



High Energy Density Lithium/Sulfur Batteries for NASA and DoD Applications

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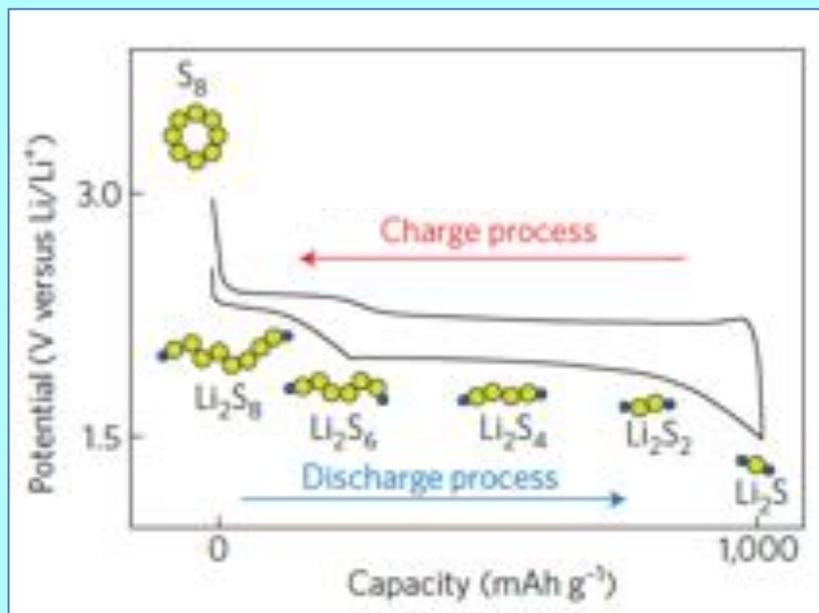
Phoenix, Arizona

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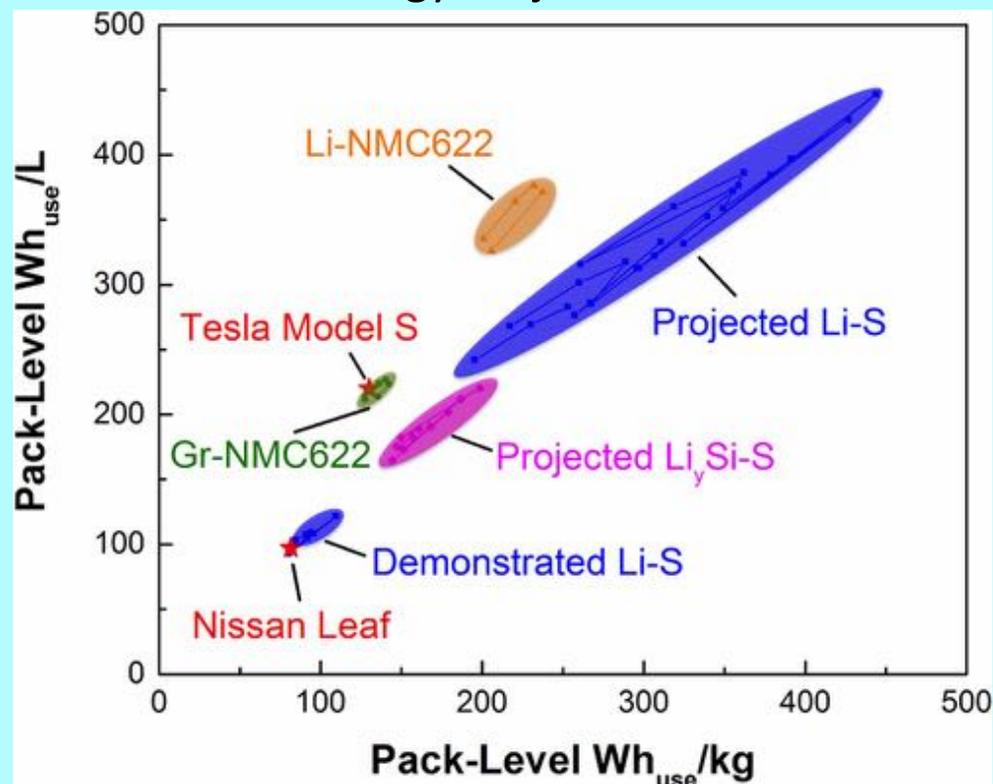
Why Lithium-Sulfur Batteries?

Sulfur Cathode



- High specific capacity of 1670 mAh/g; High theoretical specific energy of 2567 Wh/kg
- 250-400 Wh/kg realized in practical cells.
 - Higher specific energy cells have generally shorter cycle life

Energy Projections

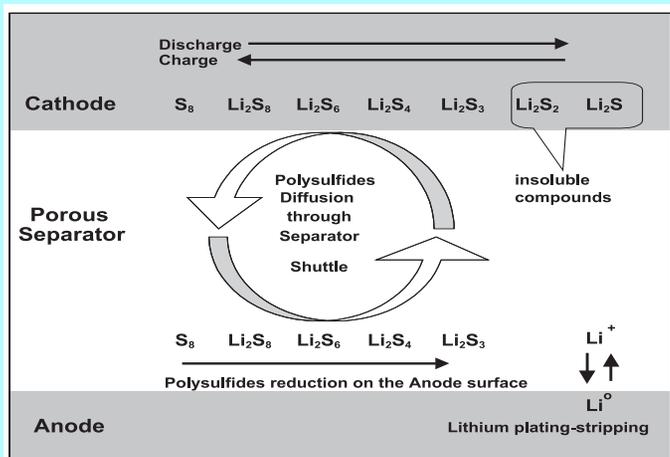


Projected pack-level Wh/kg and Wh/l for a 100 kWh, 80 kW and 360 V Li-S battery with higher loadings (>8 mAh/cm² and 7 mg S/cm²) vs. estimated from demonstrated cell performance (~2.5 mAh/cm² and 2 mg S/cm²)

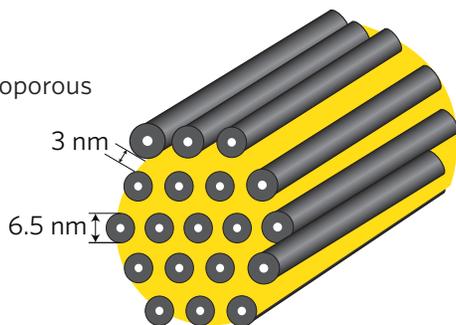
Gallagher et al J ECS, **162** (6) A982-A990 (2015)



Life-limiting Processes in a Li-S cell and the Mitigation Strategies



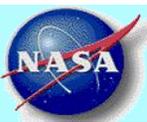
Trap discharge products in mesoporous carbon cathode.



- Anode passivation and dendrite formation.
- Sulfur expands by 79%
- Poor conductivity of S and its discharge products.
- Polysulfides are soluble in many solvents : Form Redox shuttle and insulating layer (Li_2S) on the anode

Problems	Strategies Adopted	Rationale
Poor cyclability and dendrites	Coat with protecting layer (solid electrolyte)	Blocks contact between Li and soluble sulfide species and/or mechanically inhibit Li dendrites
	Coat with protecting layer (gel polymer)	Li dendrites
Polysulfide dissolution, redox shuttle behavior	Immobilize in carbon host matrix	Strong S-C interactions trap sulfides (e.g. as S_n^{x-} chain-like species, as cyclo- S_8 allotrope does not fit inside pores)
	Use sulfide (discharge product) as cathode	Allows use of non-Li anodes
Poor Conductivity and expansion	Meso/microporous carbon support for S	High electronic conductivity of C mitigates poor S conductivity
Passivation	Use sulfide (discharge product) as cathode	Allows use of non-Li anodes
Soluble sulfides affecting anode stability and performance	Organic electrolyte with additives (e.g. $LiNO_3$, P_2S_5)	Good conductivity, additives react preferentially with sulfide species and passivate Li surface, depassivate cathode
	Ionic liquid electrolyte	Sulfides are insoluble in certain ionic liquids
	Solid-state electrolyte	Blocks contact between Li and soluble sulfide species and/or mechanically inhibit Li dendrites

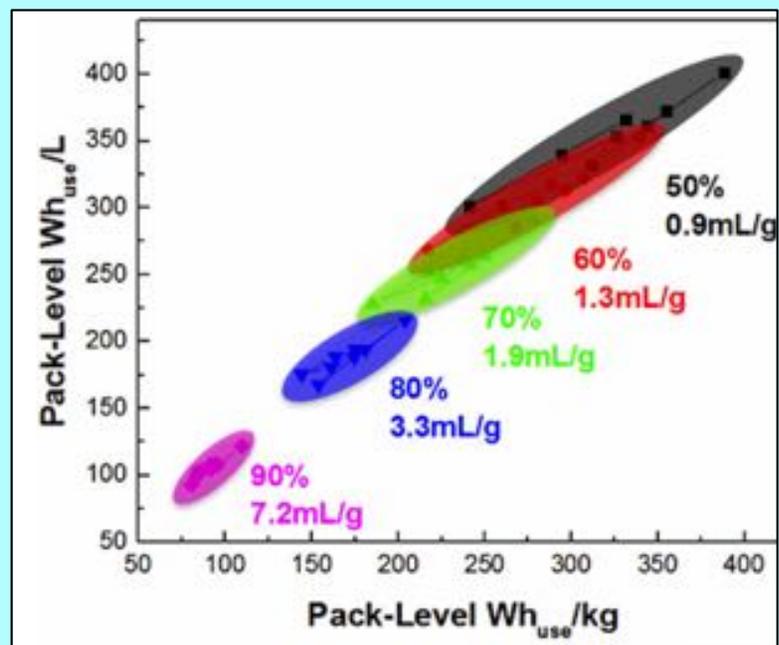
- **Some of these approaches have shown improved cycle life, but only with low sulfur loadings (2-3 mg/cm²)**



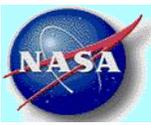
Design Considerations for a 400 Wh/kg Li-S cell

Cathode Loading

- Cathode loading in a Li-ion cell (nickel cobalt aluminum oxide, NCA): $\sim 15 \text{ mg/cm}^2$, i.e., $\sim 2.23 \text{ mAh/cm}^2$ 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 $\sim 6.2 \text{ mAh/cm}^2$ 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 $< 5 \text{ mg/cm}^2$ (mostly $2\text{-}3 \text{ mg}\cdot\text{cm}^{-2}$) and/or with low proportion of sulfur in the cathode.

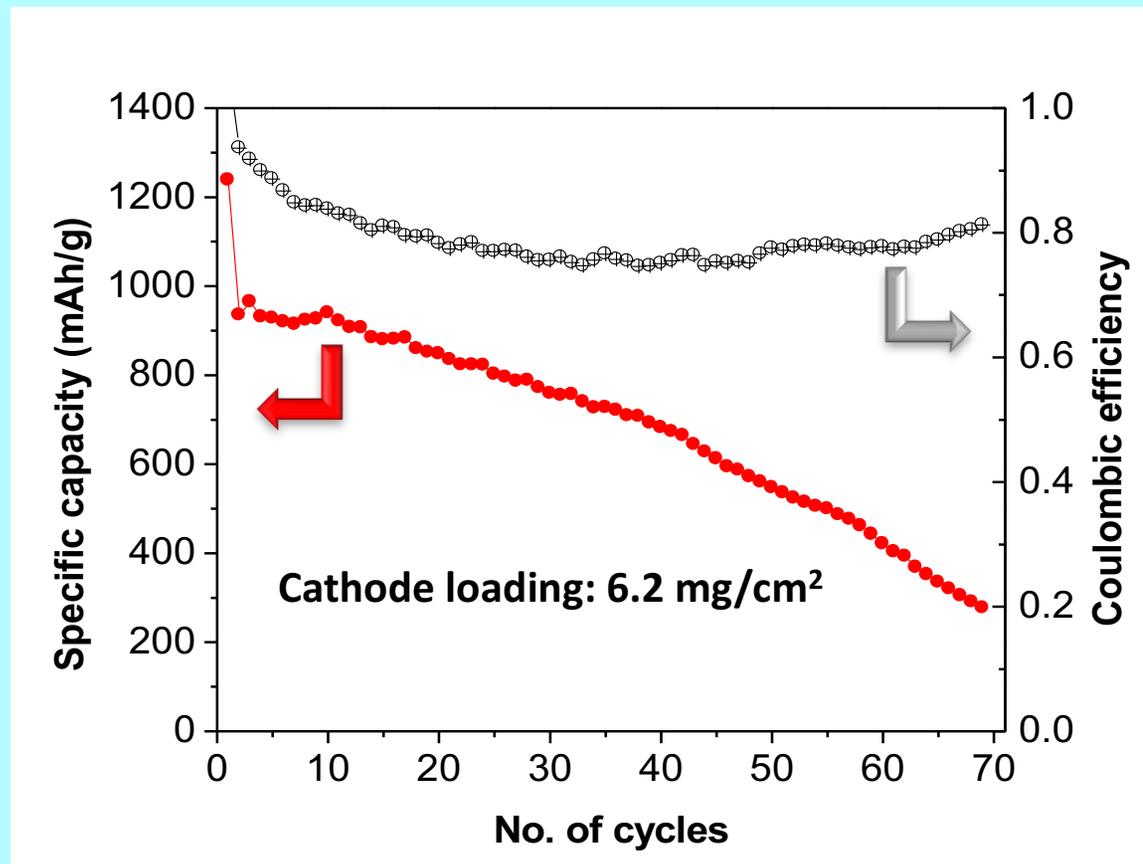


Electrolyte content needs to be reduced to 4-5 ml/g (currently 9-13 ml/g)



Performance of a S cathode with high Loading in a Li-S cell

1.0MLiTFSI+ DME (Dimethoxy Ethane) +DOL (Dioxolane) (95:5) with a Carbon Cloth

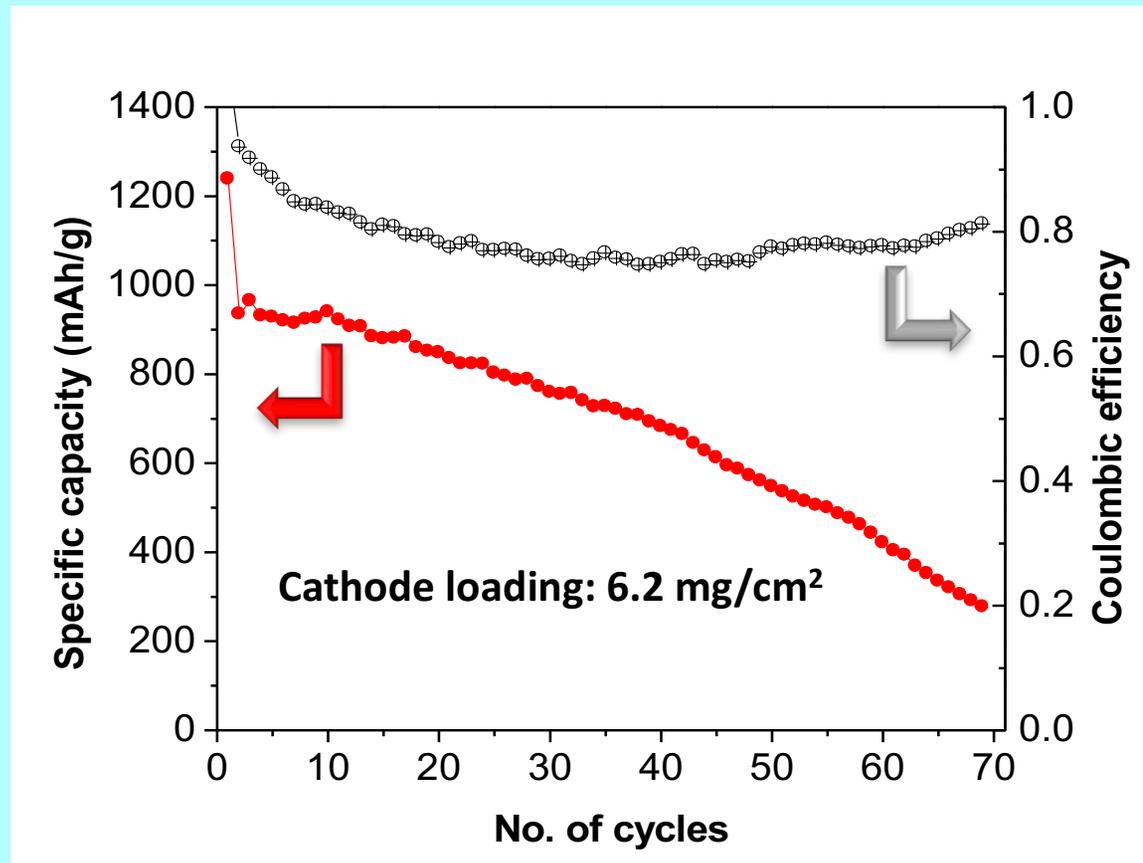


- Lower capacity and utilization of sulfur in thicker cathode even with carbon cloth interlayer and LiNO_3 .
- With denser sulfur cathodes, more polysulfides are expected to dissolve in the electrolyte.

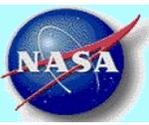


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High Area-specific Capacity Sulfur Cathode

- Our strategies to improve the cycle life sulfur cathodes with high loadings (being discussed today):
 - Modification of sulfur cathode with metal sulfide blends
 - Coating of separator with ceramic compounds (Al_2O_3 and AlF_3) and polymeric materials.
 - Protection of Li anode with ALD-deposited AlF_3
 - Assessment of high concentration electrolytes
 - Corroboration with in-situ polysulfide determination



Metal Sulfide Blended S Cathodes

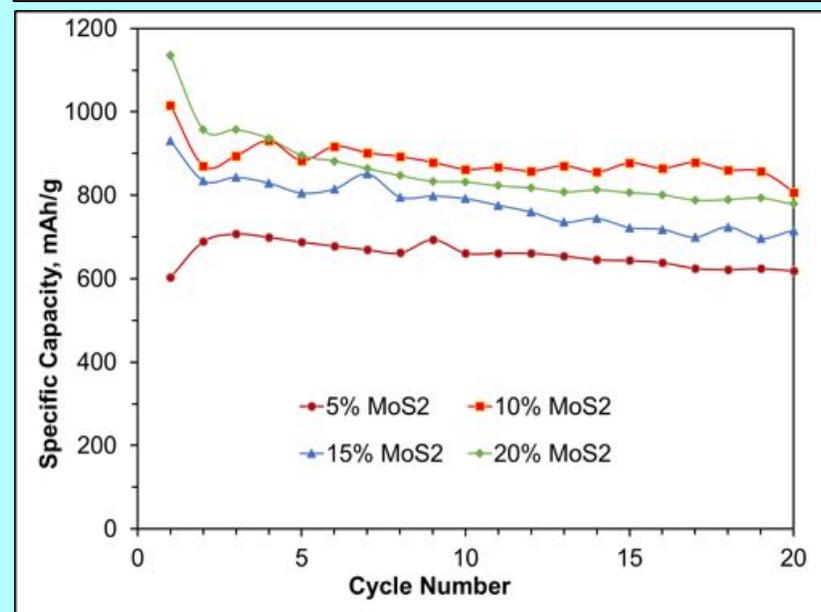
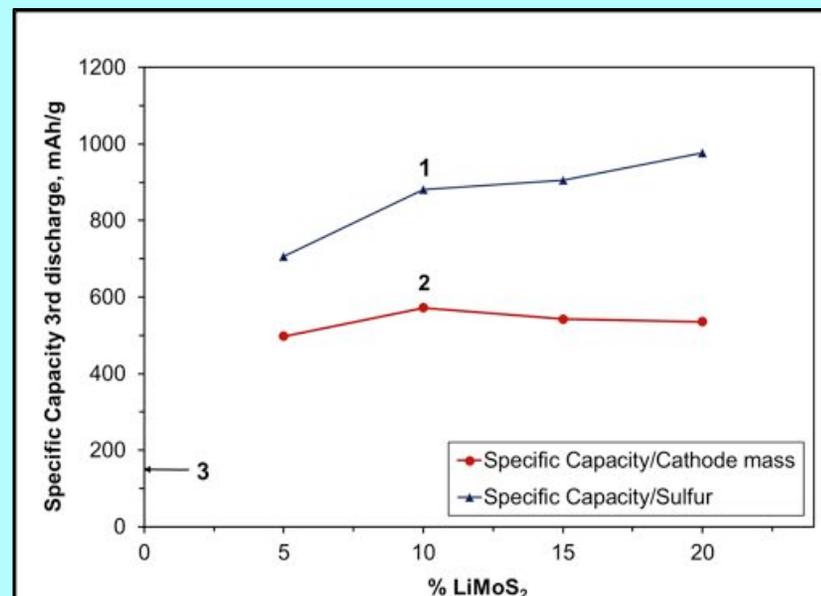
- Transition metal sulfide undergoes reversible reactions around the same voltage range and can add to the cathode capacity and also mediate the sulfur redox reaction.
 - TiS_2 (Manthiram and Cui et al) , VS_2 , ZrS_2 (Cui et al) with low loadings ($<5\text{mg}/\text{cm}^2$), CuS_2 (Takeuchi et al)
- Metal sulfide provides some electronic/ionic conductivity
- Physical/Chemical Entrapment of S (Cui et al: Nature material Nature Communications 2014 | 5:5017 | DOI: 10.1038)
 - Strong Li–S interaction (between the Li atoms in Li_2S and S atoms in TiS_2), as well as strong S–S interaction between the S atoms in Li_2S and S atoms in TiS_2).
 - The binding energy between Li_2S and a single layer of TiS_2 was calculated to be 2.99 eV. This value is 10 times higher than that between Li_2S and a single layer of carbon-based graphene, which is a very common encapsulation material used.
 - The much stronger interaction between Li_2S and TiS_2 can be explained by their similar ionic bonding and polar nature, unlike graphene which is covalently bonded and nonpolar in nature.
 - Entities that bind strongly to Li_2S exhibit strong binding with Li_2S_n species as well owing to their similar chemical bonding nature.

Screened several sulfides : TiS_2 , MoS_2 have shown to improve sulfur utilization and cycle life



Sulfur Cathode With Different amounts of MoS₂

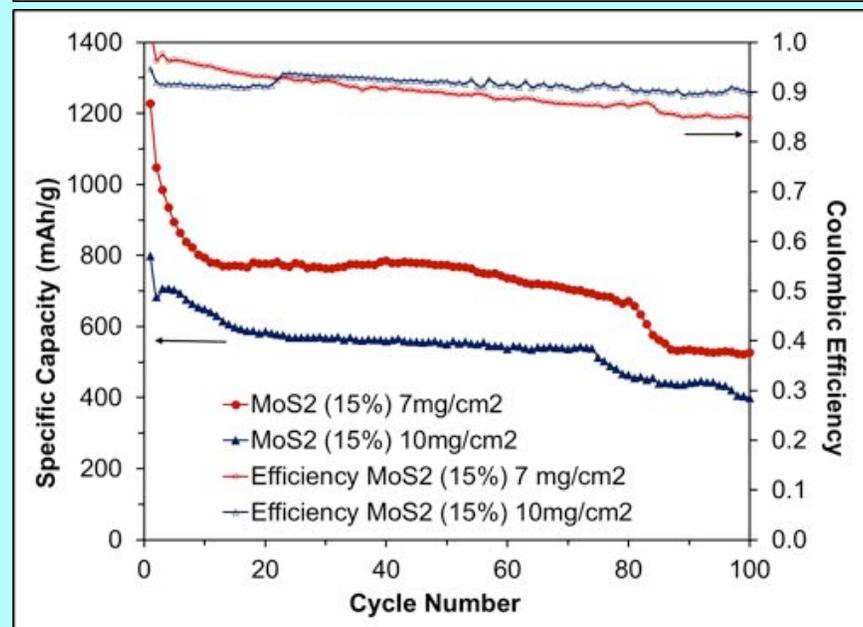
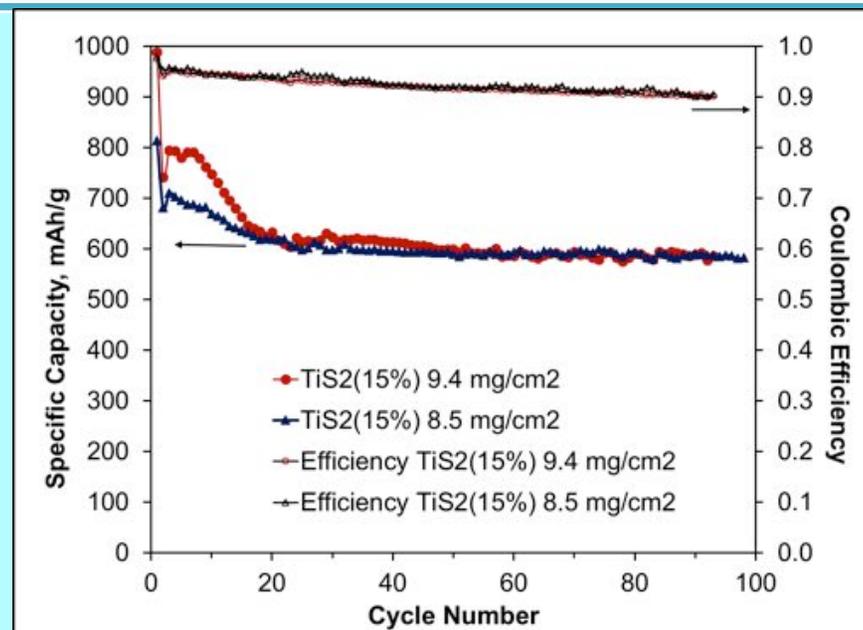
- The ratios of S and MoS₂ were varied from 55:20, 60:15, 65:10 and 70:5, while keeping the carbon and PVDF binder the same at 20% and 5%, respectively (55:20:20:5, 60:15:20:5, 65:10:20:5 and 70:5:20:5 for S:MoS₂:C:PVDF at ~9 mg/cm² (compared to Li-ion cathode powder, NCA)
- Specific capacity of sulfur increases with MoS₂ loading, but specific capacity of total cathode decreases at high loadings.
- High sulfur utilization and capacity retention during cycling with 10-15% of MoS₂ in the cathode (65% sulfur)

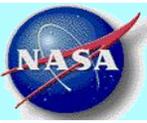




TiS₂- MoS₂ Blended Sulfur Cathode

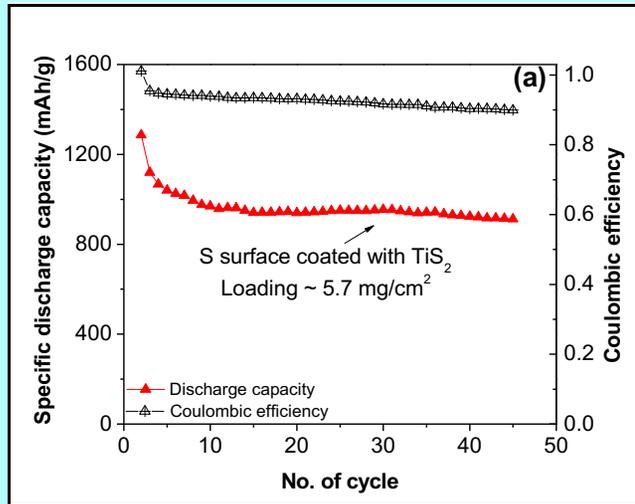
- Good performance considering the high cathode loading and high proportion of sulfur (4.6 mAh/cm² per side)
- High coulombic efficiency suggests polysulfide trapping.
- The XRD spectra for TiS₂ electrodes showed a transition from TiS₂ to LiTiS₂ after discharge and transition from LiTiS₂ to TiS₂ after charge.
- Similar to the baseline and MoS₂ electrodes the S-MoS₂ cathode showed the presence of sulfur peaks after charging and disappearance of the same peaks after discharging.
- No change in the MoS₂ peaks



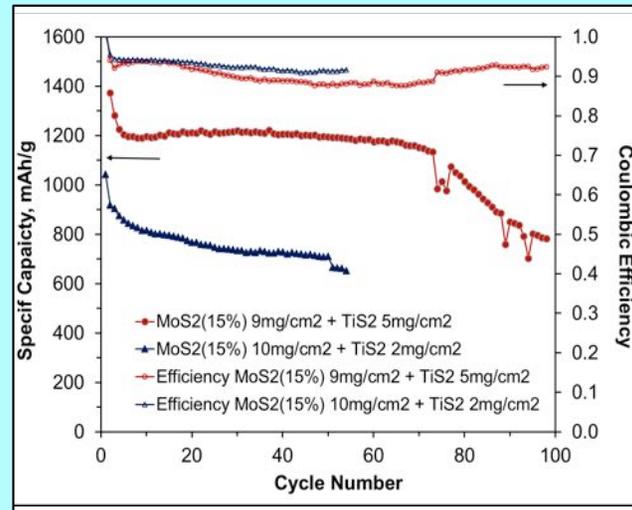


Metal Sulfide Coating on S Cathode

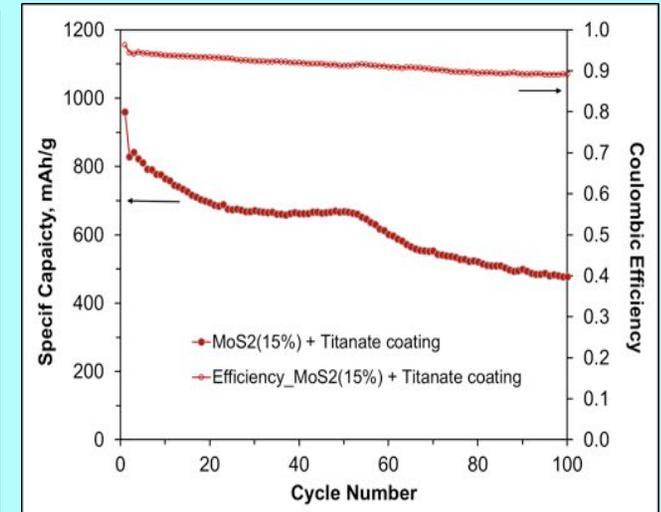
S coated (S:C:PVDF 55:40:5)+
1.5 mg/cm² TiS₂ from spin
coating



MoS₂-S (S:MoS₂:C:PVDF
65:15:15:5 + TiS₂ from spin
coating)



MoS₂-S (S:MoS₂:C:PVDF
65:15:15:5) coated with
lithium titanate.

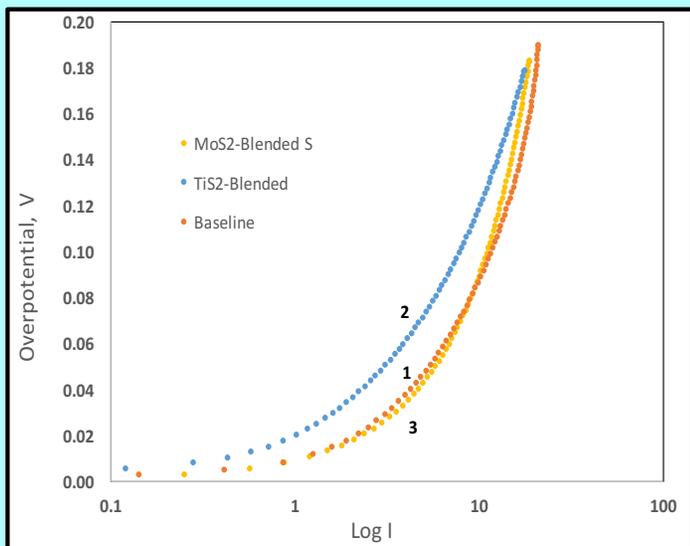


- Coatings with the metal sulfides TiS₂ and MoS₂) and lithium titanate also seem to have beneficial effect of the cycling of sulfur cathode.



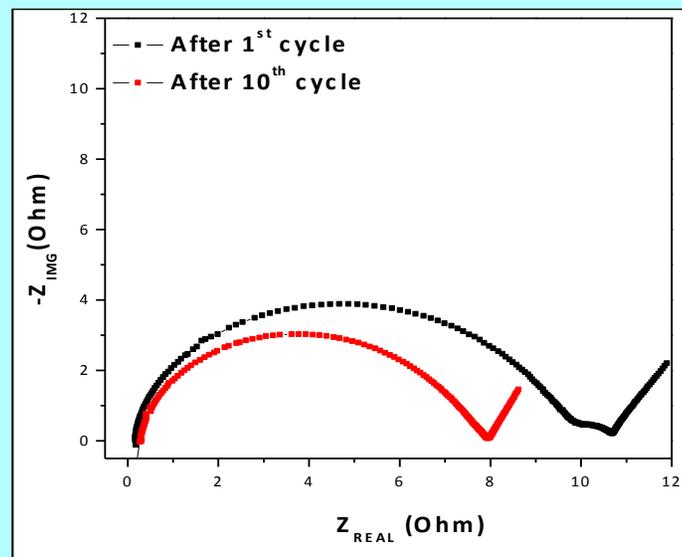
Kinetics of Sulfur Cathode

Kinetics Tafel Polarization

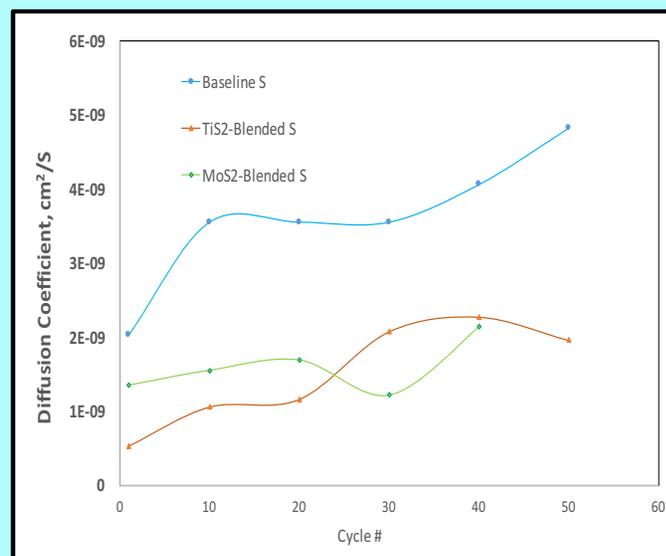


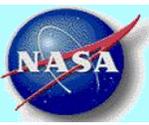
- Identical kinetics for sulfur reduction
- The exchange current density of pristine sulfur cathode is 0.19 mA/cm². In contrast, the exchange current densities of the composite cathodes with TiS₂ and MoS₂ blends are 0.21 mA/cm² and 0.23 mA/cm², respectively
- Similar kinetics for Li diffusion in the cathodes.

EIS of MoS₂-Blended S Cathode



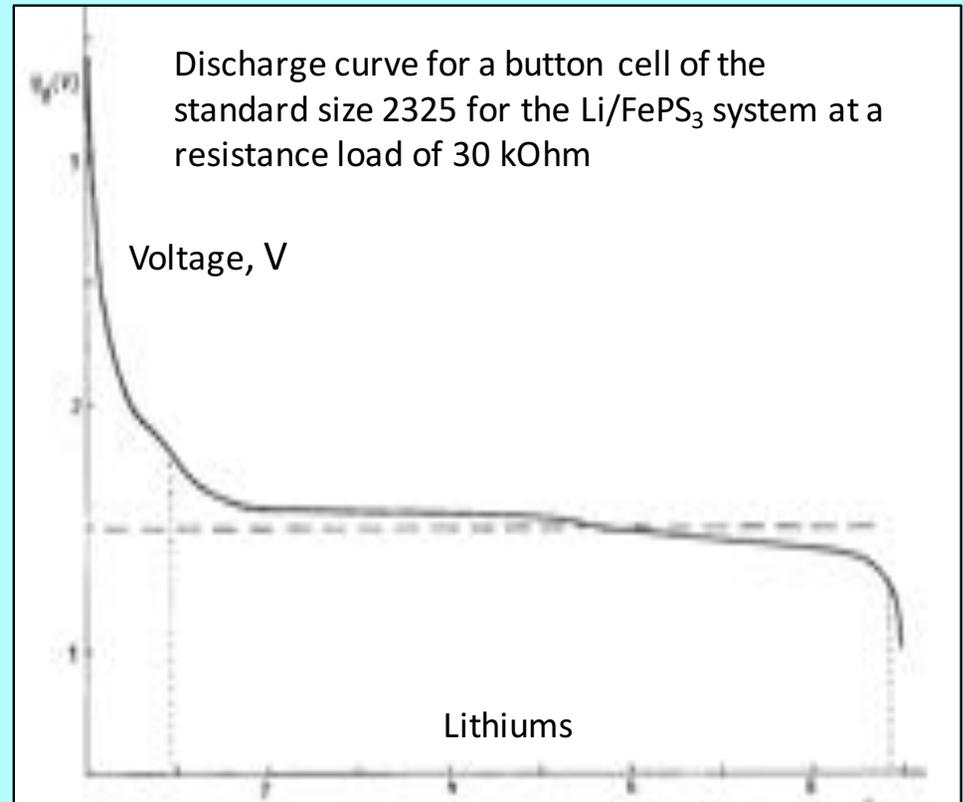
- Stable interface and lower impedance upon cycling





Metal Phosphorus Trisulfides for Composite Sulfur Cathodes

- Rationale: Involve reactions with multiple lithiums in the same voltage range as the sulfur cathode
- Synthesis: 'one-zone' heating at 973-1023 K of a stoichiometric mixture of suitable components in evacuated ampoules for five and more days followed by a very slow cooling
- Synthesized several metal trisulfides: FePS_3 , NiPS_3 , CoPS_3 and MnPS_3 . Composition confirmed from XRD

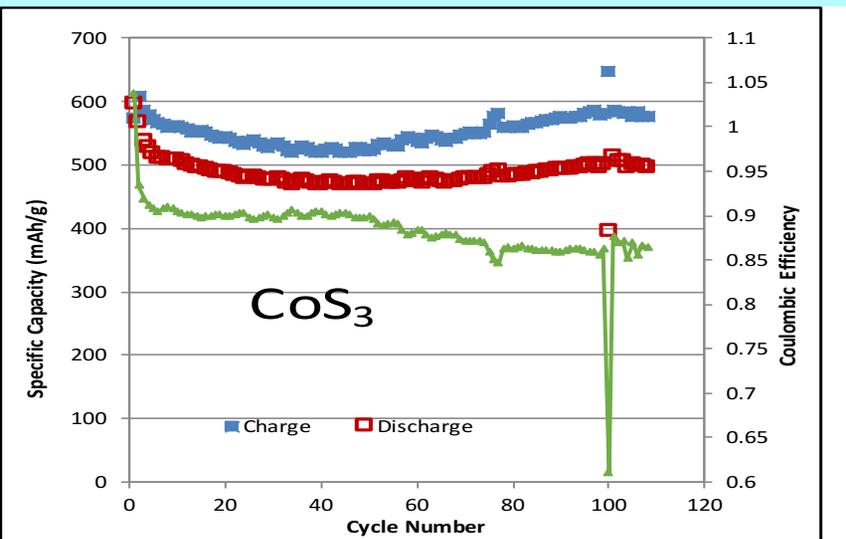
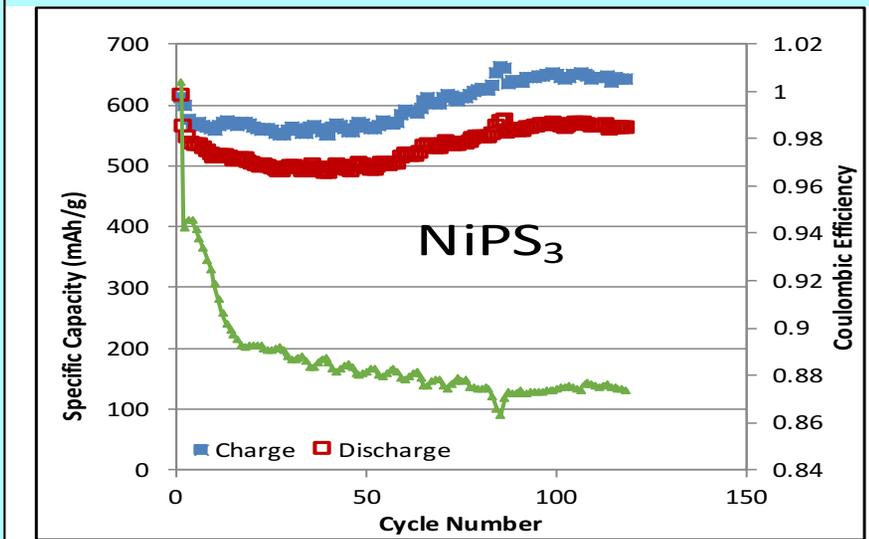
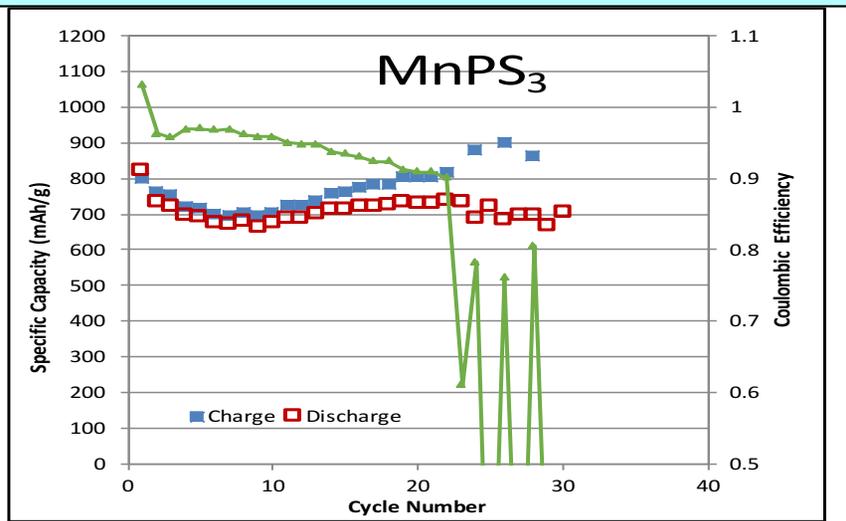
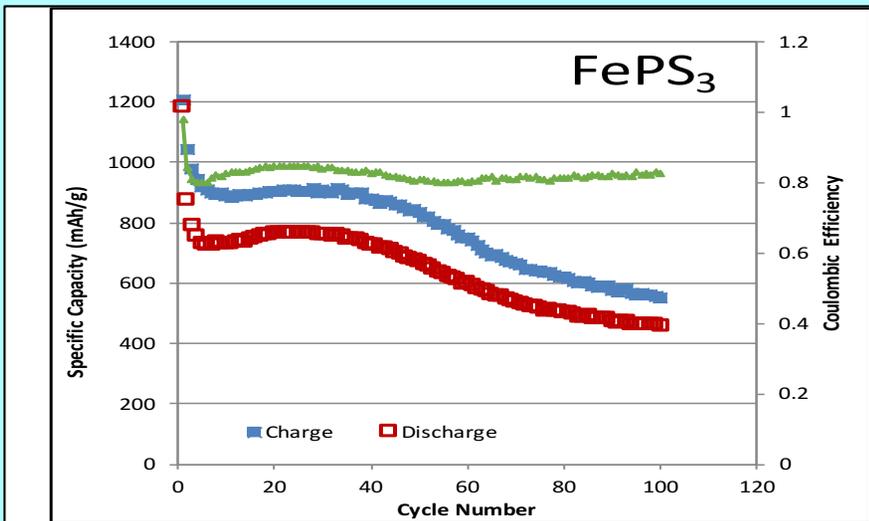


Two lithiums (reversible) and nine lithiums (irreversible)

Kuzminskii et al, J. Power Sources, 55, 133 (1995)



Metal Phosphorus Trisulfides for Composite Sulfur Cathodes

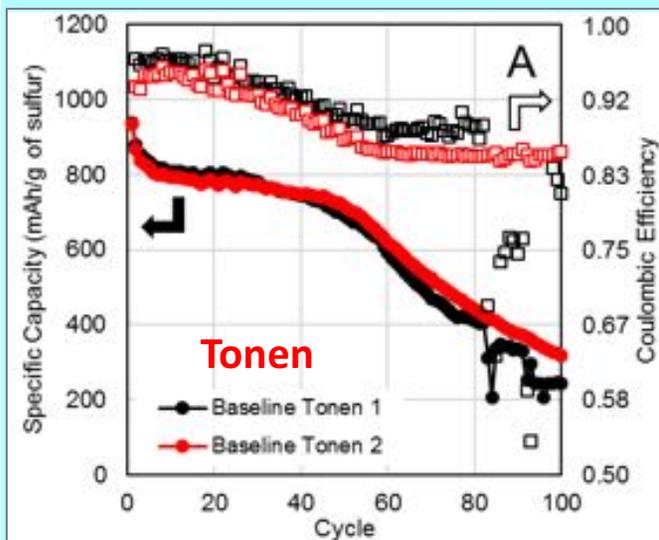


Composition:(S:MPS₃:C:PVDF=65:15:15:5); loading 5 mg/cm²

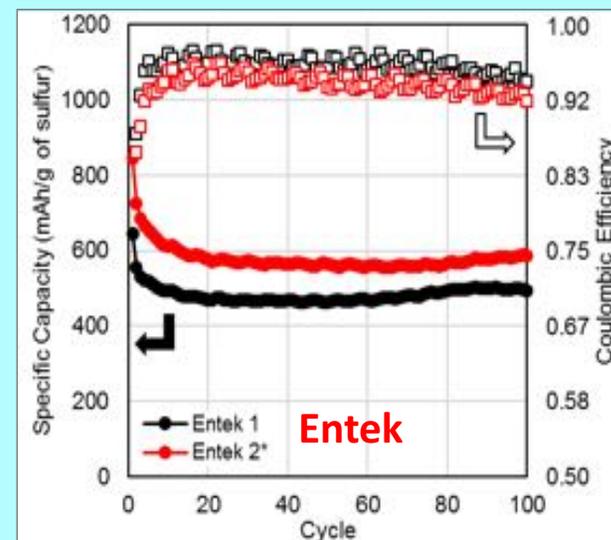
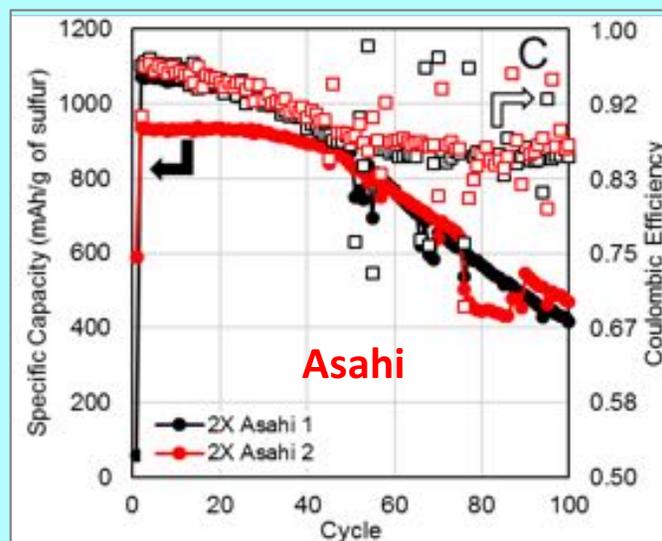


Li-S cells with Al₂O₃-coated separator (Asahi and Entek)

Tonen Separator



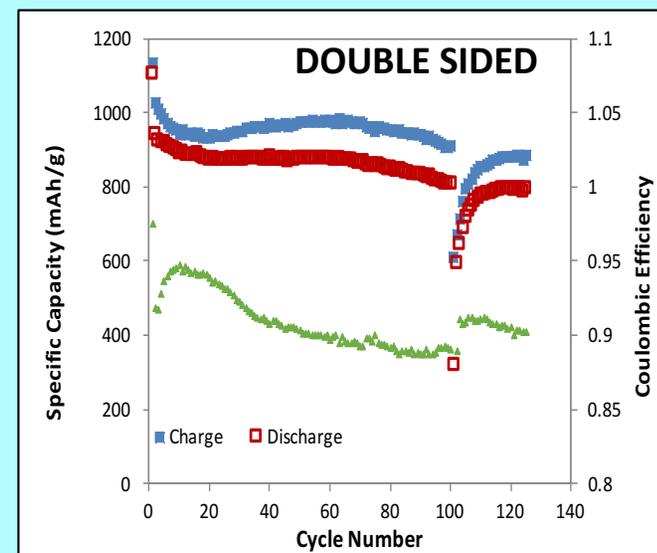
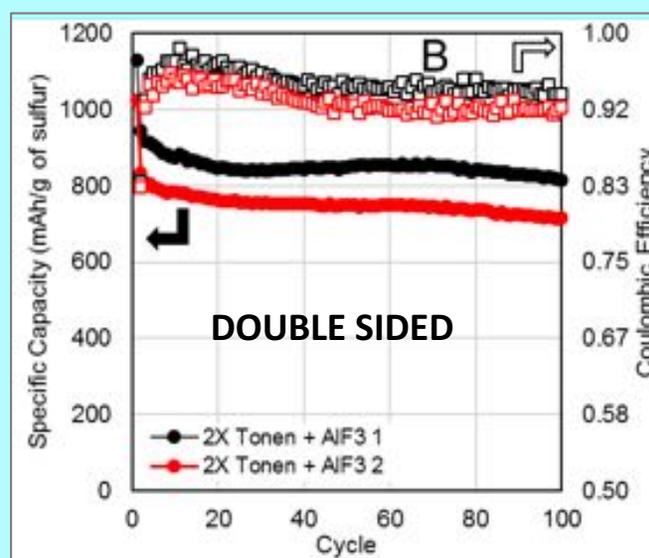
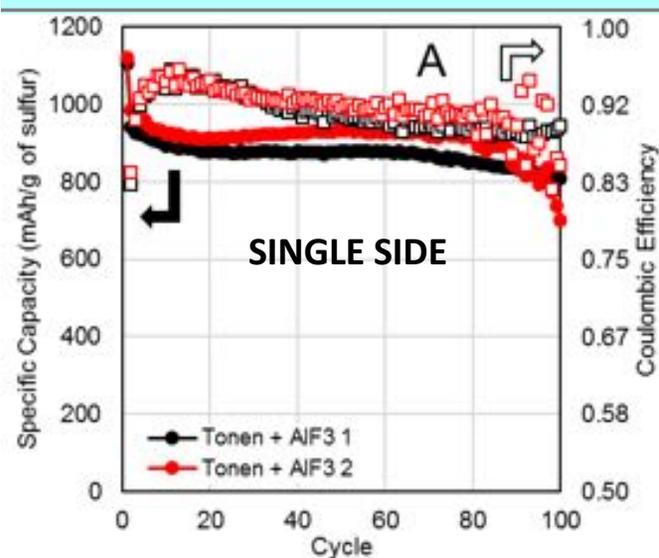
Al₂O₃ Coated –Two layers



- Motivation:
 - Al₂O₃-coated Celgard separator blocks the diffusion of the polysulfide anions by physical adsorption and electrochemical deposition (Zhang et al., Electrochim. Acta 129, 55 2014)
 - Wixom et al (Navitas): Coating with Titanium nitride for aiding in the electrochemical reduction of polysulfides.
- Separator coated with Al₂O₃ on one side (typically used on the cathode side)
- Improved performance with two layers of Asahi) separator
- Entek separator gives lower but stable capacity



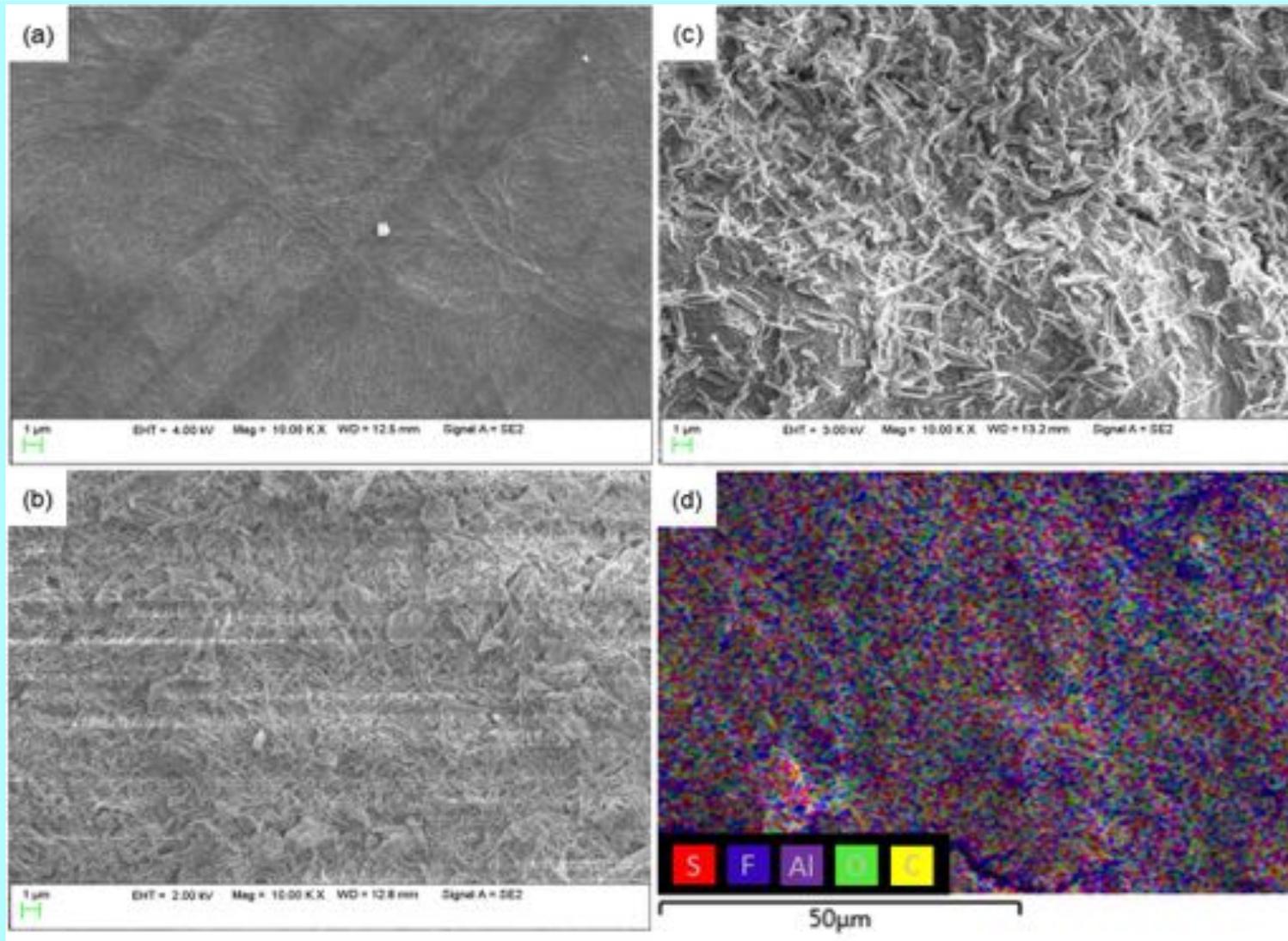
AlF₃-coated Tonen separator (spray coated)



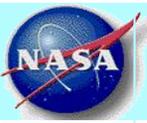
- AlF₃ is used as coating for high voltage cathodes in Li-ion cells.
- Li-S coin cells containing sulfur cathode of composition S:CB:PVDF(55:40:5), 6.45mg/cm² and AlF₃-coated Tonen separator (spray coated)
- Good cycle life with high coulombic efficiency
- Also, good capacity recovery after test interruption for 3 weeks



AlF₃-coated Separators from Cycled Cells

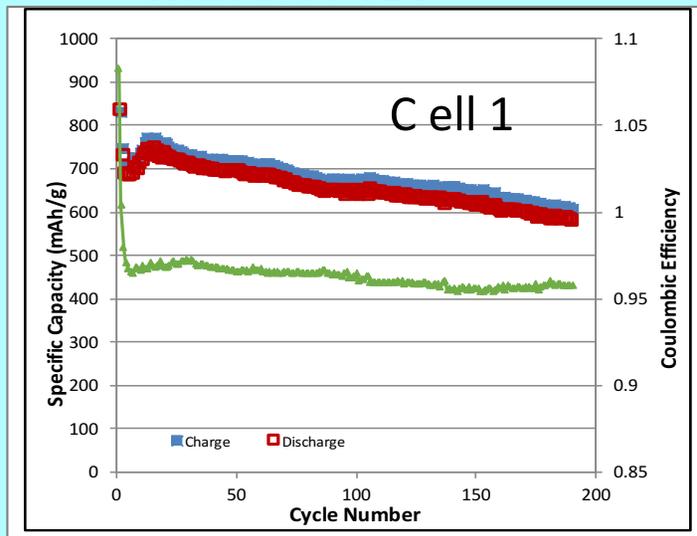


SEM images of (a) fresh Tonen separator, (b) Tonen separator coated with AlF₃ and (c) AlF₃-coated Tonen separator after 100 cycles showing AlF₃ material present on the surface after coating, and deposition of sulfur-containing species on the surface of these particles after cycling. EDS in (d) indicates approximately uniform distribution of sulfur-containing species across the surface of the coated separator.

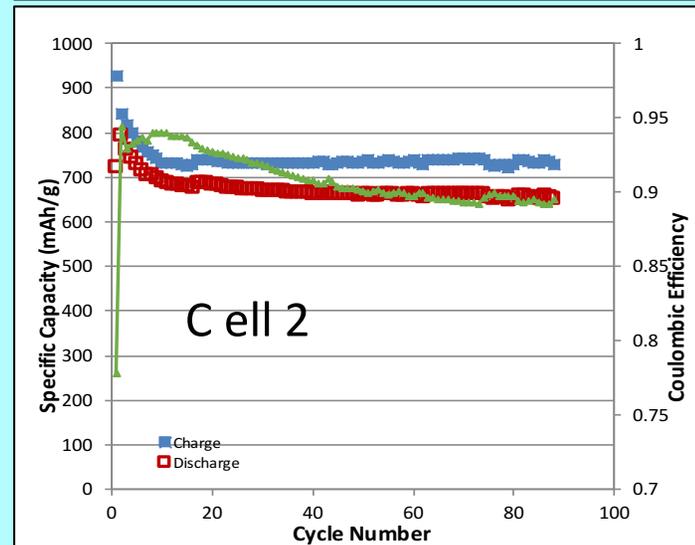
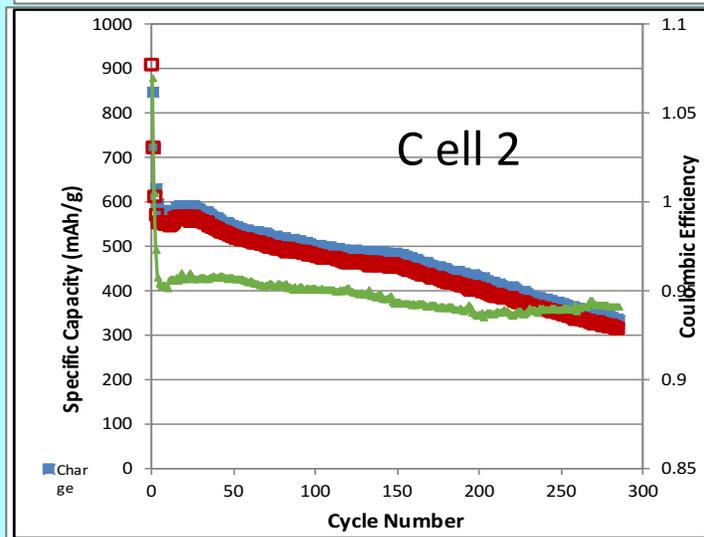
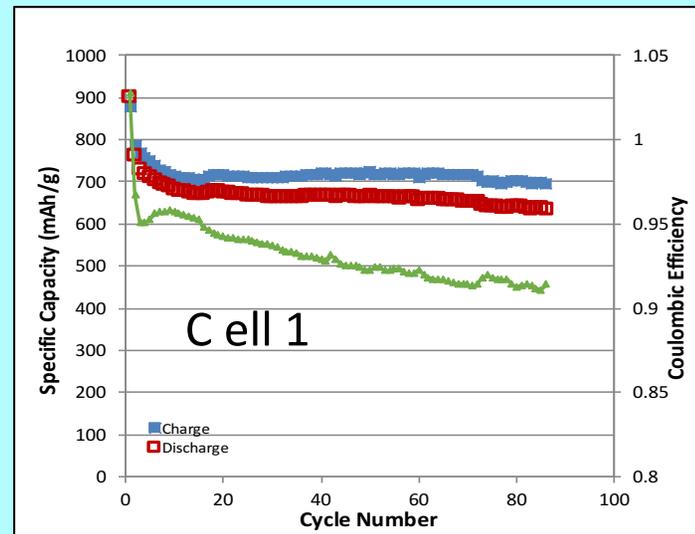


Li-S Coin cells with AlF_3 -coated separator (doctor blade)

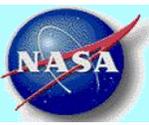
With 5% PVDF



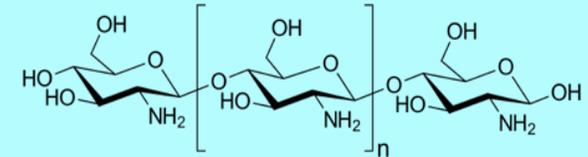
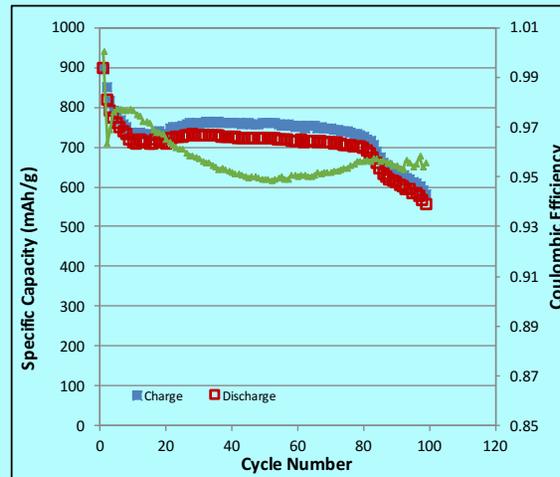
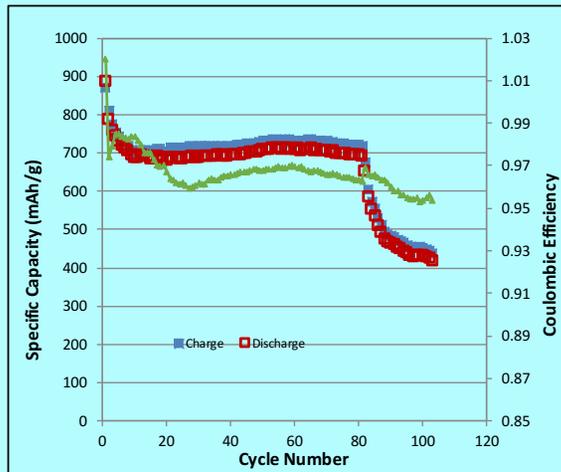
With 2% PVDF



- Good cyclic stability and high coulombic efficiency
- The coating needs to be optimized to improve the initial capacity, may be with reduced binder content.
- Capacity has improved with 2% binder, binder the efficiency is lowered slightly (till over 90 %)

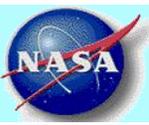


Li-S cells with Chitosan coated separator (Asahi)

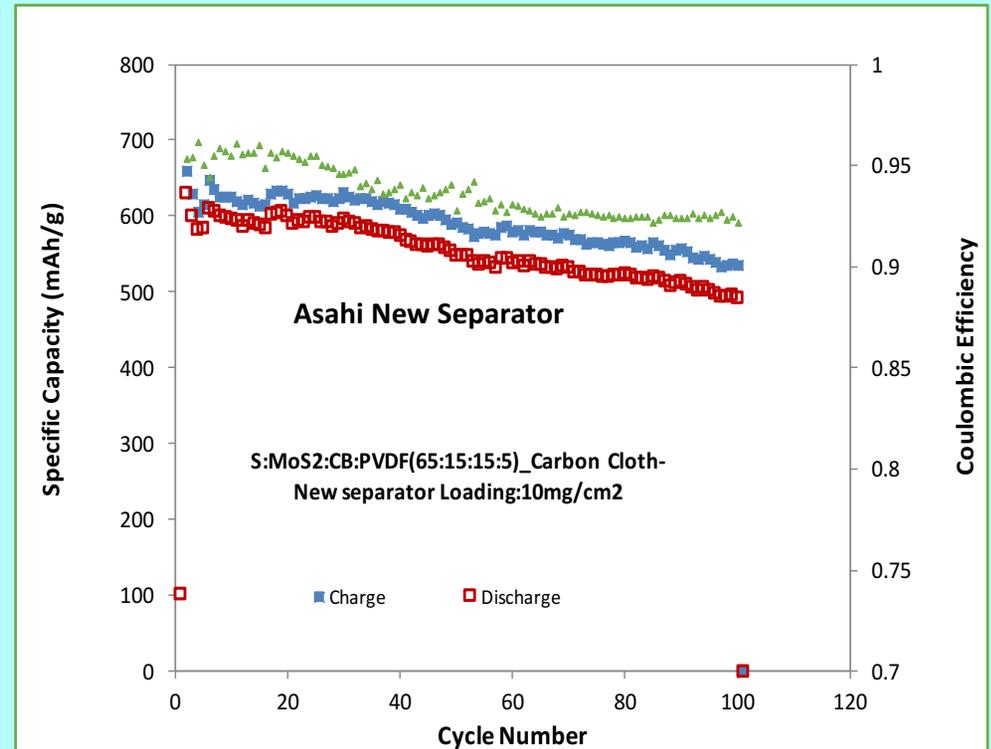
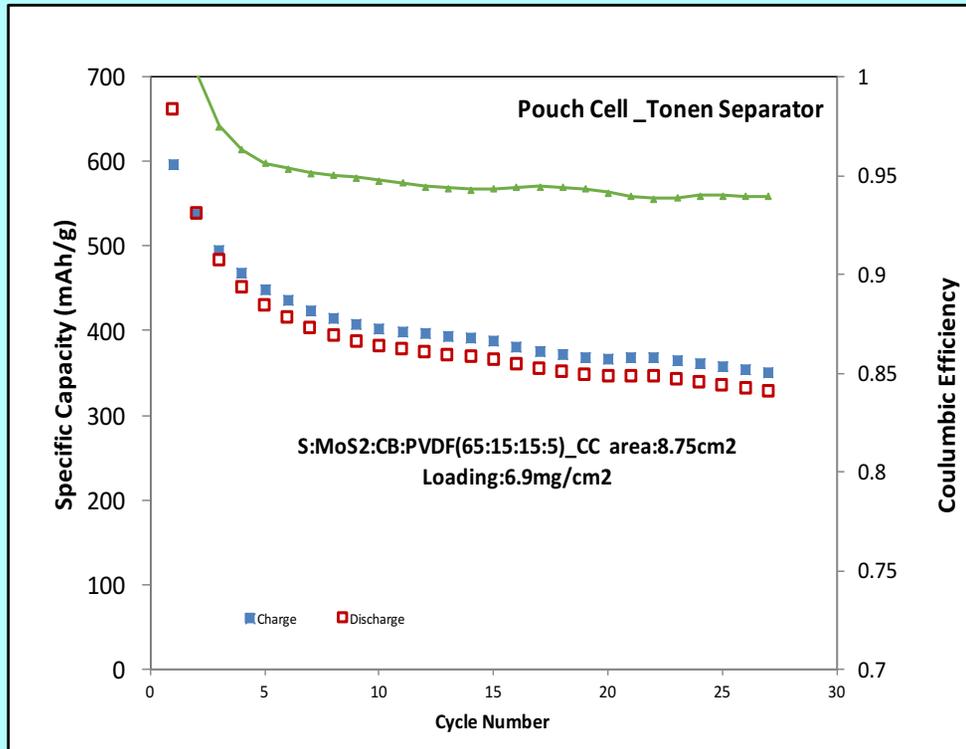


Commercially available polymer,
used in agriculture and medicine,

- Separator coated with Chitosan on one side (typically used on the cathode side)
- Stable cycle life with high coulombic efficiency



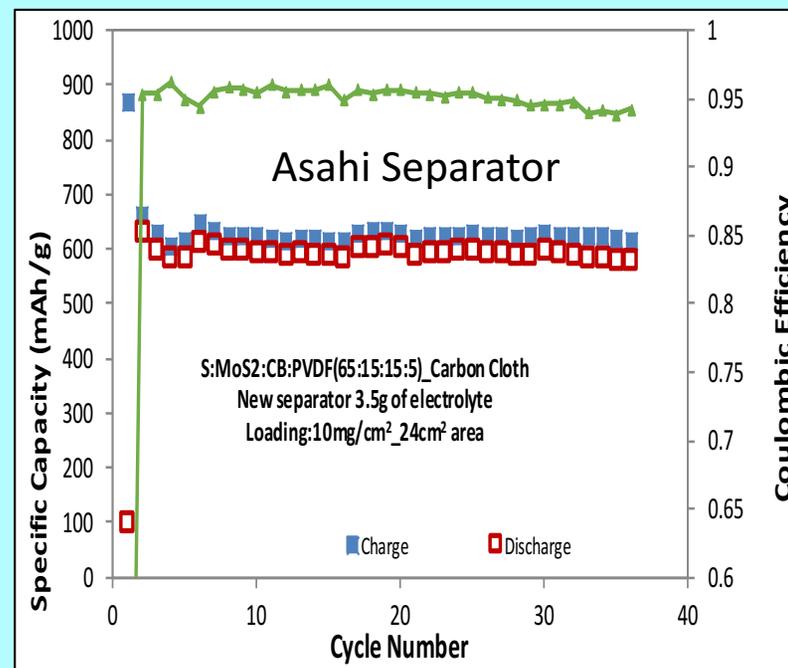
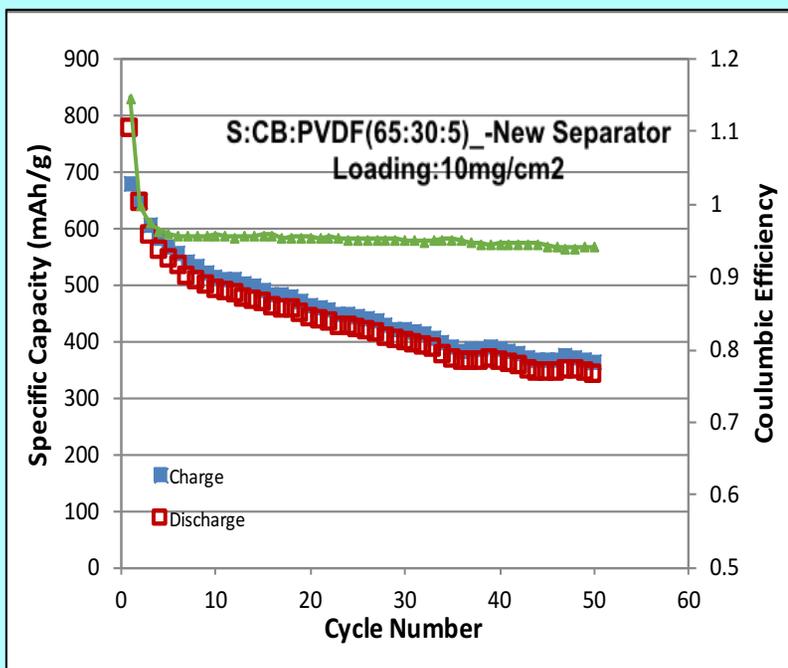
Li-S pouch cells with sulfur cathode with different separators



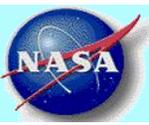
- Cell with S-MoS₂ cathode (10 mg/cm² loading) and Asahi separator outperforms Cell with S-MoS₂ cathode (7 mg/cm² loading) and Tonen separator.



Li- S Pouch Cells

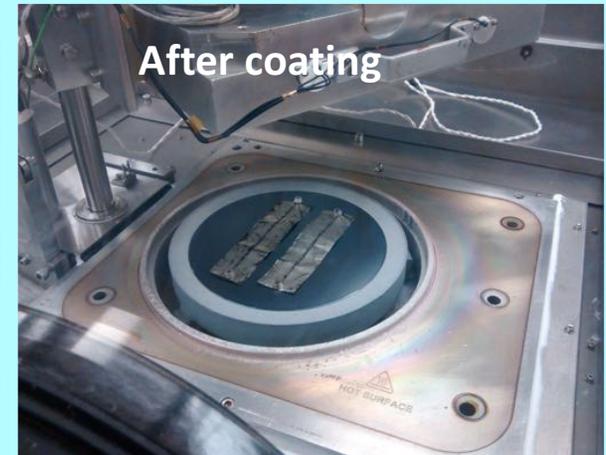
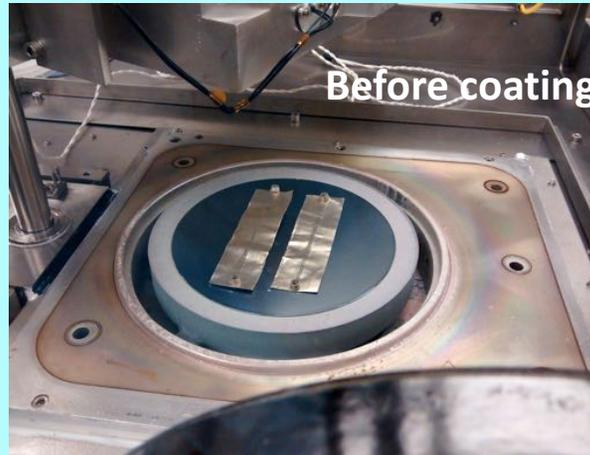


- Good coulombic efficiency but a high fade rate with the baseline sulfur
- Cell with S-MoS₂ cathode (10 mg/cm² loading) and Asahi separator outperforms Cell with baseline sulfur cathode (10 mg/cm² loading) and Tonen separator.
- Excellent performance with high sulfur content (65%) and loading (10 mg/cm²) with MoS₂ blending (15%) and new separator
- 4mAh/cm² per side (8 mAh/cm² both sides) based on the realized capacity
- Electrolyte content is ~9 ml/g of S.

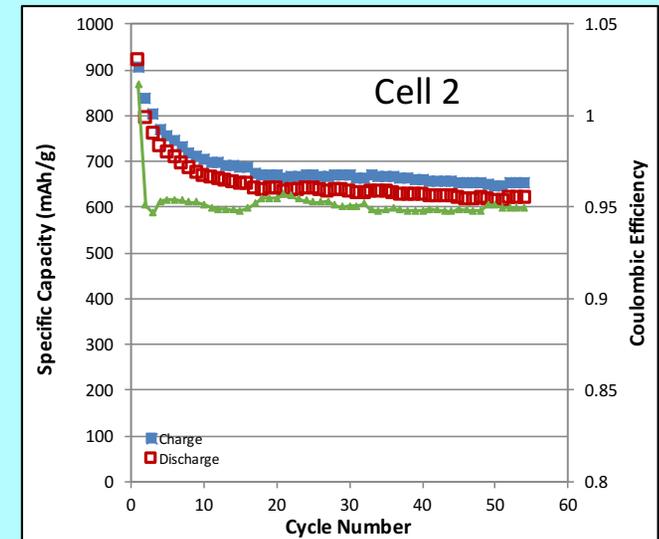
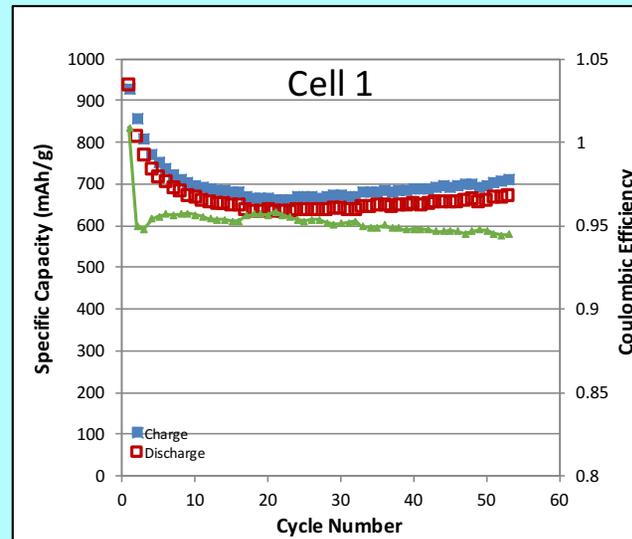


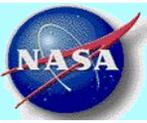
Thicker ALD Coating of AlF_3 over Li

- 15 nm thick coating.
The samples were also only heated to 75 °C instead of 100 °C

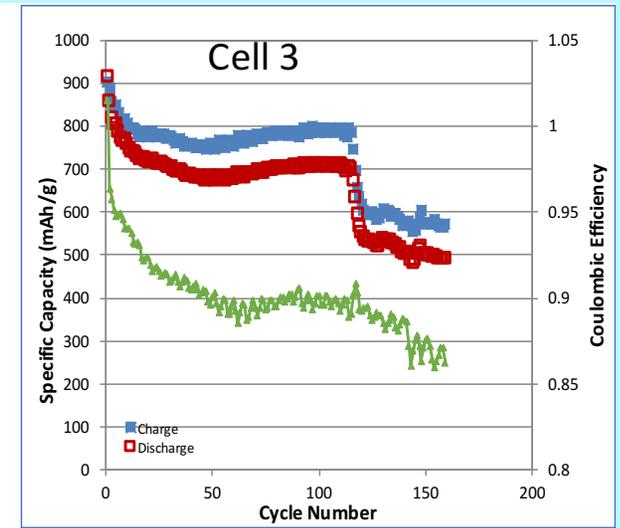
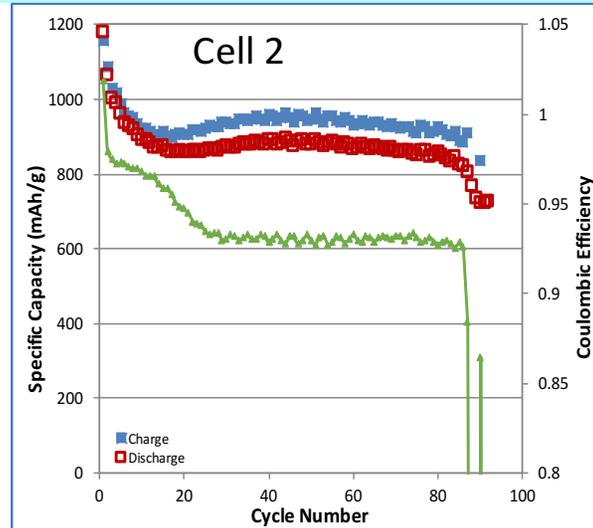
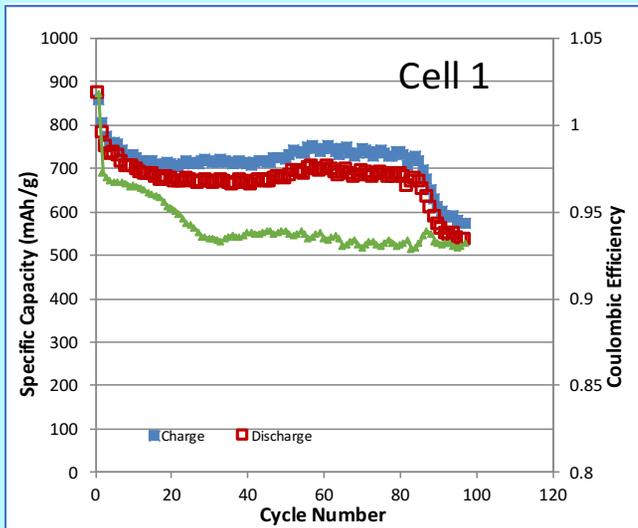


Performance of Li/S coin cells using AlF_3 coated (ALD) Li and baseline sulfur (55%) at 5 mg/cm² and with Tonen separator coated with AlF_3 :PVDF(98:2).



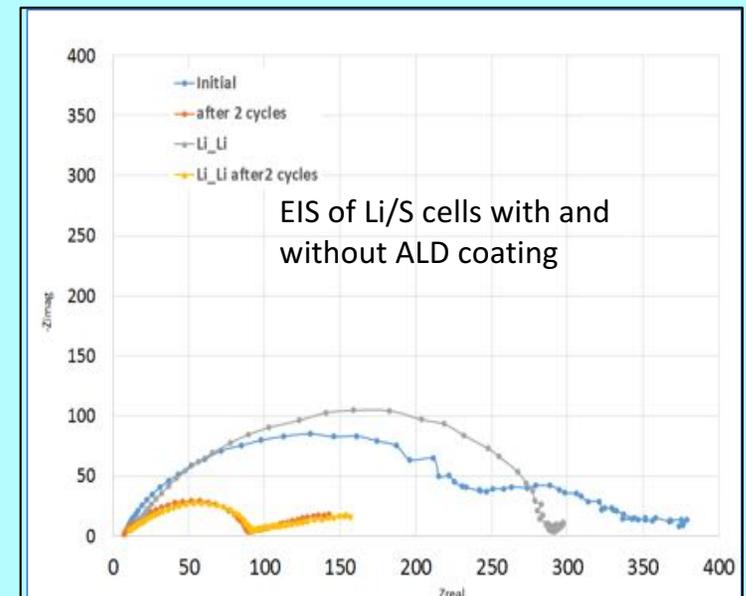


AlF₃-coated (ALD) Li Anode



Cycling of Li-S coin cells containing sulfur cathode of composition S:CB:PVDF(55:40:5), 5.65 mg/cm² with the SAFT separator in standard electrolyte with Li anode protected by an ALD coating of AlF₃.

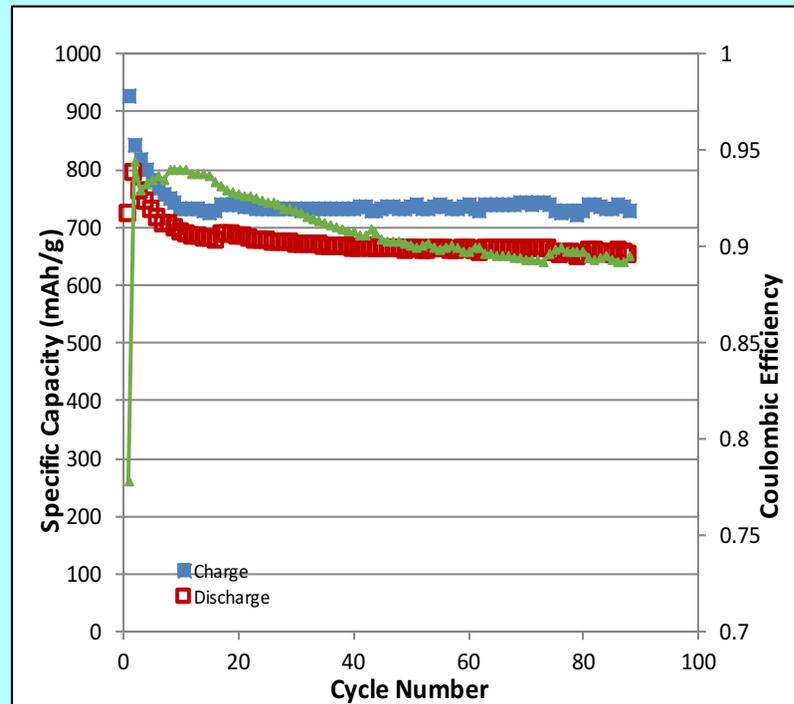
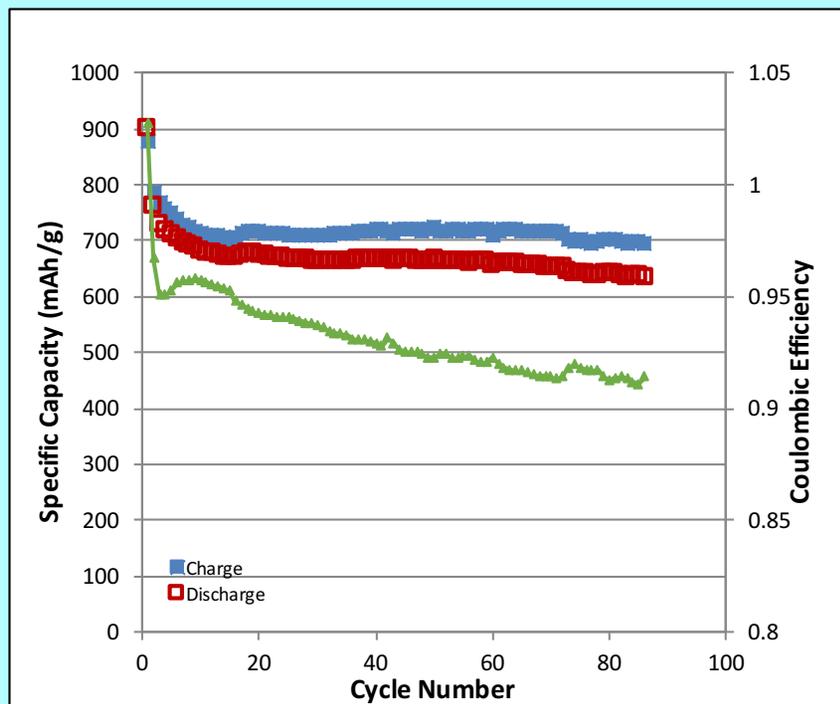
- Procedure: Pulse trimethyl aluminum Al(CH₃)₃ followed by HF in 40 times, which should have formed a 4.8 nm thick AlF₃ coating on Li based on calibration runs using on silicon wafers.



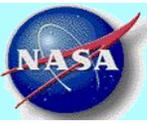


Li-S Coin cells with AlF_3 -coated separator (doctor blade)

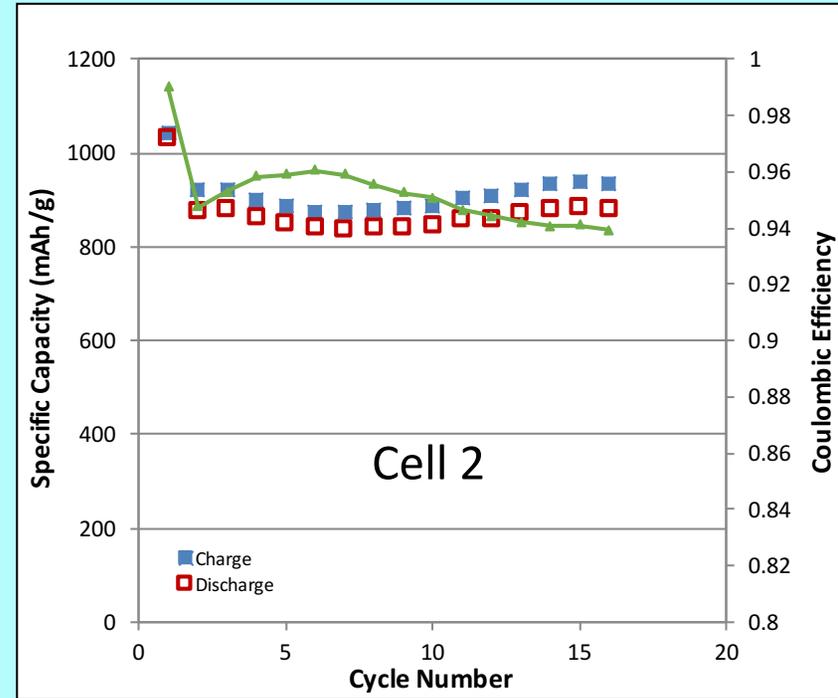
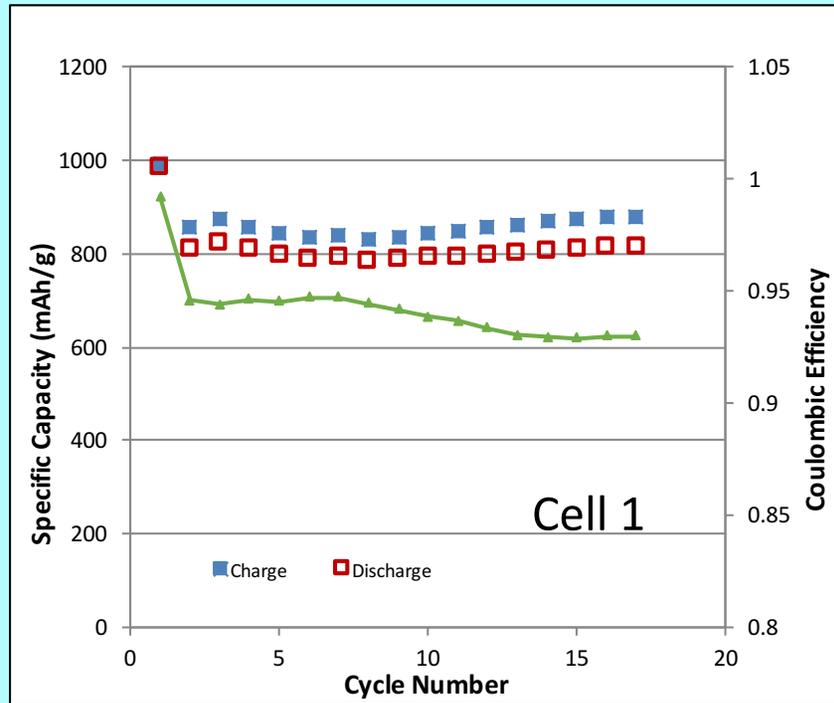
With reduced Binder in the separator coating)



Performance of Li/S coin cells using AlF_3 coated (ALD) Li and baseline sulfur (55%) at 5 mg/cm^2 and with Tonen separator coated with AlF_3 :PVDF(98:2).



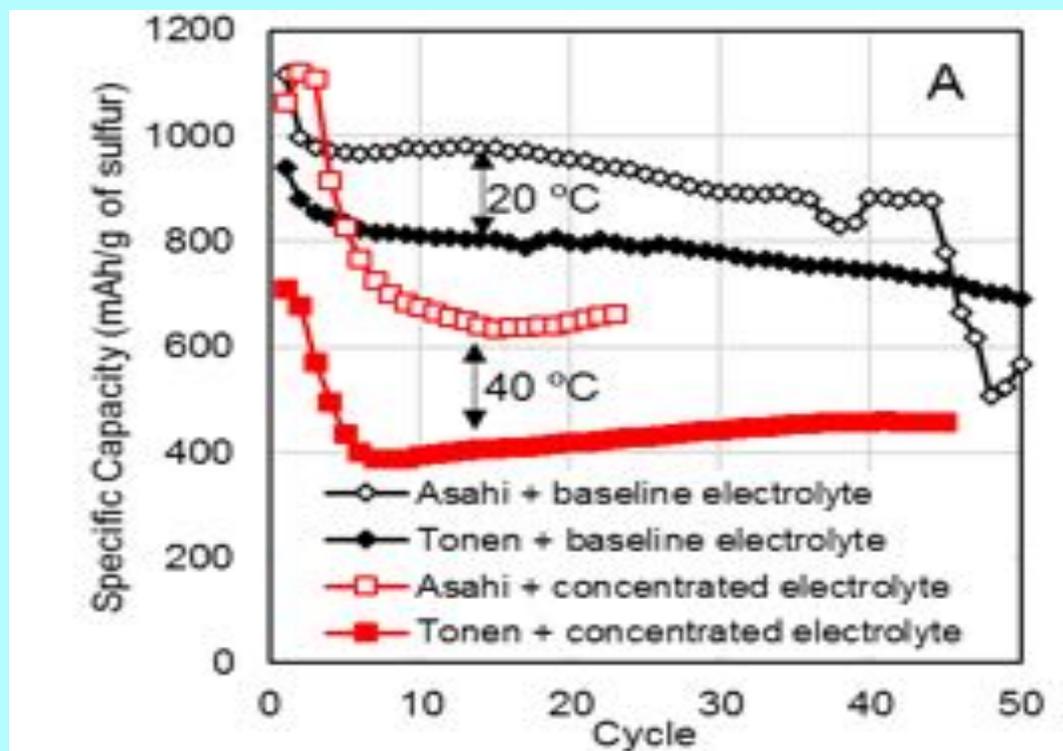
Li(ALD)/AlF₃-Tonen/S-MoS₂



- Good performance (high capacity and efficiency) of Li/S coin cells using AlF₃ coated Li and MoS₂-blended sulfur (65% with 15% MoS₂) at 11.2 mg/cm².
- High area specific capacity is 6 mAh/g per side.

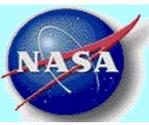


Concentrated Electrolytes

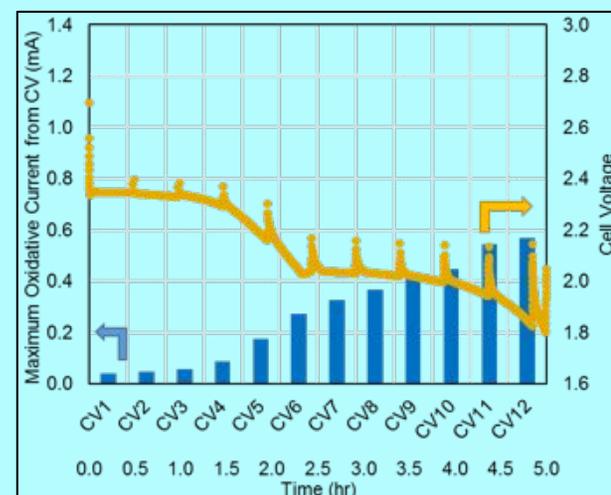
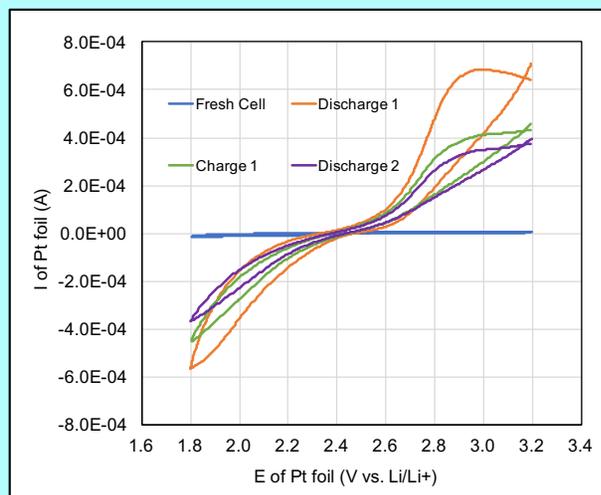
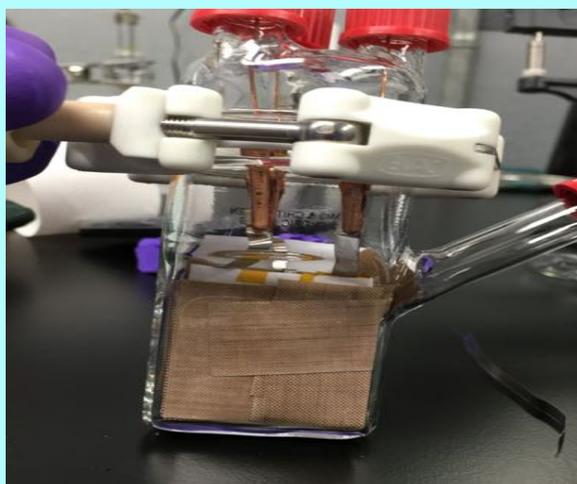


- Highly concentrated electrolytes (solvent in salt) reportedly prevent Li dendrites on the anode and polysulfide shuttle on the cathode.
- Poor performance observed at room temperature in 4M-7M solutions (poor conductivity)
- Slightly improved performance at 40°C with interestingly high coulombic efficiency. May be an option for low power long-life applications.

Liumin Suo, Yong-Sheng Hu, Hong Li, Michel Armand and Liqun Chen, "A new class of Solvent-in-Salt electrolyte for high-energy rechargeable metallic lithium batteries", NATURE COMMUNICATIONS | 4:1481 | DOI: 10.1038/ncomms2513 | www.nature.com/naturecommunications



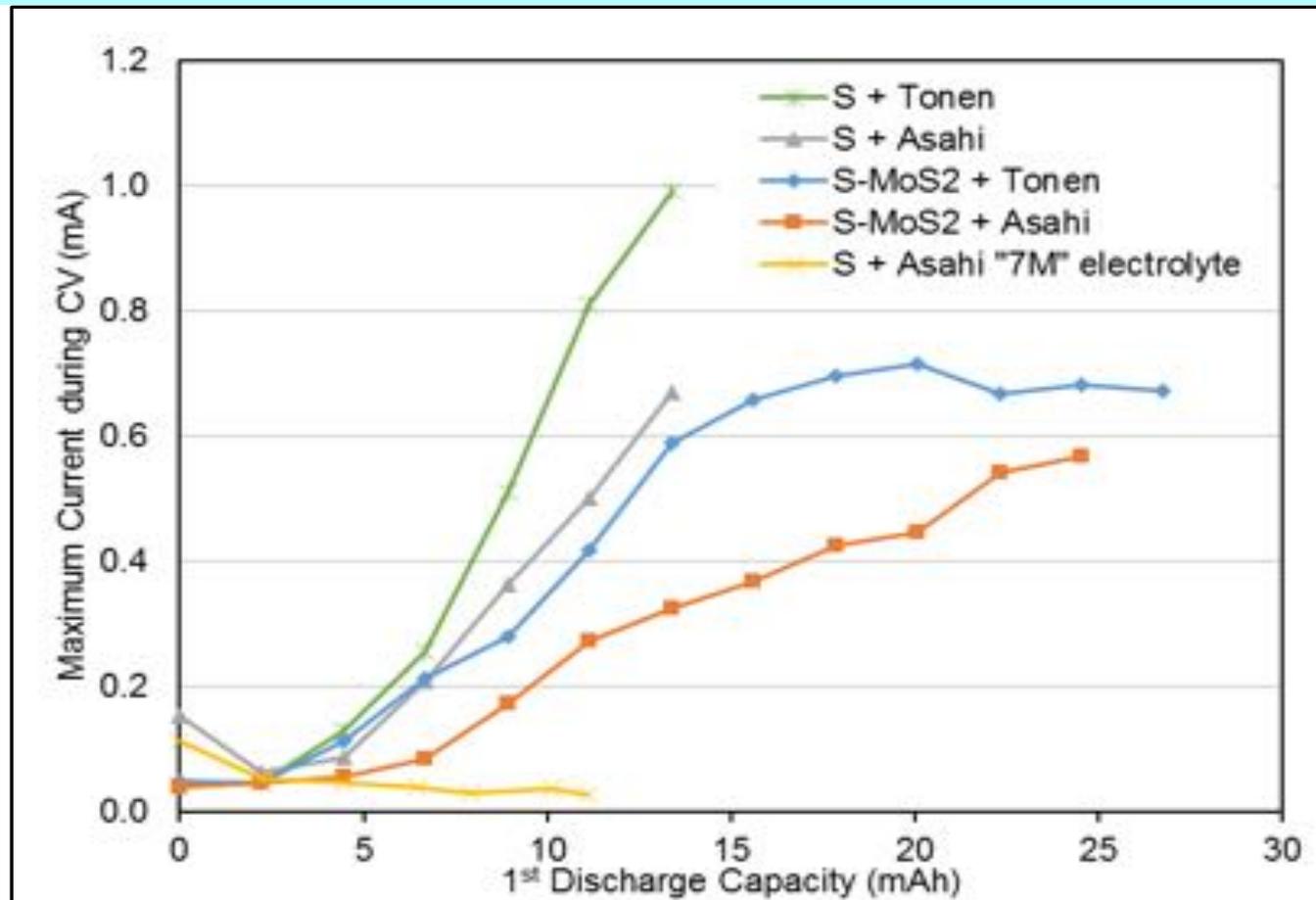
Four-Electrode Li-S cells for Polysulfide Estimation



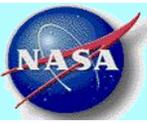
- Four-electrode glass prismatic cell to quantify polysulfides through cyclic voltammetry (right)



Comparison of Polysulfides with different separators/cathodes

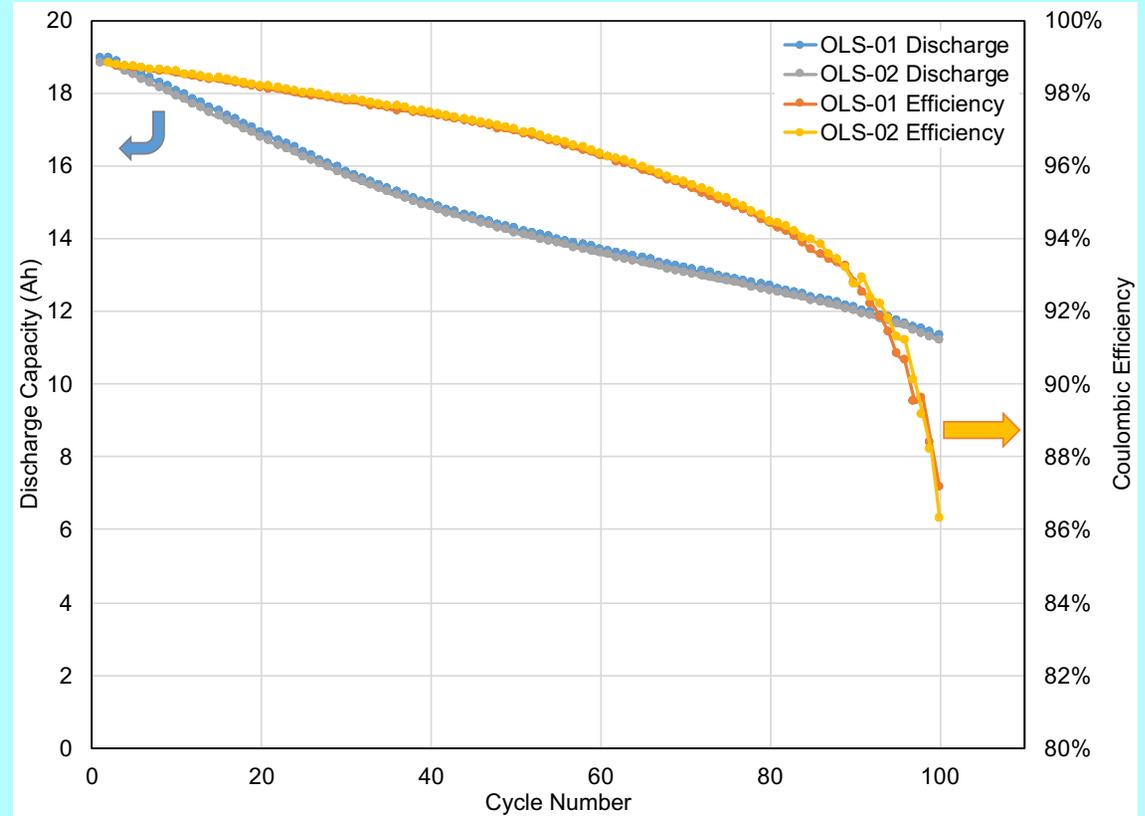


Comparison of CV results from 4-electrode cells incorporating various electrodes, separators, and electrolytes.



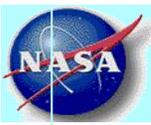
Li/S Prototype Cells from Oxis Energy

- Ten 20 Ah cells received from Oxis and are being tested at JPL



Test Plans

Test:	# cells:	Temp(s):	Rate(s):	Cycles:	C/D Voltage:	EIS:	comment:
Initial test	10	20	C/5	3	2.6/1.9	after	Oxis suggested
Cycle life	2	20	C/5	100	2.6/1.9	every 25 cycles	
Low temp	2	20, 10, 0, -10, -20	C/5, C/20 lowT	3 per Temp	2.6/1.9	after each temp	charge at RT, followed by discharge, then two cycles at low temp
Discharge rate	2	20	C/20, C/10, C/5, C/2, C	2 per Rate	2.6/1.9	after	charge at C/5 then discharge twice at each rate starting with C/20
Charge rate	2	20	C/20, C/10, C/5, C/2, C	2 per Rate	2.6/1.9	after	discharge at C/5 then charge twice at each rate starting with C/20
DOD/EIS	2	20	C/5	1	2.6/1.9	every 10% cap	characterize EIS + polysulfide shuttle as function of DOD
	->	20	storage	1	2.6/1.9	none	self discharge test
	->	20	C/5	20	2.6/?	none	capacity based discharge cycling



Summary

- Novel sulfur/metal sulfide (TiS_2 and MoS_2) and sulfur composite cathodes display high capacity of ≥ 800 mAh/g (based on sulfur content), high coulombic efficiency and good cycle life ($>75\%$ retention through 100 cycles of 100% depth of discharge) at C/3 rate.
 - High cathode loadings (11 mg/cm² or ~ 6 mAh/cm² per side) were demonstrated in Li-S cells containing composite cathodes with good utilization
 - Result in a high specific energy of 400 Wh/kg in prototype cells.
- Metal sulfide coatings also improve the cycle life by minimizing the polysulfides in the electrolyte.
- New separators with ceramic coating (Al_2O_3 and AlF_3) offer interesting opportunities for further improving in this technology. Will augment the composite sulfur cathodes



Acknowledgements

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