Performance Assessment of Prototype Lithium-Sulfur Cells from Oxis Energy

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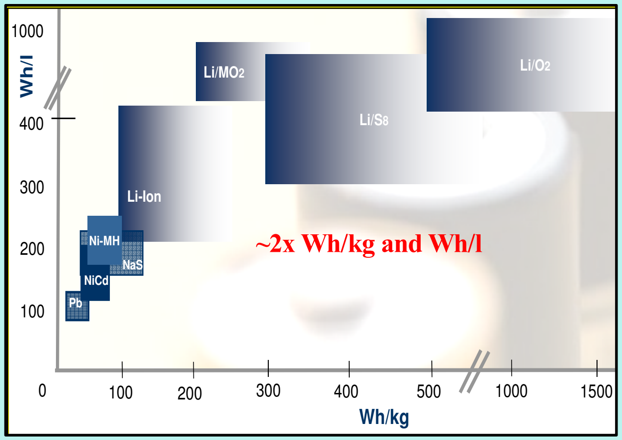
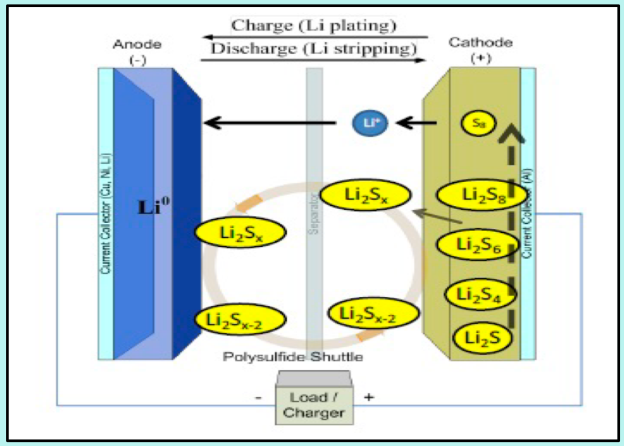
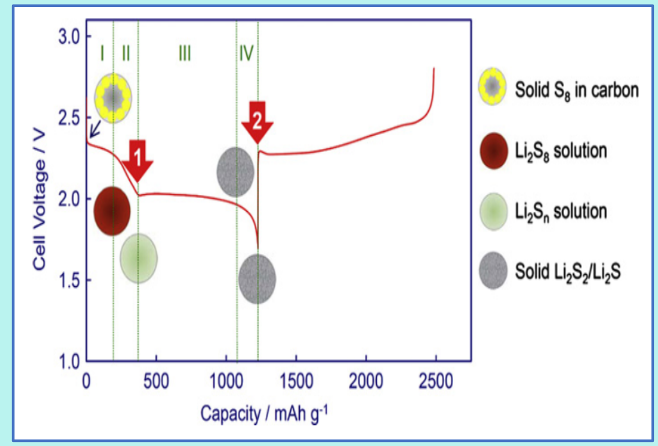
Li-S Cell Chemistry

Technology Challenges



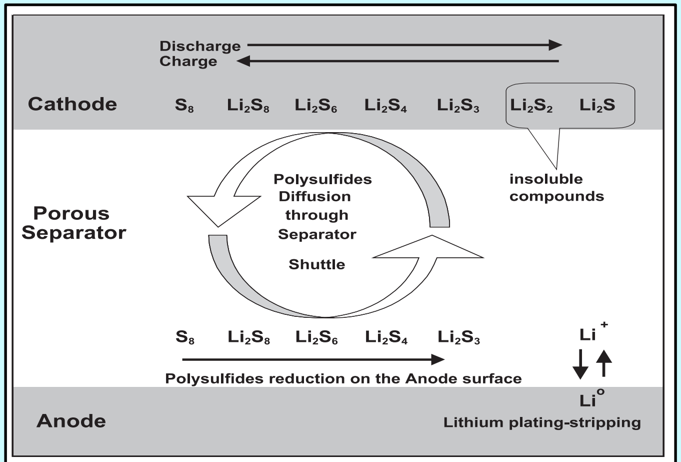




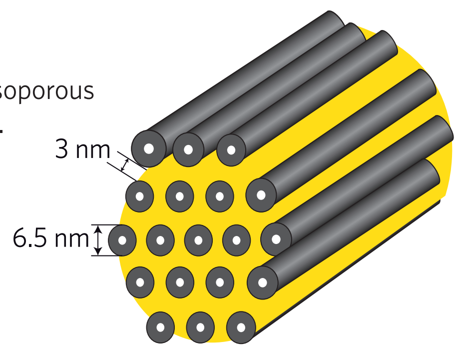
- High capacity of 1670 vs. <300 mAh/g for Li-ion cathodes;
- High theoretical Sp. energy of 2567 vs ~1200 Wh/kg for Li-ion

- Intermediate discharge products (polysulfide species) are soluble in most organic electrolyte systems
- Polysulfide species can react with anode forming redox shuttle
- Affects cycle life and coulombic efficiency and increases anode interfacial impedance
- Essential to extract full capacity from cathode

Approaches to Mitigate Sulfide Shuttle



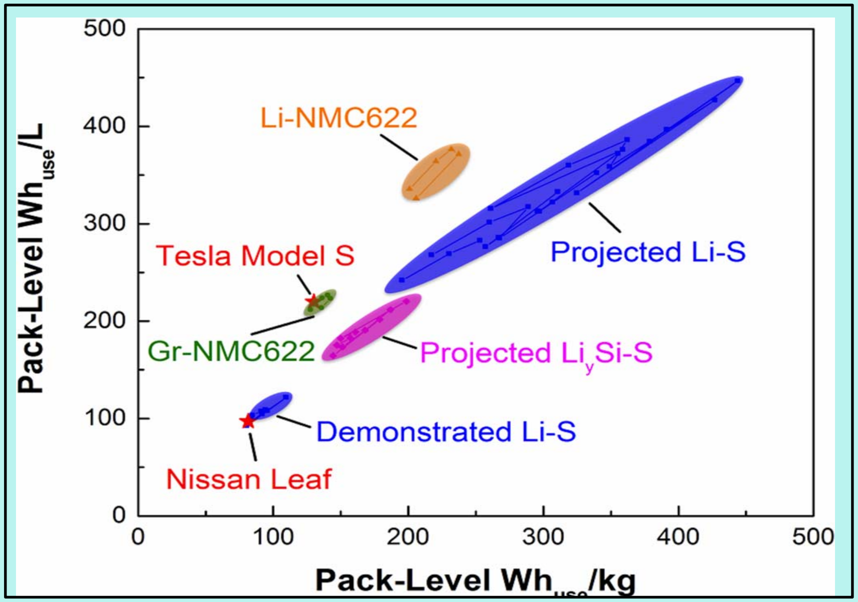
Trap discharge products in mesoporous carbon cathode.

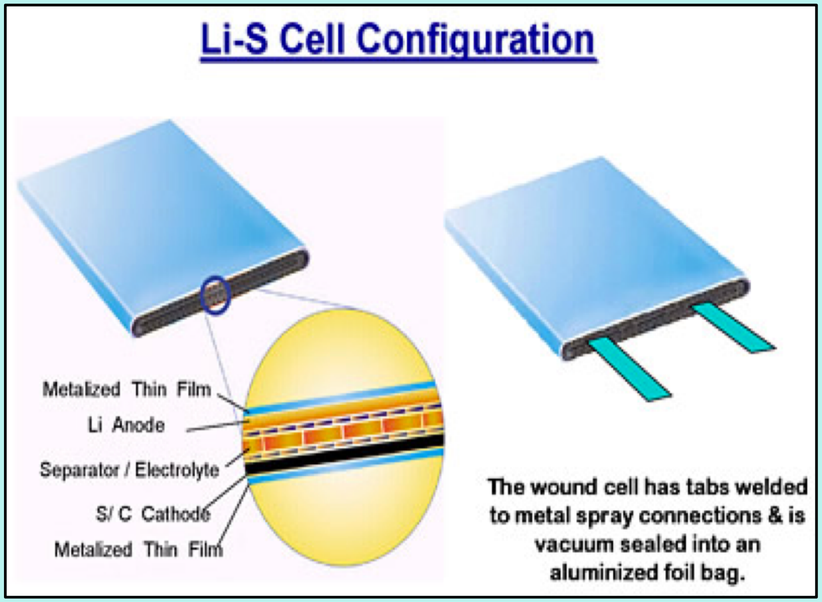


Component	Problems	Strategies Adopted
S cathode	Polysulfide dissolution-and Shuttle	Hierarchally-porous carbon (HPC) host
		Immobilize polysulfide in carbon host matrix
		Use sulfide (discharge product) as cathode
	Sulfur Passiavtion	Use sulfide (discharge product) as cathode
Li anode	Poor cyclabaility and dendrites	Coat with protecting layer (polymer or solid electrolyte)
Electrolyte	Soluble sulfides affecting performance	Organic electrolyte with additives (e.g. $LiNO_3$, P_2S_5)
		Ionic liquid electrolyte
		Solid-state electrolyte
Other components	Soluble sulfides affecting performance	Carbon, V_2O_5 (MnO_2) interlayers

- Some of these approaches have shown improved cycle life, but only with low sulfur loadings (2-3 mg/cm^2)

State of Art Li-S cells





- Low experimental energy density due to low sulfur loading (1-2 mg/cm^2)
- High loading (7mg/cm^2) --> 400 h/kg, which is the objective here

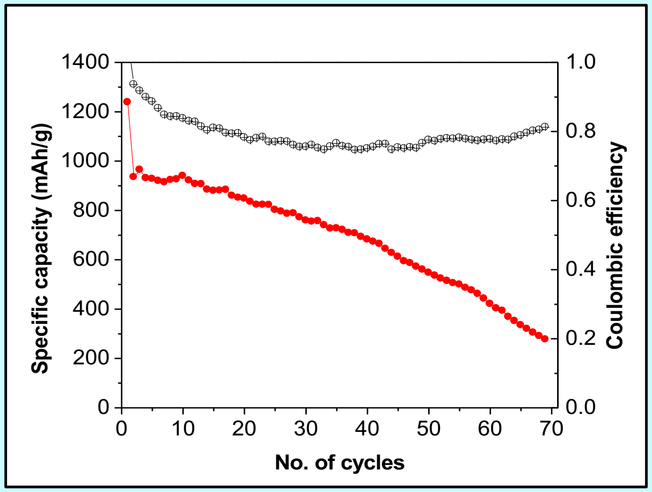
- Current developmental cells are pouch cells with 250-400 WH/kg.
- Higher Wh/kg will lower cycle life

Design Considerations for a 400 Wh/kg Li-S cell

Cathode Loading

- Cathode loading in a Li-ion cell (nickel cobalt aluminum oxide, NCA): ~15 mg/cm^2, i.e., ~2.23 mAh/cm^2 or 8.9 mWh/cm^2 per side
- For 400 Wh/kg, i.e.,1.5 times the specific energy vs. Li-ion cells, i.e., 13 mWh/cm^2 per side.
  - With a voltage of 2.1 V for Li-S cell, this implies an areal capacity of ~6.2 mAh/cm^2 for the sulfur cathode.
  - With 800 mAh/g from sulfur (and with a composition of 65% sulfur), the required loading is 12 mg/cm^2.
- Almost all reports of Li-S cells in the literature describe performance of sulfur cathodes with a low loading of < 5mg/cm^2 (mostly 2-3 mg.cm^{-2}) and/or with low proportion of sulfur in the cathode.
- Projected pack-level Wh/kg and Wh/l for a 100 kWh, 80 kW and 360 V Li-S battery with higher loadings (>8 mAh/cm^2 and 7 mg S/cm^2) vs. estimated from demonstrated cell performance (~2.5 mAh/cm^2 and 2 mg S/cm^2) (Gallagher et al JECS, 162 (6) A982-A990 (2015))
- Electrolyte content needs to be reduced to 4-5 ml/g (currently 9-13 ml/g of S)

S: C: PVDF (55: 40:5) 6 mg/cm^2
1.0MLiTFSI+ DME (Dimethoxy Ethane) +DOL (Dioxolane) (95:5) with a Carbon Cloth



- Lower capacity and utilization of sulfur in thicker cathode
- With denser sulfur cathodes, more polysulfides are expected to dissolve

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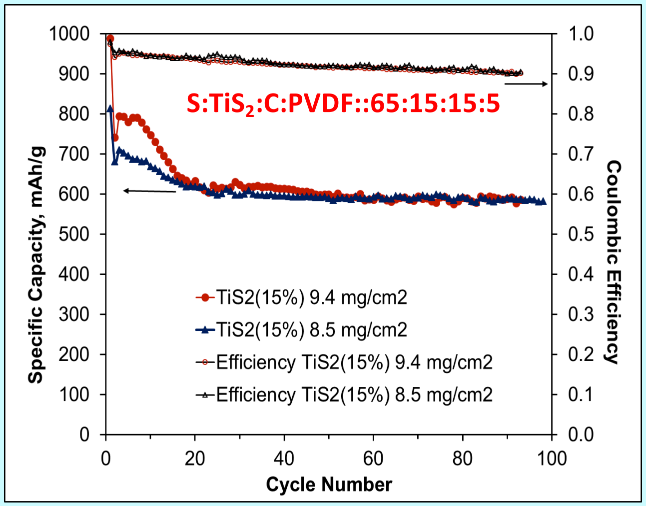
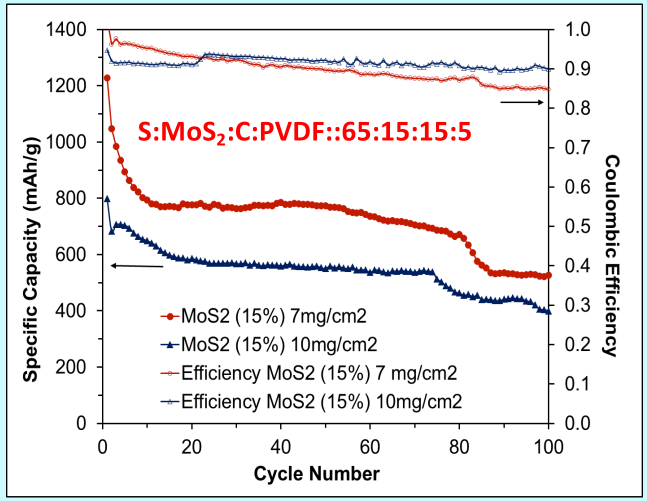
Long-Life and High Energy Li-S Battery for NASA and DoD Applications

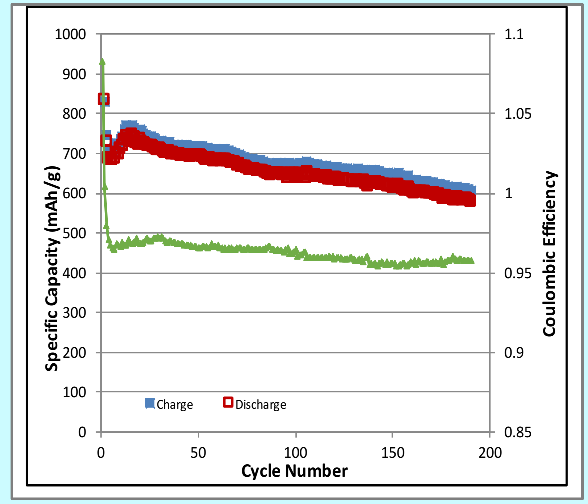
(Funded by US Army- CERDEC)

Sulfur Cathodes with High loadings (9 mg/cm^2) and high proportion (65%)





AlF$_3$-coated separators



- **Area specific capacity is 8 mAh/cm² (3-4Xof Li-ion)**

Our Approach:

- New sulfur cathodes with transition metal sulfide blends (MoS_2 and TiS_2) with sulfur cathode and/or with the coatings of metal sulfides.
- Ceramic-coated separators as Polysulfide Blocking Layers to minimize the crossover of polysulfides
- Protected Li anode with a thin coating of AlF3 by Atomic Layer Deposition or various polymer electrolyte coatings
- New electrolytes which minimize polysulfide-related shuttle effects and promote sulfur kinetics (Solvated or concentrated electrolytes)

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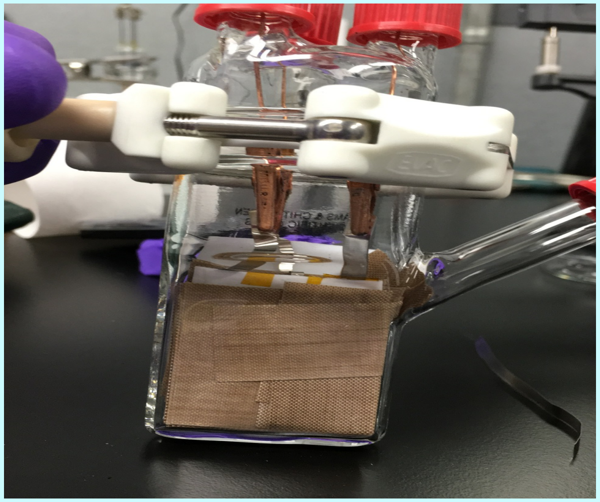
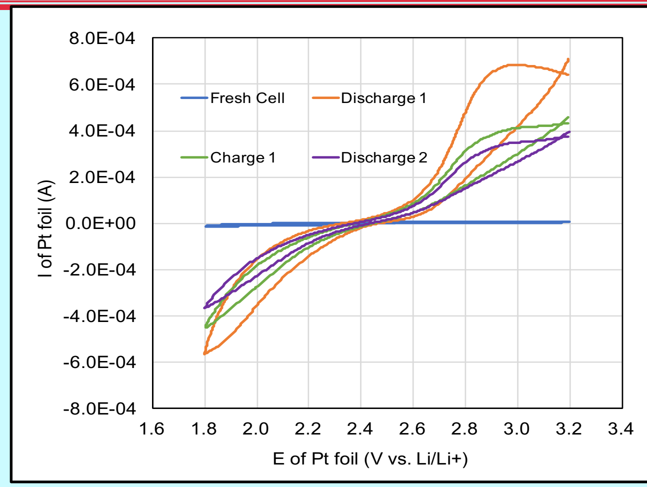
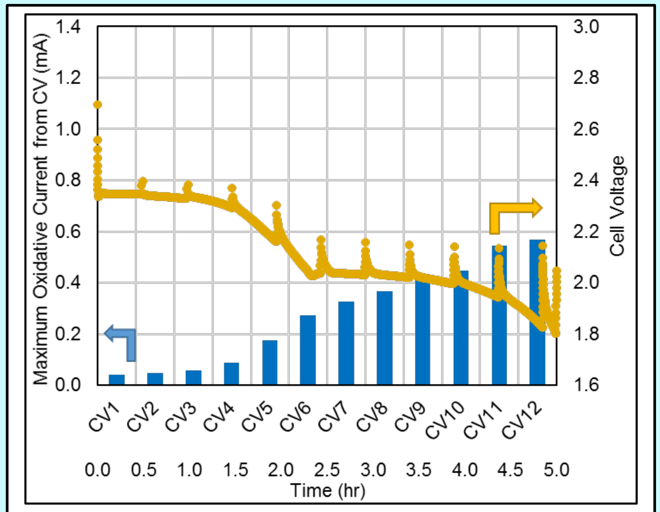
Four-Electrode Li-S cells for Polysulfide Estimation

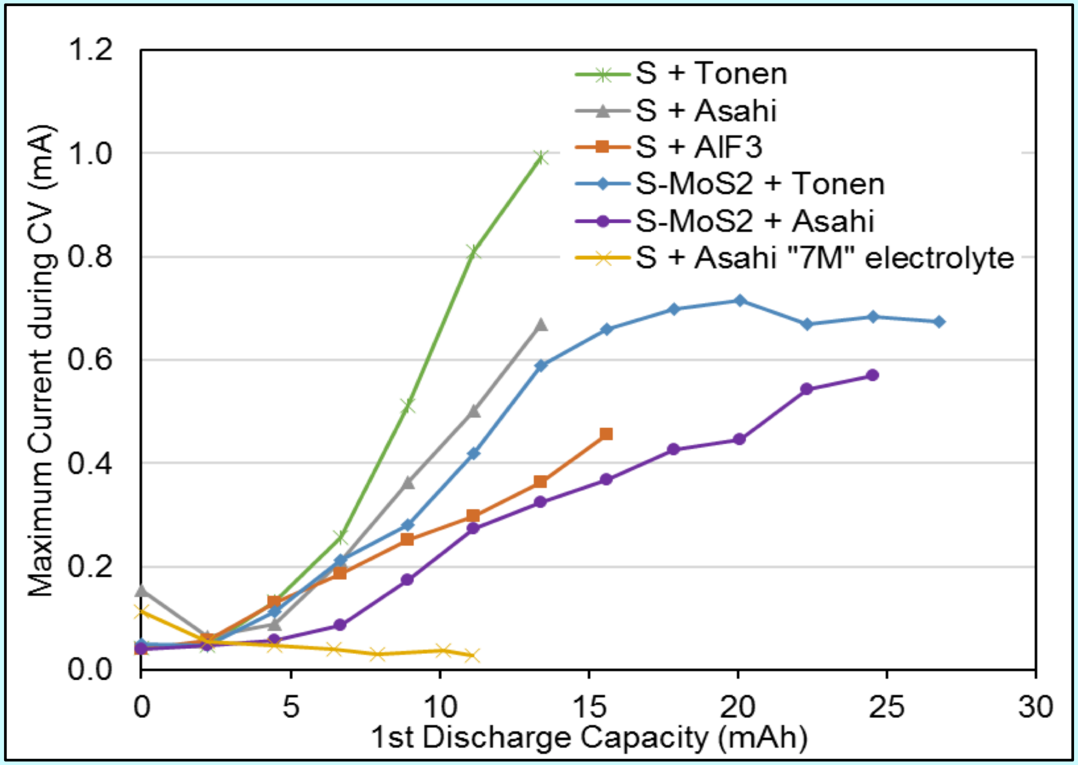


- Four-electrode glass prismatic cell to quantify polysulfides through cyclic voltammetry (right)





Comparison of Polysulfides with different separators/cathodes



- Polysulfides estimated from CV: S + Tonen > S + Asahi > S+MoS_2 + Tonen > S+MoS_2 +Asahi > S + Asahi + 7M salt
- Cycle life follows the inverse trend
- Published in the J. Phys. Chem. Lett.

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Status of Sion Power Li-S Technology

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

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

TABLE I. USABC Long Term Goals for Advanced Batteries for EVs vs Sion Power Baseline Battery.

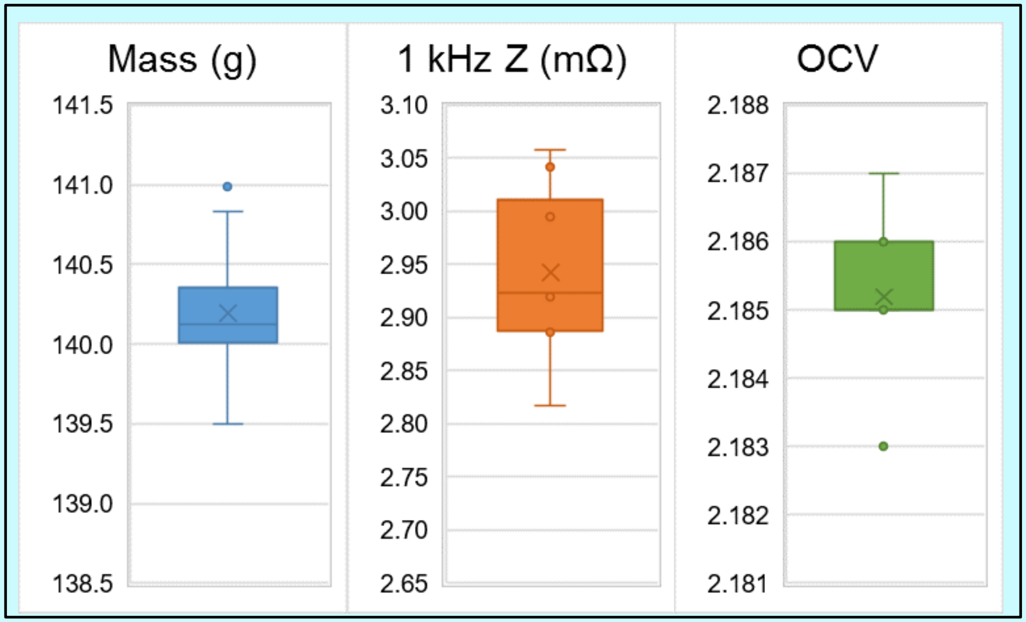
Parameter (Units) of fully burdened system	USABC Long Term Goals	Sion Power Battery
Power Density (W/L)	600	1500
Specific Power-Discharge, 80% DOD/30sec (W/kg)	400	1500
Energy Density (Wh/L)	300	320
Specific Energy (Wh/kg)	200	350
Specific Power/Specific Energy Ratio	2:1	4:1
Normal Recharge Time	3 to 6 hours	6 to 8 hours
Continuous Discharge in 1 hour (% of rated capacity)	75	90
Cycle Life – 80% DOD (Cycles)	1000	30 - 60
Operating Environment (^oC)	- 40 to +85	- 40 to +50

- Developed protective coating for Li anode and are now interested in Li-MOx chemistries

Oxis Energy: "Ultralight" pouch cells

Ultra Light POA0343 cells (300 Wh/kg)

Cell ID	Mass (g)	1 kHz Z (mΩ)	OCV
AH260917-1	140.131	3.042	2.187
AH260917-2	139.500	3.001	2.185
AH260917-3	140.195	2.995	2.185
AH260917-4	140.105	2.920	2.185
AH260917-5	140.832	3.058	2.186
BM260917-1	139.809	2.817	2.185
BM260917-2	140.179	2.886	2.183
BM260917-3	140.078	2.888	2.185
BM260917-4	140.115	2.893	2.185
BM260917-5	140.989	2.927	2.186
Average:	140.193	2.943	2.185
Stdev:	0.412	0.074	0.001



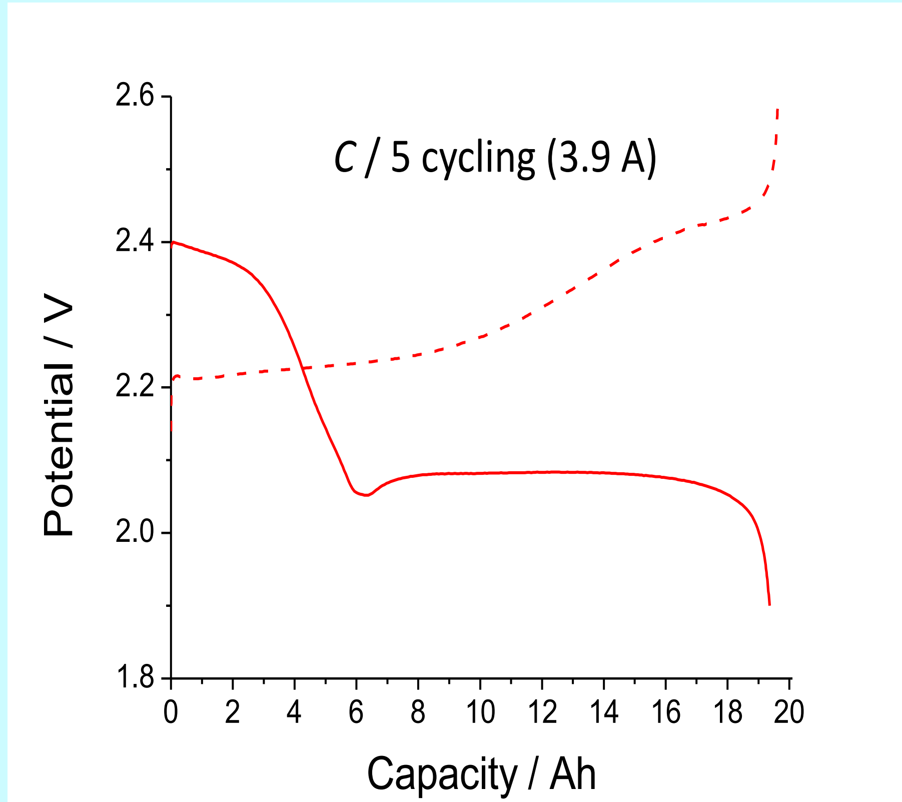
Oxis Energy: "Ultralight" pouch cells

~140g, 19.5 Ah

Self-discharge during stand test at 20 °C

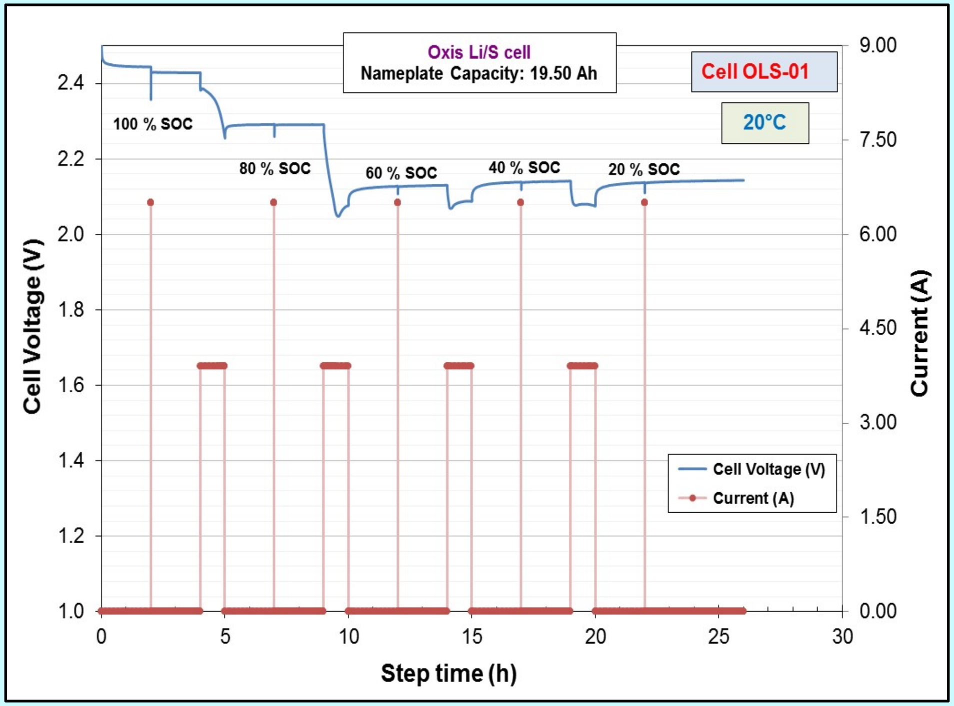
Characteristic	OLS-03	OLS-04
Initial capacity (Ah)	19.08	19.01
Capacity after 1 week (Ah)	17.03	16.75
Self-discharge (%)	10.8%	11.9%

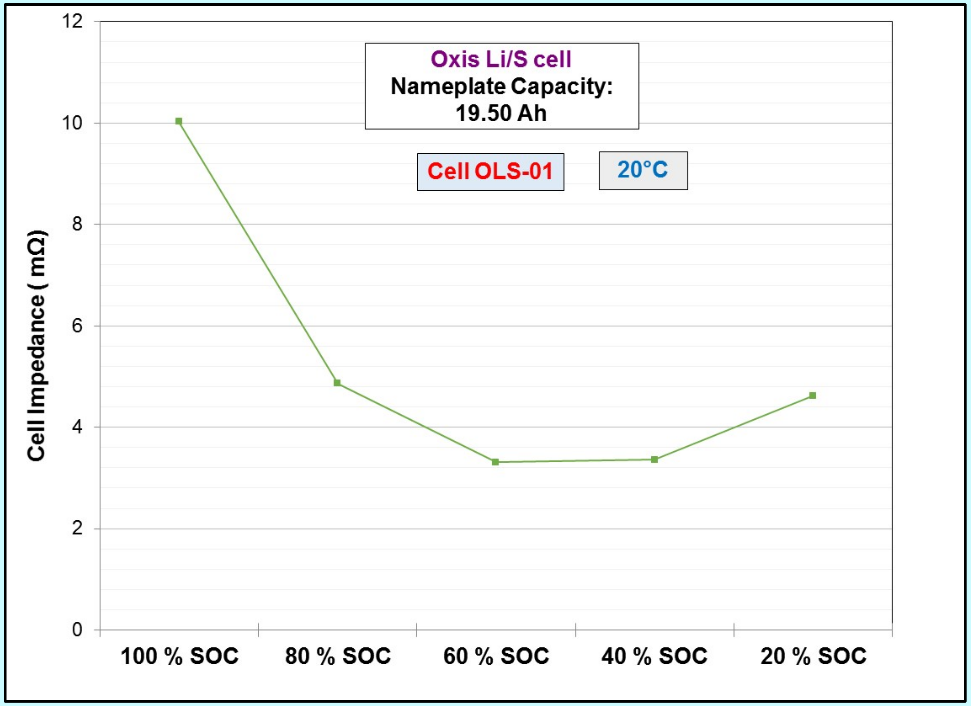
- ~11% self-discharge after 1 week standing at full charge, 20 °C



~300 Wh/kg on first cycle

DC impedance at 20 ^oC



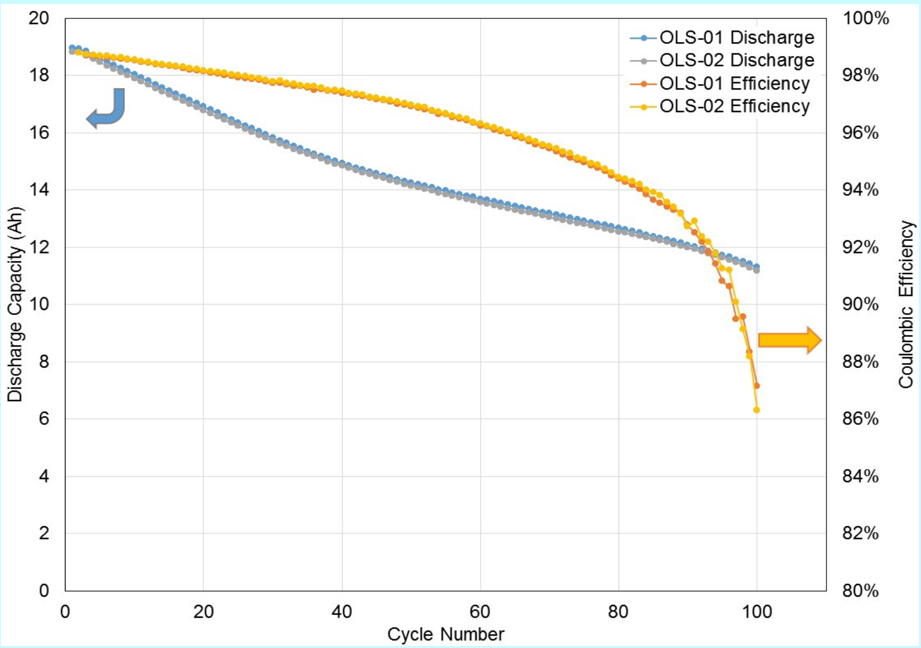


C / 3 pulses (6.5 A)

Cycling performance at 20 °C

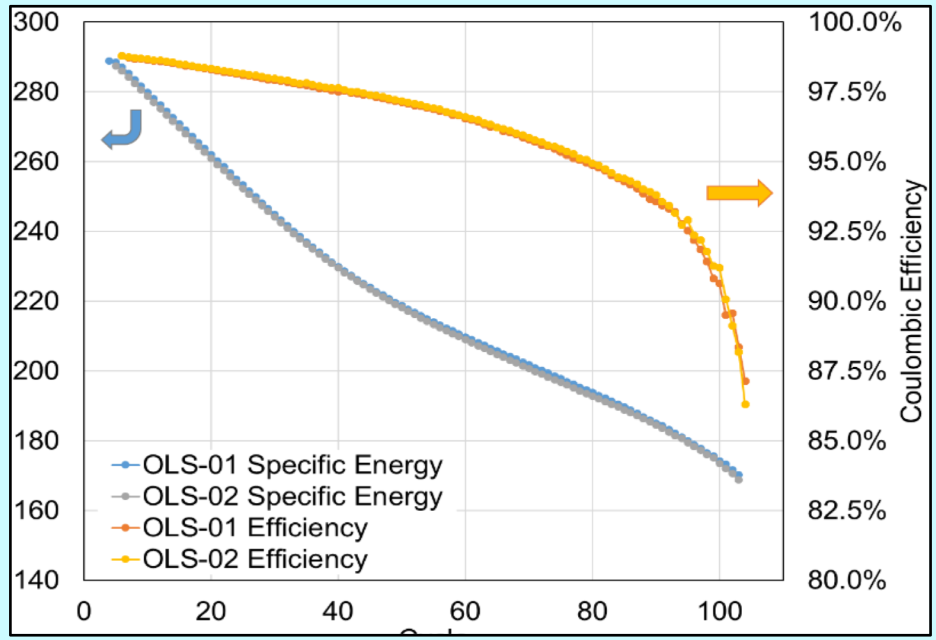
3.9 A cycling (C/5)

Capacity



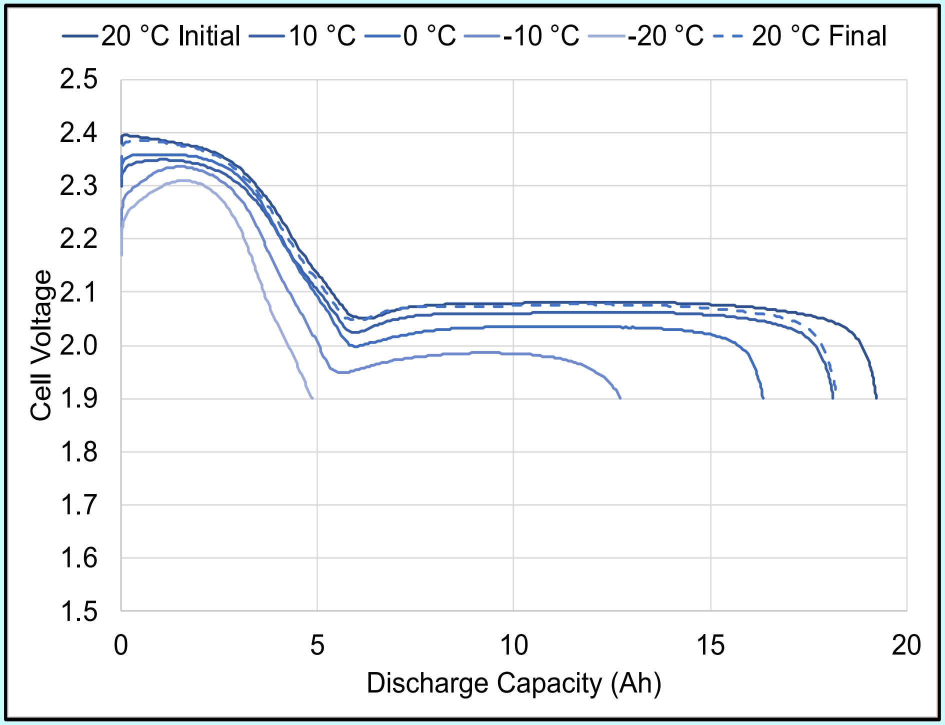
Fade ~70 mAh/cycle, 0.4%

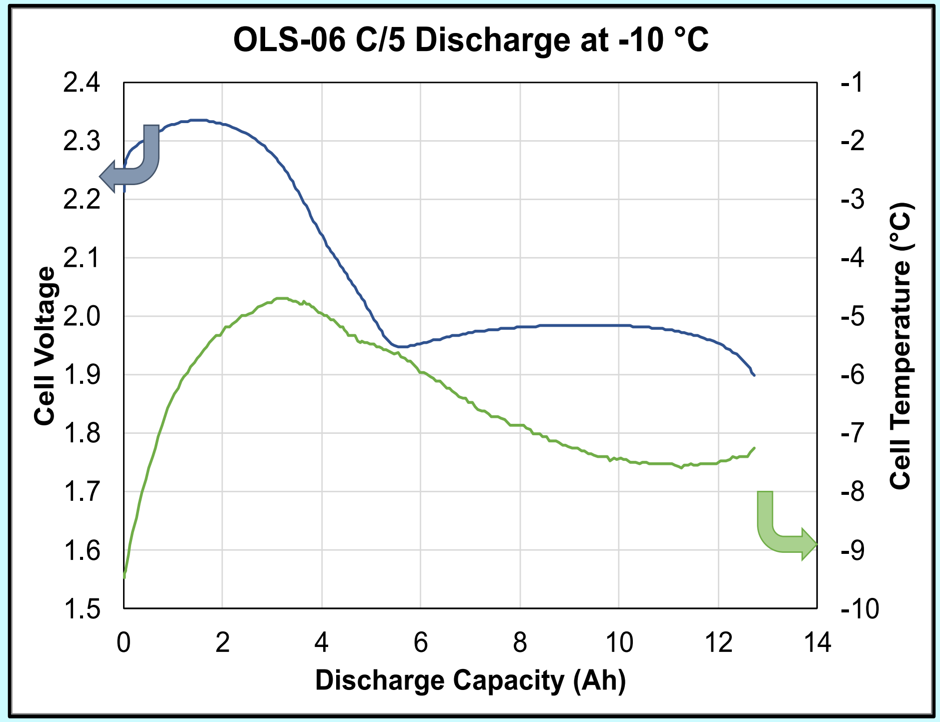
Specific Energy



~170 Wh/kg after 100 cycles

Variable-temperature discharge capacity

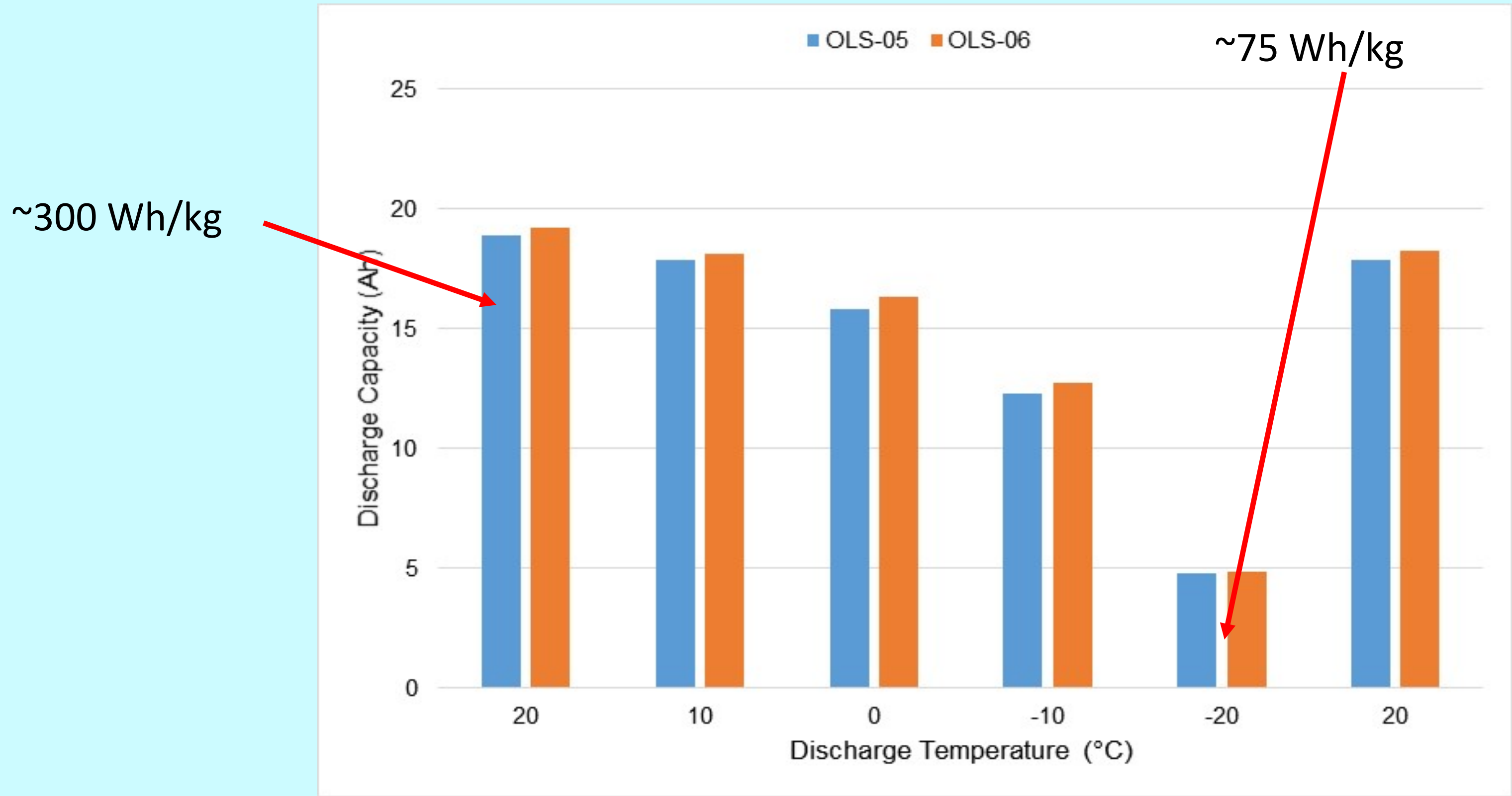




- Lower capacities at low temperature (reduced plateau)
- Noticeable heat dissipation at low temperatures

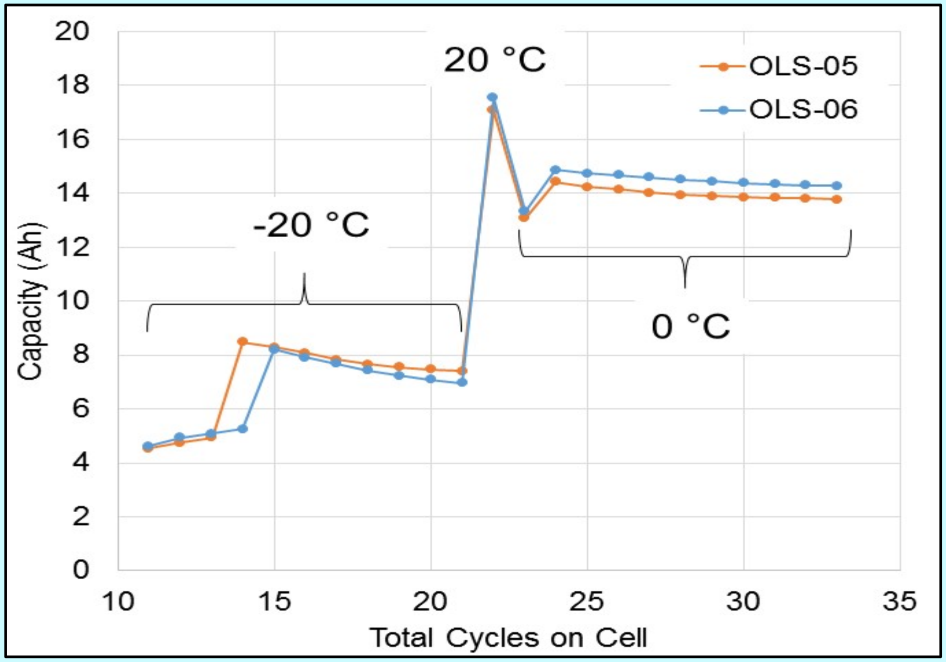
Variable-temperature discharge capacity

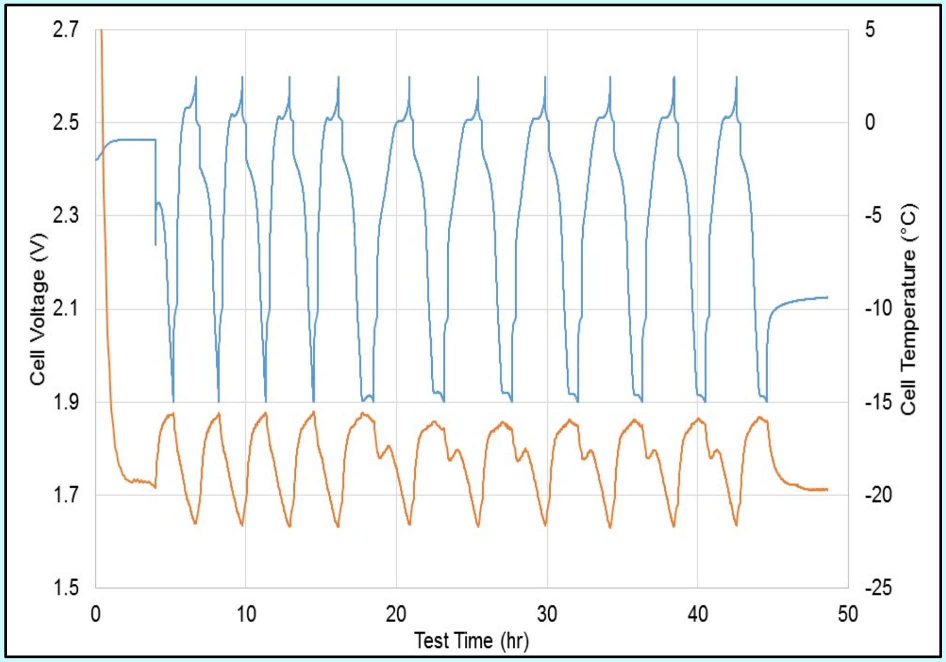
3.9 A cycling (C/5)



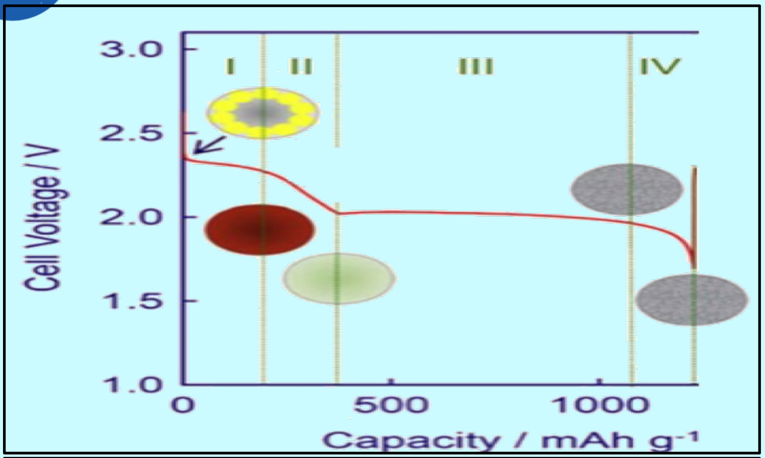
Variable-temperature cycling and thermal profile

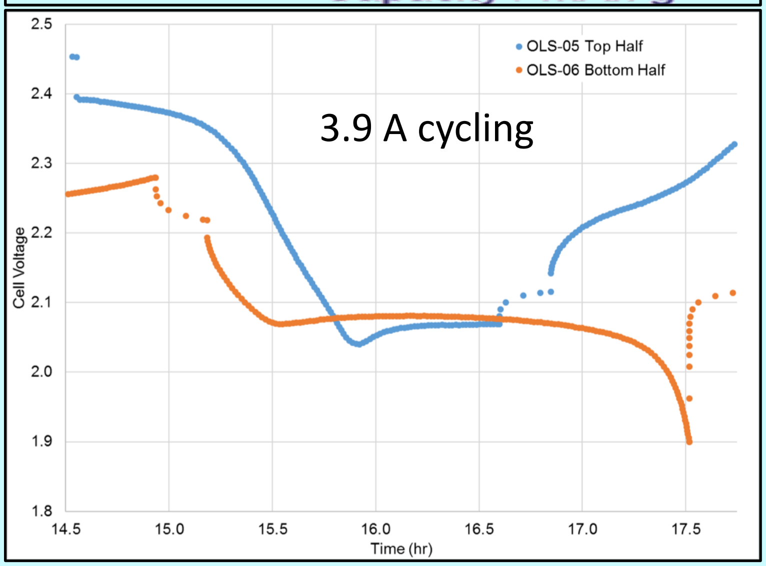
3.9 A cycling



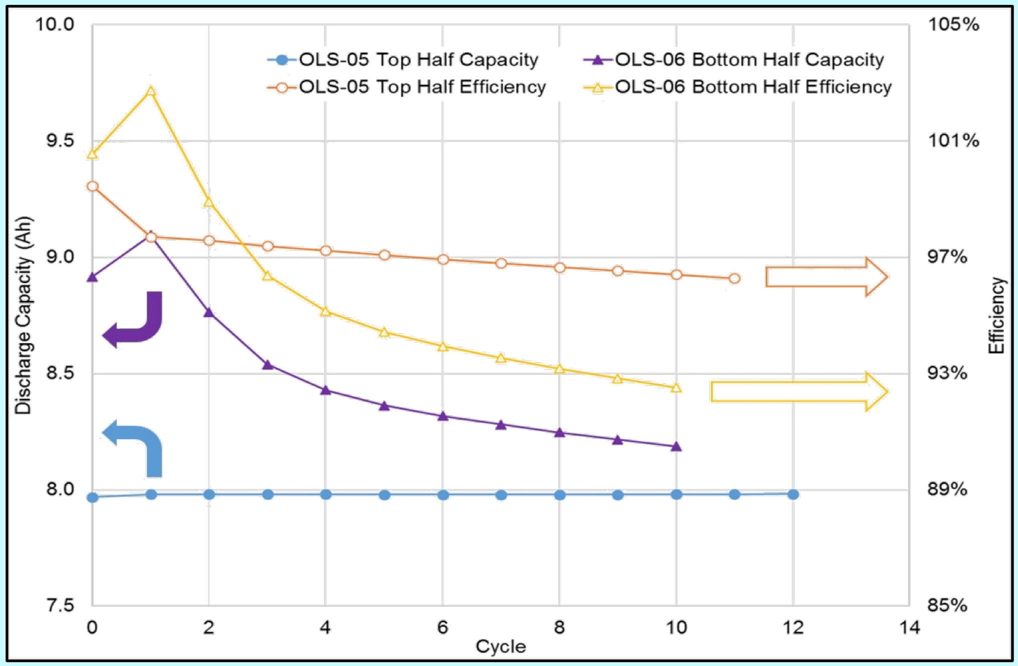


Variable-DoD Cycling





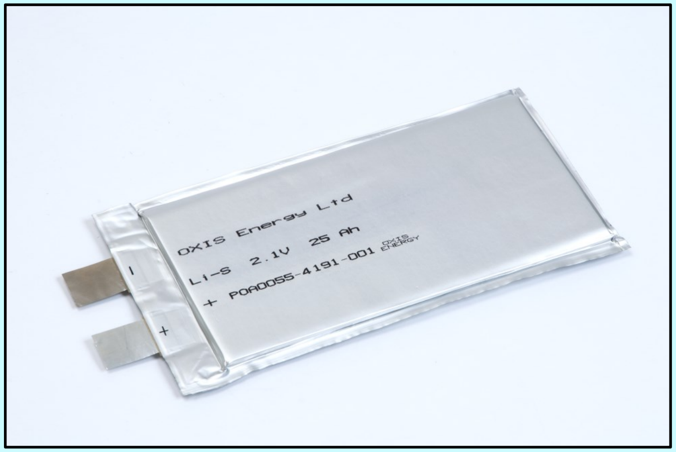
- Capacity is very flat for “top half” cycling due to discharge energy limits
- Efficiency drops rapidly for “bottom half” cycling



Conclusions

- Metal sulfide incorporation and/or separator modification can improve sulfur utilization and cycling performance in laboratory cells.
- High area specific capacities are realized in sulfur cathode blended with metal sulfides, which can lead higher specific energies
- Oxis 19.5 Ah pouch cells have been characterized across a range of operating conditions
  - Initial specific Energy is 300 Wh/kg
  - Specific energy after 100 cycles is 170 Wh/kg
  - 100 cycles at 20^{o}C,
  - Low DC impedance
  - Low temperature performance is moderate
  - "Top" *vs*. "bottom" cycling (varying insoluble species: S_8 *vs*. Li_2S)
- Planning to procure the next version (350-400 Wh/kg) Oxis Energy cells for our evaluation

Oxis Next Gen Cells



Ultra Light Cell Technology Specifications

Type	High Power	High Energy
Part Number	POA0343	POA0412
Availability	Evaluation Sample	
Operating Voltage (V)	1.9-2.6	
Nominal Voltage (V)	2.1	
Typical Capacity (Ah) 0.2C discharge at 20°C to 1.9V	19.5	14.7
Gravimetric Energy (Wh/kg)	300*	400**
Max. Peak Discharge (C) <30s, 50% SoC, 20°C	6	3
Max. Continuous Discharge (C)***	2	1
Max. Charge Rate (Hours)	4	
Cycle Life (Cycles) 100% DoD****, 80% BoL	80-100	60-100
Cycle Life (Cycles) 80% DoD, 60% BoL	~200	
Operating Temperature (°C)*****	0 to 30	
Storage Temperature (°C)	-30 to 30	
Pouch Format (mm) Length x width x thickness	151x118x10.5	145x78x10
Tab Dimensions (mm) Length x width x heigth	27x20x0.1	
Cell Weight (g)	137	85
Abuse Safety Testing	In-House to IEC62133 standard	

Key Features

- Extremely lightweight: >**400 Wh/kg** already proven
- Safe
- Full 100% Discharge Capability
- High Power type for Aviation and Automotive
- High Energy type for HAPS
- Bespoke cell sizes available

Acknowledgements

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