High Energy Density Lithium-Sulfur Batteries for Aerospace Applications

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Li-Ion Batteries in Space Missions

- Lithium-ion batteries are being widely used in the space missions
  - For the recent Mars and other planetary missions, we used batteries custom Li-ion cells (10-45 Ah) with lithium nickel cobalt oxide (NCO) cathode, MCMB anode and the low temperature ternary carbonate electrolyte
    - Excellent performance both in terms of cycle and calendar life
    - Cell balancing methods were utilized to prevent overcharge.
  - GS Yuasa cells (large-format) were also used in some of the missions
  - Also, we used batteries made from the small cylindrical cells (18650) from commercial manufacturers, after careful screening and cell matching.
    - Built-in safety devices
    - No need for charge-balance electronics
    - High degree of redundancy
    - Only Sony HC cells have been used so far, The recent high energy cells are being considered for the upcoming missions

Li-ion Batteries on NASA Missions

Project	Launch Date	Battery Size	Battery Vendor
ST-5	March 22, 2006	6 Ah, 2s6p	ABSL, UK
Interstellar Boundary Explorer (IBEX)	October 19, 2008	55 Ah, 8s1p	Yardney/Lithion
Lunar Reconnaissance Orbiter (LRO)	June 18, 2009	80 Ah, 8s84p	ABSL, UK
Solar Dynamics Observatory (SDO)	February 11, 2010	100 Ah, 8s104p	ABSL, UK
Van Allen Probes (formerly RBSP)	August 30, 2012	50 Ah, 8s1p	GSYuasa
Mars Atmosphere and Volatile Evolution (MAVEN)	November, 2013	55 Ah, 8s1p	Yardney/Lithion
Global Precipitation Measurement (GPM)	June, 2014	3 – 80 Ah, 8s84p	ABSL, US
Magnetospheric Multiscale (MMS) spacecraft	October, 2014	74 Ah, 8s60p	ABSL, US
DSCOVER (Triana)	November, 2014	10 Ah, 8s10p	ABSL, US
Geostationary Operational Environmental Satellite (GOES-R)	2015	44 Ah, 3p12s	Saft, US
Ice, Cloud, and land Elevation Satellite (ICESAT-2)	2016	134 Ah, 8s1p	EPT(GS Yuasa Cells)
Joint Polar Satellite System (JPSS)	2017	2 – 100 Ah, 8s84p	ABSL, US
James Webb Space Telescope (JWST)	2018	55 Ah, 8s44p	ABSL, US
Solar Probe Plus	2018	20 Ah, 8s20p	ABSL, US

Li-ion Batteries on NASA Missions

Project	Launch Date	Battery Size	Battery Vendor
Mars Surveyor Program Lander	Planned for 2001 (cancelled)	30 V, 62 Ah (custom cell 31 Ah cells 8S2P)	Yardney Technical Products, CT
Mars Exploration Rovers (Spirit and Opportunity)	June 2002	30 V, 20 Ah (custom cell 10 Ah cells 8S2P)	Yardney / Lithion
Mars Phoenix Lander	2007	30 V, 62 Ah (custom cell 31 Ah cells 8S2P)	Yardney / Lithion
Kepler	2009	30V, 20 Ah, (Small cells- 8S10P)	ABSL, UK
Juno	2011	30 V, 110 Ah (custom cell 55 Ah cells 8S2P)	Yardney / Lithion
Aquarius	2011	30 V, 120 Ah (4 x 8S20P small cells)	ABSL, UK
GRAIL	2011	30 V, 31 Ah (31Ah cells 8S1P)	Yardney / Lithion
NuStar	2012	30V, 40Ah, (18650 cells- 2 x 8S16P)	ABSL, US
Mars Science Laboratory (Curiosity)	November, 2012	30 V, 86 Ah (43Ah cells 8S1P)	Yardney / Lithion
SMAP	2015	30V, 90Ah, (18650 cells- 8S82P)	ABSL, US
Mars Insignt	2016	30 V, 62 Ah (31 Ah cells 8S2P)	Yardney / Lithion
Mars 2020 (MSL-II)	2020	30 V, 86 Ah (43Ah cells 8S1P)	Yardney / Lithion

There are a few human exploration missions (e.g., International Space Station)

NASA Relevance- High Energy Batteries for Extra-Vehicular Activity

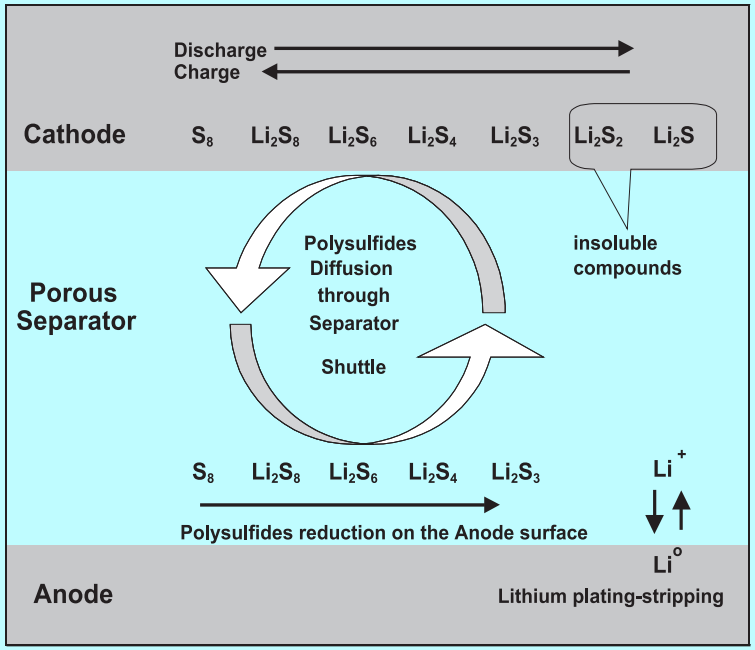
Performance Parameter	Cell Level	Battery Pack
Total Energy		1625 Wh
Specific Energy	>300 watt-hour (Wh)/kg	250Wh/kg
Cycle Life	200	200
Operational Temperature	0 to 30^0 C	0 to 30^0 C
Volume		4 Liters
Mass		6.5 Kg
Voltage		28V
Discharge Rate	C/10	C/10
Safety	Tolerant to Electrical and Thermal Abuse	Tolerant to Electrical and Thermal Abuse

Portable Life Support System

- **High specific energy of 400 Wh/kg at the cell level desired.**
- **Cycle life is less demanding (100-200 cycles).**
- **Li-S is the system that can possibly meet these requirements.**
- **Challenge is to advance the technology towards maturation in 3 y (demonstration in modules).**

Problems with the Current Li-S Cells

- Li-S cells have high specific energy, but the cycle life and safety are inadequate.
- Prototype cells currently being manufactured by Sion Power in the USA have specific energies of ~350 Wh/kg for <100 cycles. Oxis Energy (UK) cells are reported to have longer cycle life but the specific energy is lower (250 Wh/kg). The challenge is thus to achieve high specific energy combined with good cycle life.
- Poor reversibility of anode due to passivation and dendrite formation.
- Sulfur expands by 79% upon Li uptake, causing Li_2S to pulverize and lose electrical contact.
- Poor conductivity of S and its discharge products.
- Polysulfides dissolve in many solvents and cause adverse effects:
  - Redox shuttle behavior which lowers efficiency and cathode capacity.
  - Build-up of an insulating layer (of Li_2S_2 and Li_2S) on the anode which reduces power capability.



Component Development

- Li anode protected with a polymer electrolyte
  - Spin coating a thin layer (~1-10 μm) of pre-formed poly(3,4-ethylenedioxythiophene)-PEO block copolymer (PEDOT-co-PEO), an electronic and ionic conductor (I. S. Kang, et al, *J. Electrochem. Soc.* 161, A53 (2014)).
- Electrolyte
  - DME and DOL blends with different additives and co-solvents
  - Lithium nitrate for protecting Li anode from polysulfides
- Sulfur Cathode with high areal capacity (mAh/cm2)
- Test Cells
  - Coin cells, laboratory pouch cells and prototype pouch cells

High Loading of Sulfur cathode

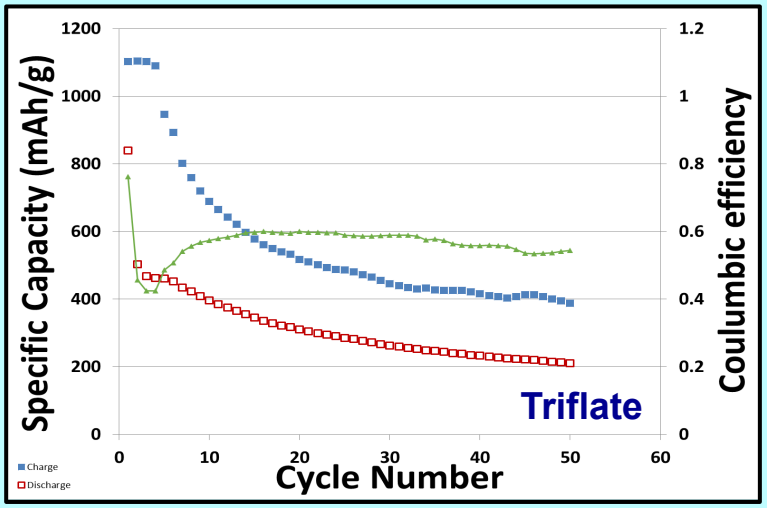
- High cathode loadings required
  - High energy Li-ion cells have cathodes (Nickel cobalt aluminum oxide, NCA) with a loading of 22 mg/cm^2, i.e., ~2 mWh/cm^2 per side of the electrode.
  - For a specific energy of 400 Wh/kg, we will need 1.5 times the specific energy compared to Li-ion cells, i.e., 18 mWh/cm^2 per side.
  - With a voltage of 2.1 V for Li-S cell, this implies an areal capacity of ~8.57 mAh/cm^2 for the sulfur cathode.
  - With 800 mAh/g from sulfur (and with a composition of 65% sulfur), the required loading is 16.5 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.

Electrolytes for Li-S Cells

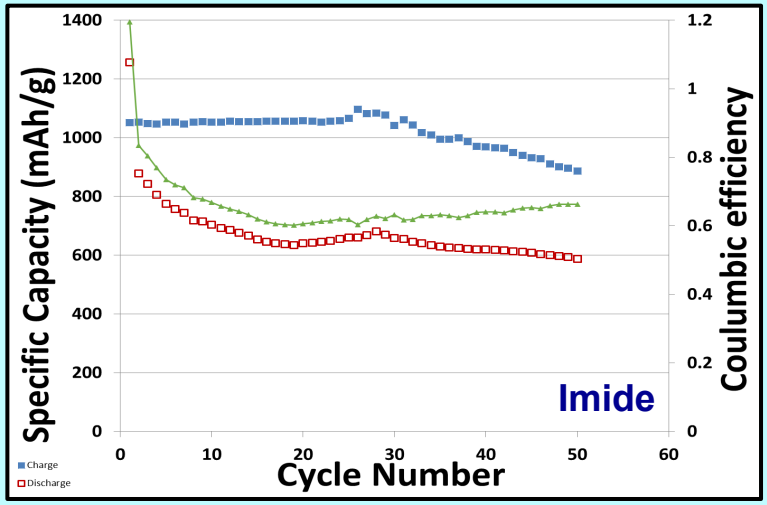
- Evaluated different electrolytes
  - Salts: lithium triflate and lithium bis(trifluoromethane)sulfonimide (TFSI)
  - Solvents: Dimethoxyethane (DME), Dioxolane (DOL). Fluoroethylene Carbonate (FEC), Trifluoroethyl butyrate (TFEB) and N-butyl- N-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (BMP-TFSI)
  - Additives: (Vinylene carbonate VC)
  - 1.0M LiOTf in DME + (DOL) (95:5 vol.)
  - 1.0M LiTFSI, DME + DOL (95:5 vol.)
  - 1.0M LiTFSI, DME + DOL (95:5 vol.) + 2% VC
  - 1.0M LiTFSI, DME + TFEB + DOL (75:20:5 vol.) (fluorinated ester co-solvent)
  - 1.0M LiTFSI, DME + FEC + DOL (75:20:5 vol.) (FEC co-solvent)
  - 1.0M LiTFSI, DME+BMP-TFSI+DOL (45:50:5 vol.) – (Ionic Liquid co-solvent)
- Cathode: Sulfur blended with carbon (Super P) with PVDF binder (55%S + 40% carbon + 5 % PVDF)
- Coin cells with Li anode and Tonen separator

Effect of Electrolyte in a Li-S Cell

1.0M LiOTf, DME+DOL (95:5 vol.)

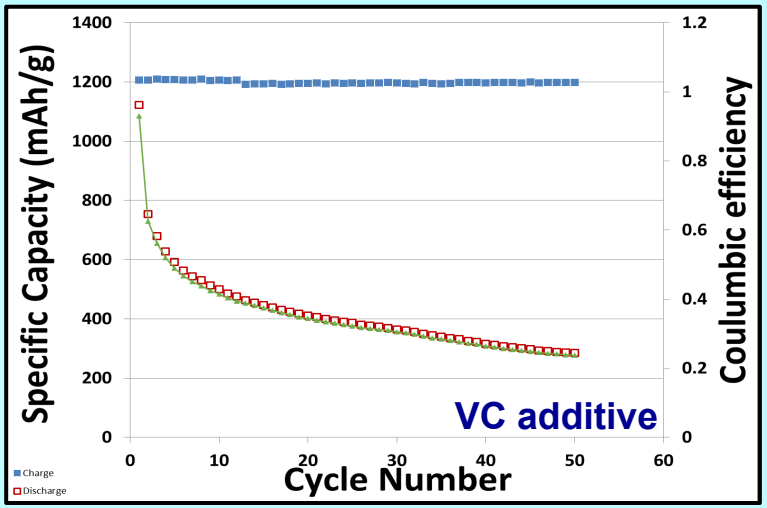


1.0M LiTFSI, DME+DOL (95:5 vol.)

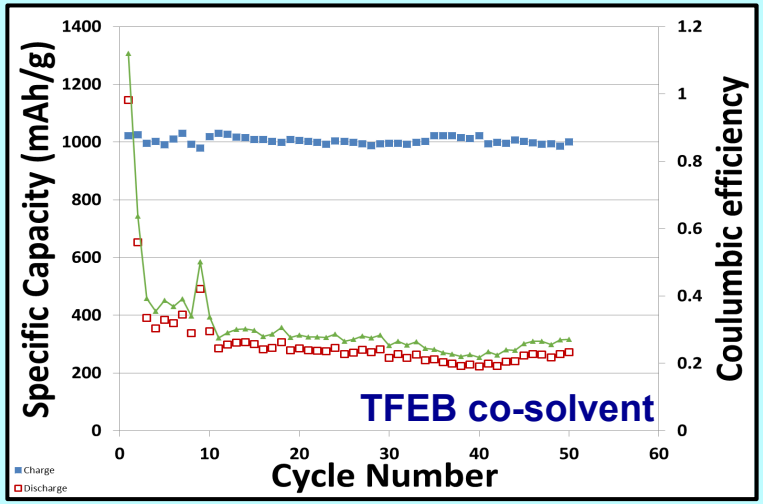


Cathode loading: 2 mg/cm^2

1.0M LiTFSI, DME+DOL (95:5 vol.) + 2% VC



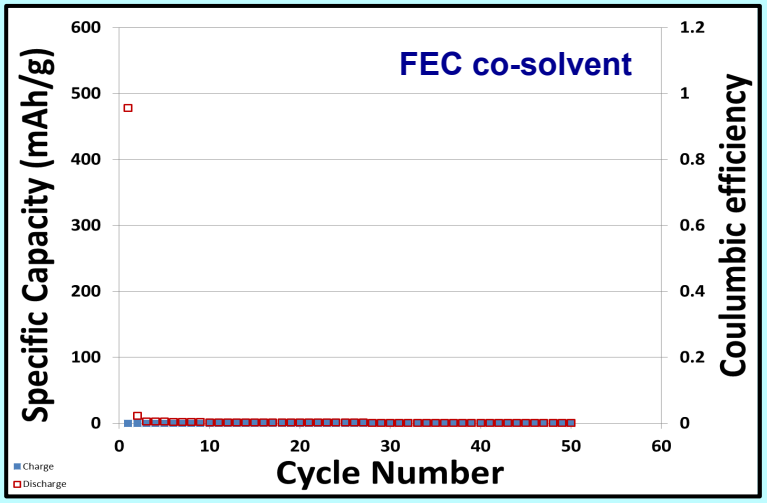
1.0M LiTFSI, DME+TFEB+DOL (75:20:5 vol.)



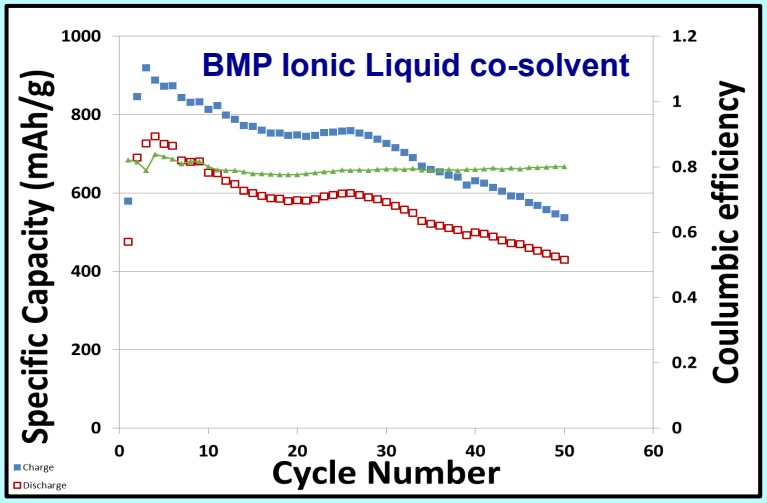
- **Imide > Triflate; Both VC additive and FEB co-solvent are not compatible.**

Effect of Electrolyte in a Li-S Cell

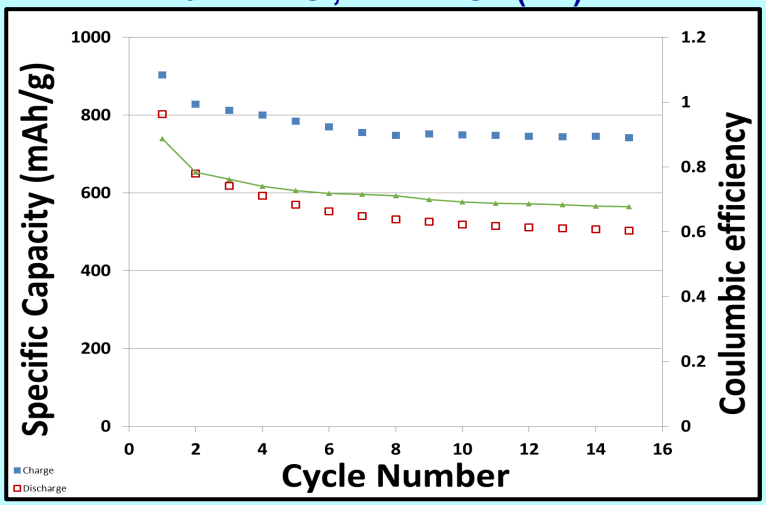
1.0M LiTFSI, DME+FEC+DOL (75:20:5 vol.)



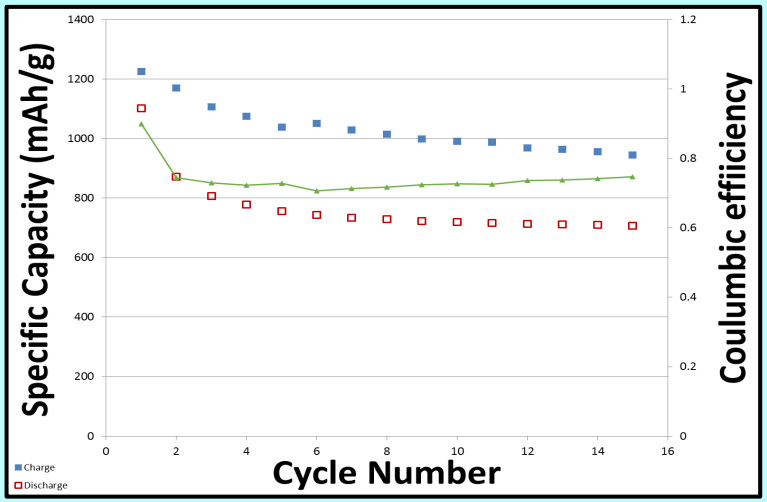
1.0M LiTFSI, DME+BMP-TFSI+DOL (45:50:5 vol.)



1.0M LiTFSI, DME+DOL (1:2)



1.0M LiTFSI, DME+DOL (2:1)

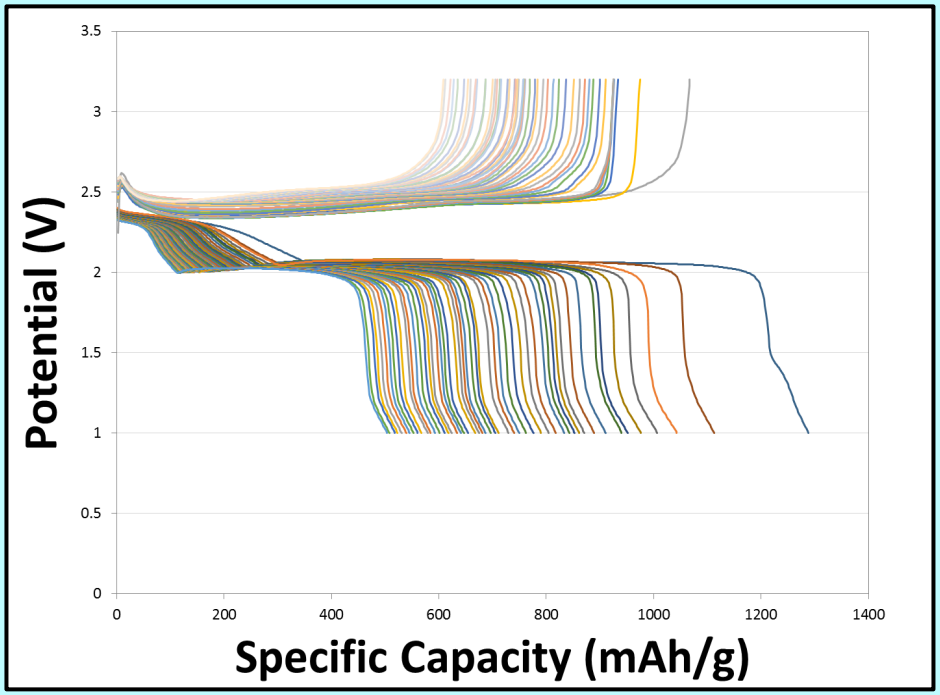


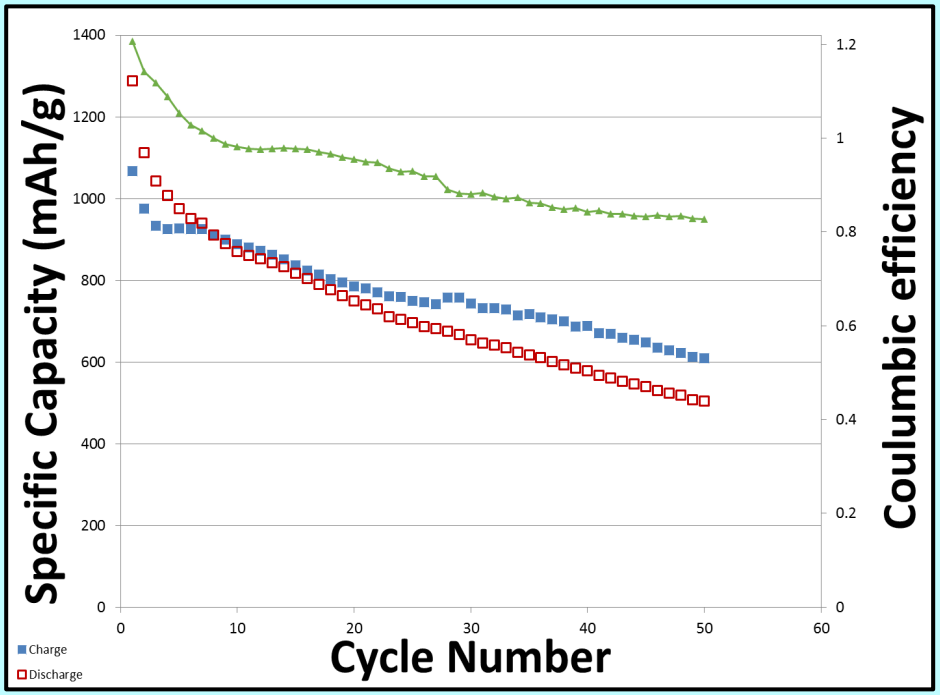
- **FEC not compatible; Performance degrades with the ionic liquid (BMP)**
- **DME: DOL (95:5 is better than 1:2 and 2:1).**

Cathode loading: 2 mg/cm^2

$LiNO_3$ Additive for Anode Protection

Electrolyte G: 1.0M LiTFSI, 0.2M $LiNO_3$, DME+DOL (95:5 vol.)



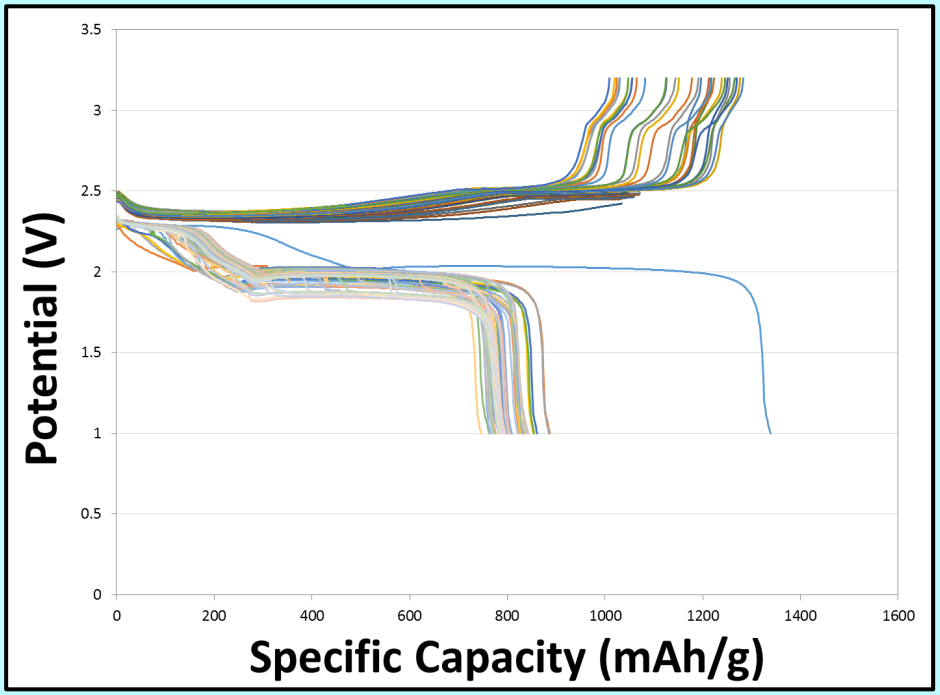


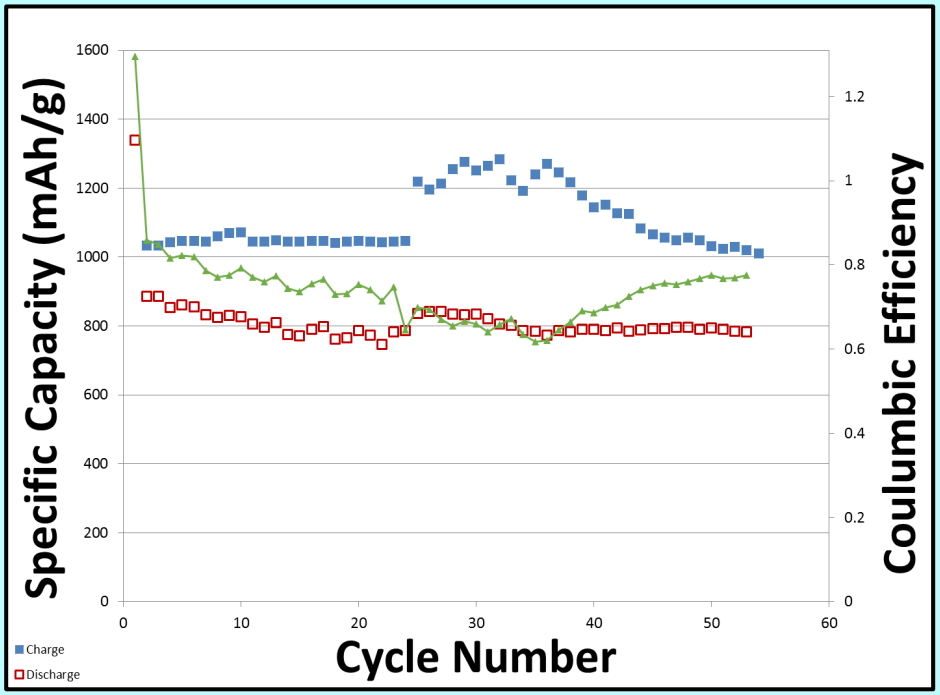
- Performance is improved with $LiNO_3$ additive (known). Coulombic efficiency has improved indicating Li anode protection

Cathode loading: 2 mg/cm^2

Carbon Inter-electrode Layer in a Li-S cell

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

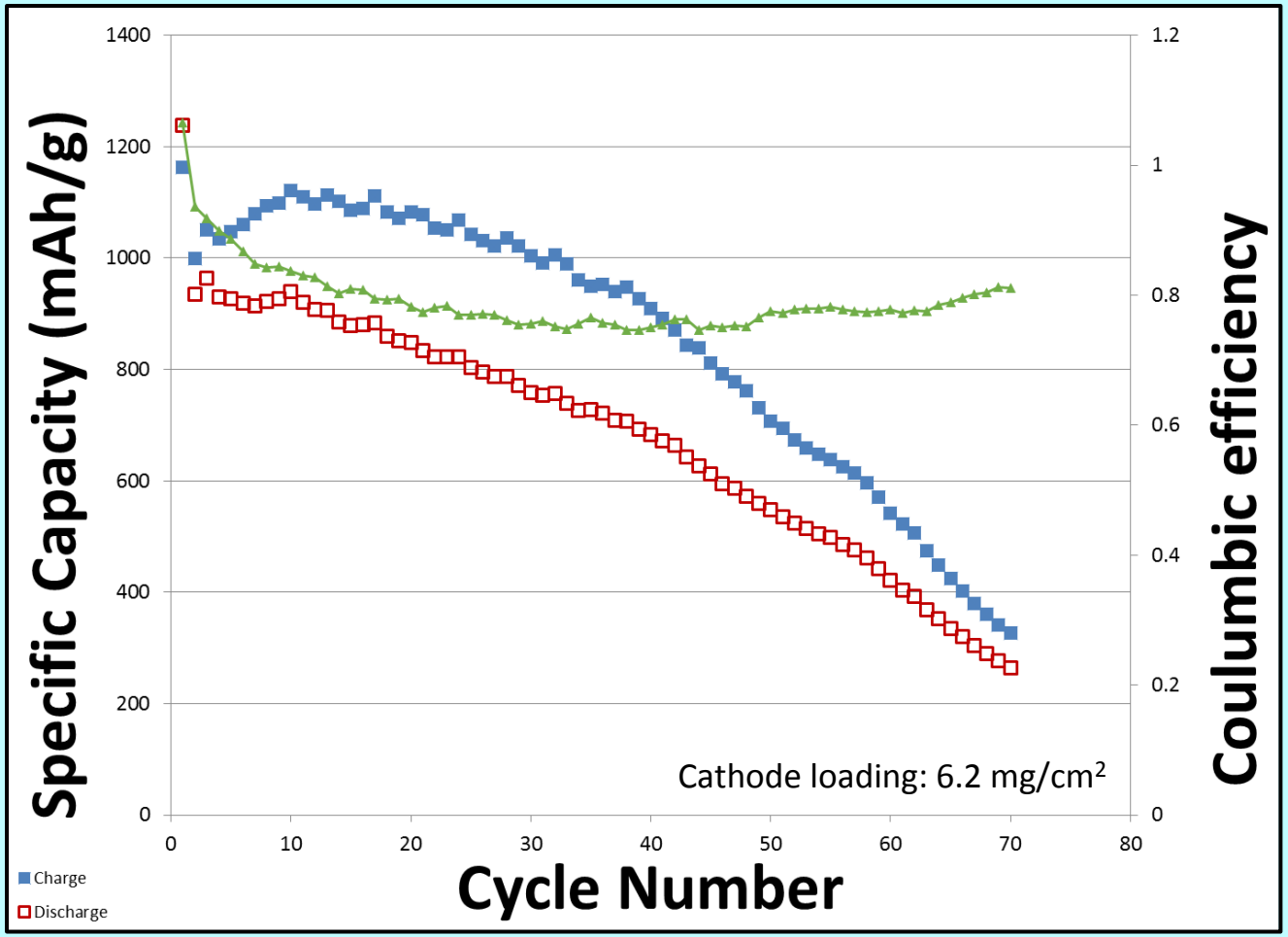




Cathode loading: 5.9 mg/cm^2

- Use of carbon interlayer between cathode and separator improves cycle life, even with a higher cathode loading (originally reported by Manthiram et al).

Sulfur Cathodes with Higher Loading and with Carbon Paper Interlayer



- Lower capacity and utilization of sulfur in thicker cathode even with carbon paper interlayer and $LiNO_3$.

High Capacity S Cathodes with Metal Sulfide Blends

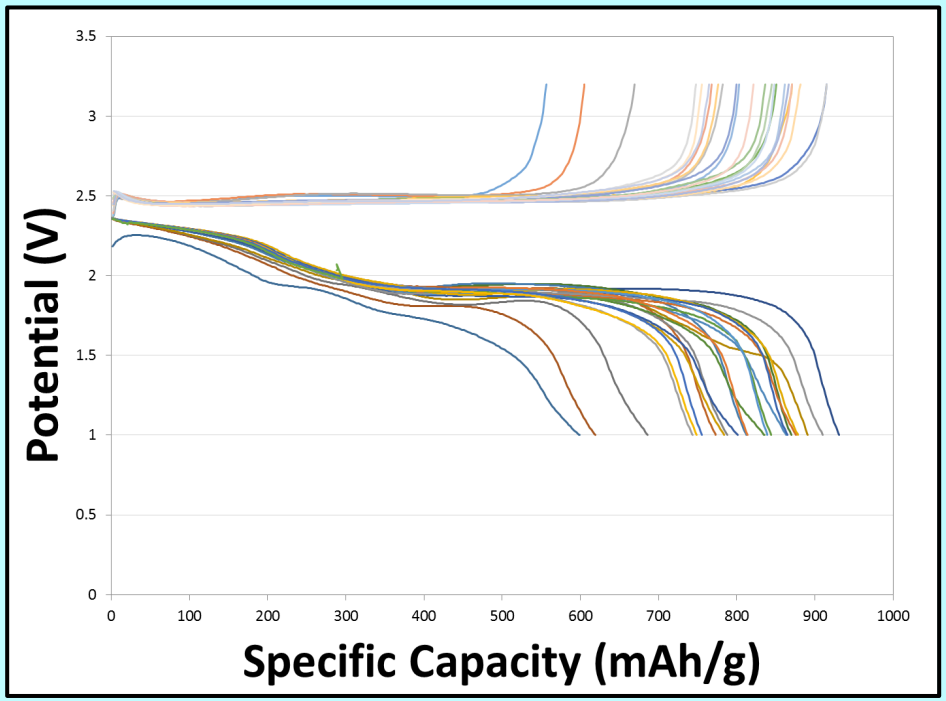
- To fabricate thick electrodes with good sulfur utilization for a high areal capacity (mAh/cm^2).

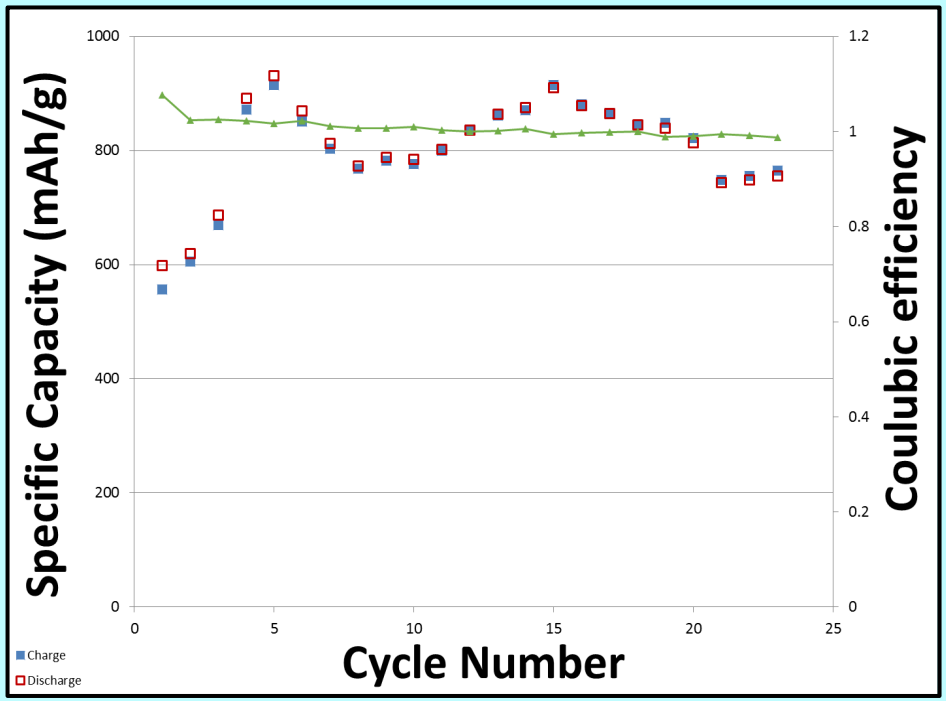
Rationale:

- Transition metal sulfide will undergo reversible reactions around the same voltage range and can mediate the sulfur redox reaction.
- Metal sulfide providing some electronic/ionic conductivity can replace carbon diluent to form dense electrodes.
- Materials Studied: TiS_2, MoS_2

Sulfur Cathode blended with TiS_2

Cathode Composition: 65%S_15%TiS2_15%CB_5%PVDF; Loading: 9.05mg/cm^2
LiNO3 electrolyte and carbon paper over cathode

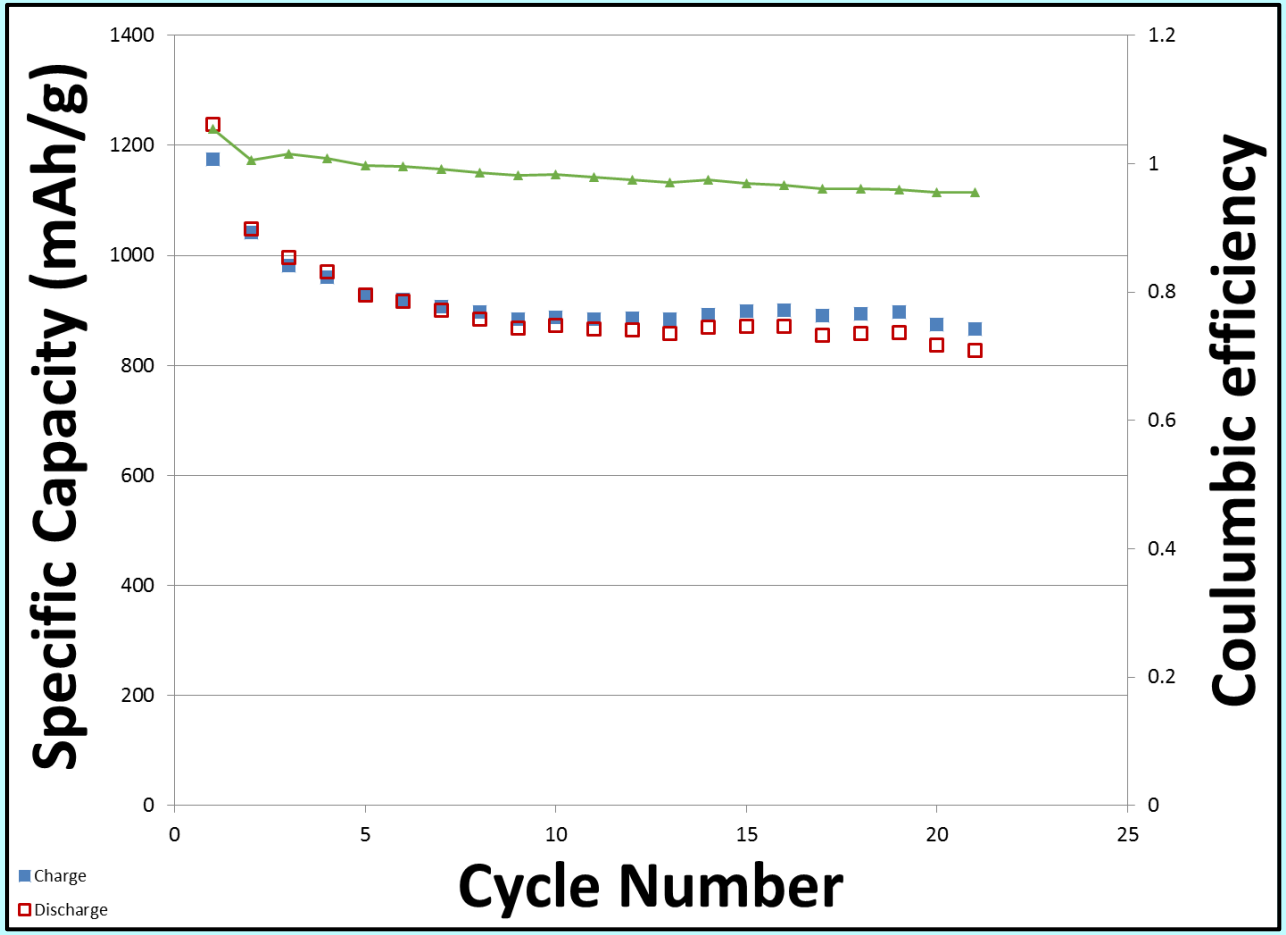




- Good performance considering the high cathode loading, high proportion of sulfur and high coulombic efficiency

Sulfur Cathode blended with MoS_2

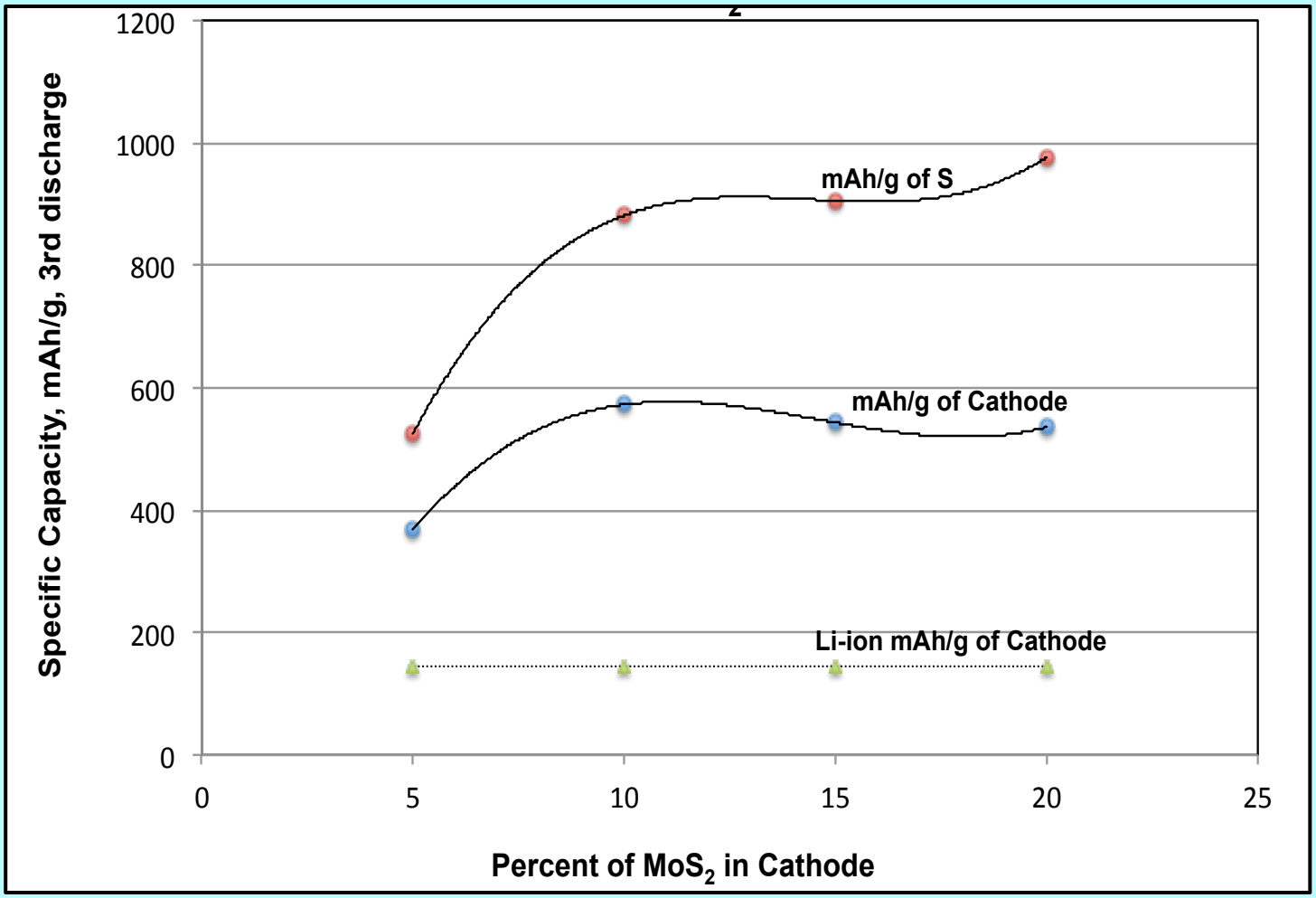
Cathode Composition: 55%S_20%MoS2_20%CB_5%PVDF; Loading: 6.45 mg/cm^2
LiNO3 electrolyte and carbon cloth over cathode



Carbon Cloth

- Good performance considering the high cathode loading, high proportion of sulfur and high coulombic efficiency.
- Performance is better with carbon cloth compared to carbon paper

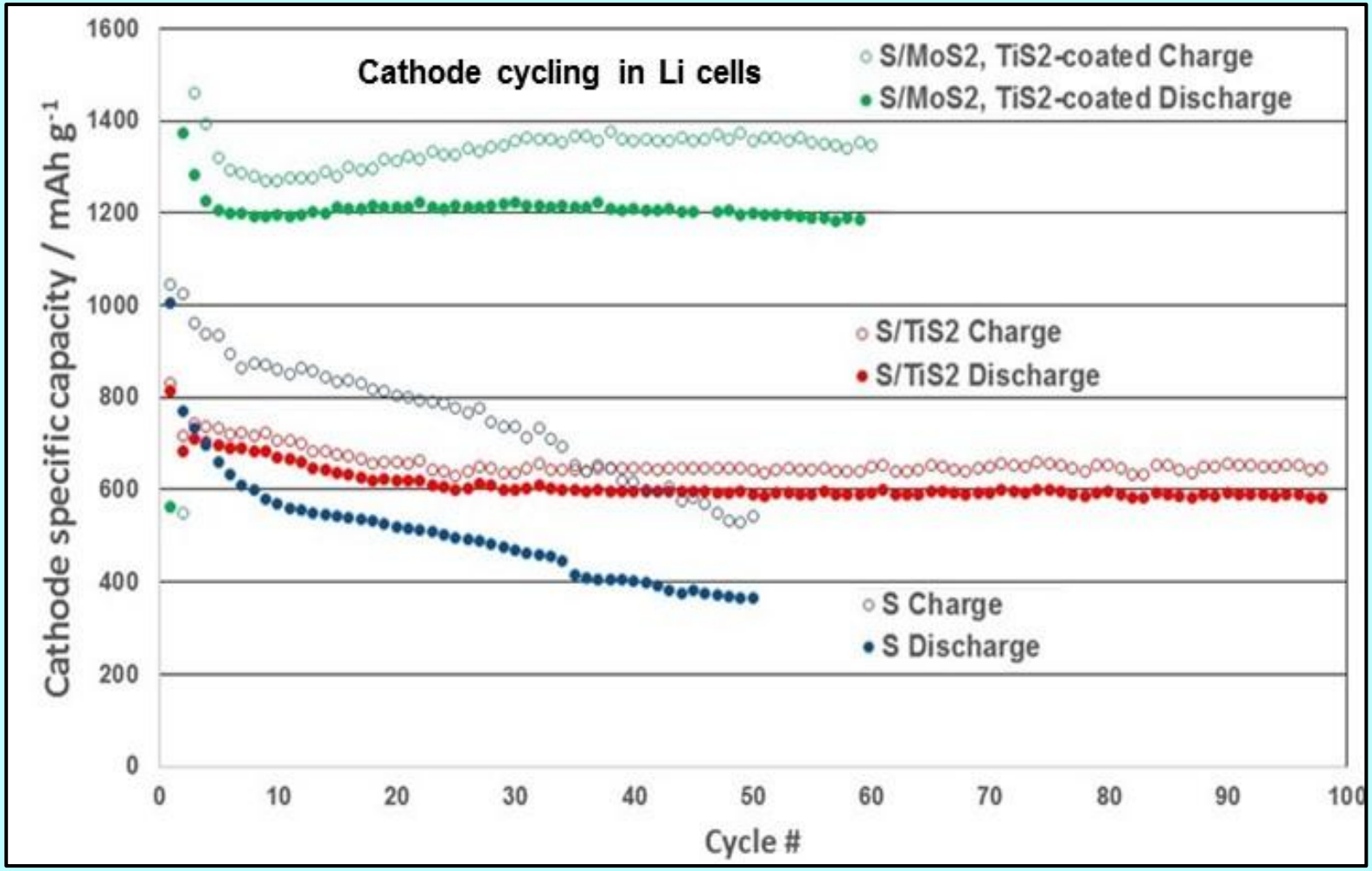
Sulfur Cathode With Different amounts of MoS_2



- Three times the capacity per gram of cathode material compared to Li-ion per gram.

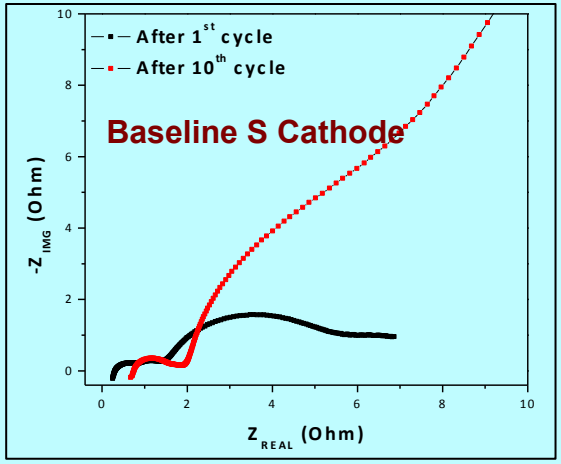
Comparison of Pristine and Sulfide-blended Sulfur Cathode

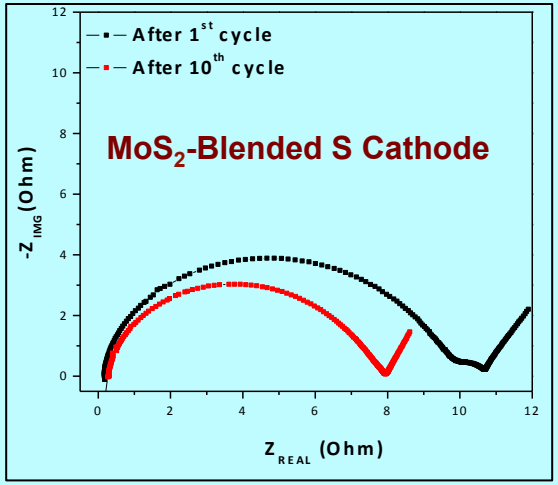
Performance of S (6 mg/cm^2, blue), S blended with TiS_2 (9 mg/cm^2, red) and S/MoS_2 coated with TiS_2 (13 mg/cm^2, green).



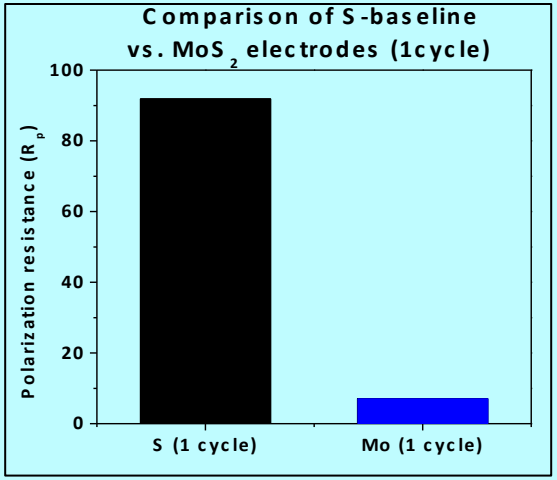
Kinetics of Baseline and MoS_2-Blended Sulfur Cathode

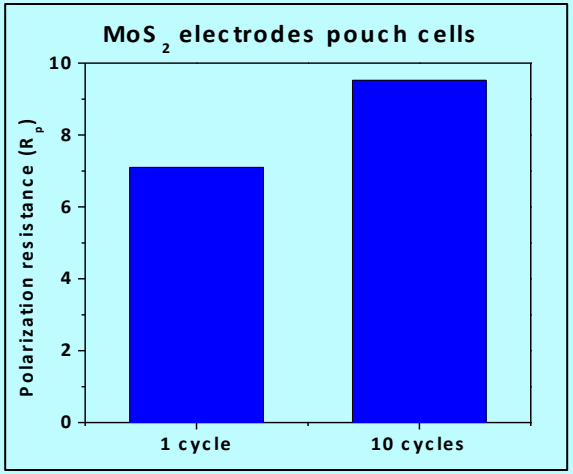
EIS



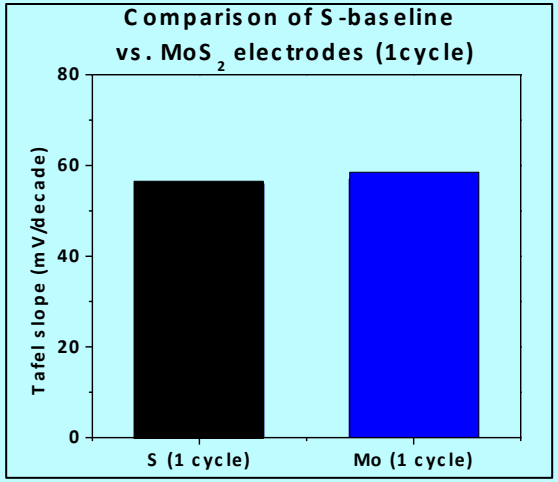


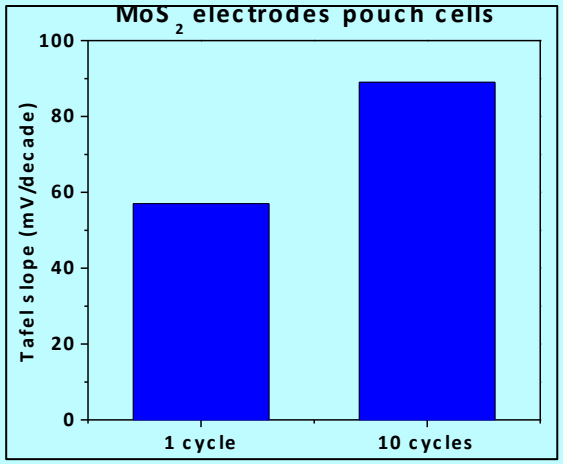
Linear Polarization





Tafel Polarization

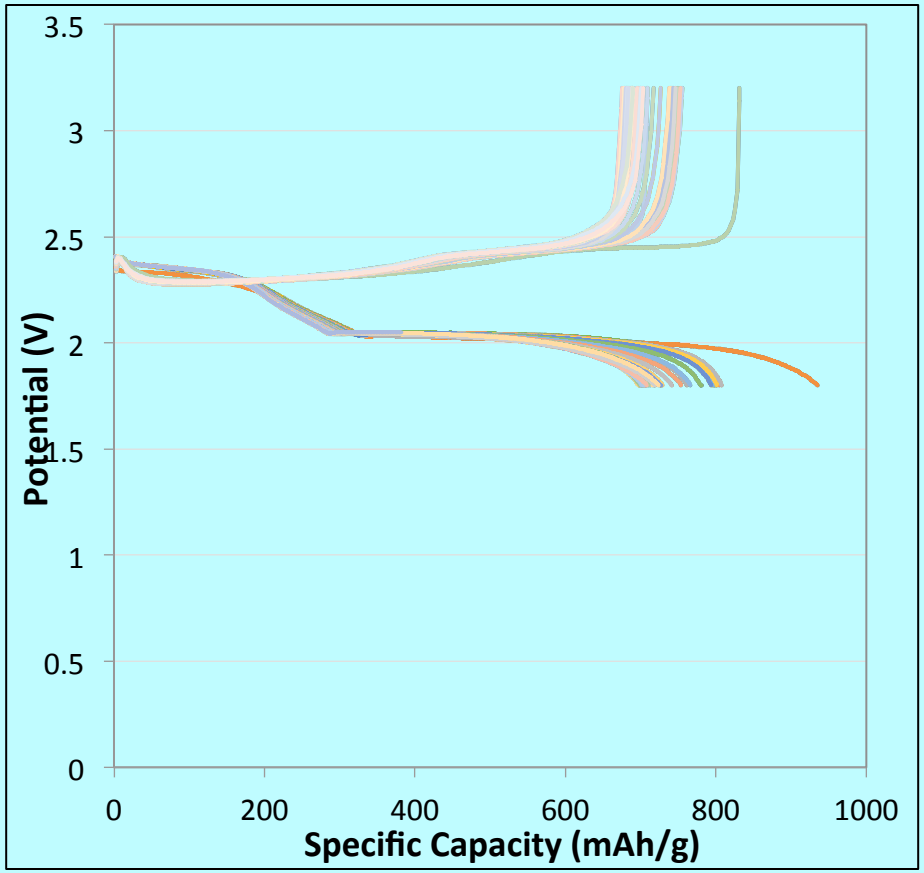


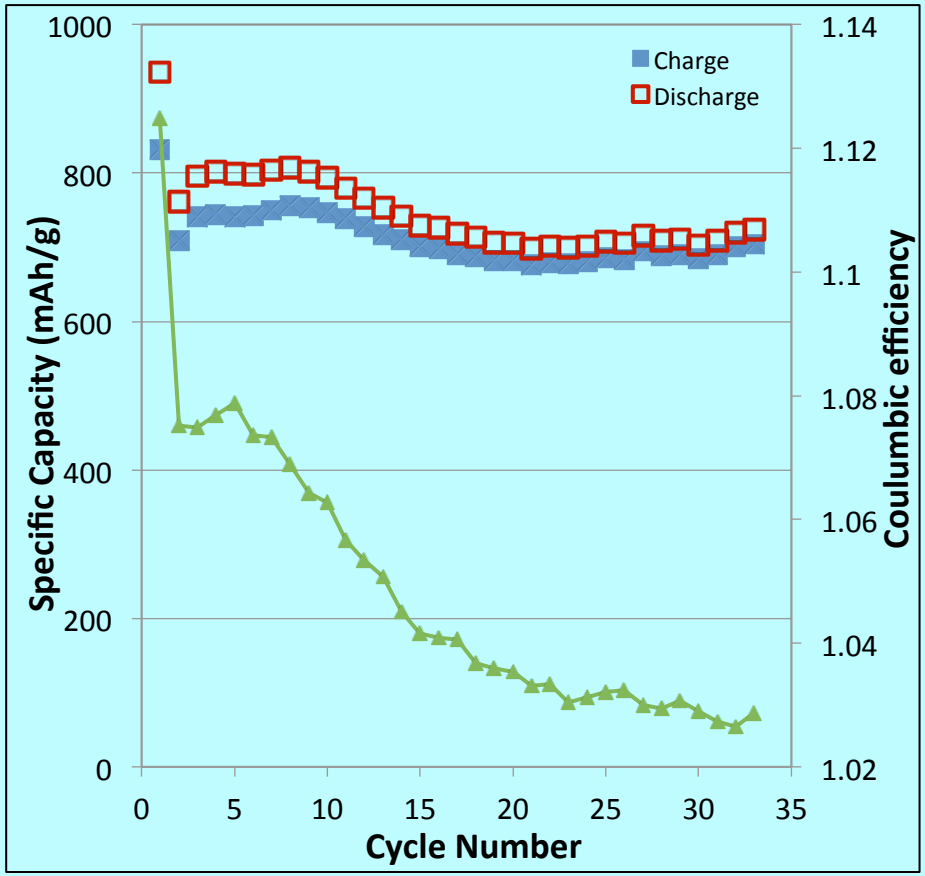


- Stable interface and lower impedance upon cycling

Sulfur Blended with MoS_2 and TiS_2

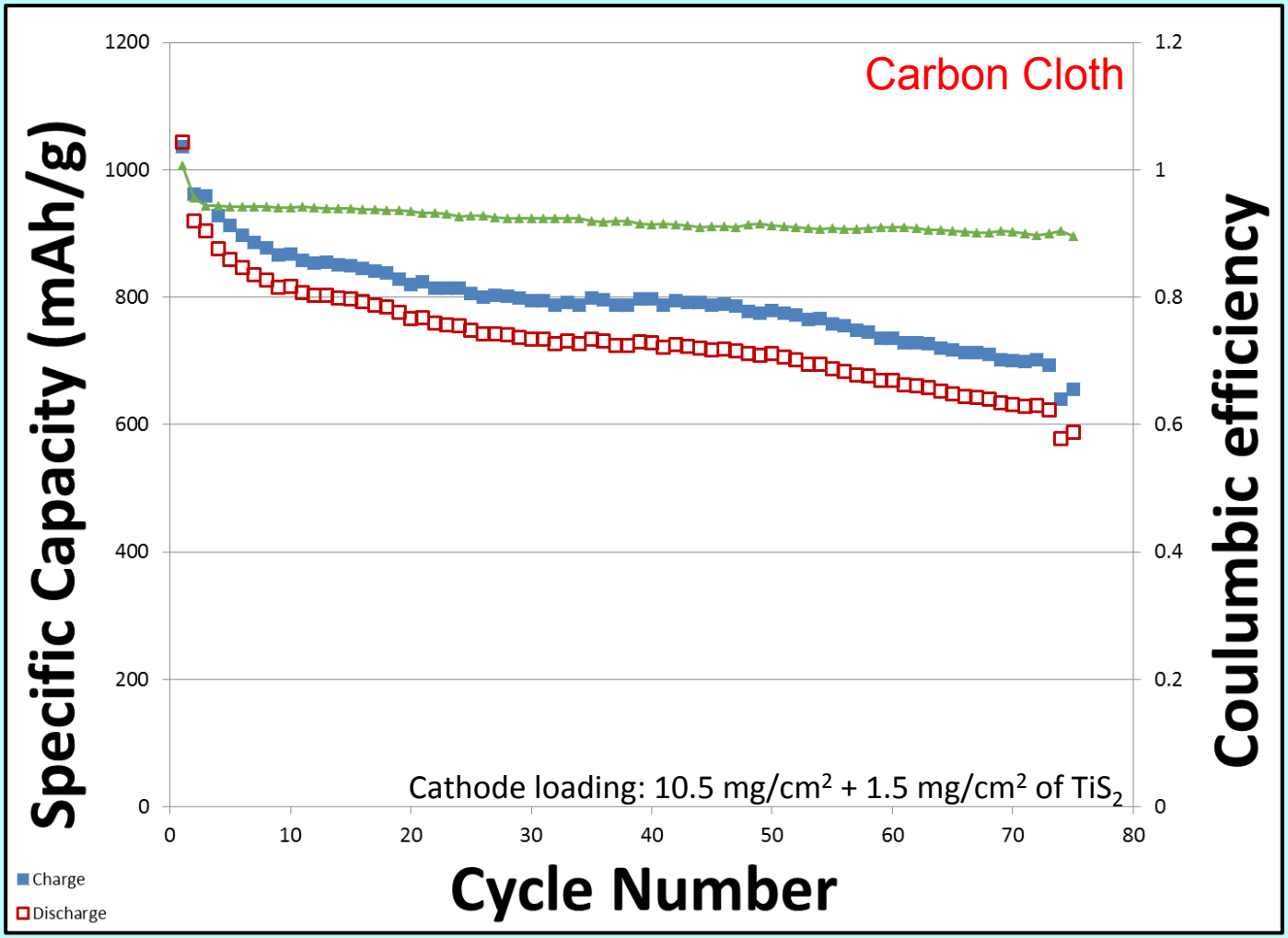
$S:MoS_2:TiS_2:CB:PVDF$ ~ 65:7.5:7.5:15:5





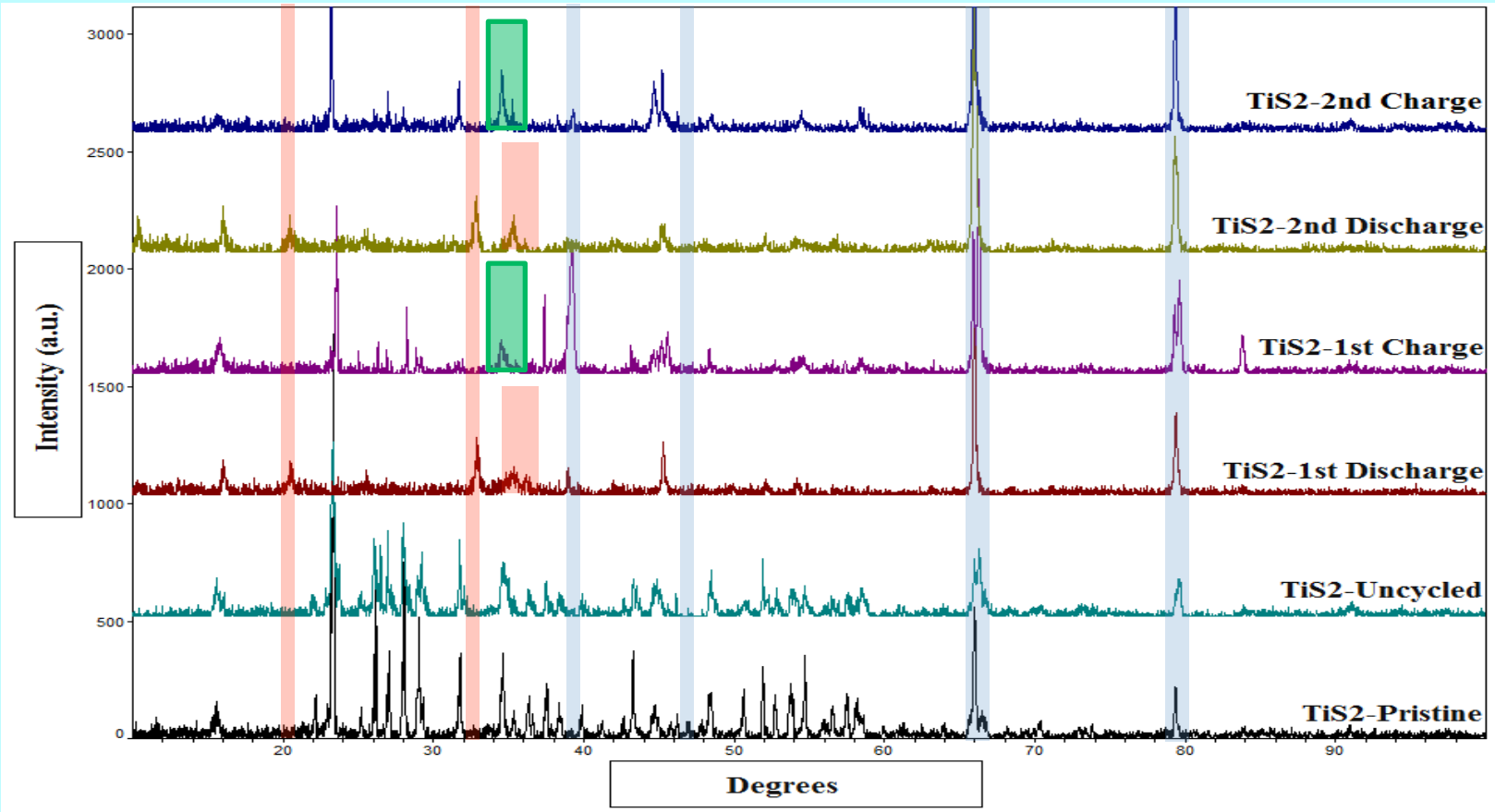
Loading ~ 10.3 mg/cm2
Voltage range ~ 1.8-3.2V
Current rate ~ C/5-Charge & C/3 Discharge

Sulfide coating on a metal sulfide –blended cathode



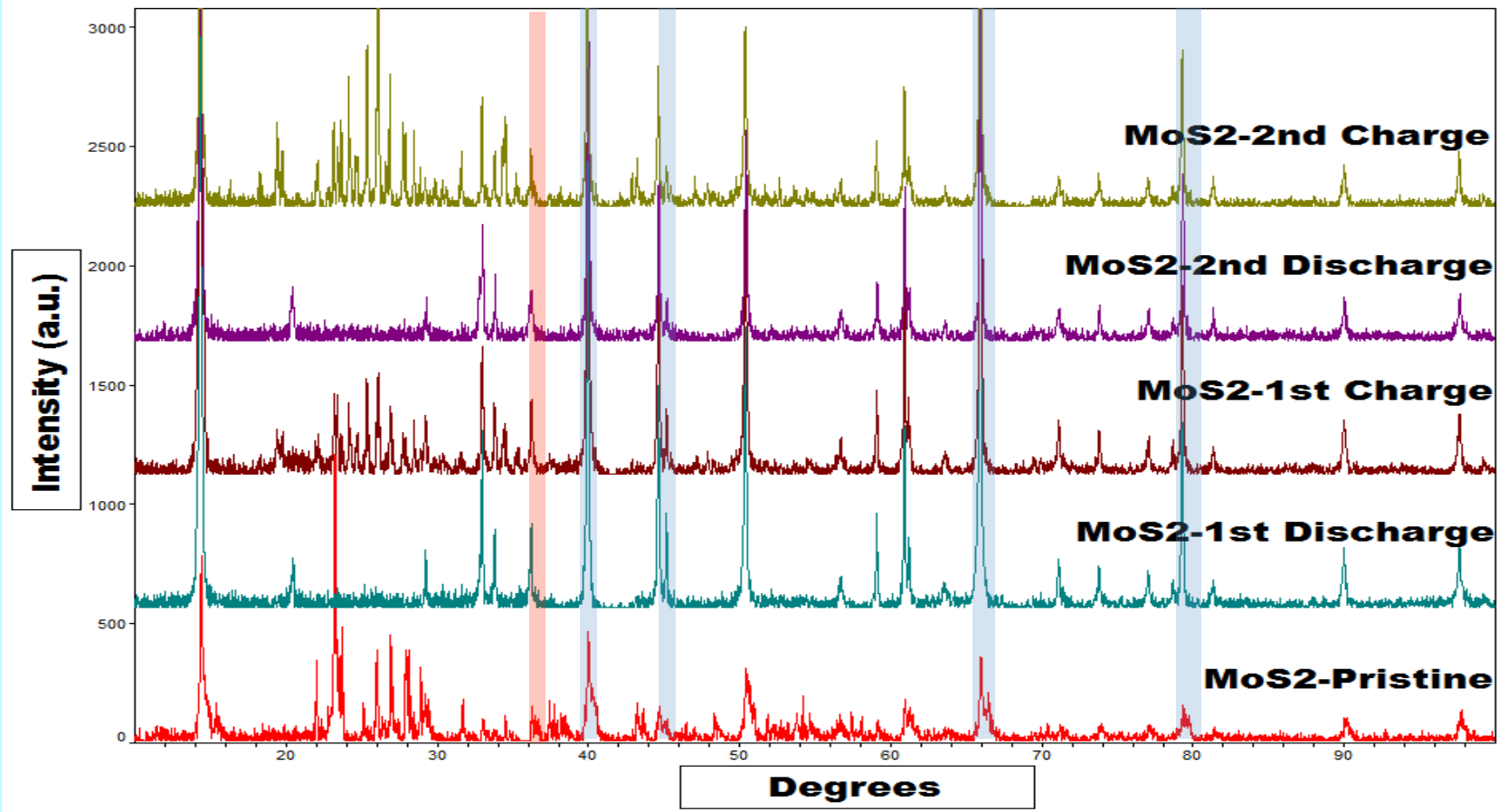
6.15 mAh/cm^2 per side

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



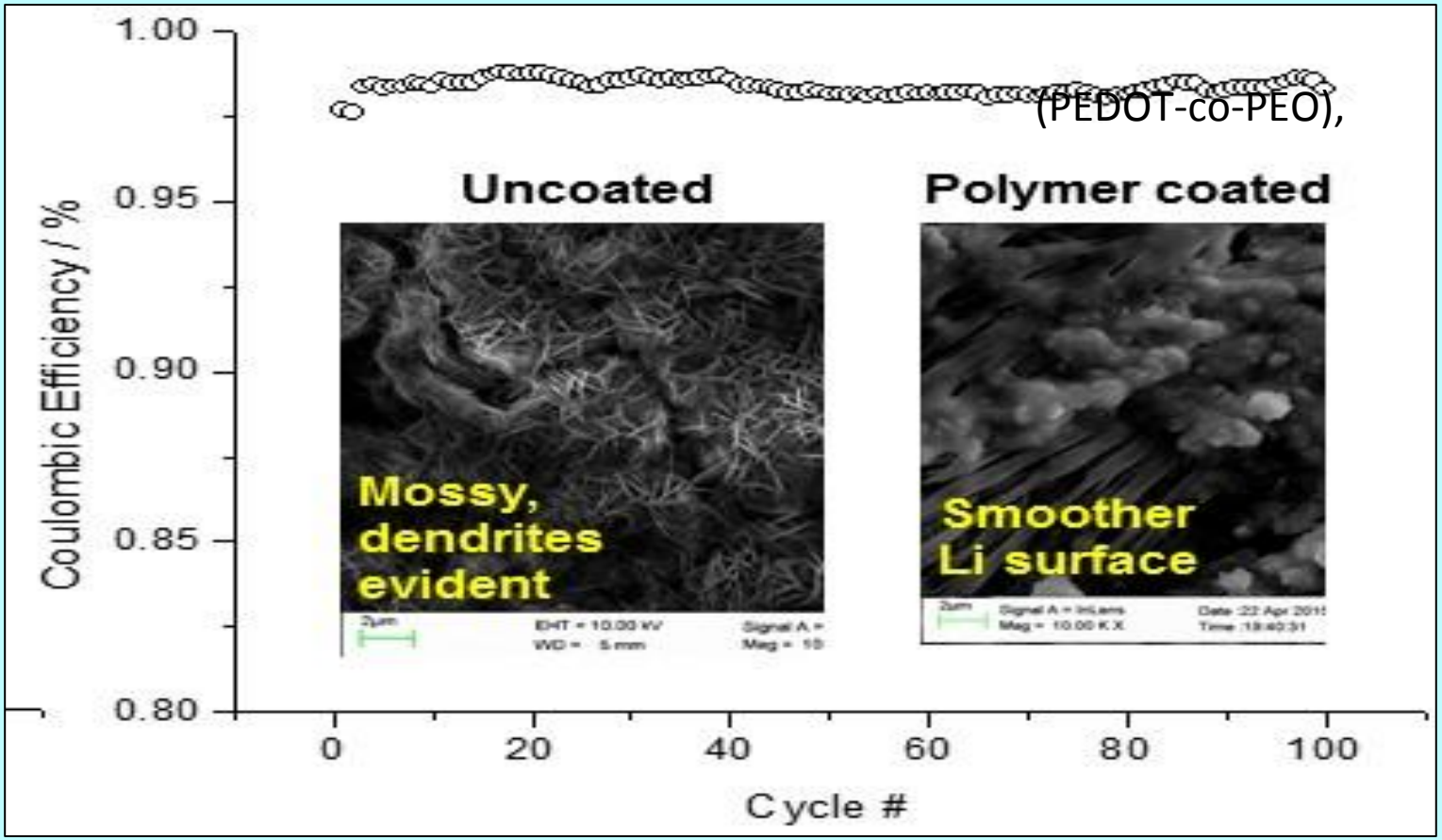
- Blue shades ~ Al foil contribution; Red Shades ~ $LiTiS_2$; Green shades ~ TiS_2
- The XRD spectra for TiS_2 electrodes showed a transition from TiS_2 to $LiTiS_2$ after discharge and transition from $LiTiS_2$ to TiS_2 after charge.

X-ray Diffraction (XRD): MoS_2- Blended Sulfur Cathode



- 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

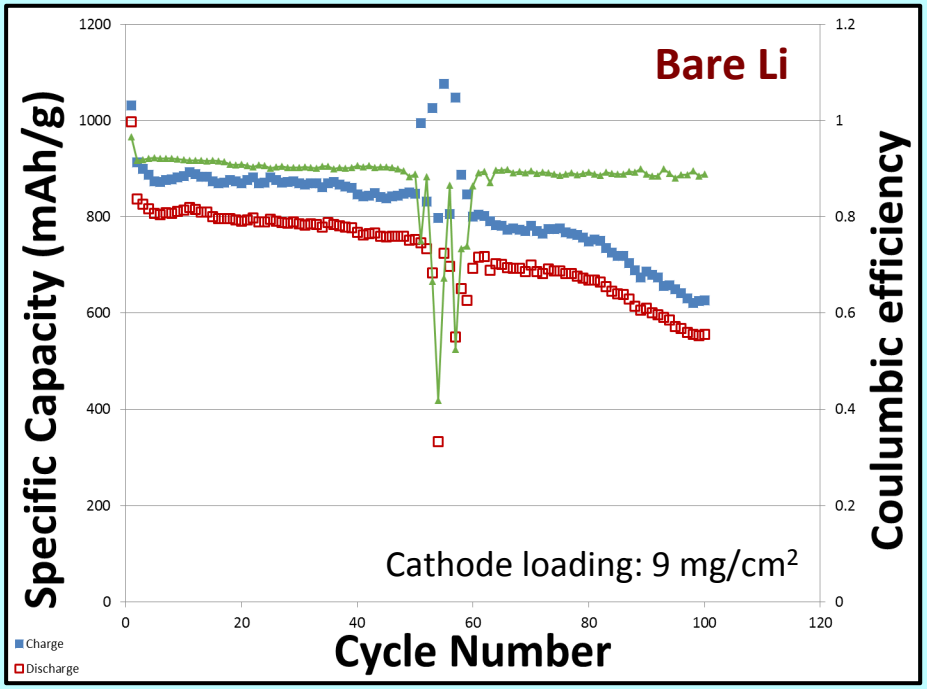
Polymer Electrolyte Coatings over Li Anode

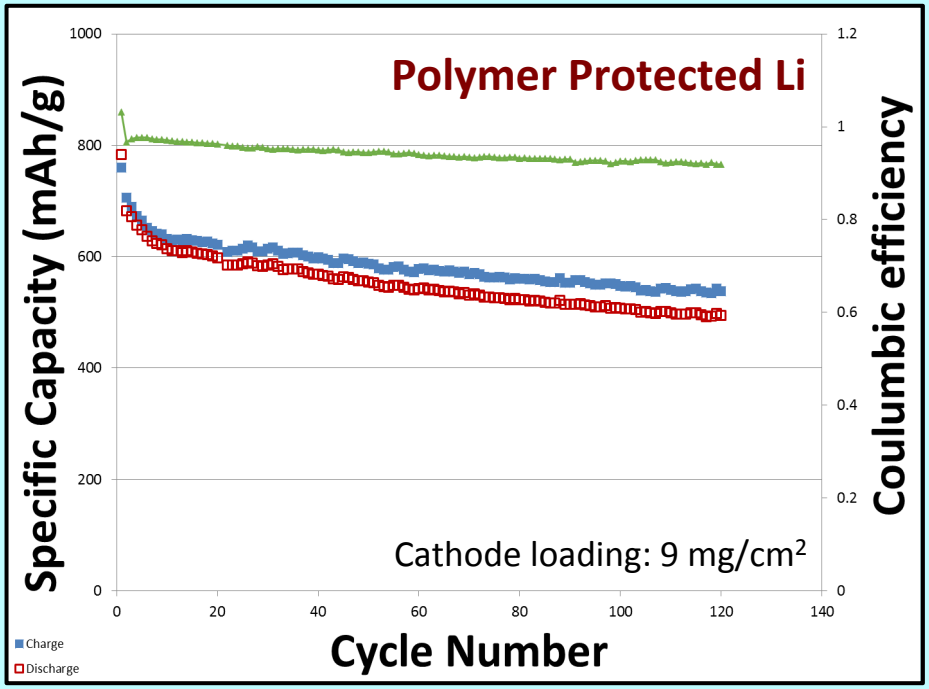


- **High coulombic efficiency in half cells**
- **Surface uniformity devoid of dendrites for the PE-coated Li anodes retrieved from cycled Li-S cells**

Polymer coating on a metal sulfide –blended cathode

3 layers of PDT-PEO Polymer spin coated on S:TiS2:CB:PVDF(65:15:15:5)

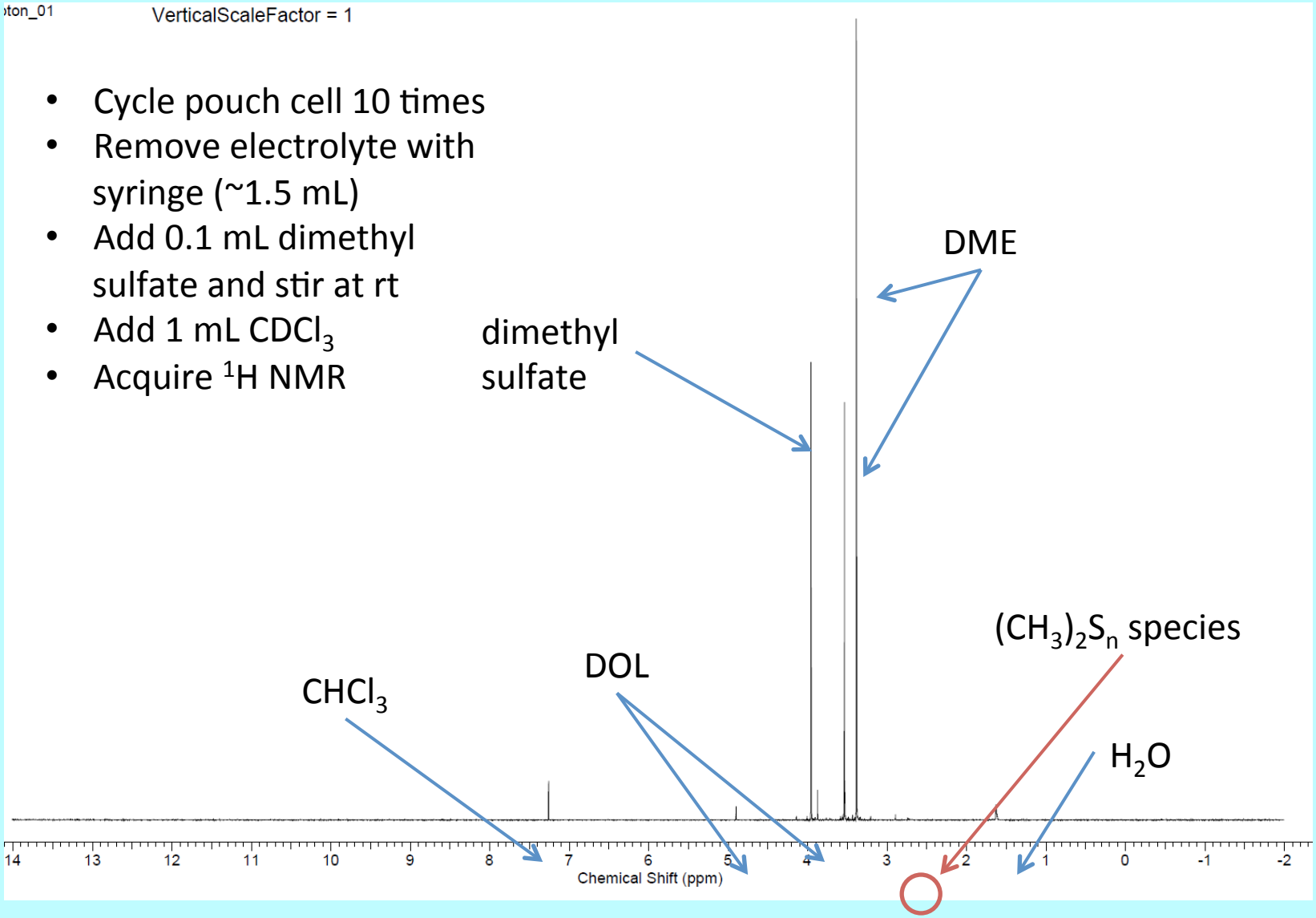




- More stable capacity with the PE-coated cathode, but slightly lower capacity than with bare Li anode

^{1}H NMR Analysis of Electrolytes for Polysulfides

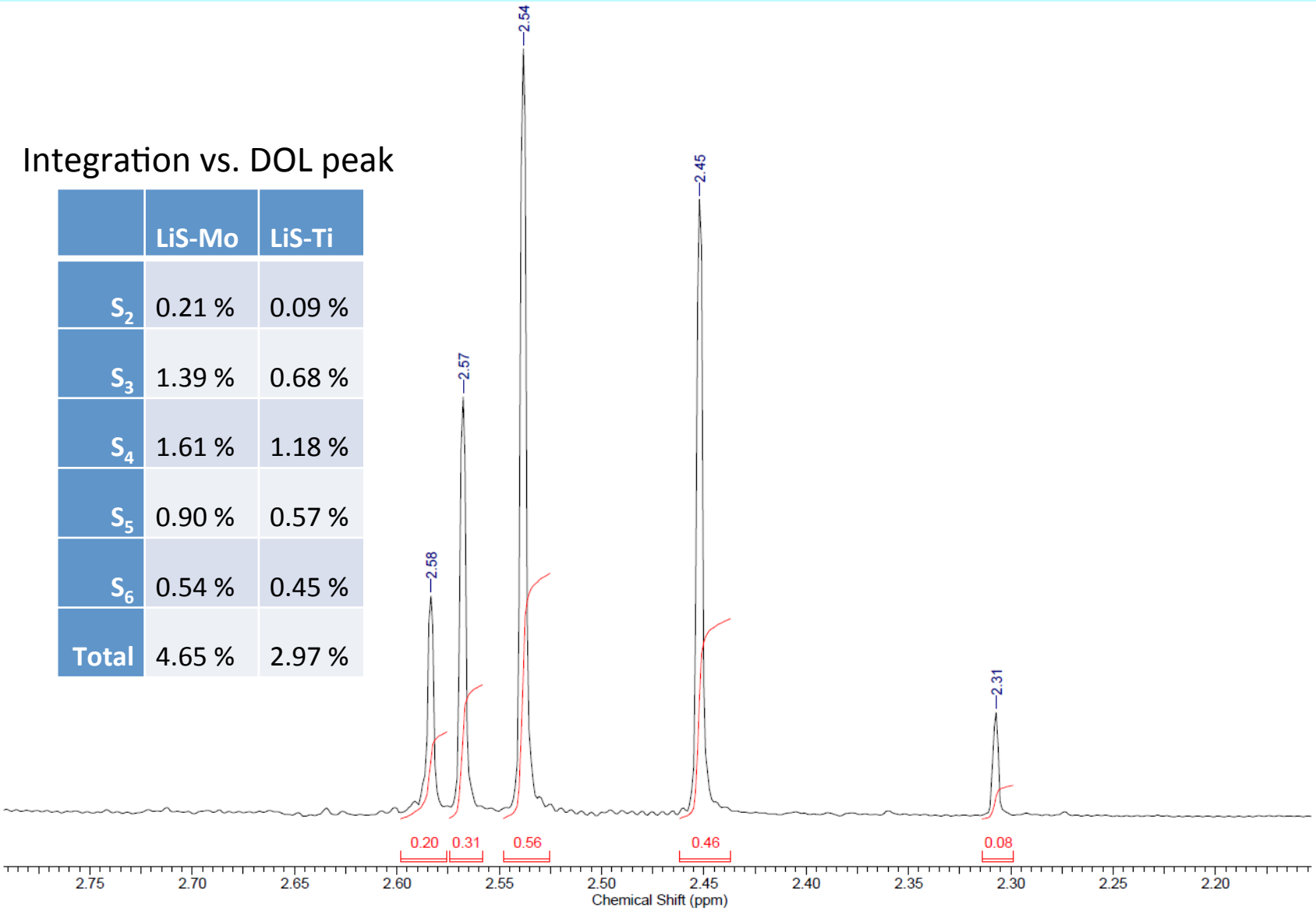
- Cycle pouch cell 10 times
- Remove electrolyte with syringe (~1.5 mL)
- Add 0.1 mL dimethyl sulfate and stir at rt
- Add 1 mL $CDCl_3$
- Acquire ^{1}H NMR



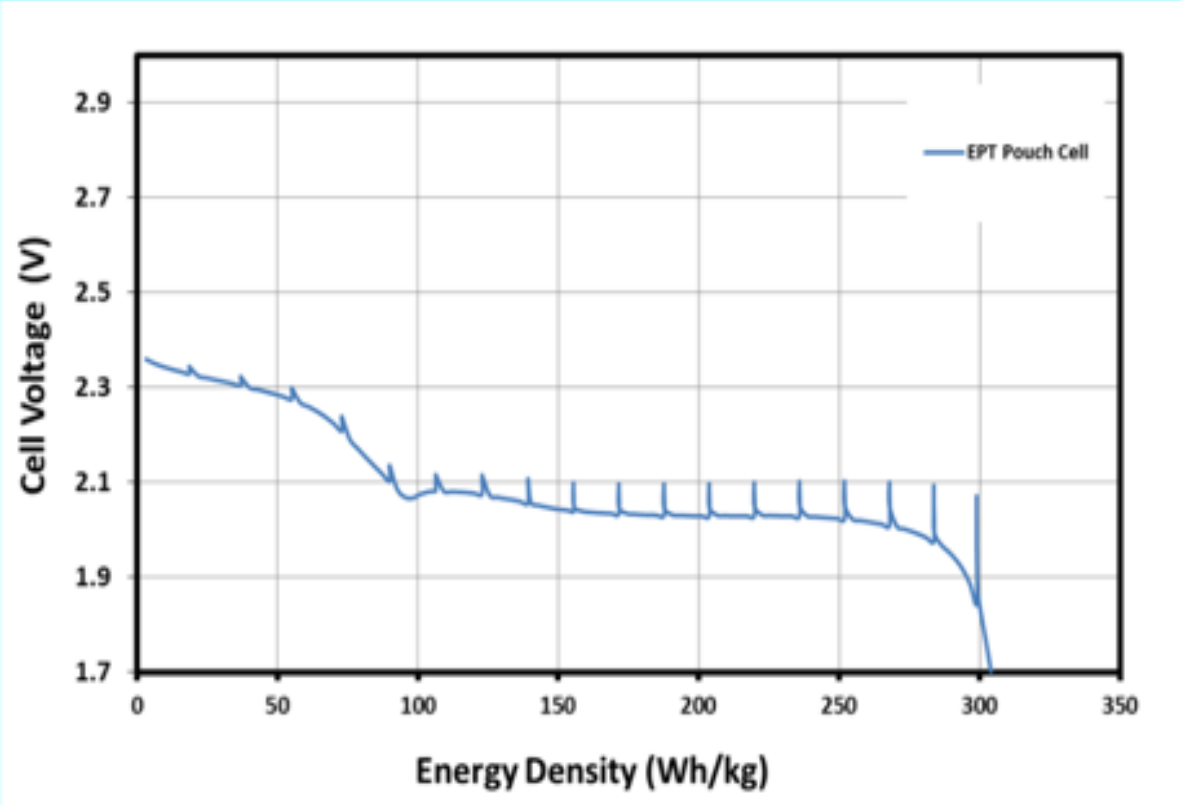
Polysulfides in cells with S-MoS_2 and S-TiS_2 Cathode

Integration vs. DOL peak

	LiS-Mo	LiS-Ti
S_2	0.21 %	0.09 %
S_3	1.39 %	0.68 %
S_4	1.61 %	1.18 %
S_5	0.90 %	0.57 %
S_6	0.54 %	0.45 %
Total	4.65 %	2.97 %



Prototype Cells



- Prototype 6Ah cells with conventional sulfur cathode show specific energy of ~300 Wh/kg.

Eagle Picher data

Summary

- Novel sulfur/metal sulfide composite cathodes display high capacity of ≥800 mAh/g (based on sulfur content), high coulombic efficiency and good cycle life (>75% retention through 80 cycles of 100% depth of discharge) at C/3 rate.
- High cathode loadings (12 mg/cm^2 or ~6 mAh/cm^2 per side) were demonstrated in Li-S cells with good utilization -required to achieve a specific energy of 400 Wh/kg in prototype cells.
- PEDOT-co-PEO polymer-coated Li provides protection from polysulfide in full Li-S cells and improves cycle life.
- Baseline 6 Ah pouch cells showed 300 Wh/kg with conventional materials, which can be increased to 400 Wh/kg cell with the metal sulfide blended sulfur cathode.

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