Improved Cycle life of Li-S cells with High Areal Capacity Cathodes

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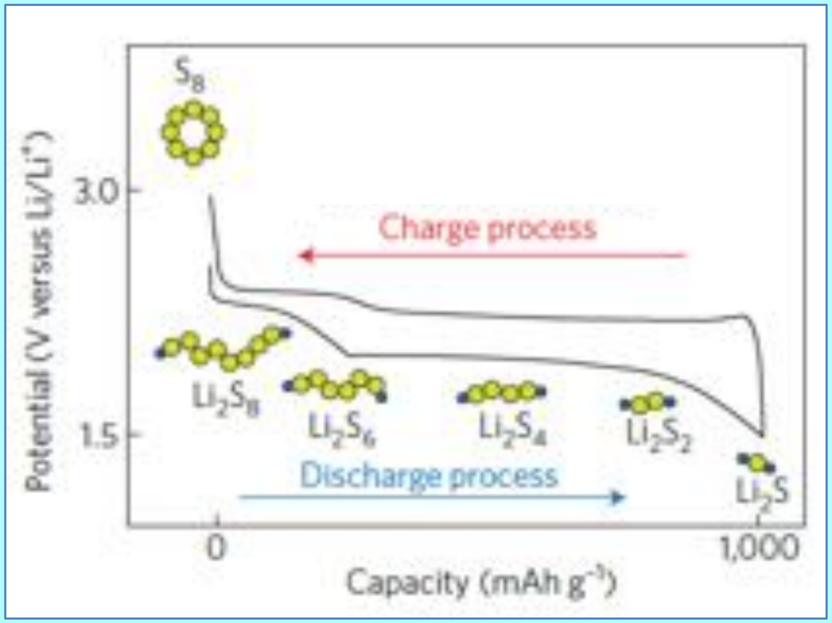
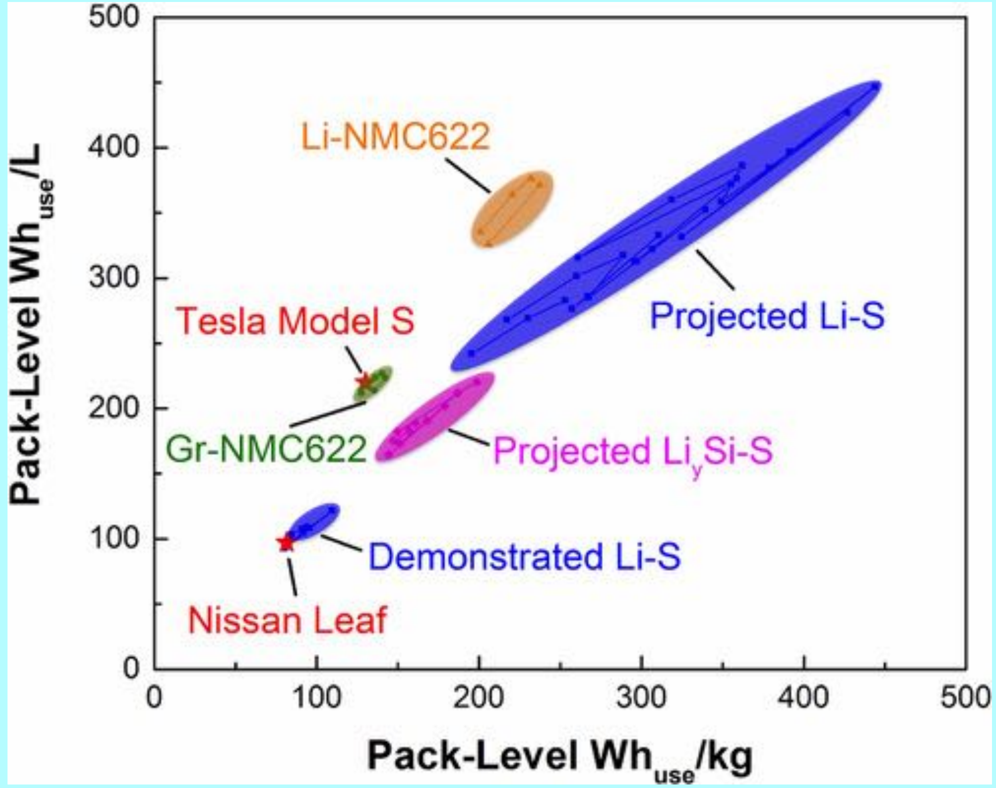
Why Lithium-Sulfur Batteries?

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

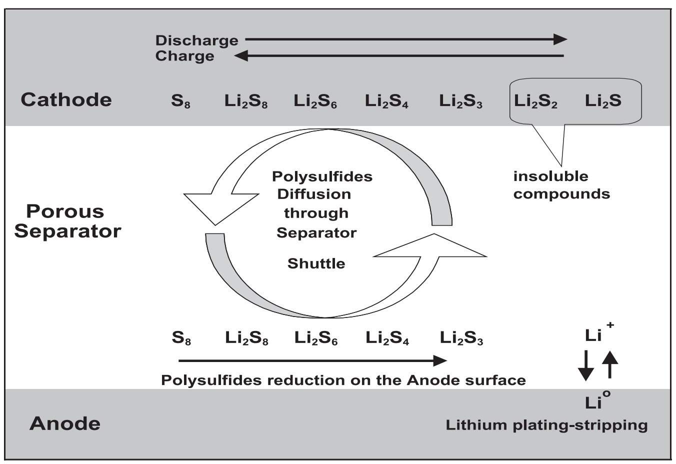
Energy Projections

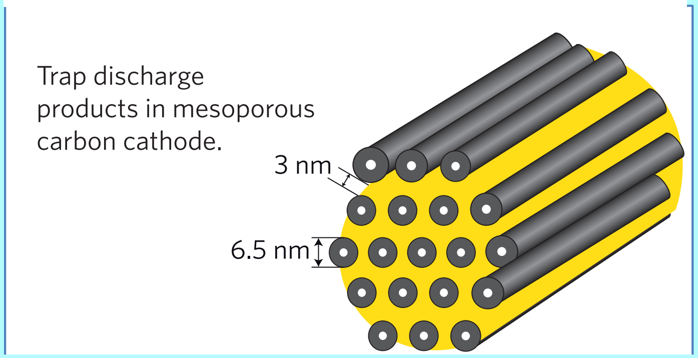


Projected pack-level Wh/kg and Wh/l for a 100 kWh, 80 kW and 360 V Li-S battery (>8 mAh/cm^2 and 7 mg S/cm^2) vs. estimated from demonstrated cell performance (~2.5 mAh/cm^2 and 2 mg S/cm^2)

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

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





- 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

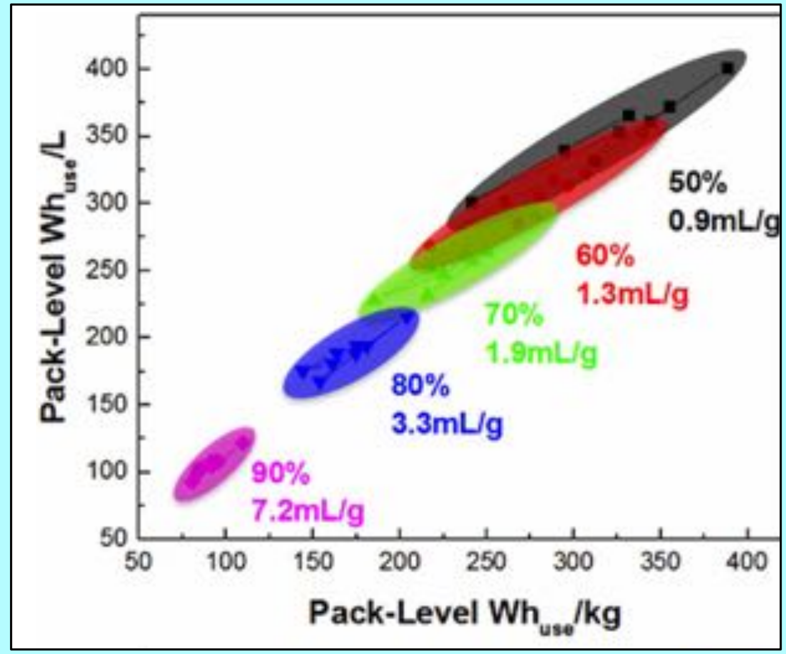
Problems	Strategies Adopted	Rationale
Poor cyclabaility and dendrites	Coat with protecting layer (solid electrolyte)	Blocks contact between Li and soluble sulfide species and/or mechanically inhibit Li dendrites
	Coat with protecting layer (gel polymer)	
Polysulfide dissolution, redox shuttle behavior	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 Conductvity 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/cm^2)**

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

Cathode Loading

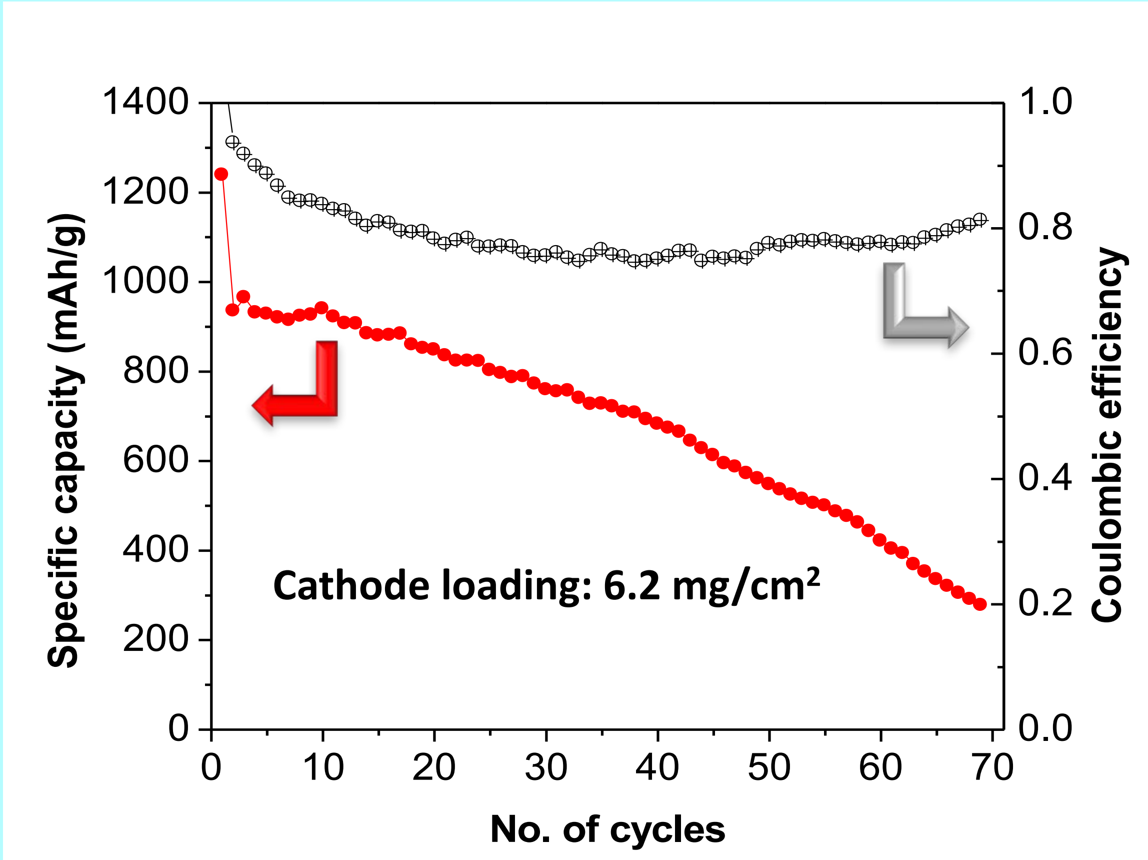
- Cathode loading in a Li-ion cell (nickel cobalt aluminum oxide, NCA): ~15 mg/cm^2, i.e., ~2.23 mAh/cm^2 or 8.9 mWh/cm^2 per side
- For 400 Wh/kg, i.e.,1.5 times the specific energy vs. Li-ion cells, i.e., 13 mWh/cm^2 per side.
- With a voltage of 2.1 V for Li-S cell, this implies an areal capacity 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.



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

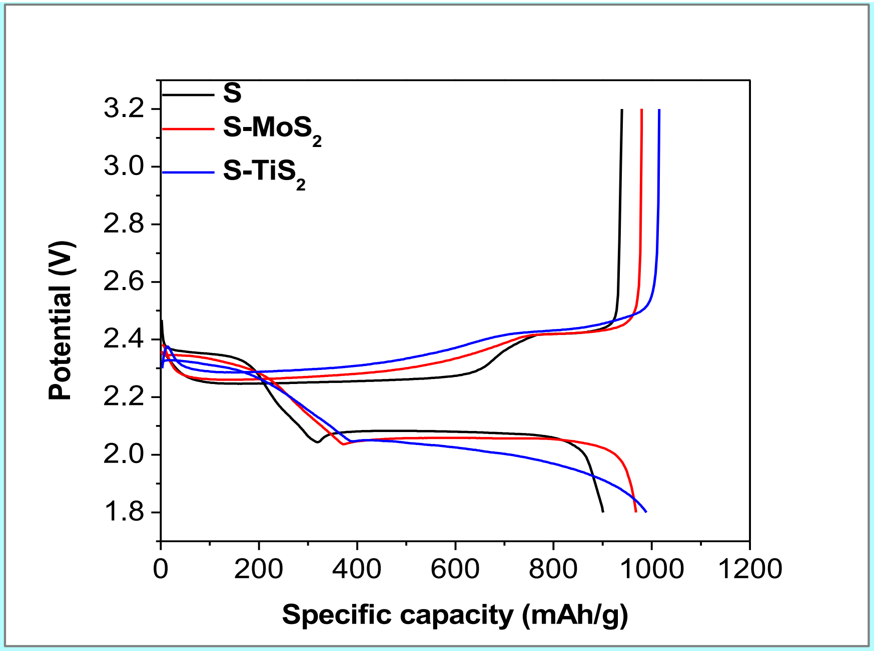
Performance of a S cathode with high Loading in a Li-S cell

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



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

High Areal Capacity 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.
- Metal sulfide provides some electronic/ionic conductivity and can replace a portion of the carbon.
    - Easier to make dense electrodes with the metal sulfide additions in place of carbon.
- TiS_2 (Manthiram and Cui et al) , VS_2, ZrS_2 (Cui et al) with low loadings (<5mg/cm^2), CuS_2 (Takeuchi et al)

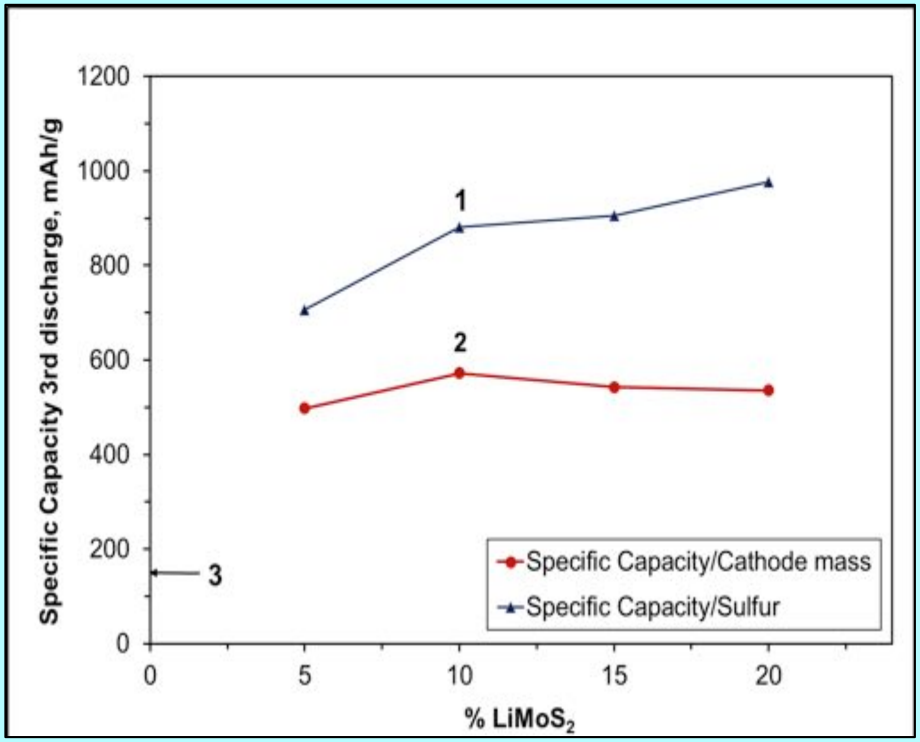
- Screened several sulfides : TiS_2, MoS_2 have shown to be beneficial

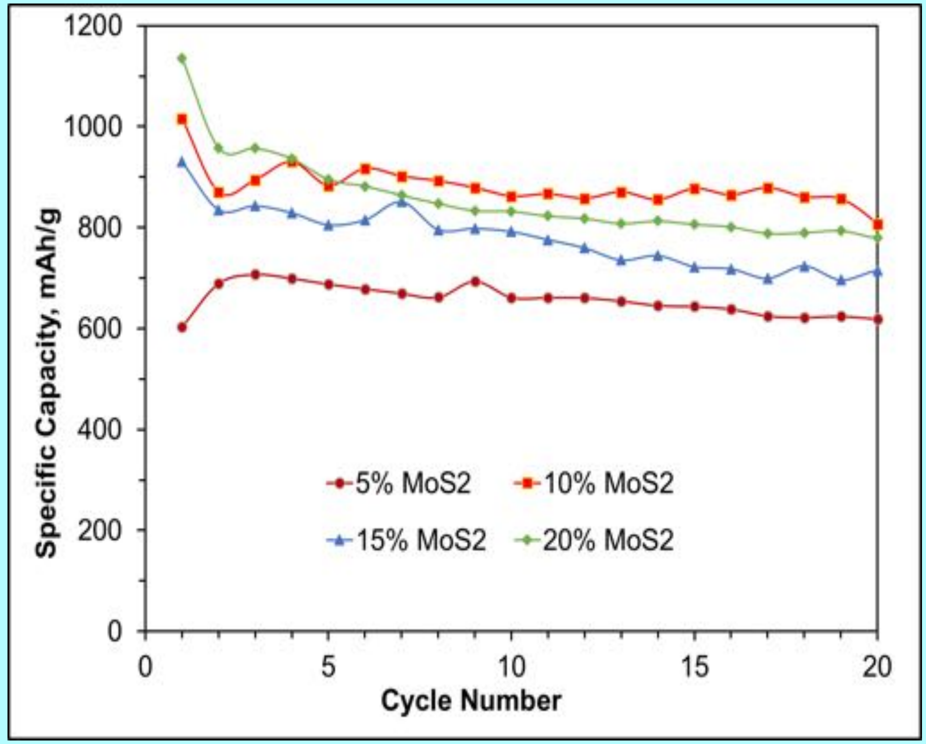
Physical and Chemical Entrapment with TiS_2

- 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.

Cui et al: Nature material Nature Communications 2014 | 5:5017 | DOI: 10.1038

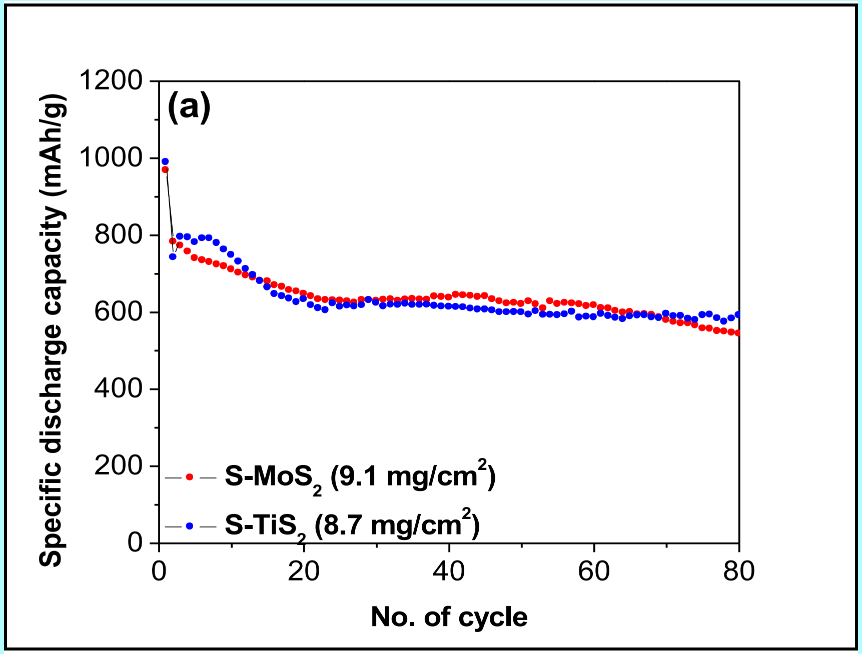
Sulfur Cathode With Different amounts of MoS_2

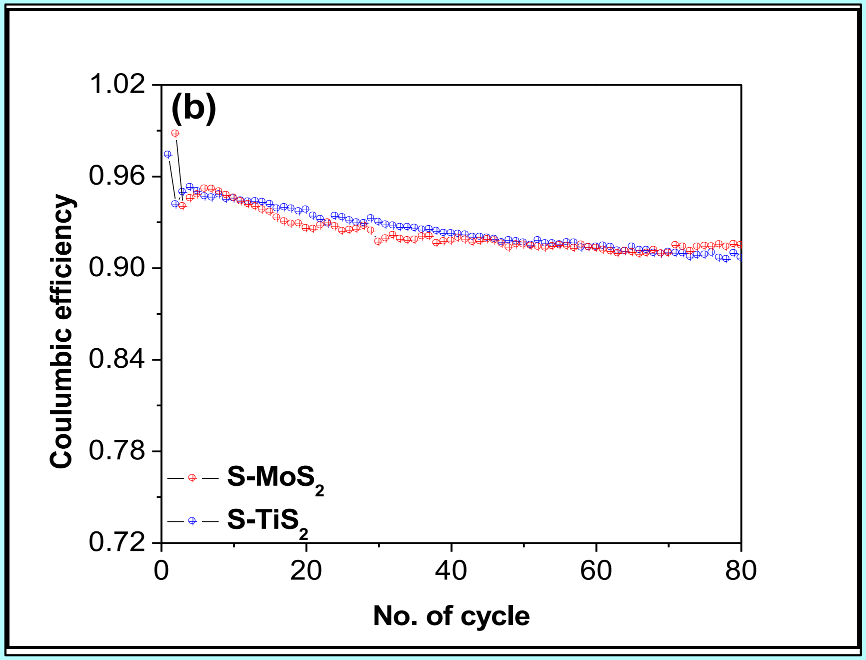




- Three times the capacity per gram of cathode material compared to Li-ion cathode powder (NCA)
- Specific capacity of sulfur increases with MoS_2 loading, but specific capacity of total cathode decreases at high loadings.
- High sulfur utilization and capacity retention during cycling with 10-15% of MoS_2 in the cathode (65% sulfur)

Sulfur blended with MoS_2 and TiS_2 (15w%)

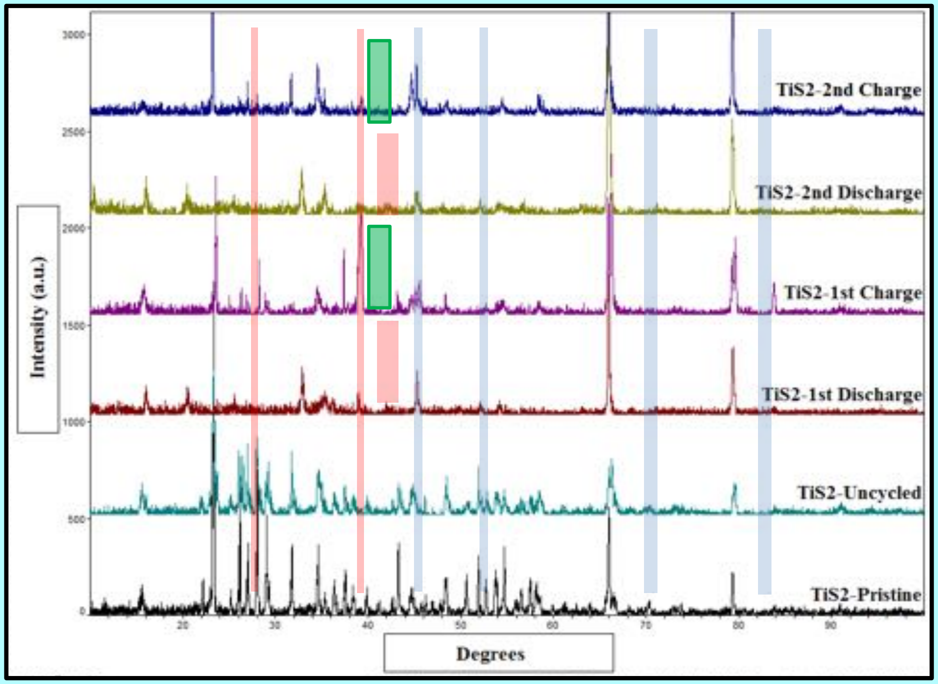




- Good performance considering the high cathode loading and high proportion of sulfur (4.6 mAh/cm^2 per side)
- High coulombic efficiency suggests polysulfide trapping.

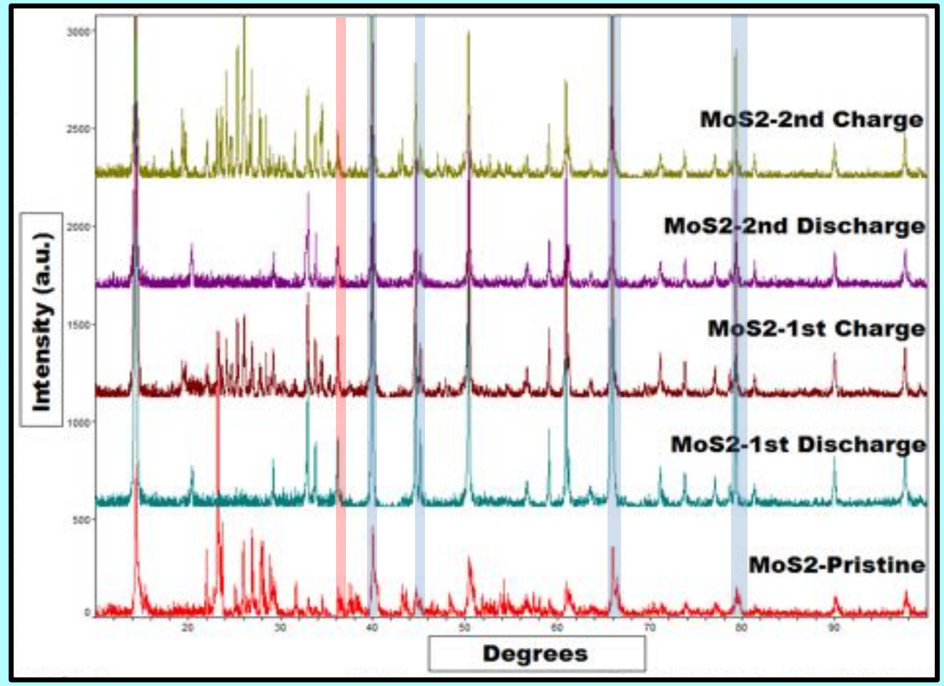
X-ray Diffraction (XRD): TiS_2 - Blended Sulfur Cathode

TIS_2-Blended Sulfur



- Blue shades ~ Al foil contribution; Red Shades ~ $LiTiS_{2;}$ Green shades ~ TiS_2
- The XRD spectra for TiS_2 electrodes showed a transition from TiS_2 to $LiTiS_2$ after discharge and transition from $LiTiS_2$ to TiS_2 after charge.

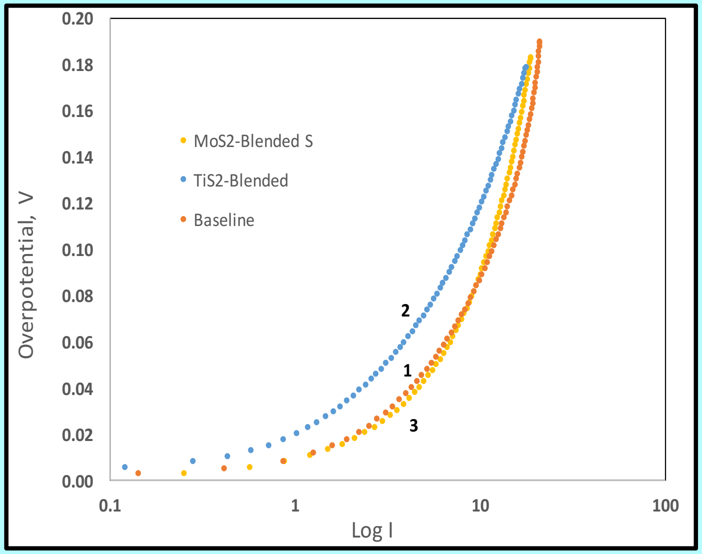
MoS_2-Blended Sulfur



- Blue shades ~ Al foil contribution; Red Shades ~ MoS_2.
- Similar to the baseline and MoS_2 electrodes the S-MoS_2 cathode showed the presence of sulfur peaks after charging and disappearance of the same peaks after discharging.
- No change in the MoS_2 peaks

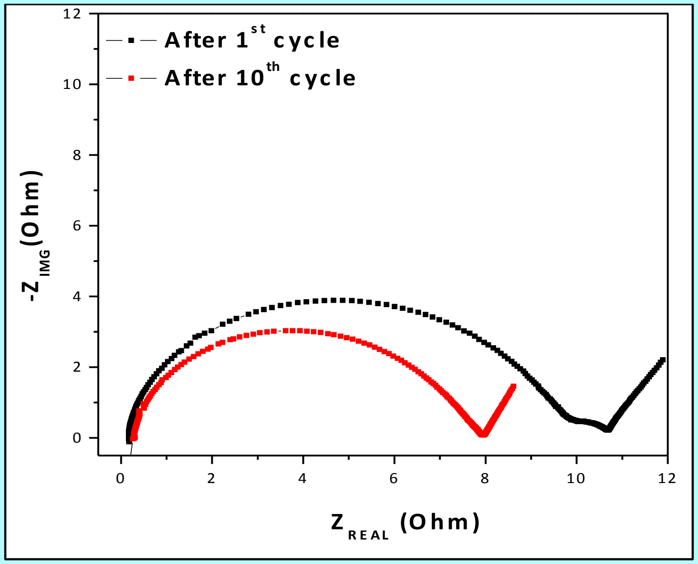
Kinetics of Sulfur Cathode

Kinetics Tafel Polarization

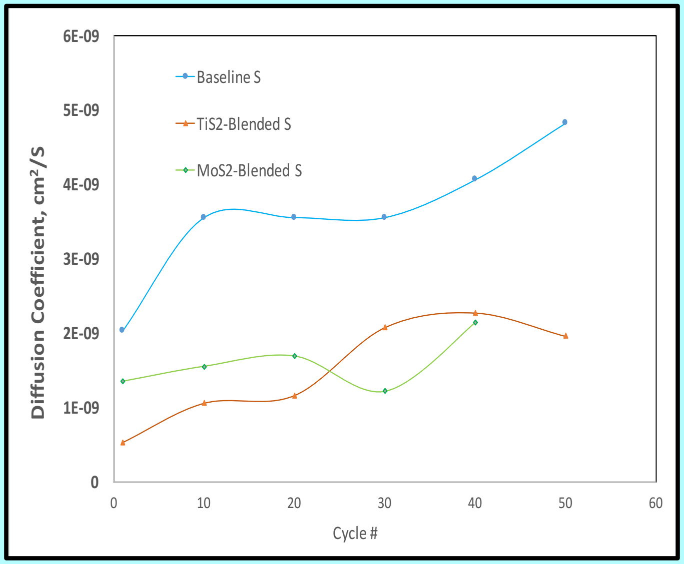


- Identical kinetics for sulfur reduction
- The exchange current density of pristine sulfur cathode is 0.19 mA/cm^2. In contrast, the exchange current densities of the composite cathodes with TiS_2 and MoS_2 blends are 0.21 mA/cm^2 and 0.23 mA/cm^2, respectively

EIS of MoS_2-Blended S Cathode



- Stable interface and lower impedance upon cycling



- Similar kinetics for Li diffusion in the cathodes.

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

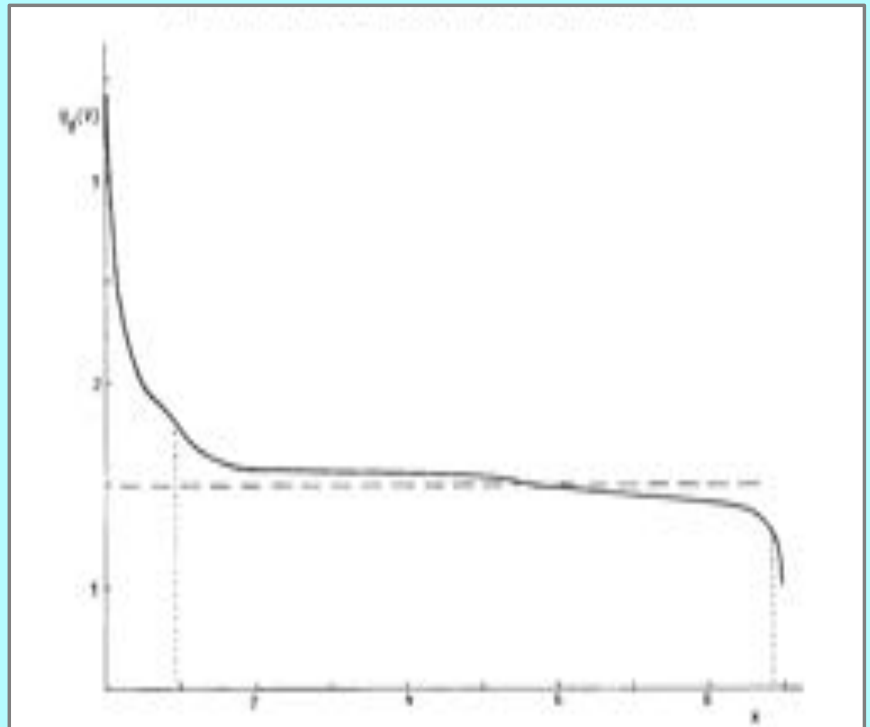
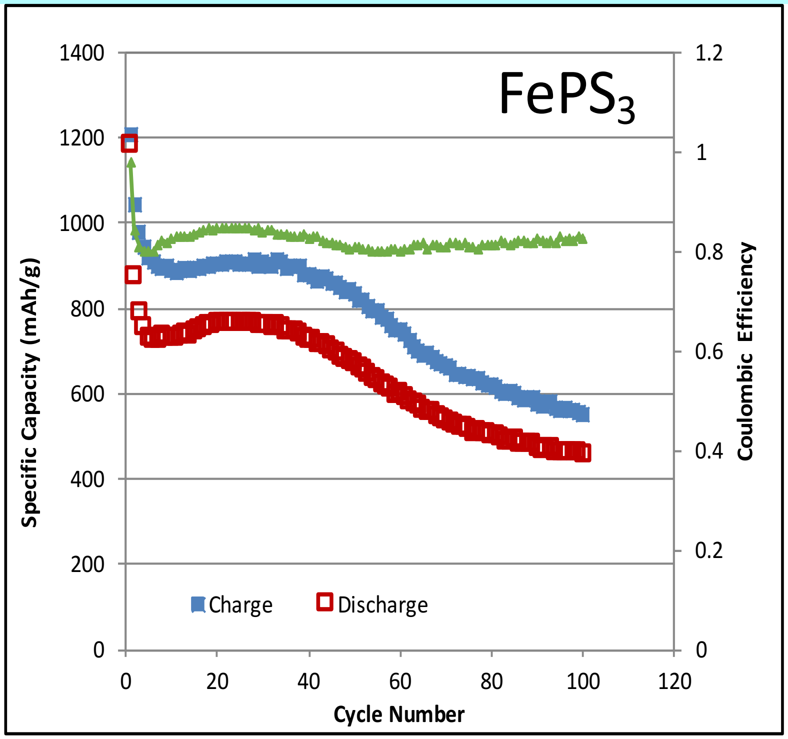
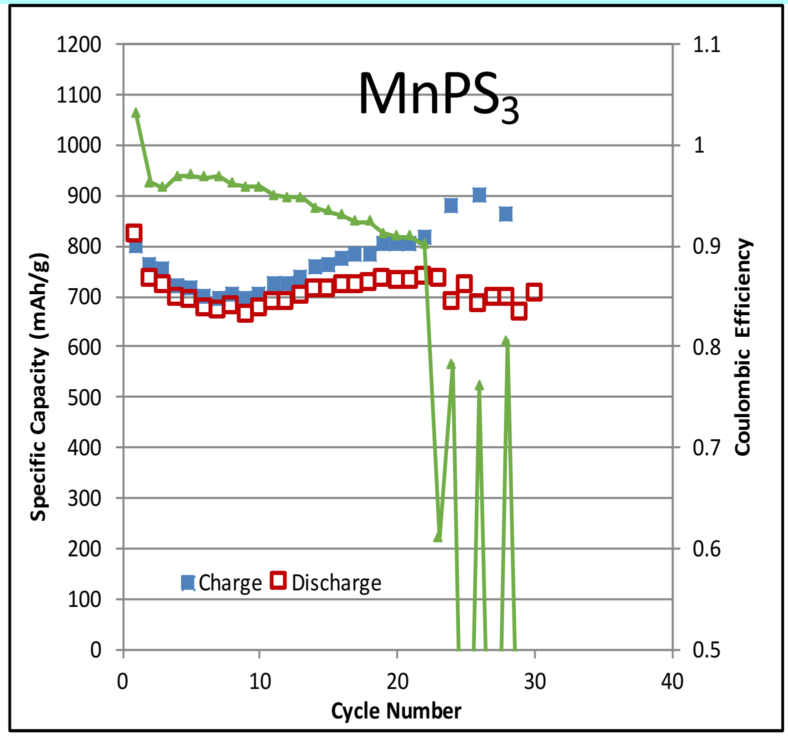


Fig. 5. Discharge curve for a button cell of the standard size 2325 for the $Li/FePS_3$ system at a resistance load of 30 kΩ. The vertical dashed lines bound the portion of the curve where the discharge voltage varies from 1.8 to 1.2 V.

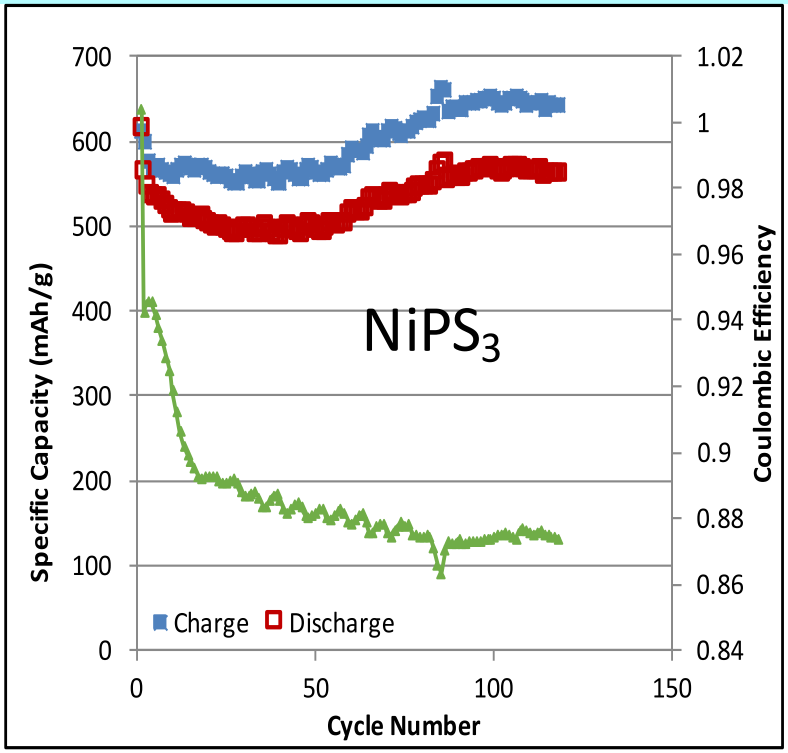
Metal Phosphorus Trisulfides for Composite Sulfur Cathodes

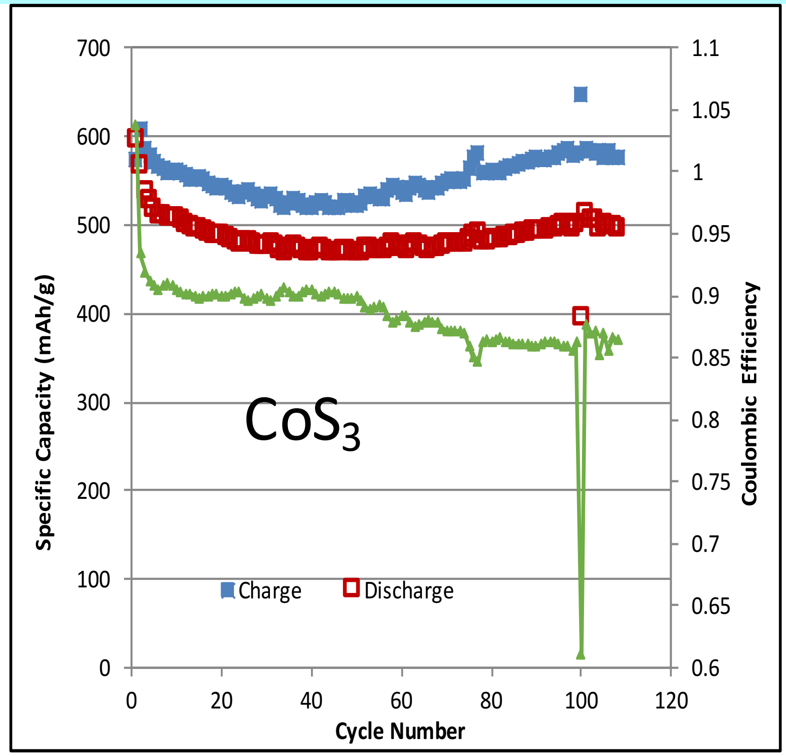




Composition:(S:MPS_3:C:PVDF=65:15:15:5); loading 5 mg/cm^2

Metal Phosphorus Trisulfides for Composite Sulfur Cathodes

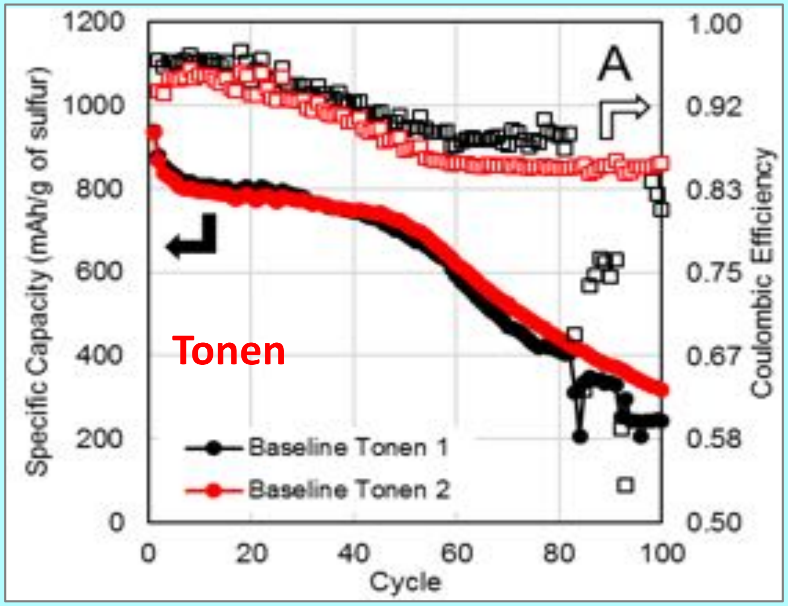




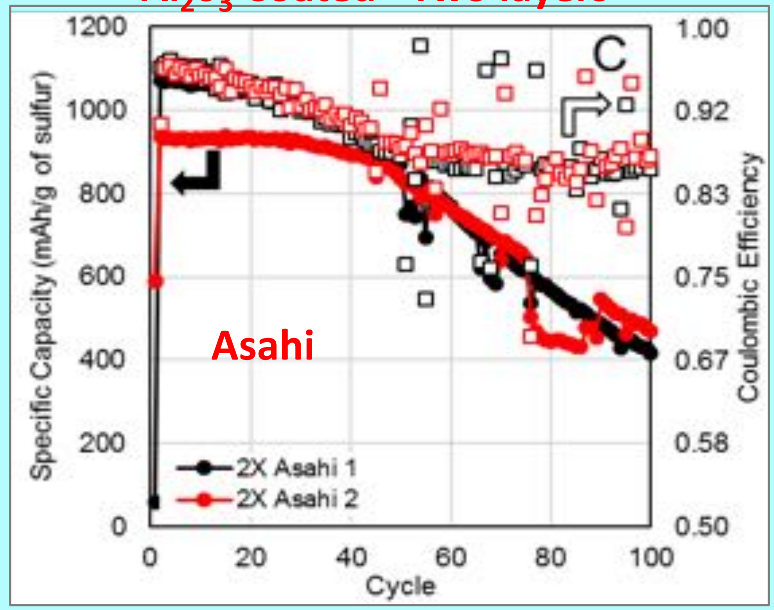
Composition: ($S:MPS_3:C:PVDF=65:15:15:5$); loading 5 mg/cm^2

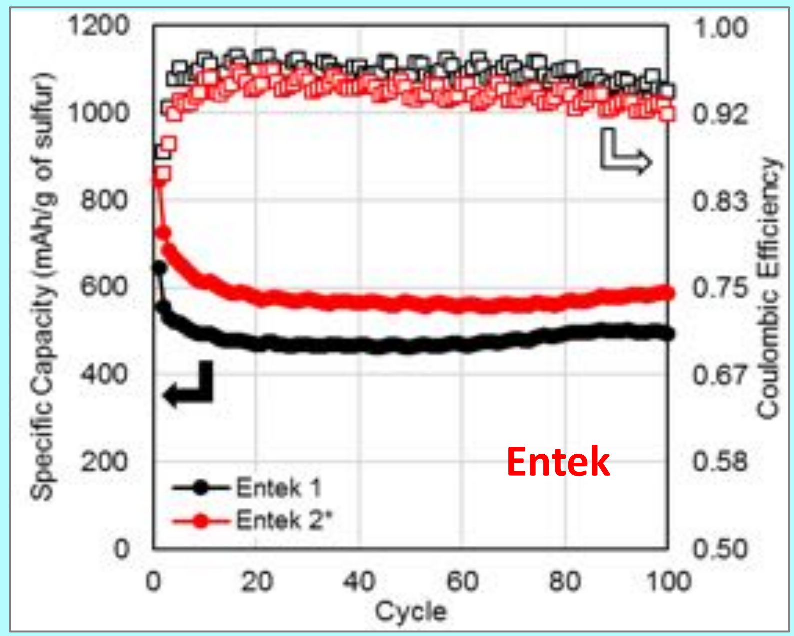
Li-S cells with Al_2O_3-coated separator (Asahi and Entek)

Tonen Separator



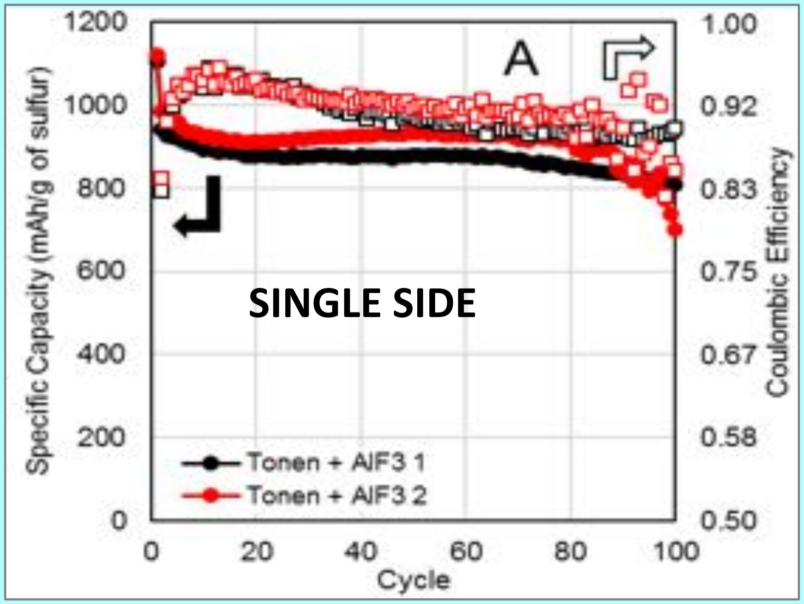
Al_2O_3 Coated –Two layers

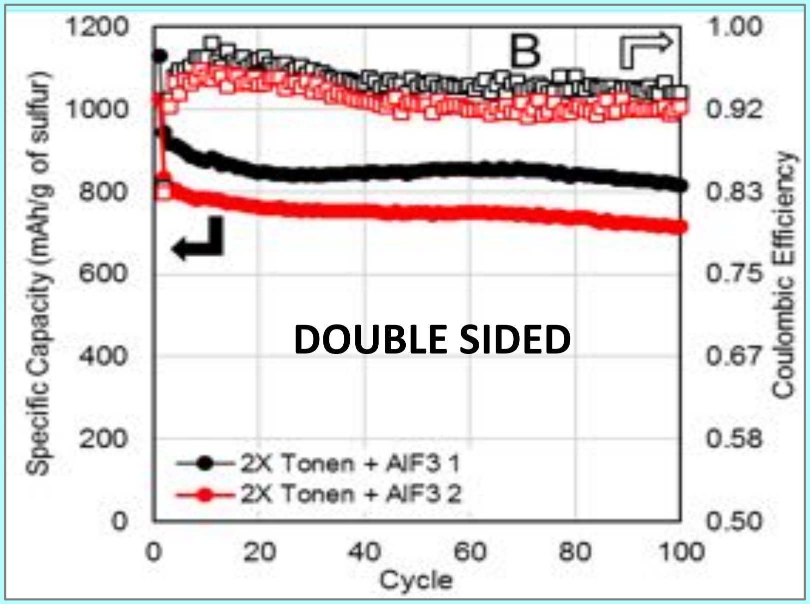




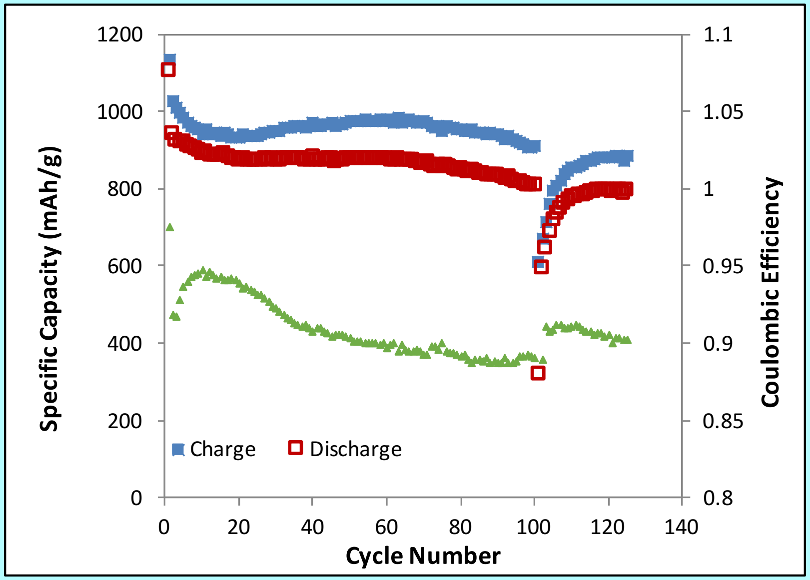
- Separator coated with Al_2O_3 on one side (typically used on the cathode side)
- Improved performance with two layers of separator
- Entek separator gives lower but stable capacity

AlF_3-coated Tonen separator (spray coated)

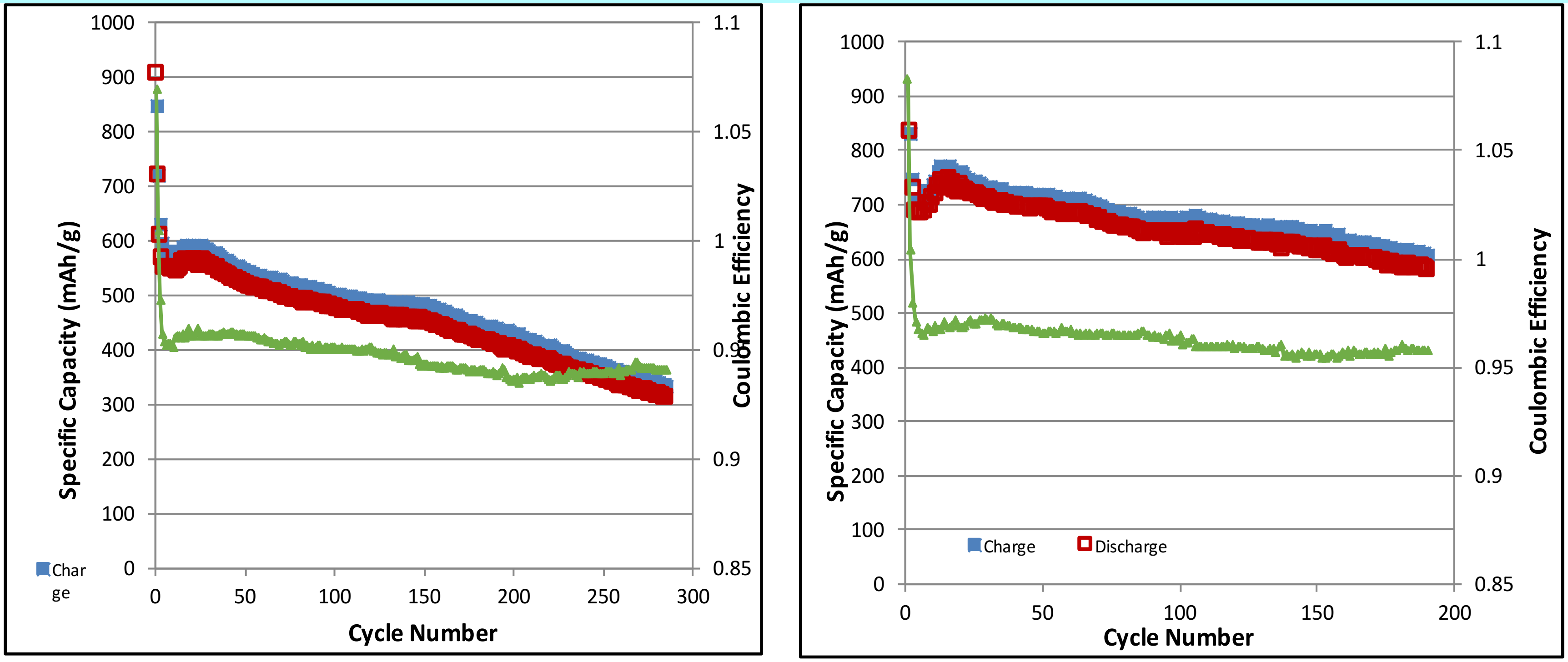




- Li-S coin cells containing sulfur cathode of composition S:CB:PVDF(55:40:5), $6.45 mg/cm^2$ and AlF_3-coated Tonen separator (spray coated)
- Good cycle life with high coulombic efficiency
- Good capacity recovery after test interruption



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

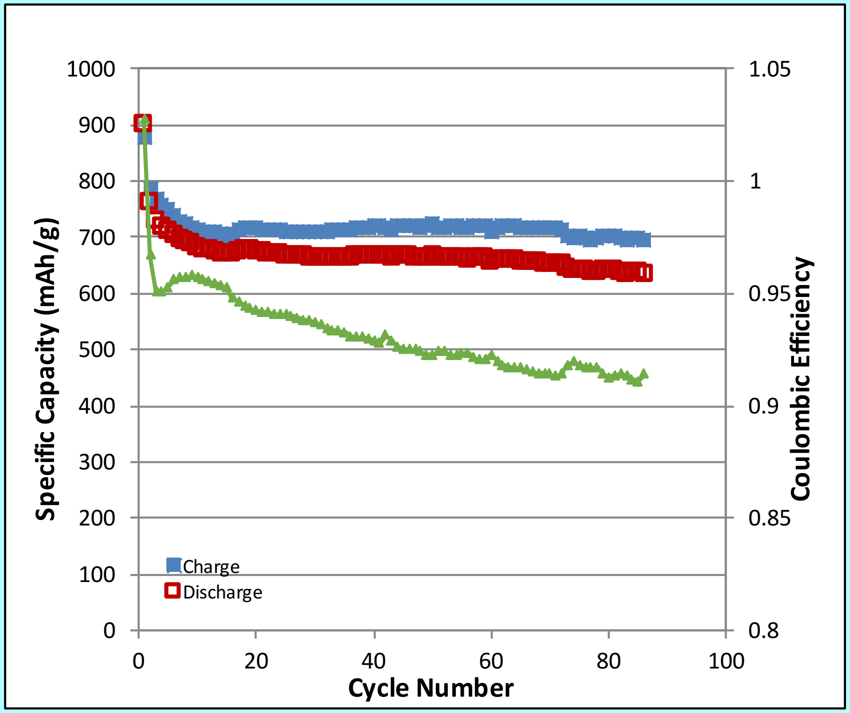


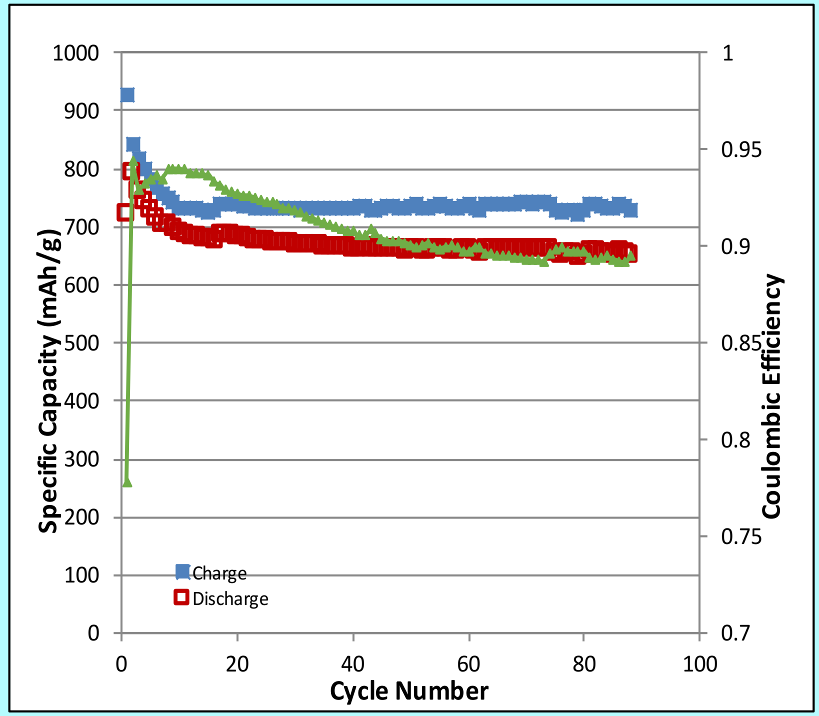
Discharge capacity of Li-S coin cells with the standard sulfur cathode (S:CB:PVDF=55:40:5) and with Tonen separator-coated with AlF_3 (doctor-blade)

- Good cyclic stability but the coating needs to be optimized to improve the initial capacity (reduce PVDF)

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

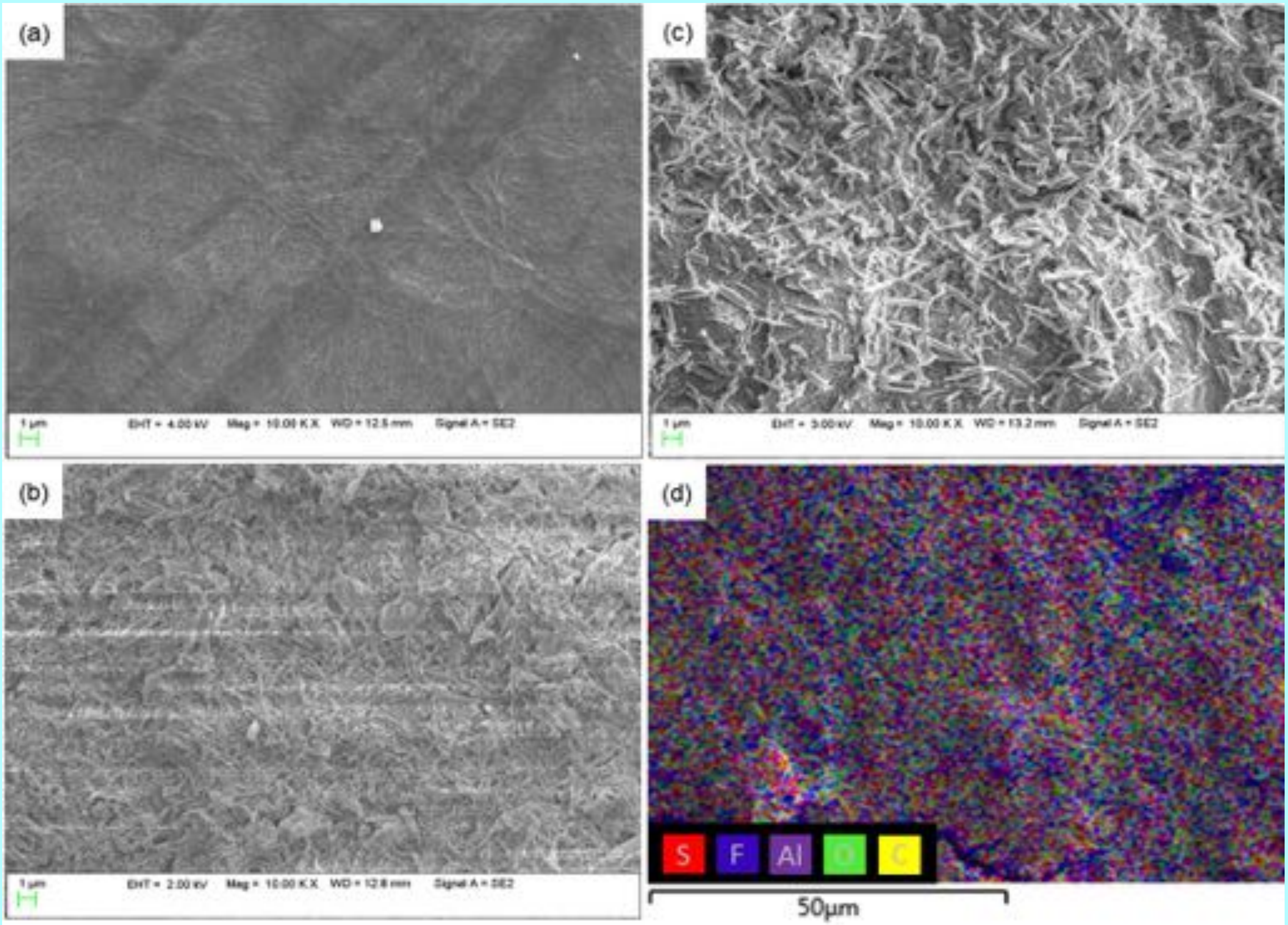
With reduced Binder in the separator coating)





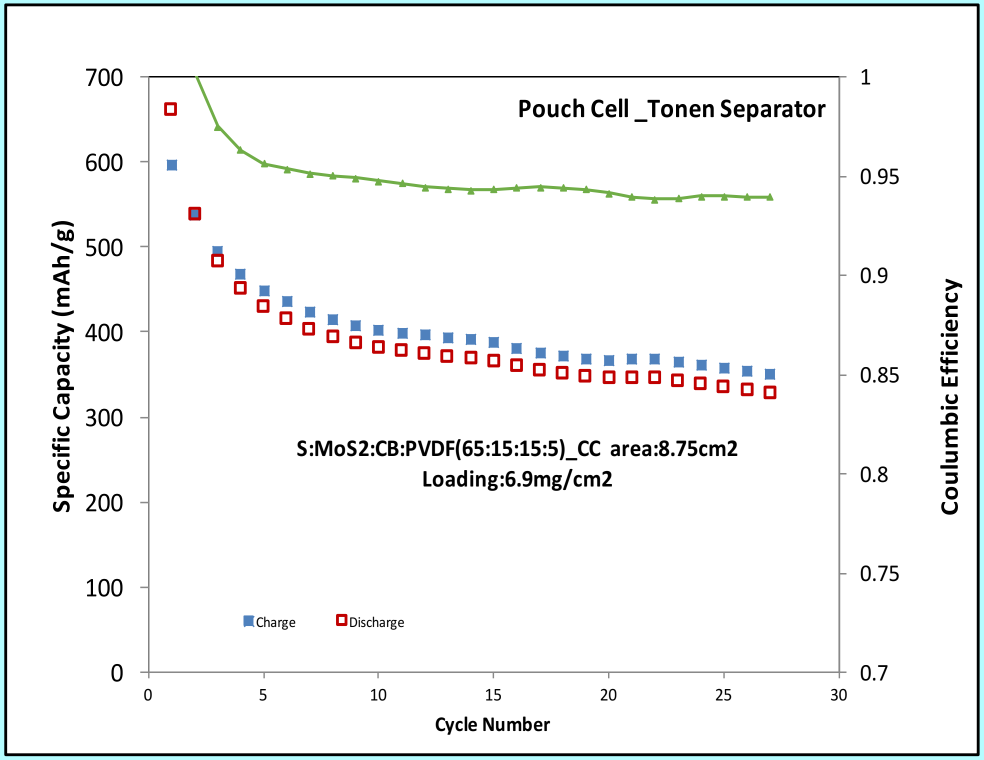
Performance of Li/S coin cells using AlF_3 coated (ALD) Li and baseline sulfur (55%) at 5 mg/cm^2 and with Tonen separator coated with AlF_3:PVDF(98:2).

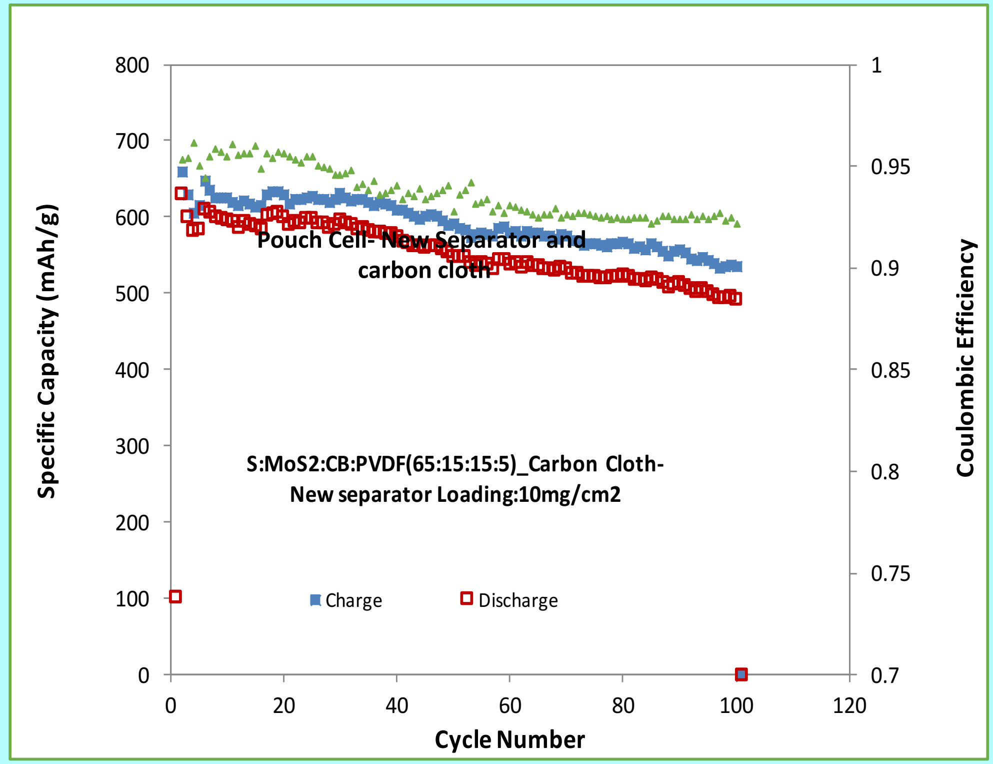
AlF_3-coated Separators from Cycled Cells



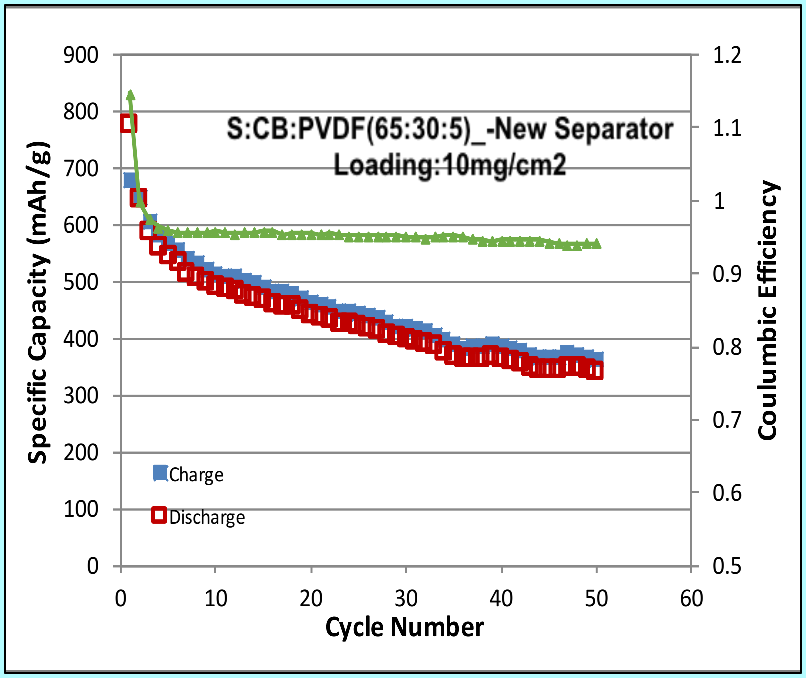
SEM images of (**a**) fresh Tonen separator, (**b**) Tonen separator coated with AlF_3 and (**c**) AlF_3-coated Tonen separator after 100 cycles showing AlF_3 material present on the surface after coating, and deposition of sulfur-containing species on the surface of these particles after cycling. EDS in (**d**) indicates approximately uniform distribution of sulfur-containing species across the surface of the coated separator.

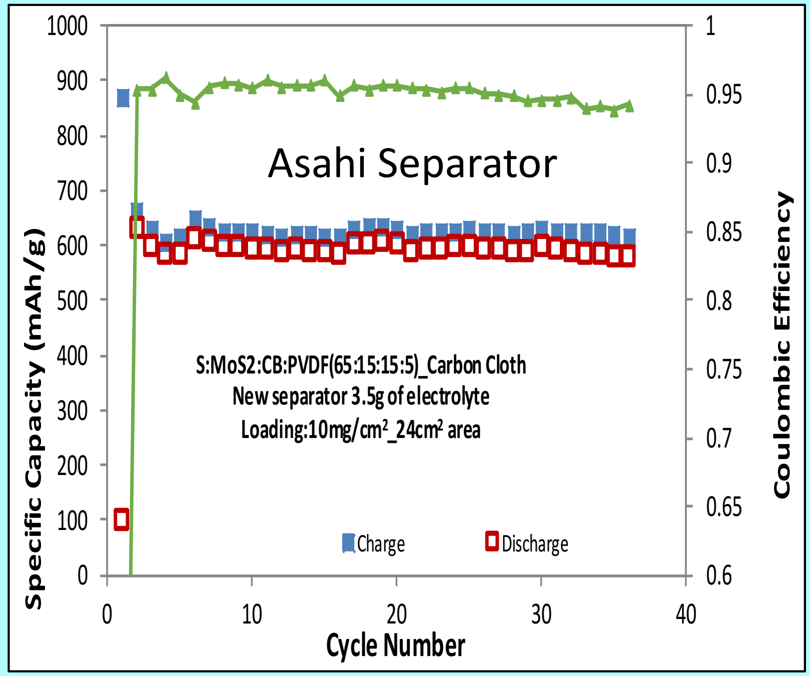
Li-S pouch cells with sulfur cathode with different separators





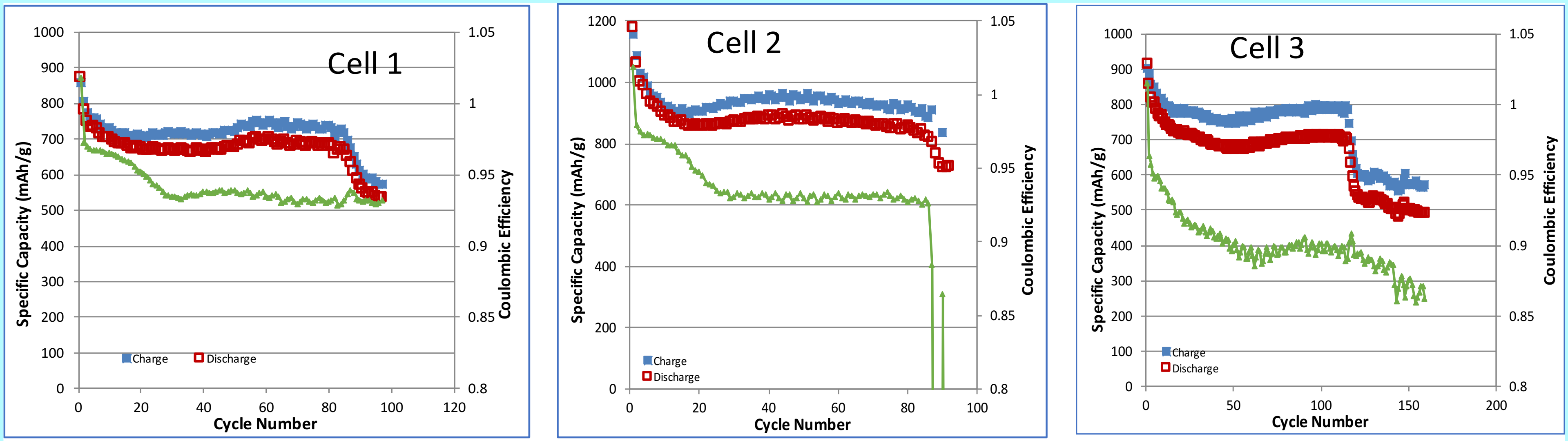
Li- S Pouch Cells





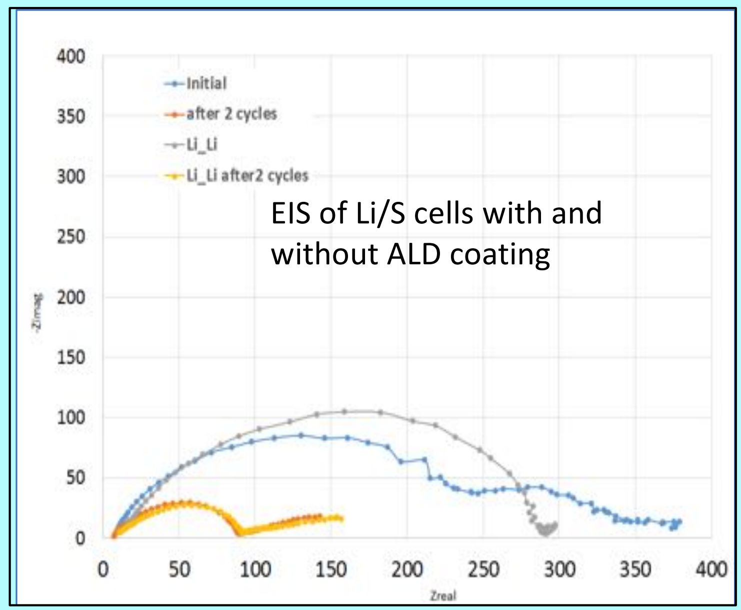
- Good coulombic efficiency but a high fade rate with the baseline sulfur
- Excellent performance with high sulfur content (65%) and loading (10 mg/cm^2) with MoS_2 blending (15%) and new separator
- 4mAh/cm^2 per side (8 mAh/cm^2 both sides) based on the realized capacity

AlF_3-coated (ALD) Li Anode



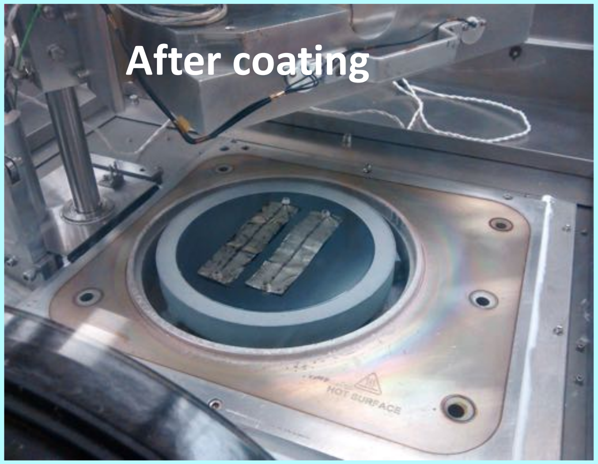
. Cycling of Li-S coin cells containing sulfur cathode of composition S:CB:PVDF(55:40:5), 5.65 mg/cm^2 with the SAFT separator in standard electrolyte with Li anode protected by an ALD coating of AlF_3.

- Procedure: Pulse $Al(CH_3)_3$ followed by HF in 40 times, which should have formed a 4.8 nm thick AlF_3 coating on Li based on calibration runs using on silicon wafers.

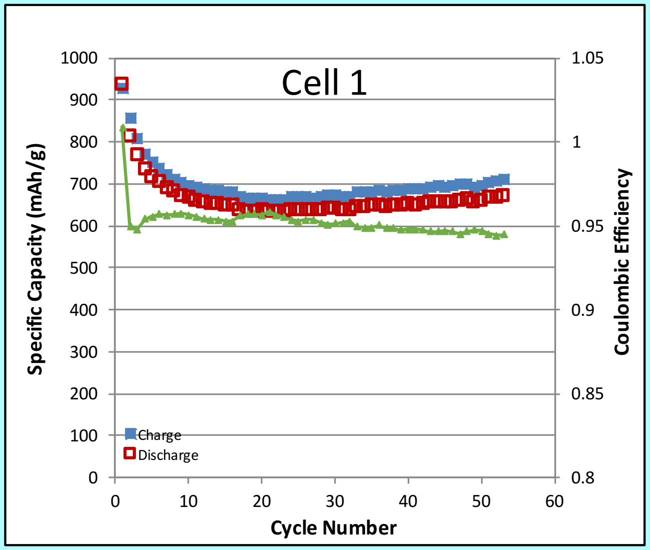


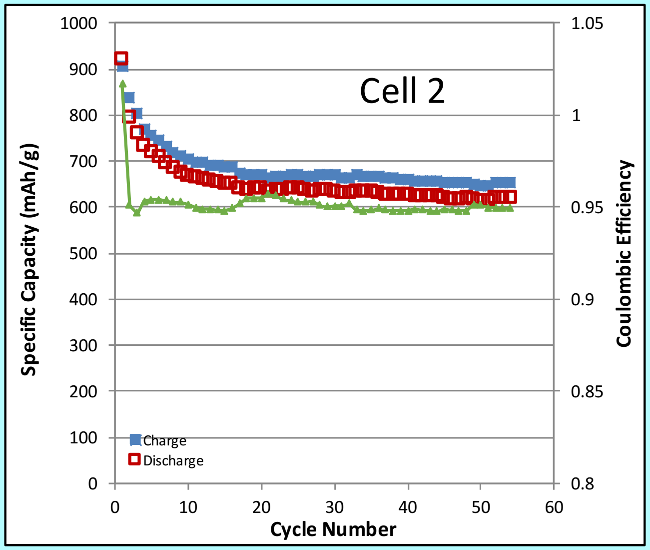
Thicker ALD Coating of AlF_3 over Li

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

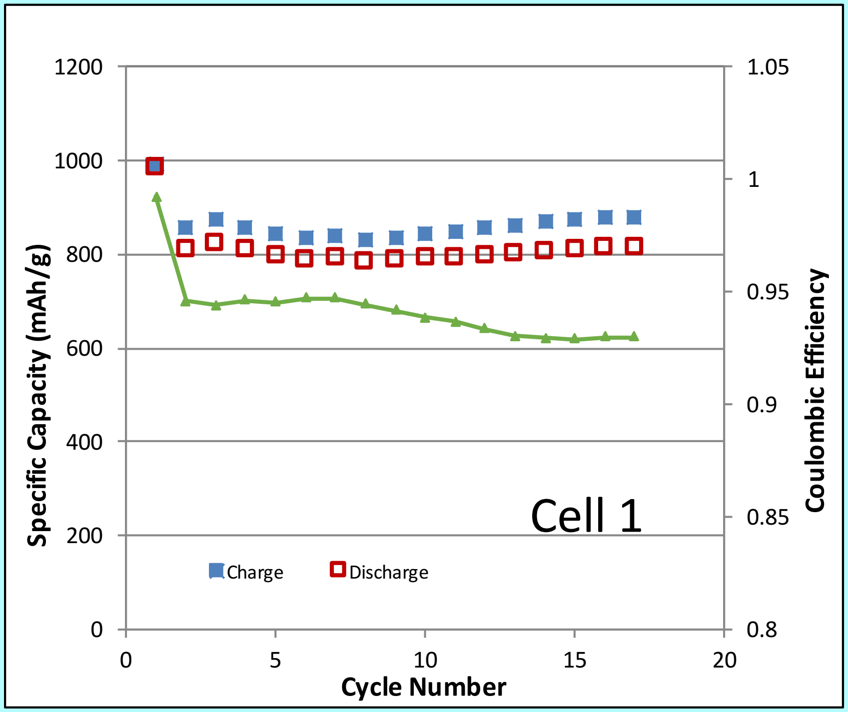


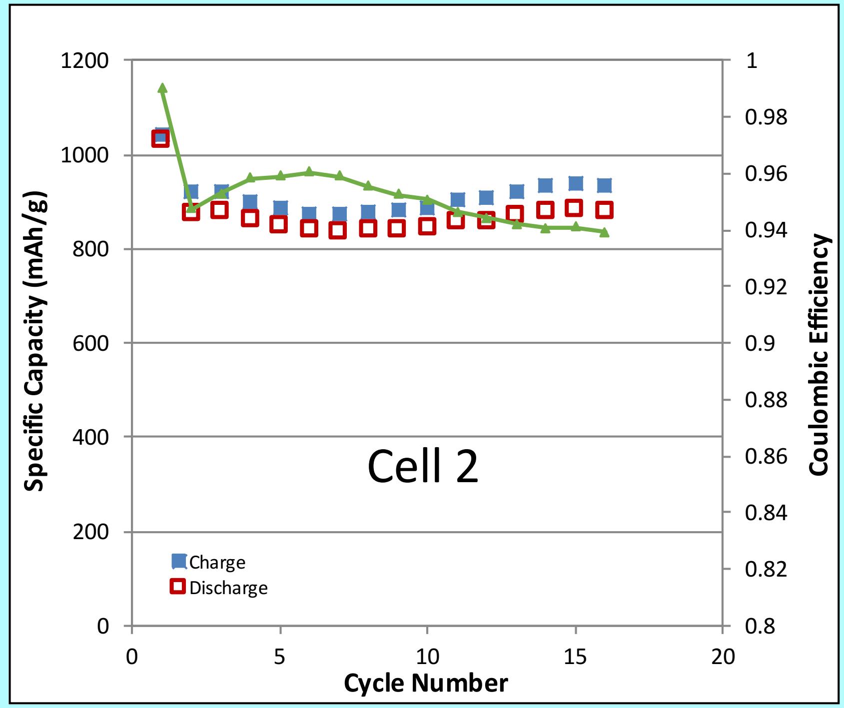
Performance of Li/S coin cells using AlF_3 coated (ALD) Li and baseline sulfur (55%) at 5 mg/cm^2 and with Tonen separator coated with AlF_3:PVDF(98:2).





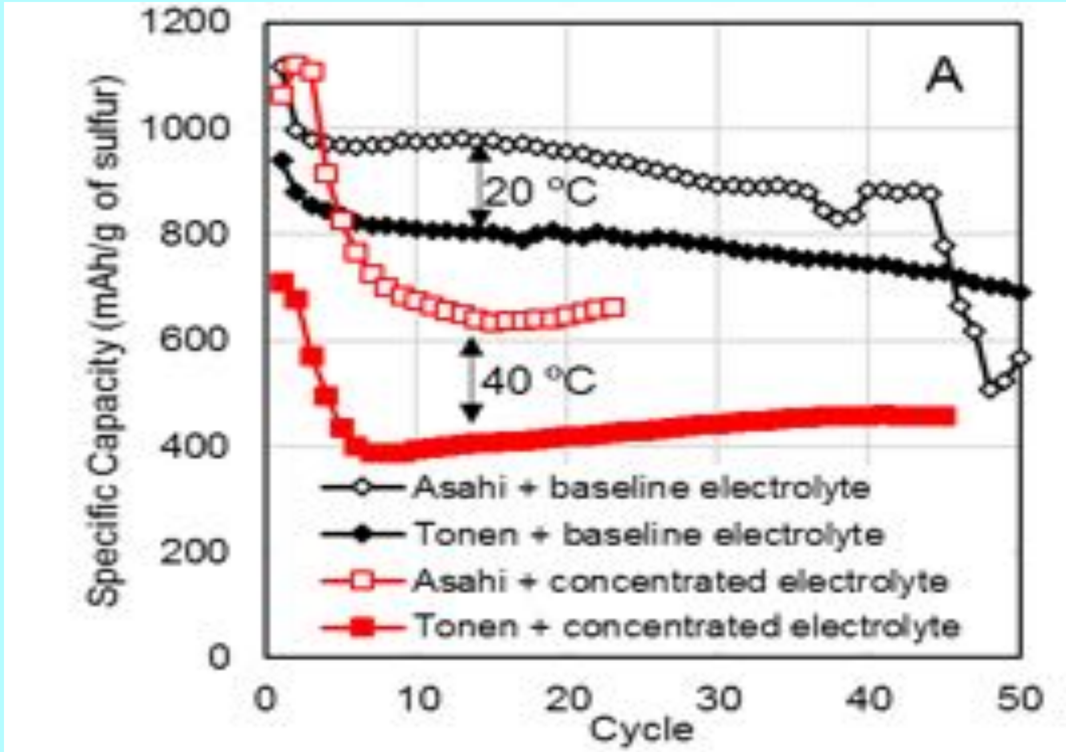
Li(ALD)/AlF_3-Tonen/S-MoS_2





- Good performance (high capacity and efficiency) of Li/S coin cells using AlF_3 coated Li and MoS_2-blended sulfur (65% with 15% MoS_2) at 11.2 mg/cm^2.
- High area specific capacity is 6 mAh/g per side.

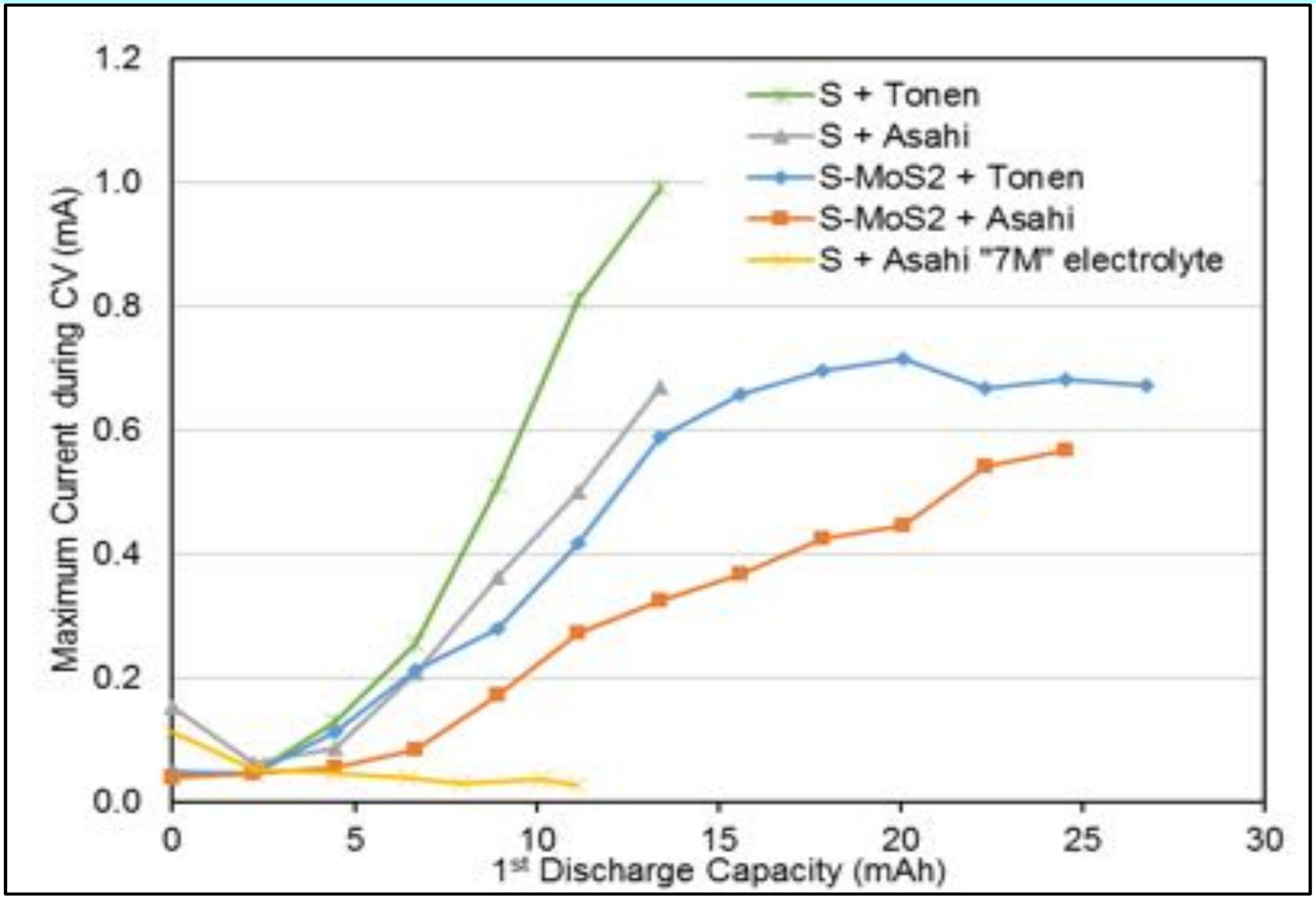
Concentrated Electrolytes



- 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 Liquan 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

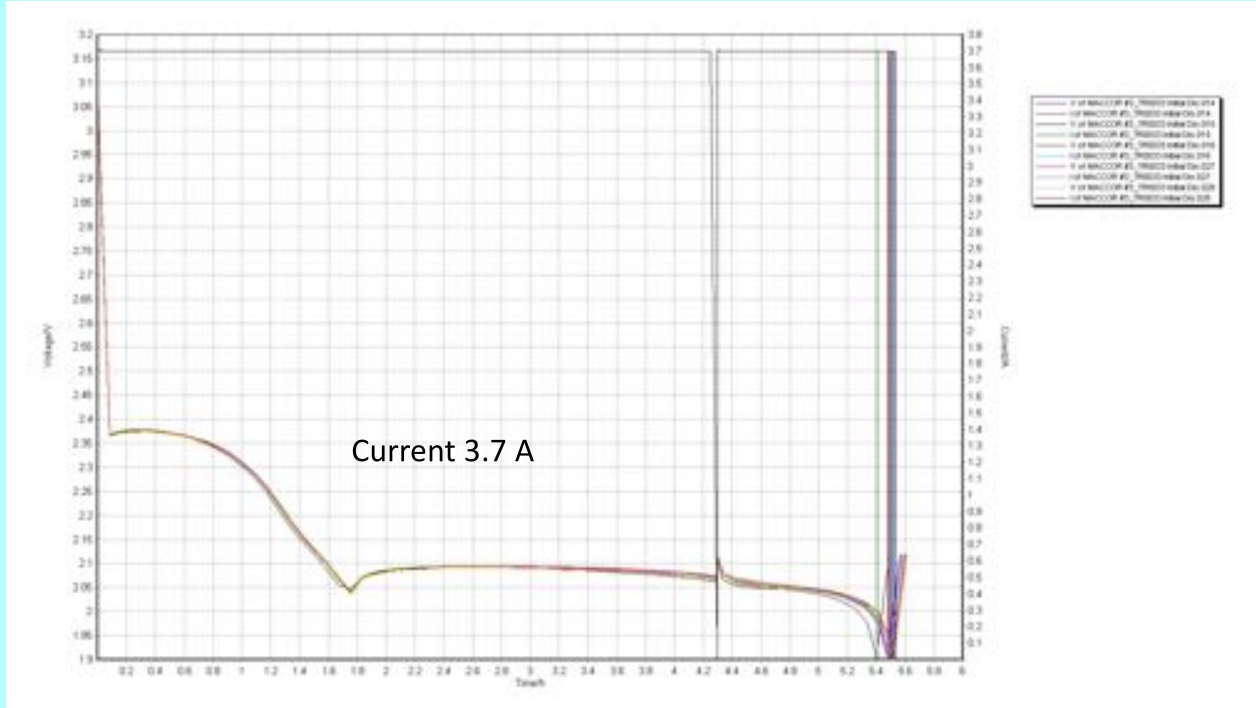
Comparison of Polysulfides with different separators/cathodes



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 will be tested at JPL



Test Pans

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/cm^2 or ~6 mAh/cm^2 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

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