increase rate capability

SION POWER


SION
POWER
TM