SAND2019-14391C

JCESR | JOINT CENTER FOR ENERGY STORAGE RESEARCH

Linking New Electrolyte Polarity Models to the Electrolyte-Driven Li-S Discharge Mechanism

(*SWRM-RMRM 2019*)

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12/3/2019

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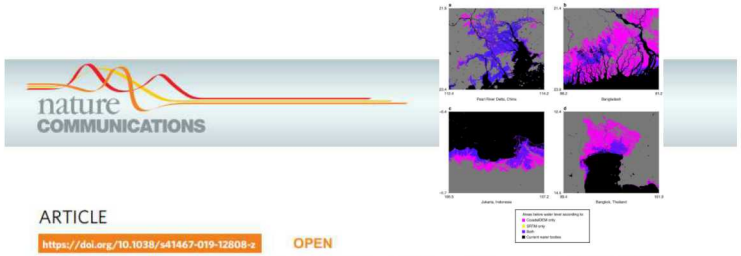
Crucial Need for Better Energy Storage Options



nature COMMUNICATIONS

ARTICLE

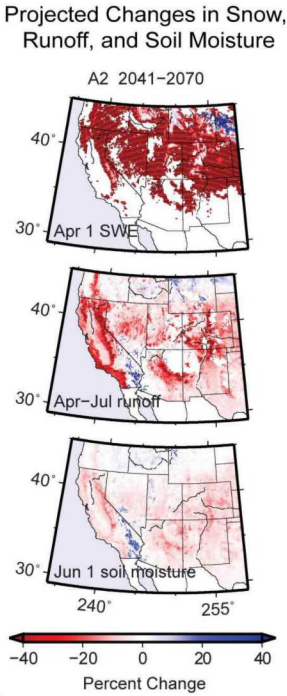
https://doi.org/10.1038/s41467-019-12808-z OPEN

New elevation data triple estimates of global vulnerability to sea-level rise and coastal flooding

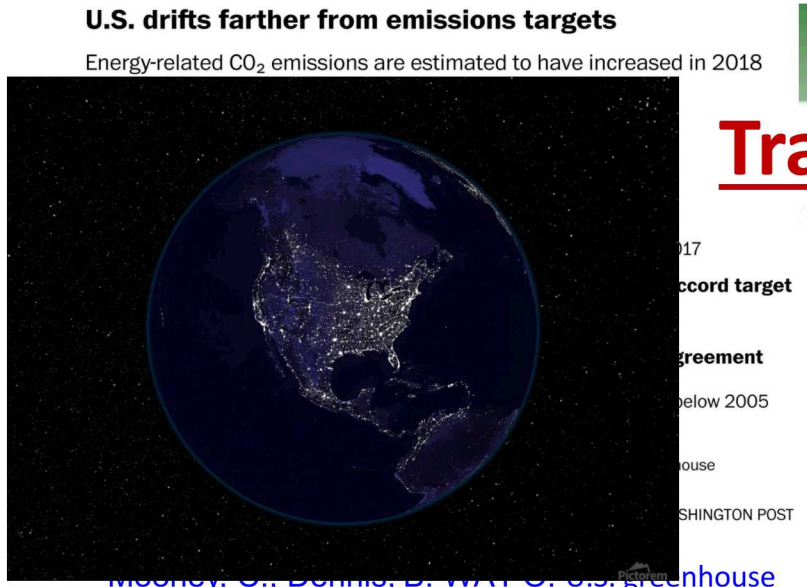
Scott A. Kulp[1]* & Benjamin H. Strauss[1]

"190 M people (150–250 M, 90% CI) currently occupy global land below projected high tide lines for 2100 under low carbon emissions…"

Kulp, S.A., Strauss, B.H. Nat Commun. 10, 4844 (**2019**)



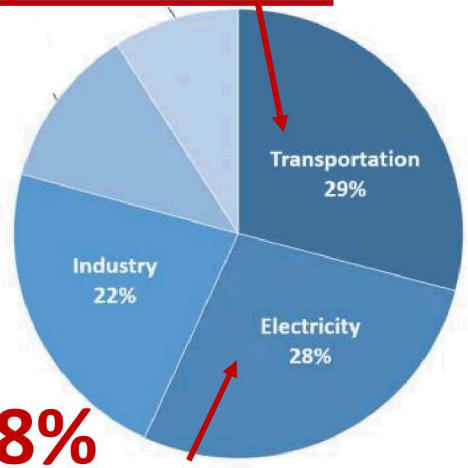
https://nca2014.globalchange.gov



Mooney, C., Dennis, B. WAPO. U.S. greenhouse gas emissions spiked in 2018 — and it couldn't happen at a worse time. Jan. 8, **2019**.

Sources of Greenhouse Gas Emissions in 2017

Transportation 29%



Electric Grid 28%

EPA. https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions

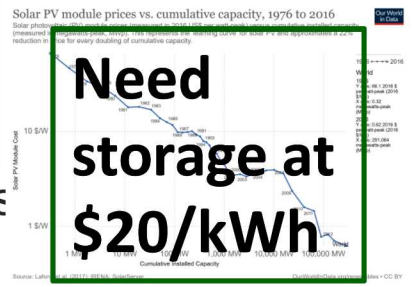
Range: 220 miles
Price: $35,490

Tesla Model 3

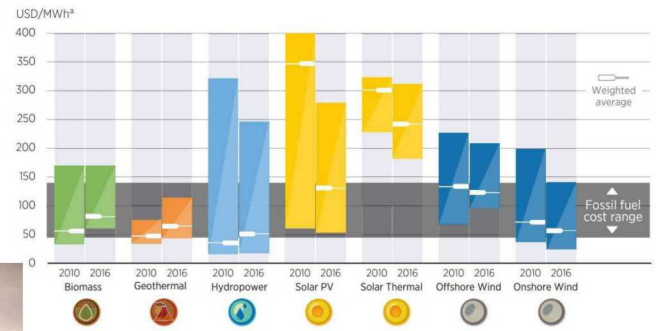
Need EVs at $20k

Range: 258 miles
Price: $36,950

Hyundai Kona



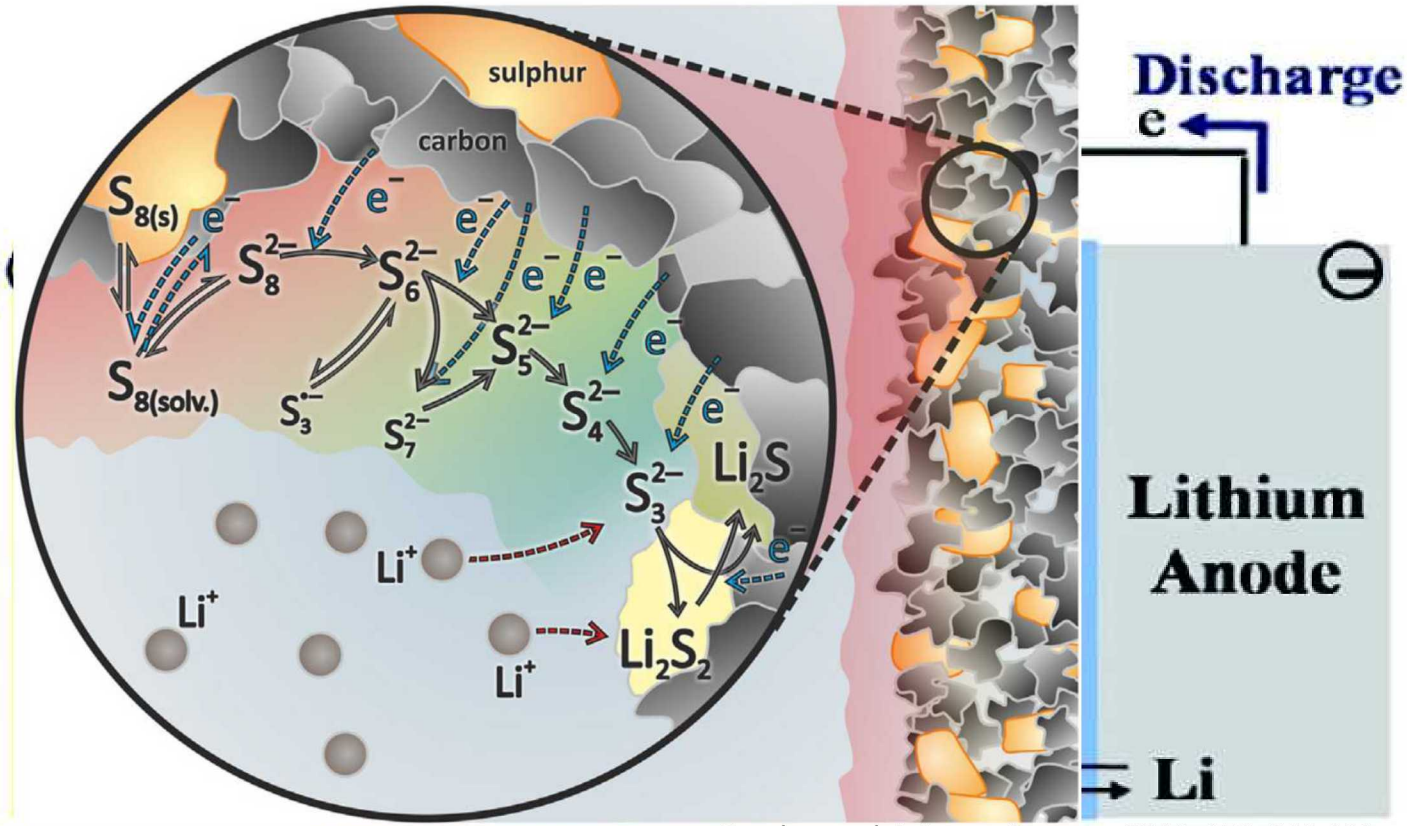
Need storage at $20/kWh



https://ourworldindata.org/energy-production-and-changing-energy-sources

https://insideevs.com/features/378975/most-efficient-electric-cars/4465484/

The "Conventional" Li-S Battery



Xu *et al*. J. Mater. Chem. A. **2014**, 2, 19941-19962.

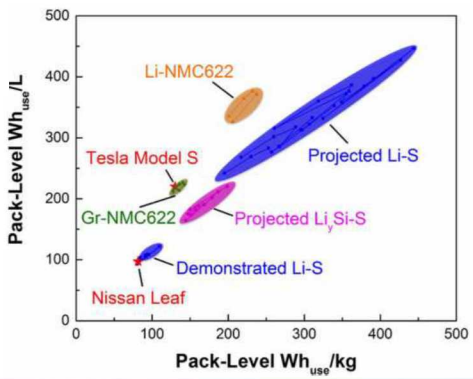
Busche *et al*. J. Power Sources. **2014**, 259, 289-299

Niche market penetration

Zephyr UAV (Powered by Sion's Li-S battery)

http://insideevs.com/sion-power-to-supply-airbus-ds-with-350-whkg-li-s-batteries/

ED_{Theory}: 2600 Wh/kg (5x Li-ion)



Eroglu *et al*. J. Electrochem. Soc. **2015**, 162, A982-A9990.

Primary Challenges:

Critical Mechanism Drivers:

I. End Products (Sulfur and Li_2S) are insulators.
II. Dissolved intermediates cause self discharge.
III. Li metal reactive with electrolytes.

I. LiPS solubility
II. PS Speciation

Li-S Electrolytes Have Been Divided Into 4 Categories

I) **Dilute Electrolytes (~0.5–1.5 M)**
   - i. **High EPD** Solvents
     - Ex. **DMF**, DMA, DMSO
   - ii. **Moderate EPD** Solvents
     - Ex. **DOL:DME**, THF, Glymes
   - iii. **Low EPD** Solvents
     - Ex. ACN, Sulfolane

II) **Solvate Electrolytes**
   - Ex. **$ACN_2LiTFSI$**, $THF_2LiTFSI$, SIS7 (DOL:DME), Glyme-based Solvate ILs & sub-Ils

IIb?) Water in Salt

III) **Ionic Liquids**

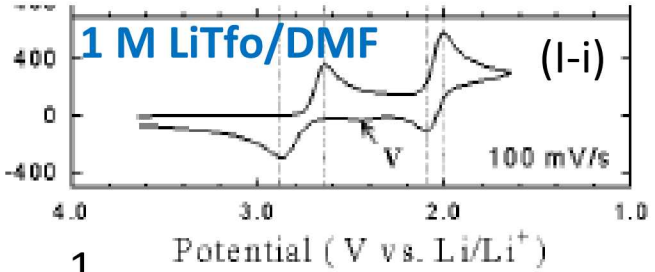
IV) **Solid-State**

Higher 1st reduction potential
Lower 2nd reduction potential

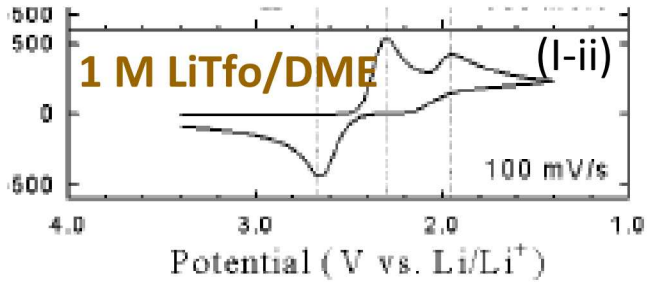
Higher solubility

Greater stability for $S_3^{\bullet-}$

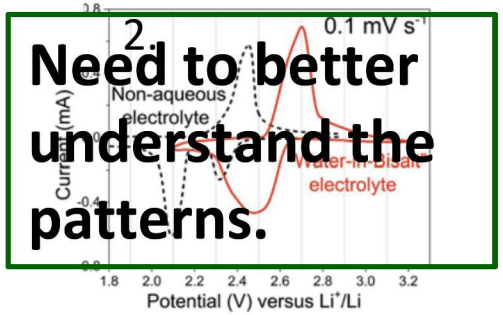
Tendencies



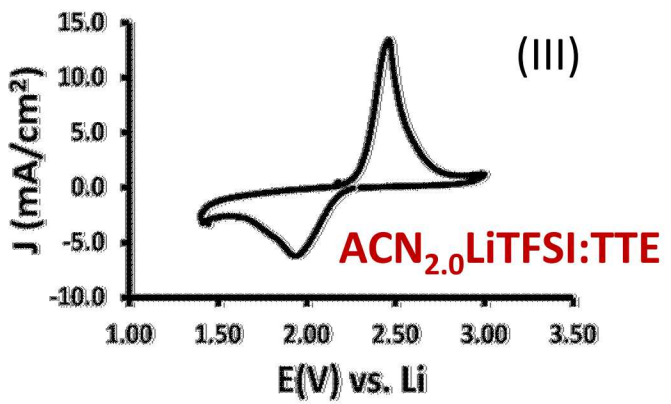
1.



2.



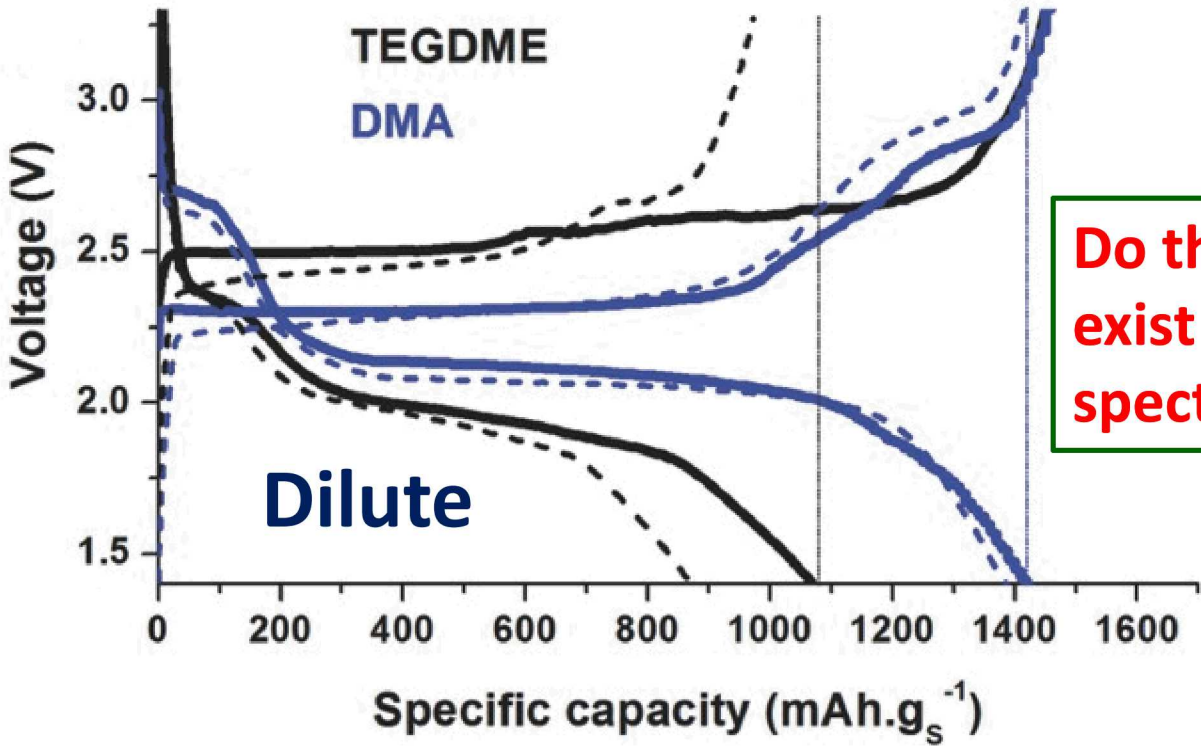
Need to better understand the patterns.



1. Jung et. al. *Int. J. Electrochem. Sci., Vol. 3, **2008** (Kwak Group, Korea)*
2. *Yang et. al. PNAS. **2017**, 114 (24) 6197 (Wang Group ANL; Xu ARL)*

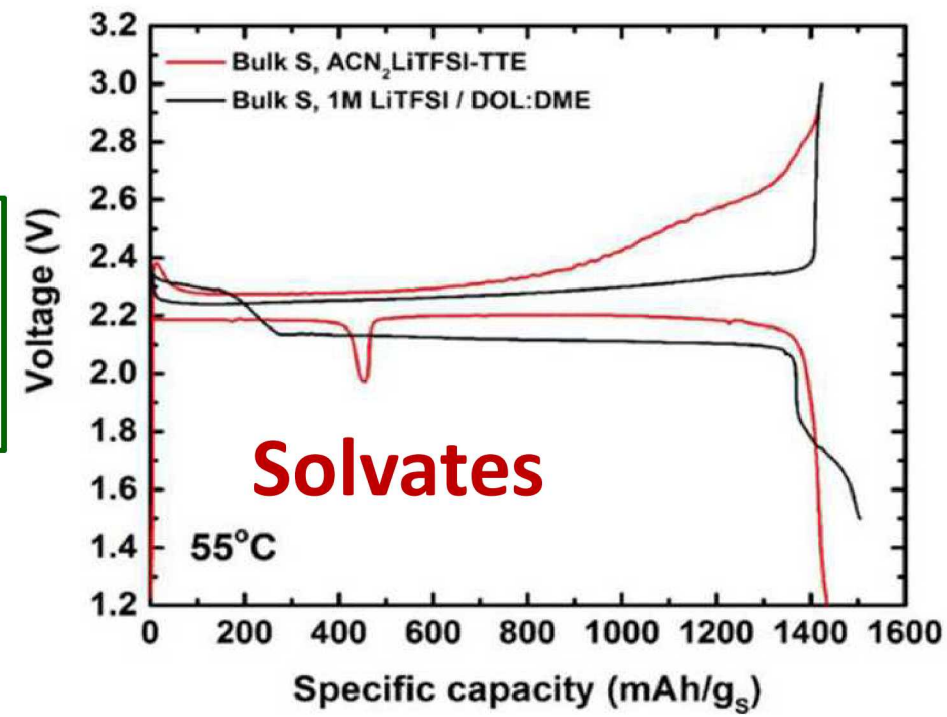
Each “Class” Generates a Unique Discharge Signature

1.



Do the “classes exist on a spectrum?

2.



Lower 1st reduction potential
Higher 2nd reduction potential

Lower solubility

Equilibrium does not favor $S_3^{\bullet-}$

1. Cuisinier et. al. Adv. Energy Mater., ***2015,*** *5 (Nazar Group, Waterloo)*
2. *Lee et. Al. ACS Cent. Sci. 2017, 3, 605-613 (Nazar, Waterloo;* Balasubramanian, ANL)

Electrolytes Exist on a "Solvation" Continuum

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- i. **High EPD** Solvents
  - Ex. **DMF**, DMA, DMSO
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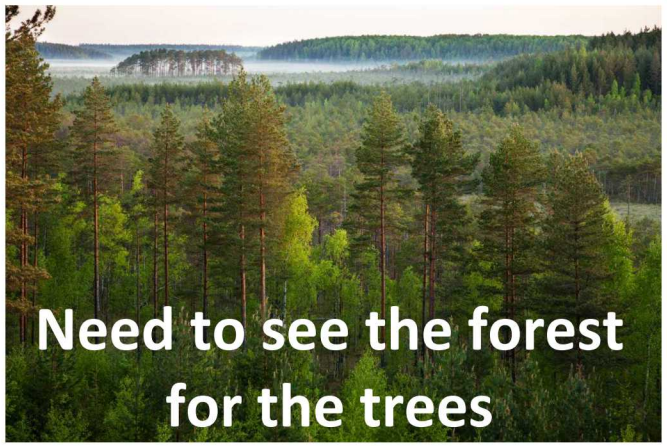
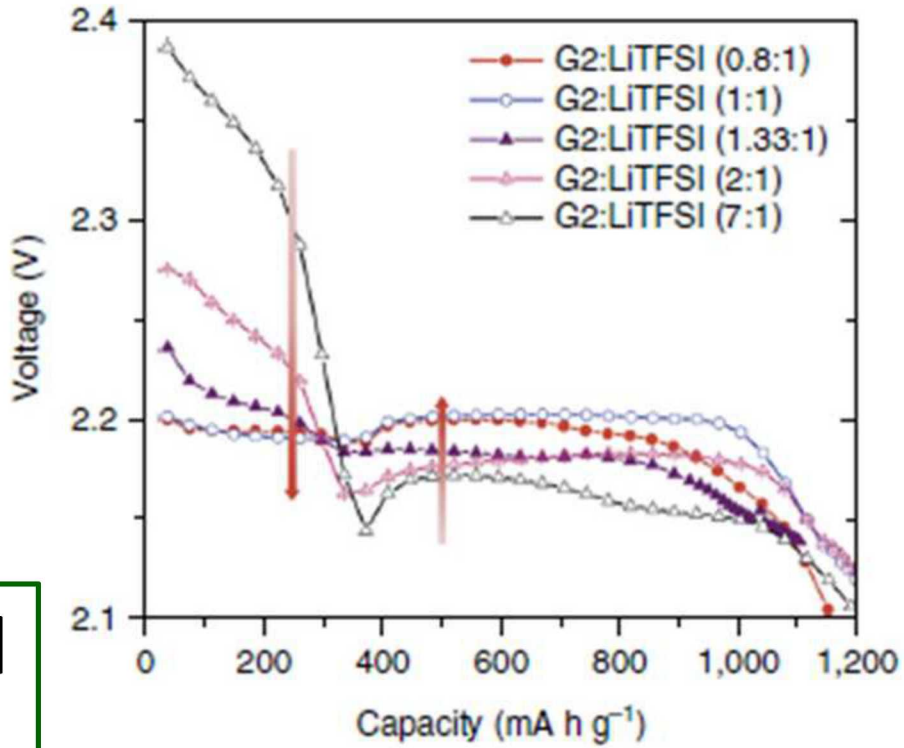
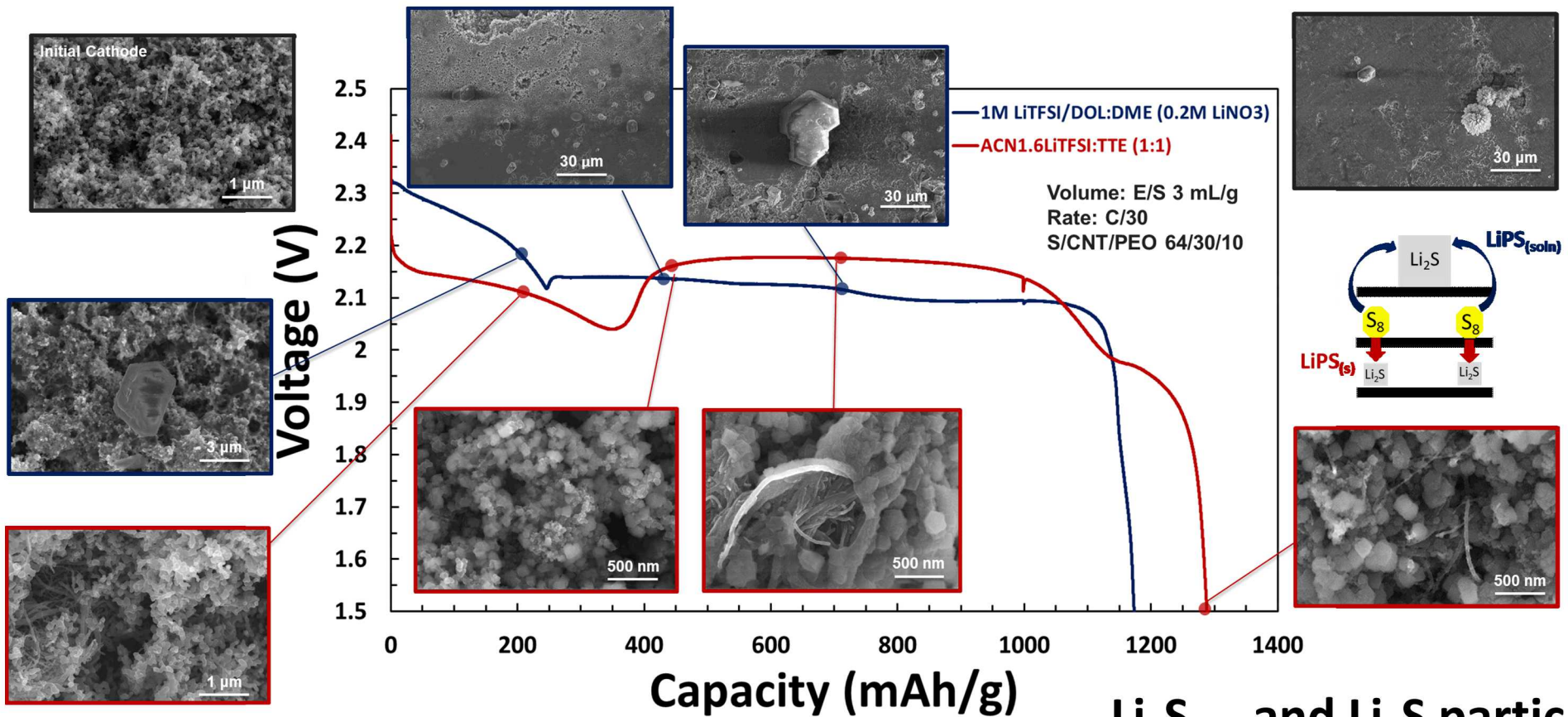




Pang *et. al.* Nat. Energy, ***2018,*** *3 (Nazar Group, Waterloo)*

Properties are tunable and outcomes should be predictable.

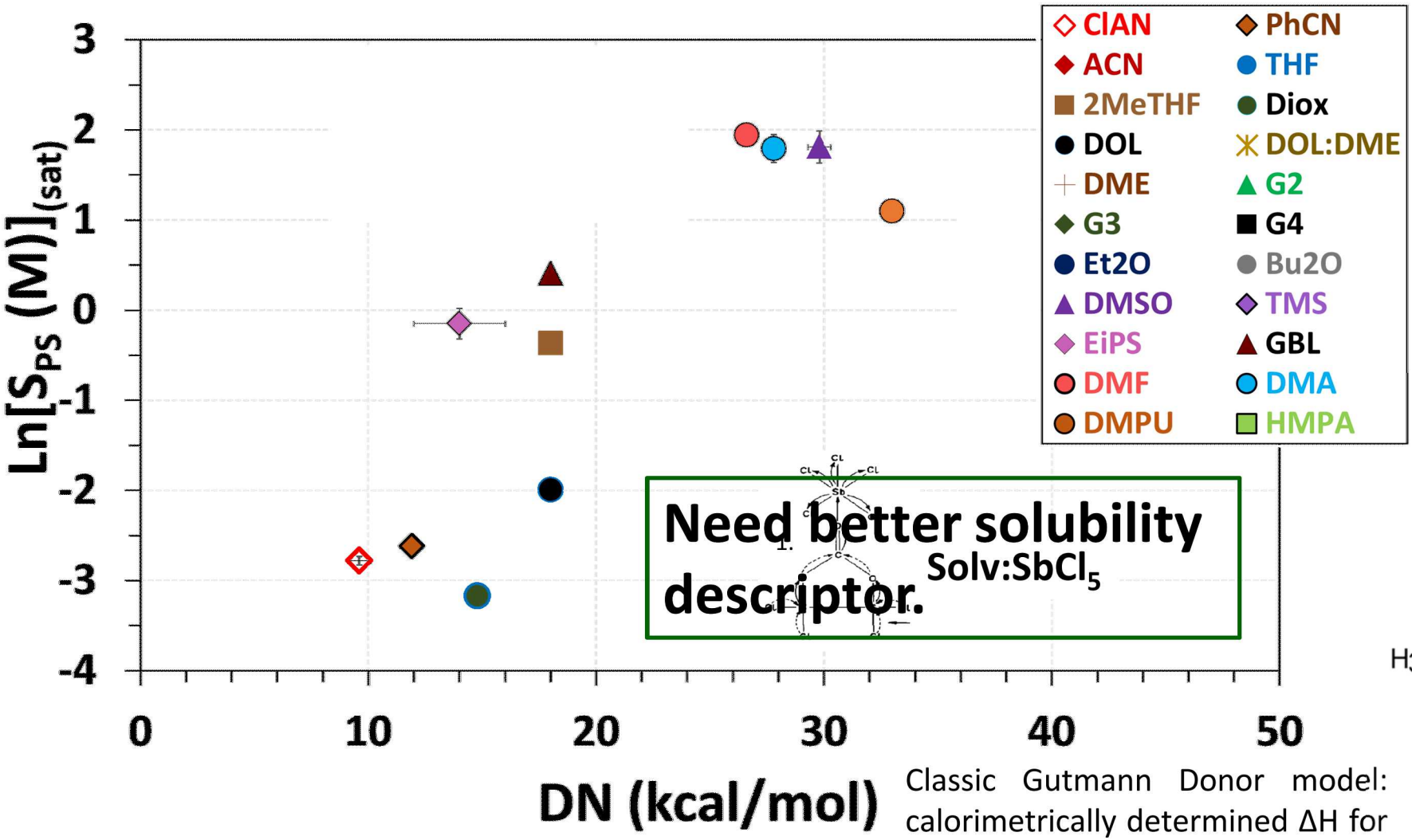
Solubility Plays a Critical Role in Mechanism

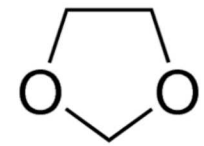


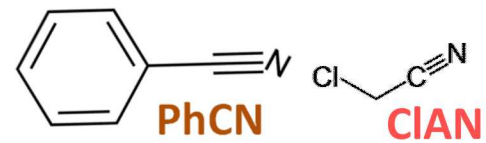
$Li_2S_{y(s)}$ and Li_2S particle size is dependent on solubility

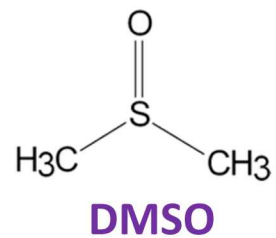
Control over solubility means control of material movement

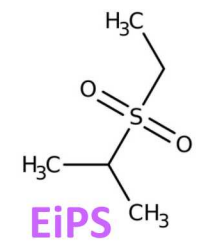
DN is a Poor Descriptor of LiPS Solubility



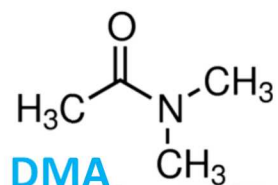






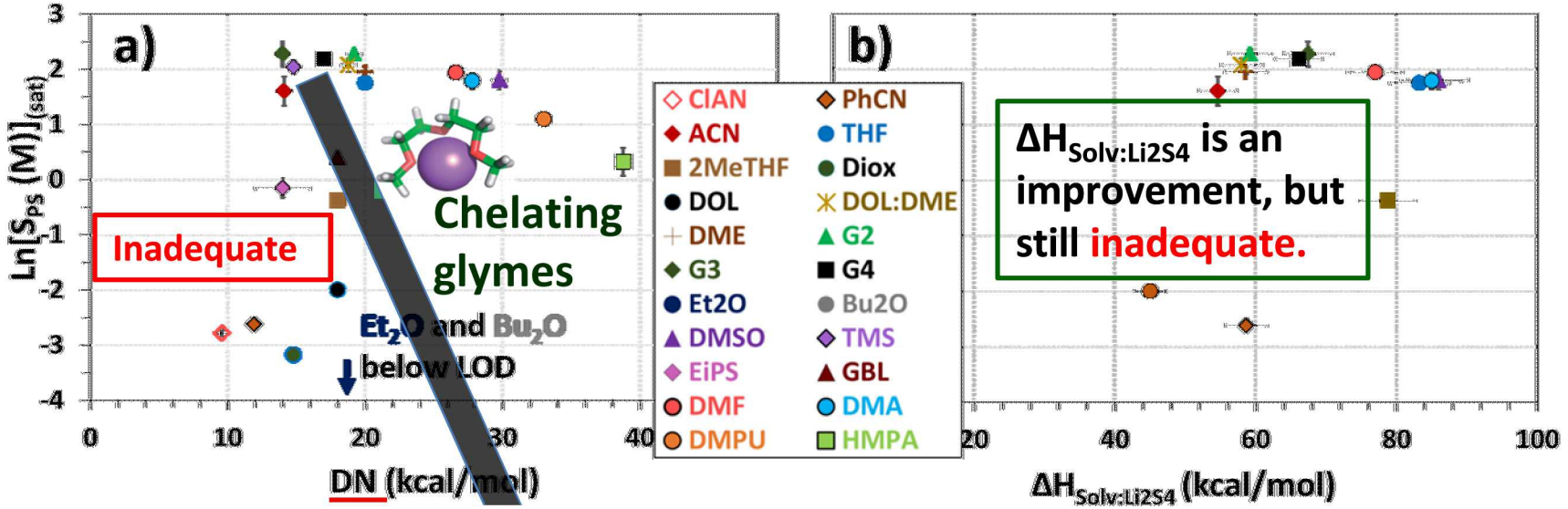


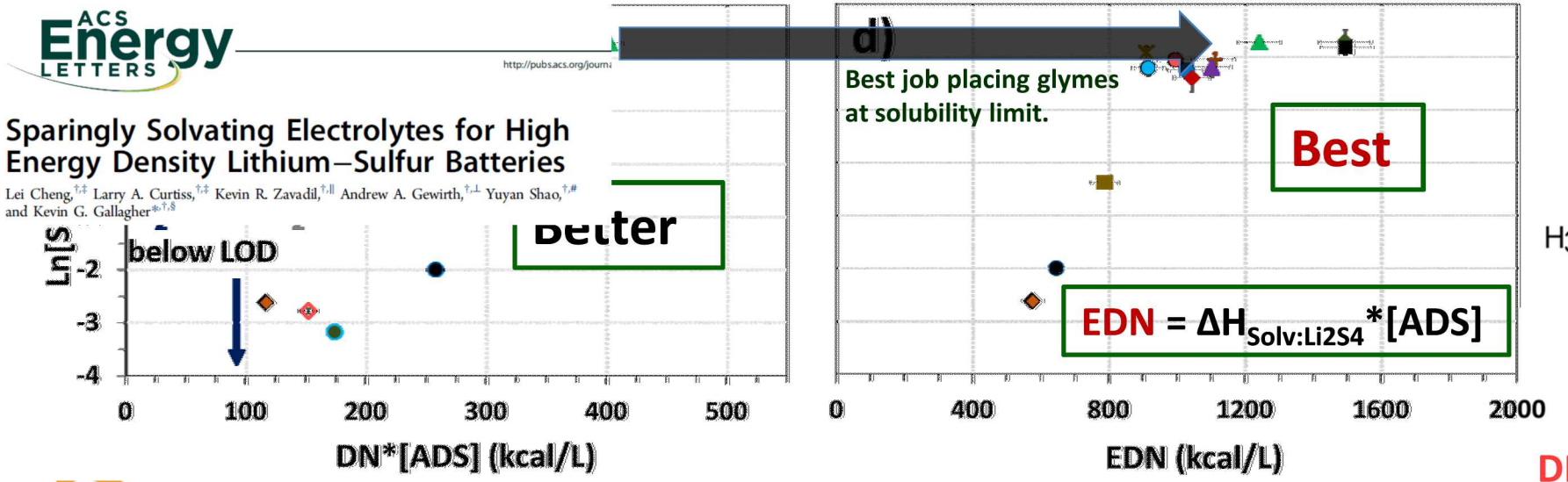
Classic Gutmann Donor model: calorimetrically determined ΔH for ***coordinative bond with $SbCl_5$.***

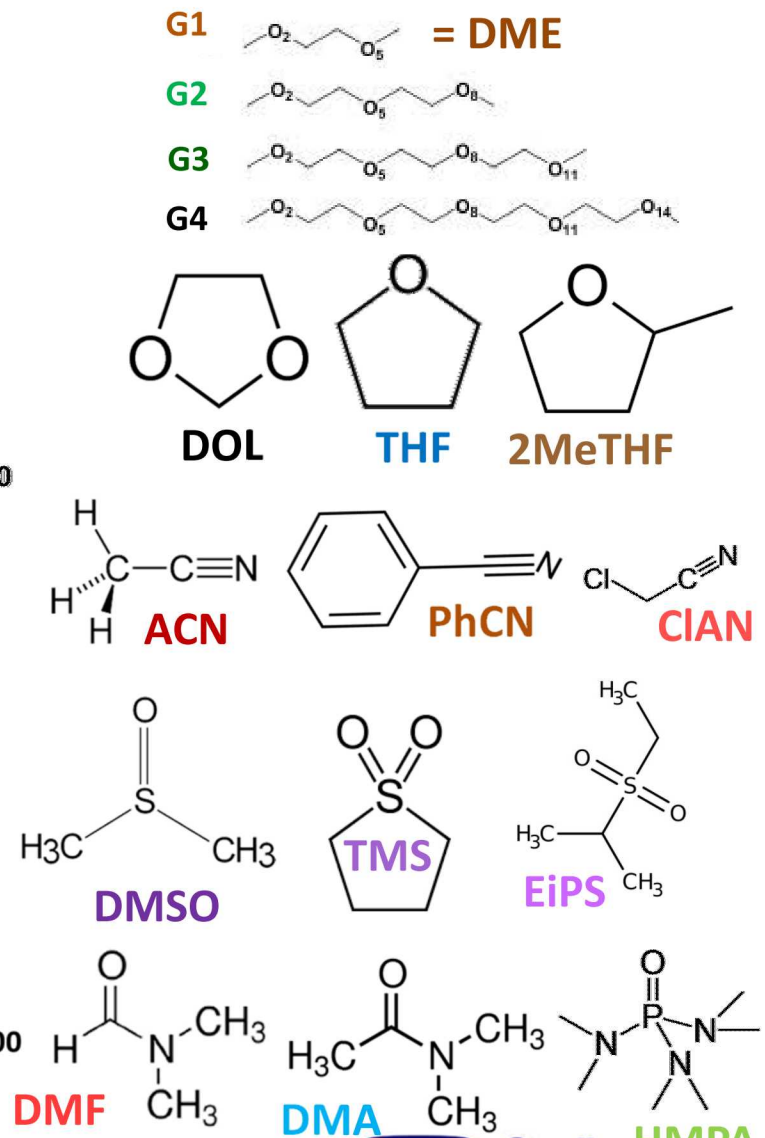


1. Gutmann, V. Electrochimica Acta. 1976, 21, 661-670

LiPS Solubility Best Described by $\Delta H_{Solv:Li2S4}$*[ADS]

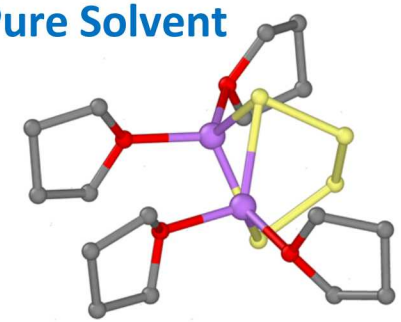




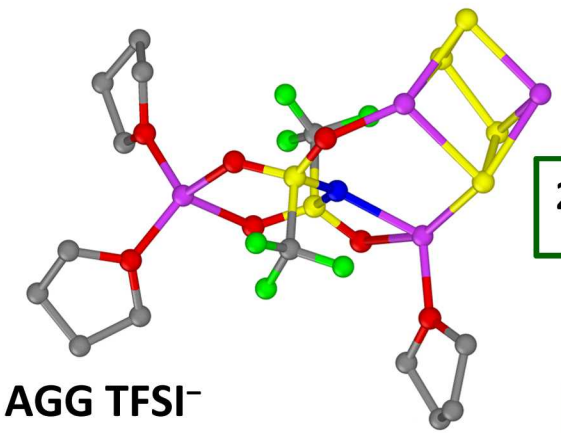


Complexation with Li_2S_4 a Better Descriptor for Solvation Enthalpy ($\Delta H_{Solv:Li2S4}$)

w/ Pure Solvent

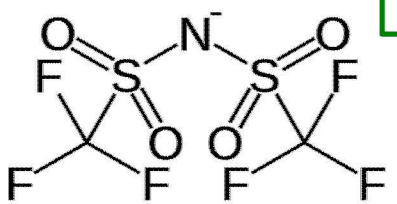


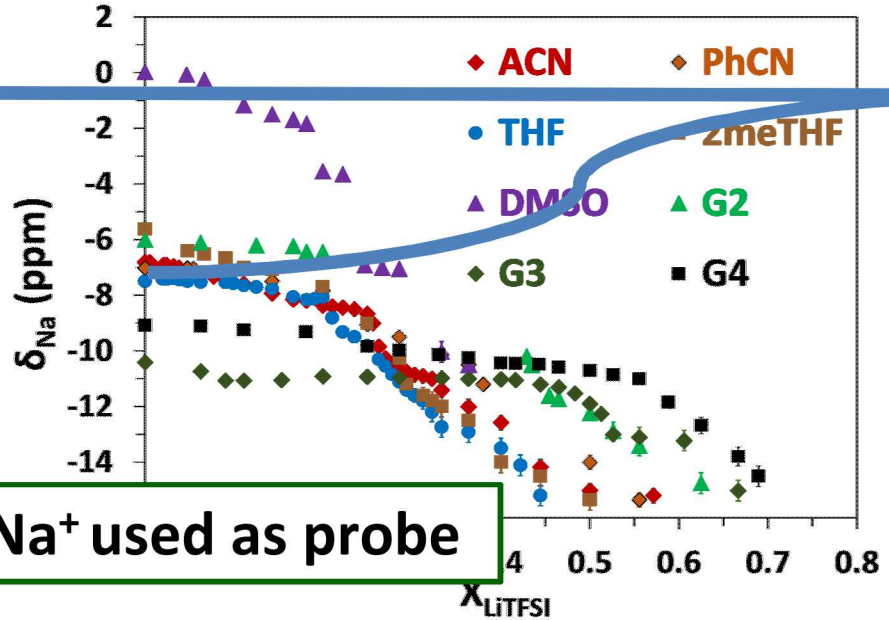
$\Delta H_{THF:Li2S4}$ = -83.3 kcal/mol



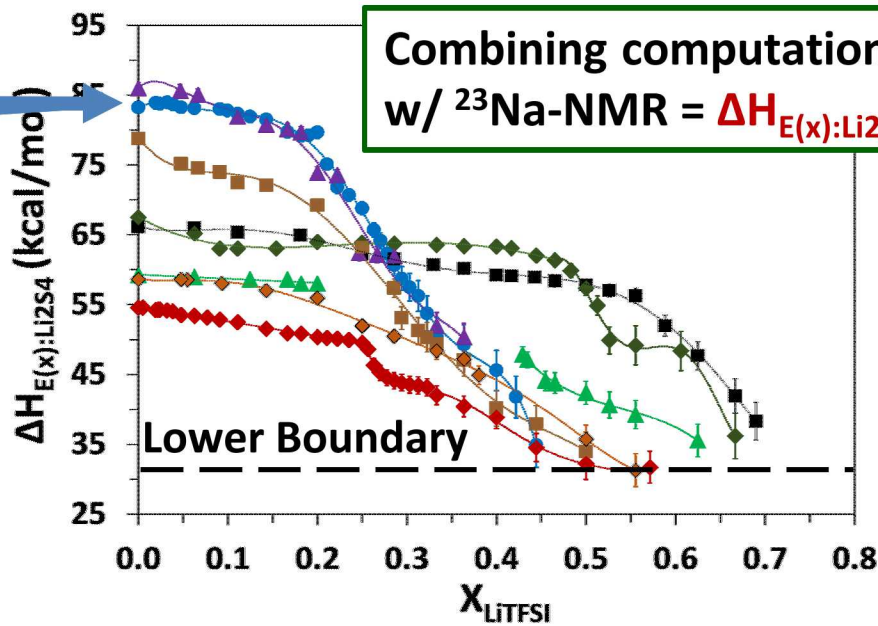
w/ AGG $TFSI^-$

$\Delta H_{AGG:Li2S4}$ = -32.8 kcal/mol





$^{23}Na^+$ used as probe



Combining computation w/ ^{23}Na-NMR = $\Delta H_{E(x):Li2S4}$

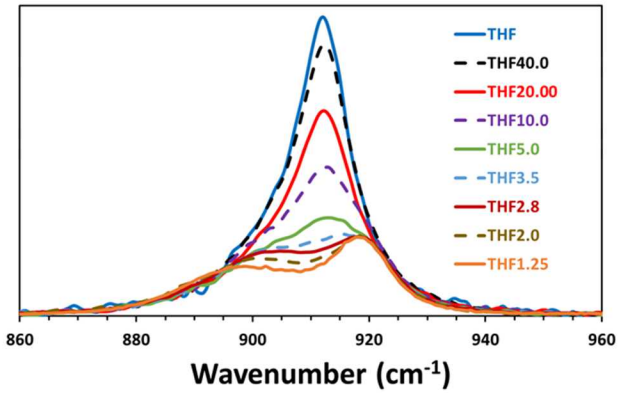
$\sigma_{p\text{-}23Na}$ = -270 ppm >> $\sigma_{d\text{-}23Na}$ = +9.7 ppm, $\sigma_{d\text{-}7Li} \approx \sigma_{p\text{-}7Li}$

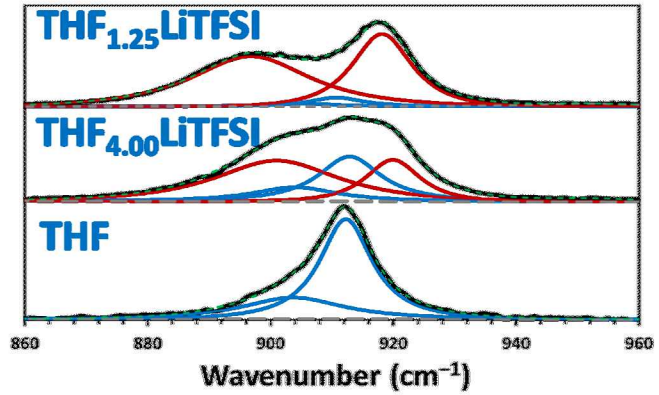
$$\Delta H_{E(x):Li2S4} = \left[\frac{\delta_{Na:E(x)} - \delta_{Na:E(AGG)}}{\delta_{Na:Solv} - \delta_{Na:E(AGG)}}\right] * \Delta H_{Solv:Li2S4} + \left[\frac{\delta_{Na:Solv} - \delta_{Na:E(x)}}{\delta_{Na:Solv} - \delta_{Na:E(AGG)}}\right] * \Delta H_{AGG:Li2S4}$$

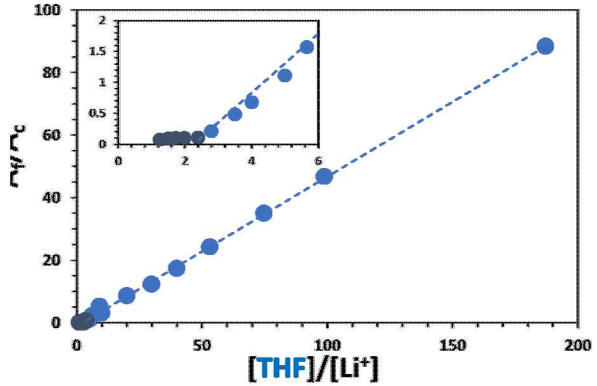
Upper Boundary

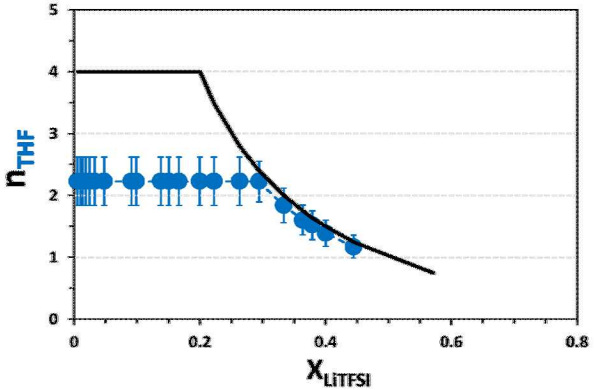
Lower Boundary

Raman Fits Determine Coordinated Fractions of Solvents

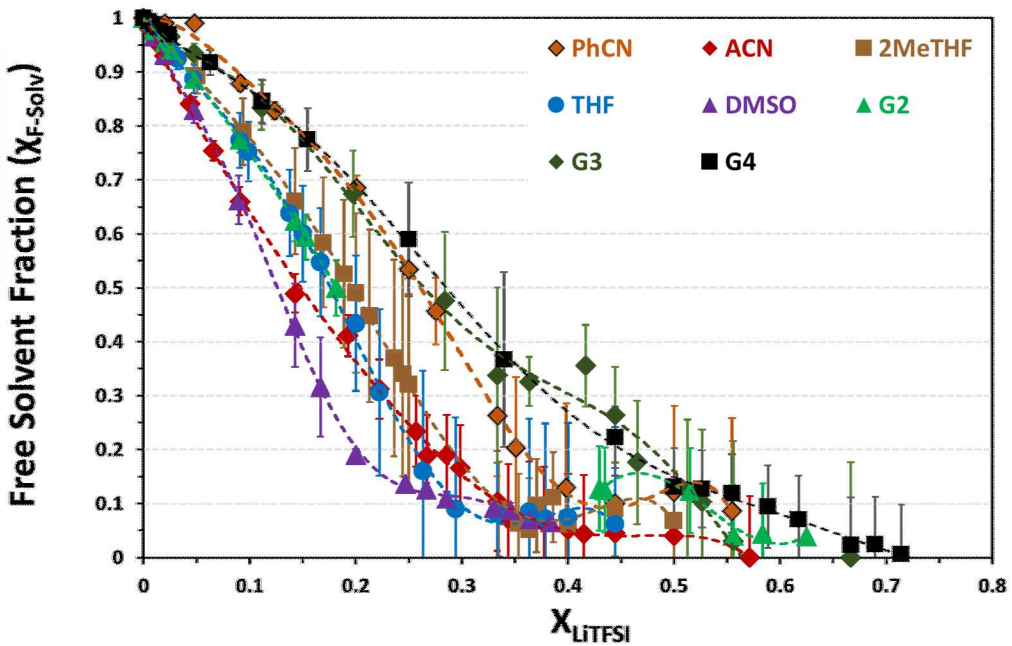








Vibrational spectroscopy unveils elyte structure.



$$\left(\frac{A_f}{A_c}\right) = \left(\frac{J_f}{J_c}\right)\left(\frac{1}{n}\right)\left(\frac{[Solv]}{[Li^+]}\right) - \left(\frac{J_f}{J_c}\right)$$

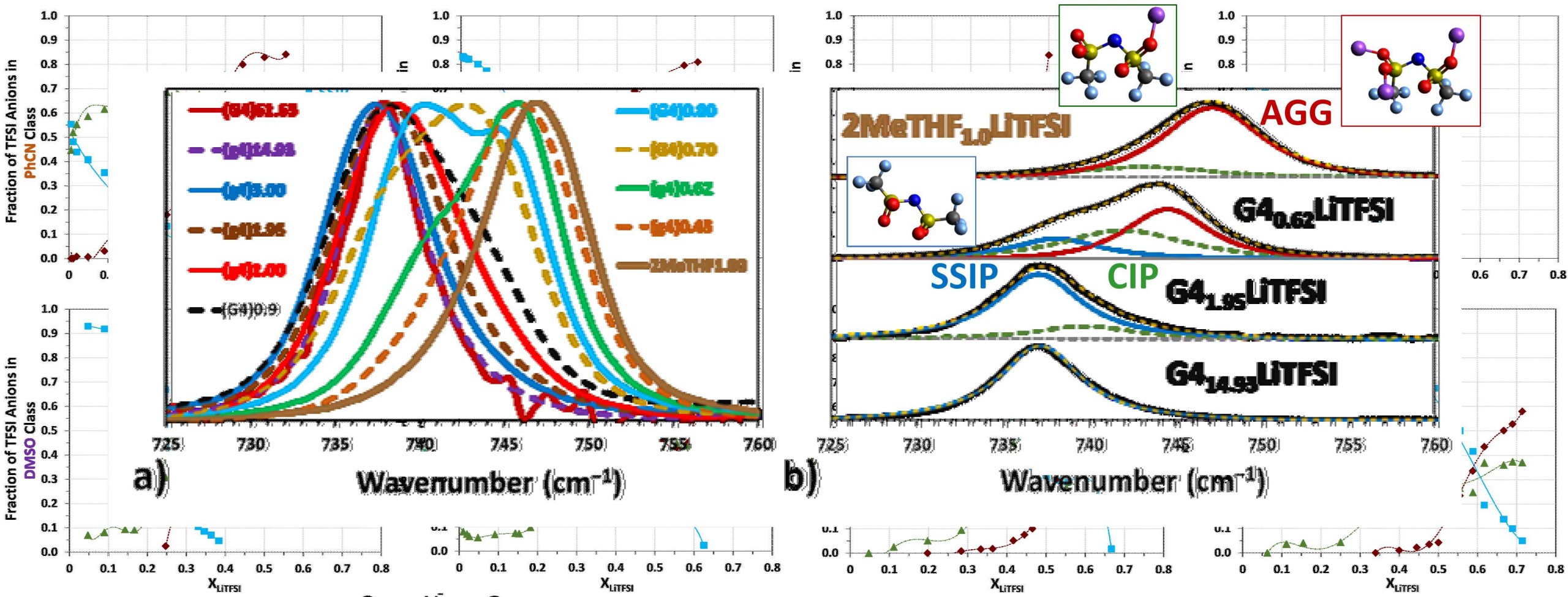
n = Coordination Number

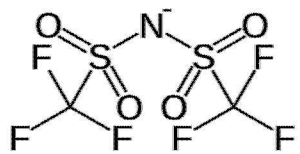
J_f = Free Scattering Coeff.

J_c = Coordinated Scattering Coeff.

$$[Solv_f] = [Solv] - n[Li^+]$$

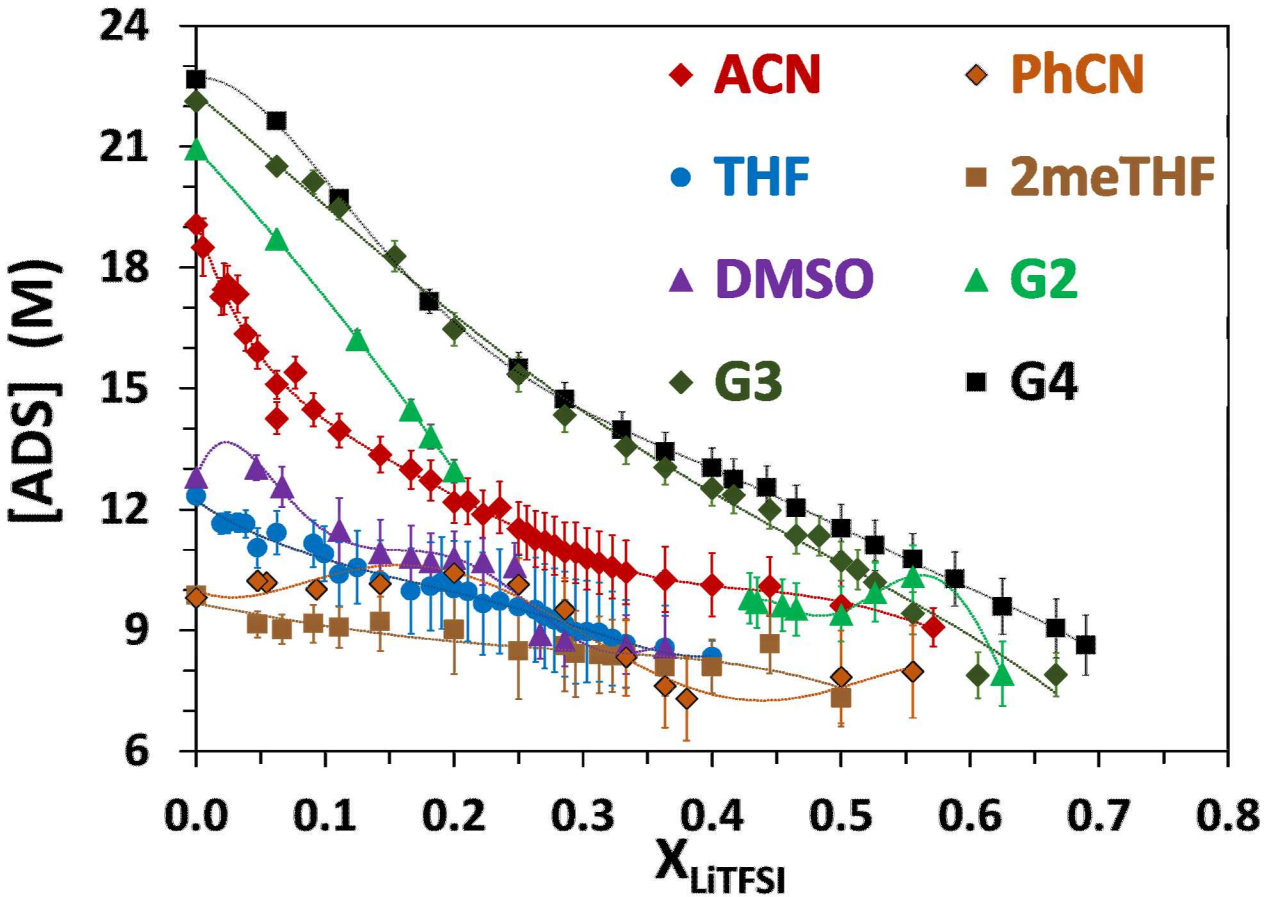
Raman Fits Determine Coordinated Fractions of $TFSI^-$

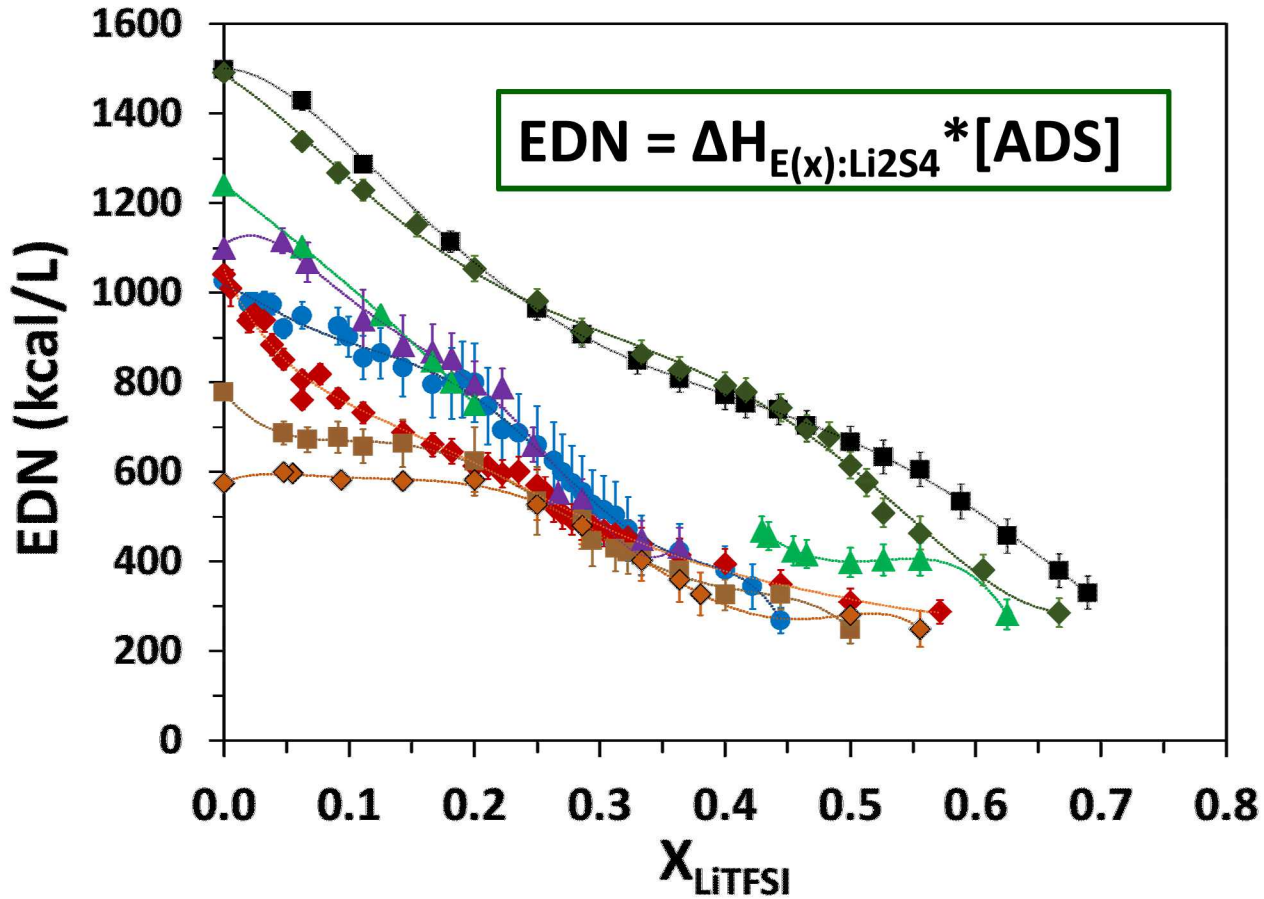




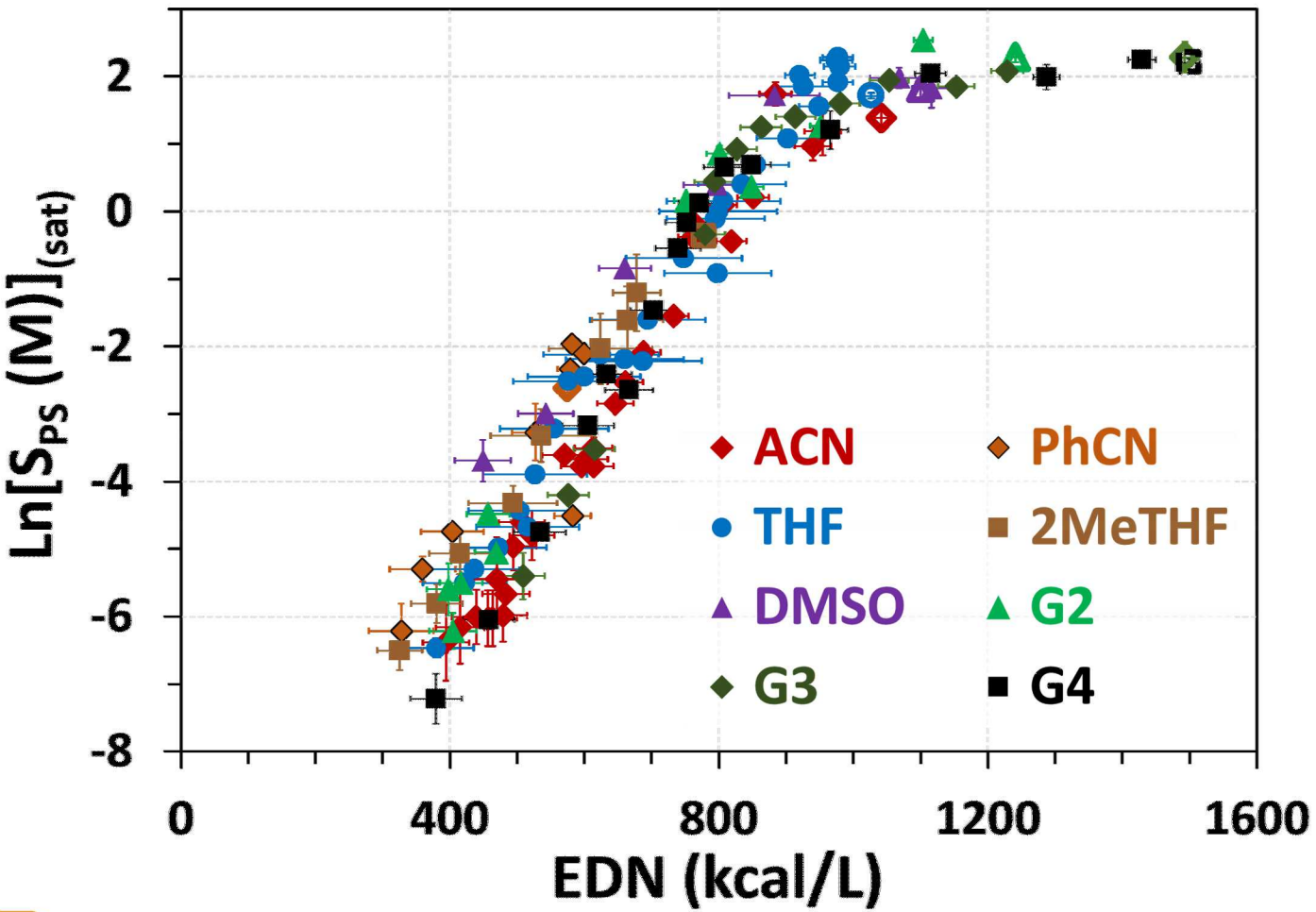
Vibrational spectroscopy unveils elyte structure.

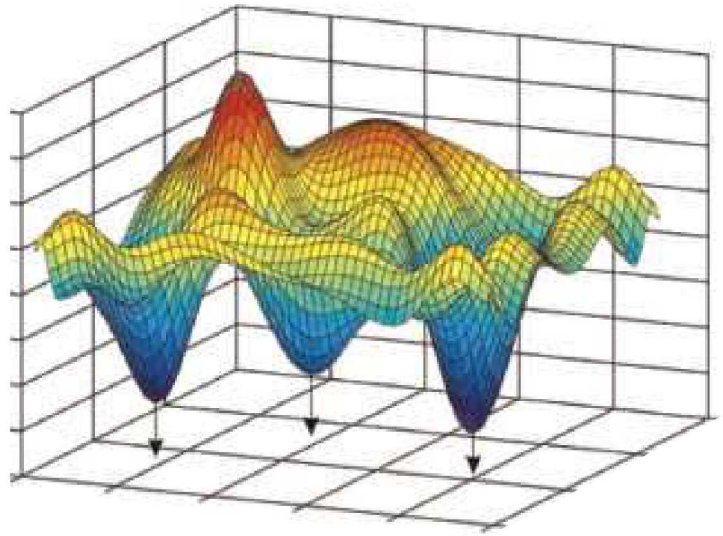
Complex Enthalpy and Structure Produce EDN





EDN is a Good Descriptor for $[S_{LiPS}]_{sat}$

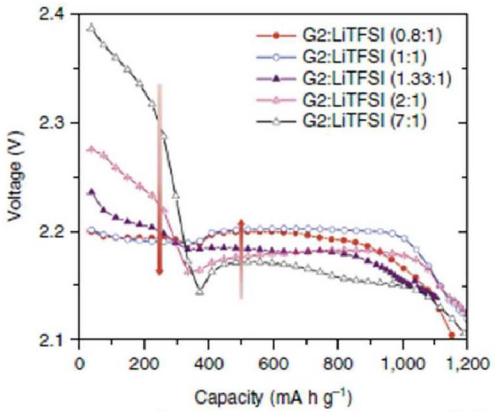




EDN as an energy landscape

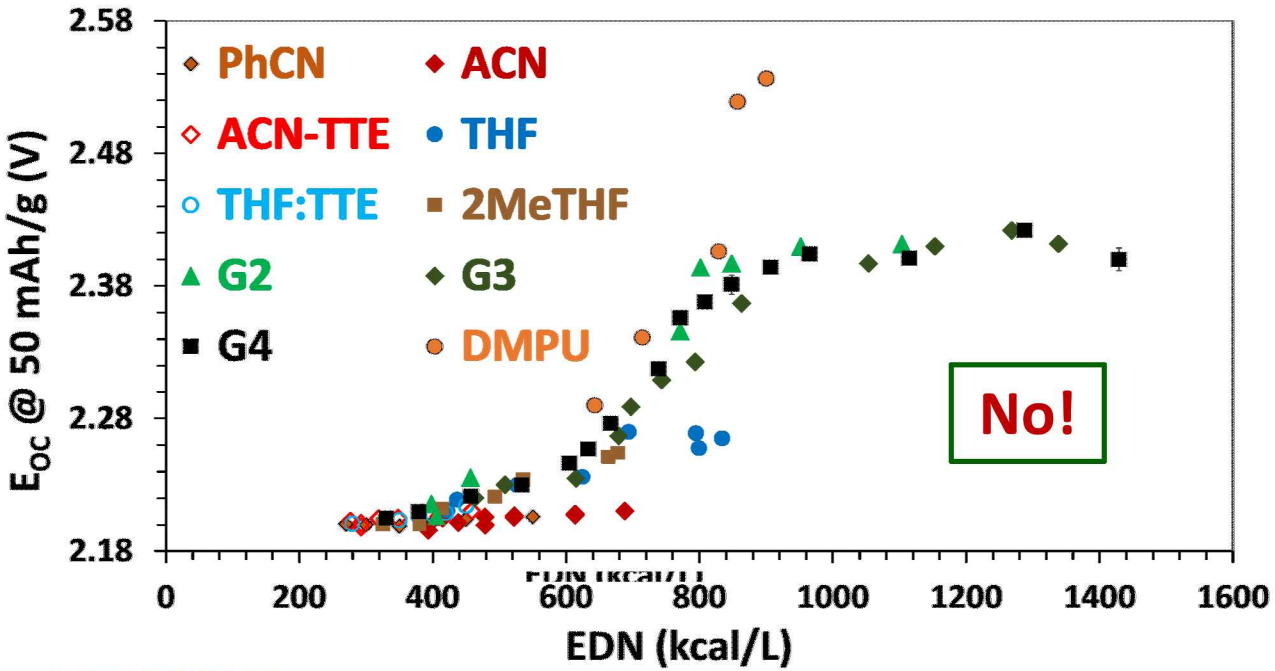
EDN ↑ by ↑ average well depth and/or ↑ density of wells

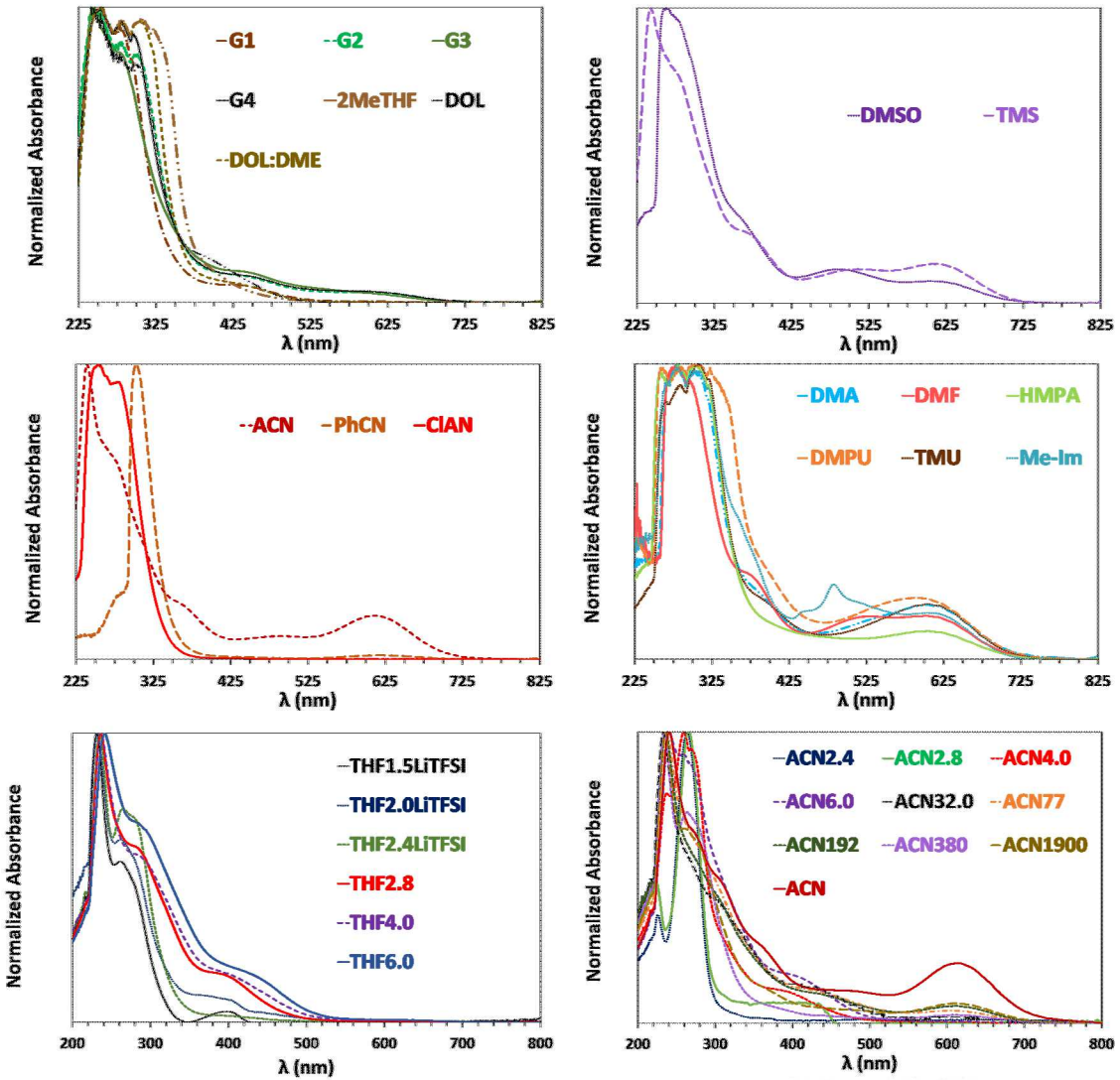
Is Solubility the Main Driver of Mechanism?



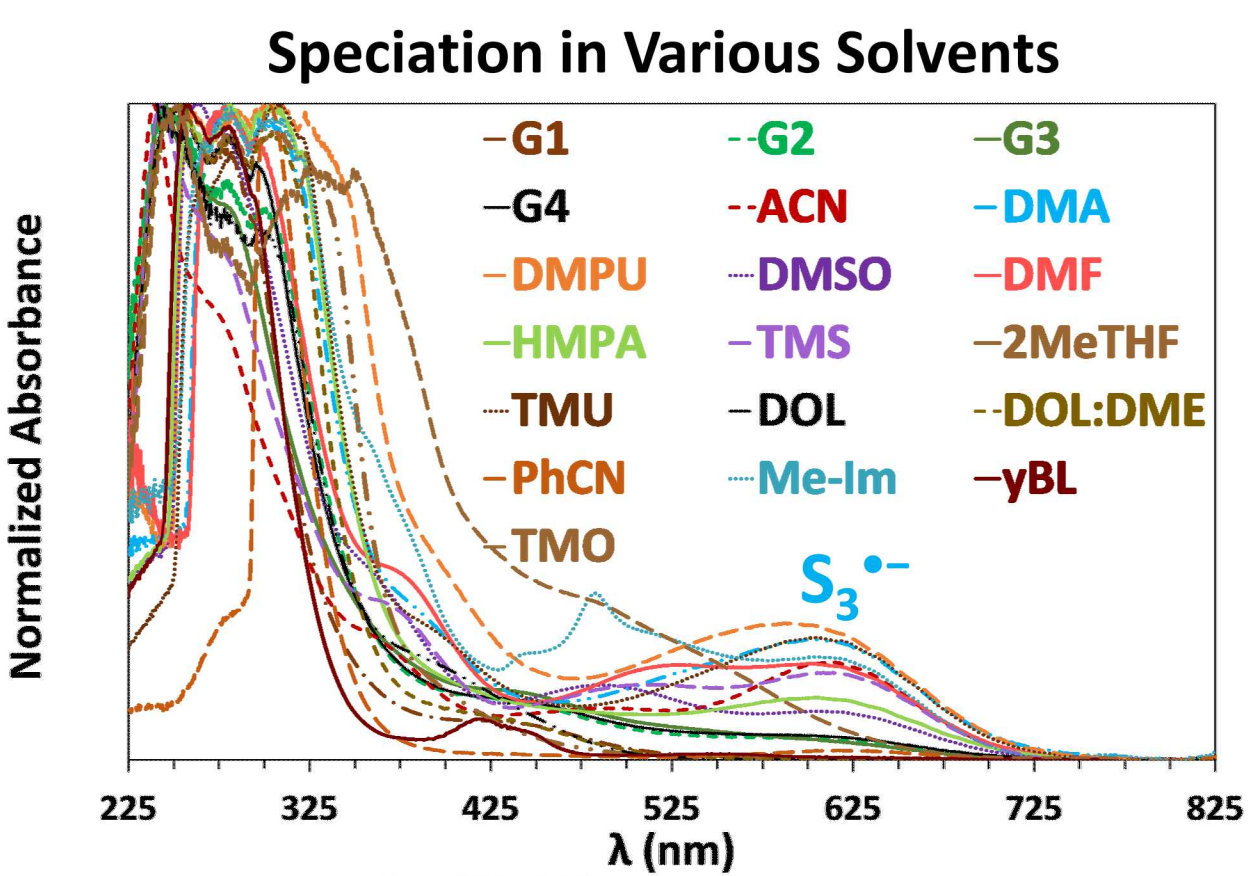
PS speciation is the second critical factor

Pang et. al. Nat. Energy, ***2018,*** *3 (Nazar Group, Waterloo)*

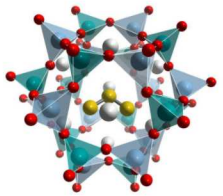


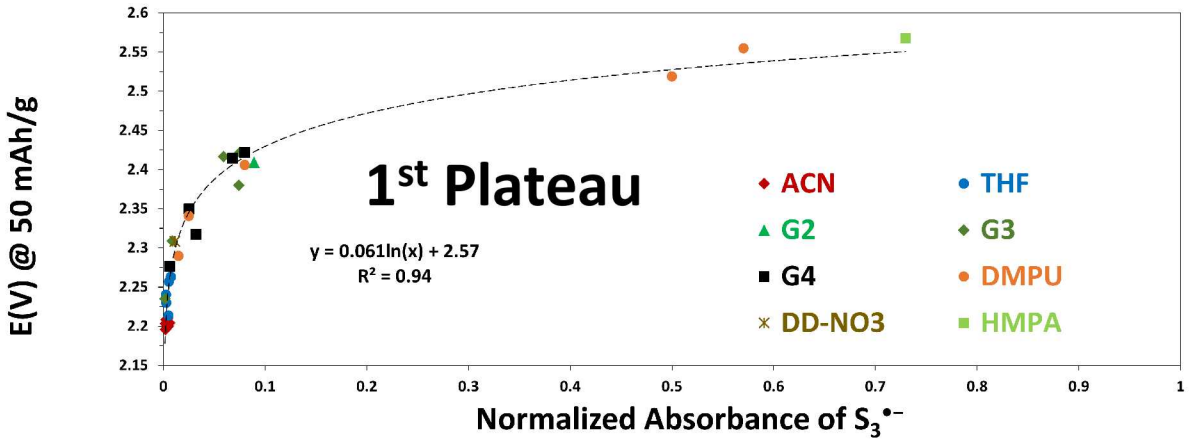


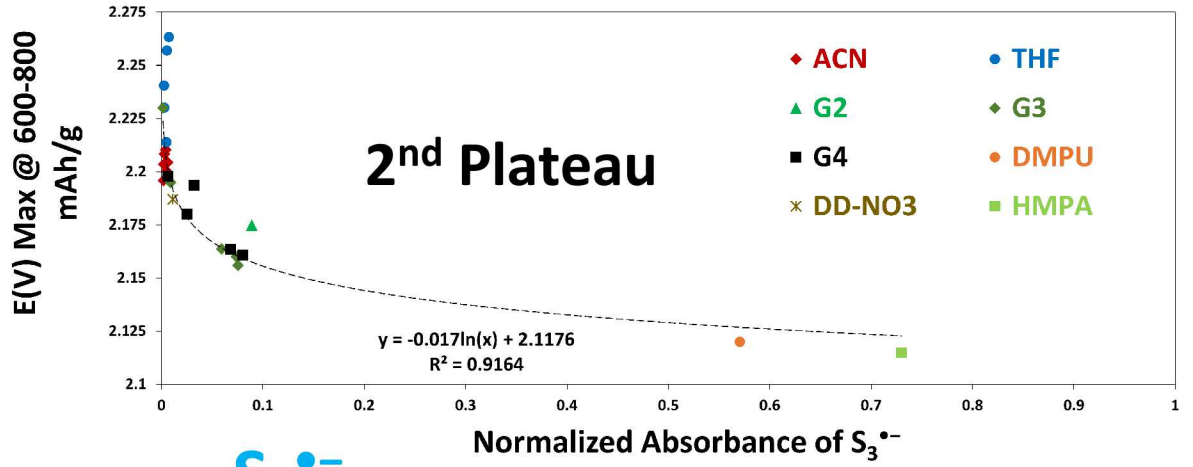
Independent of Solvent, $S_3^{\bullet-}$ in solution is linked to cell potential



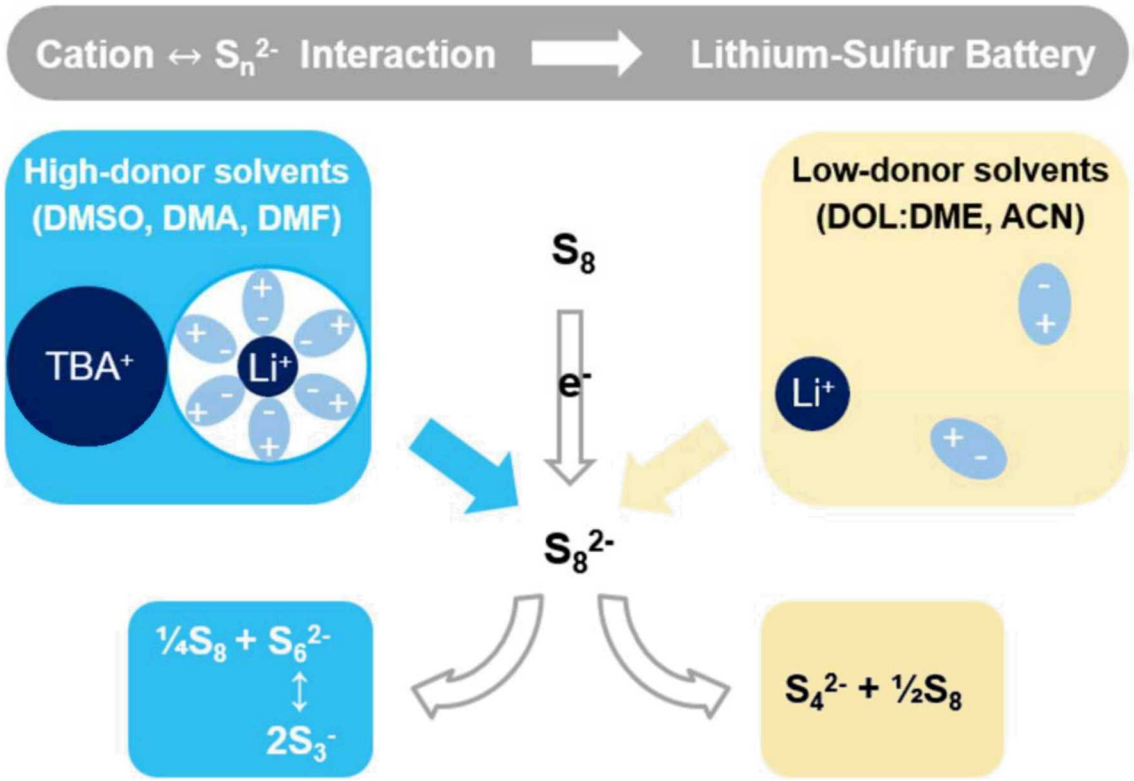
$S_3^{\bullet-}$ found in Lazurite

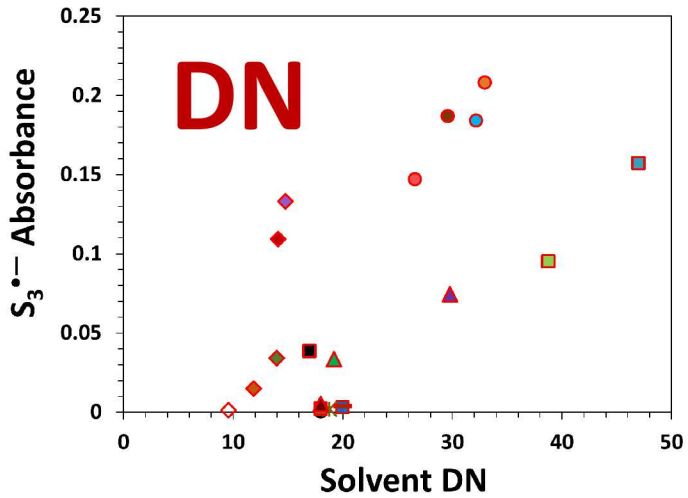


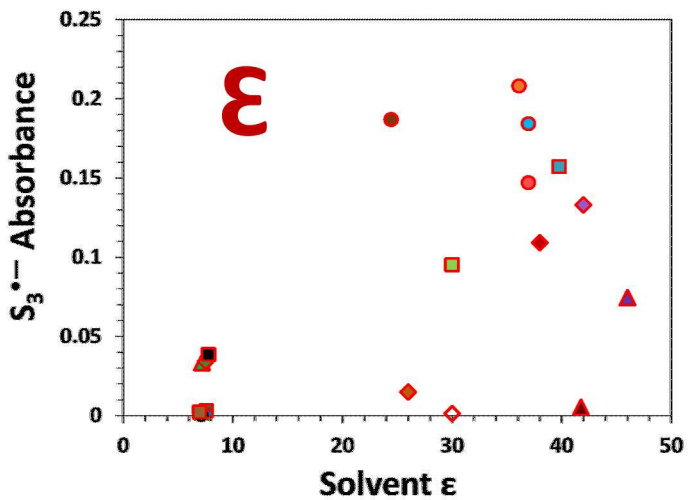


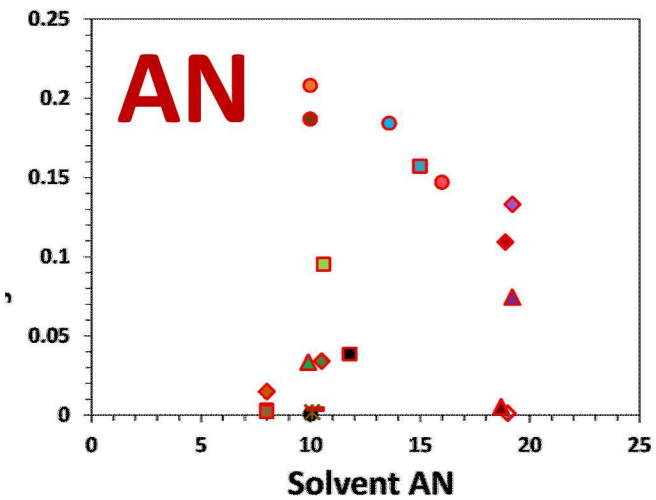


Gutmann DN is not a complete descriptor for $S_3^{\bullet -}$ in solution







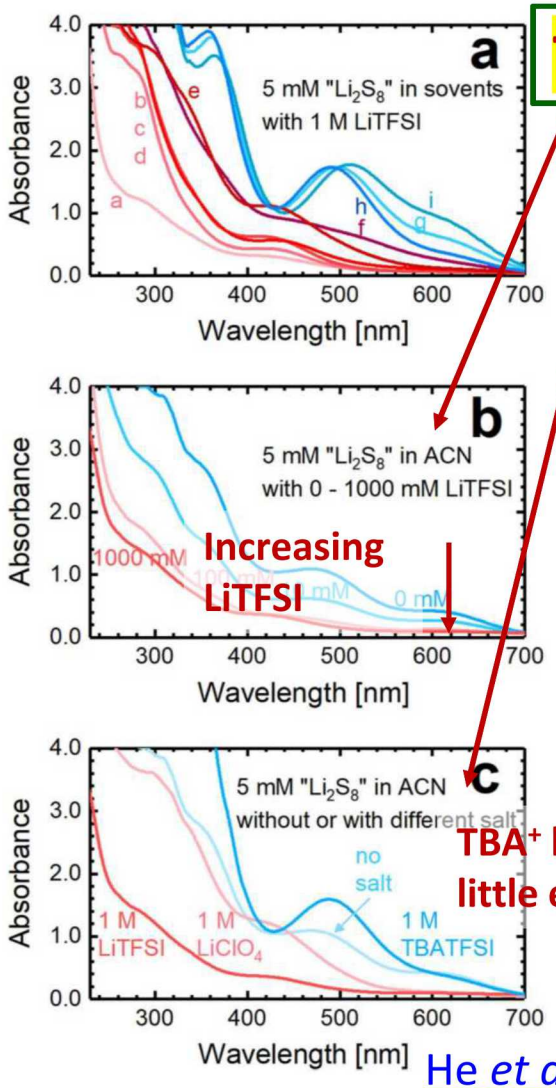


There is no single descriptor

He *et al.* J. Electrochem. Soc., **165** (16) A4027-A4033 (2018)

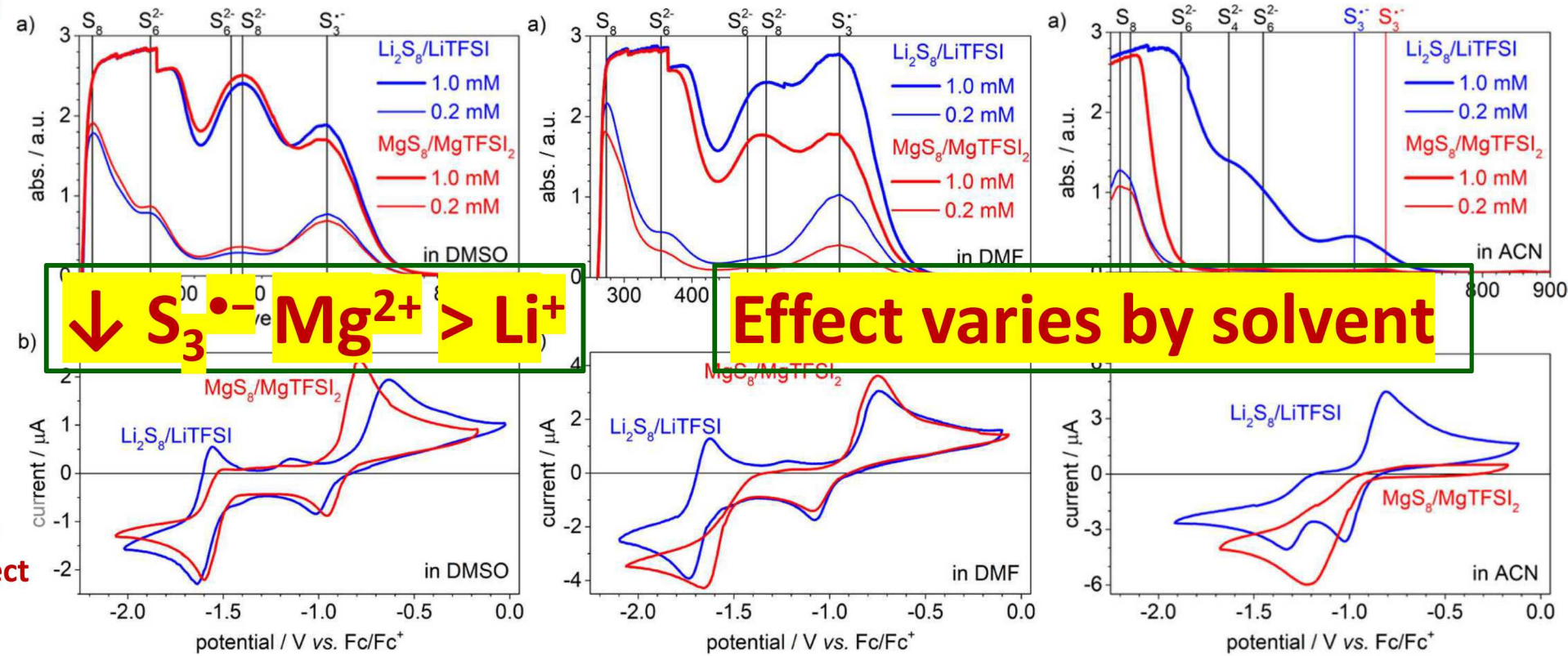
Speciation is clearly dependent on other characteristics

The salt and its concentration play a significant role.



TBA⁺ has little effect

Comparison of LiTFSI to $Mg(TFSI)_2$ in various solvents



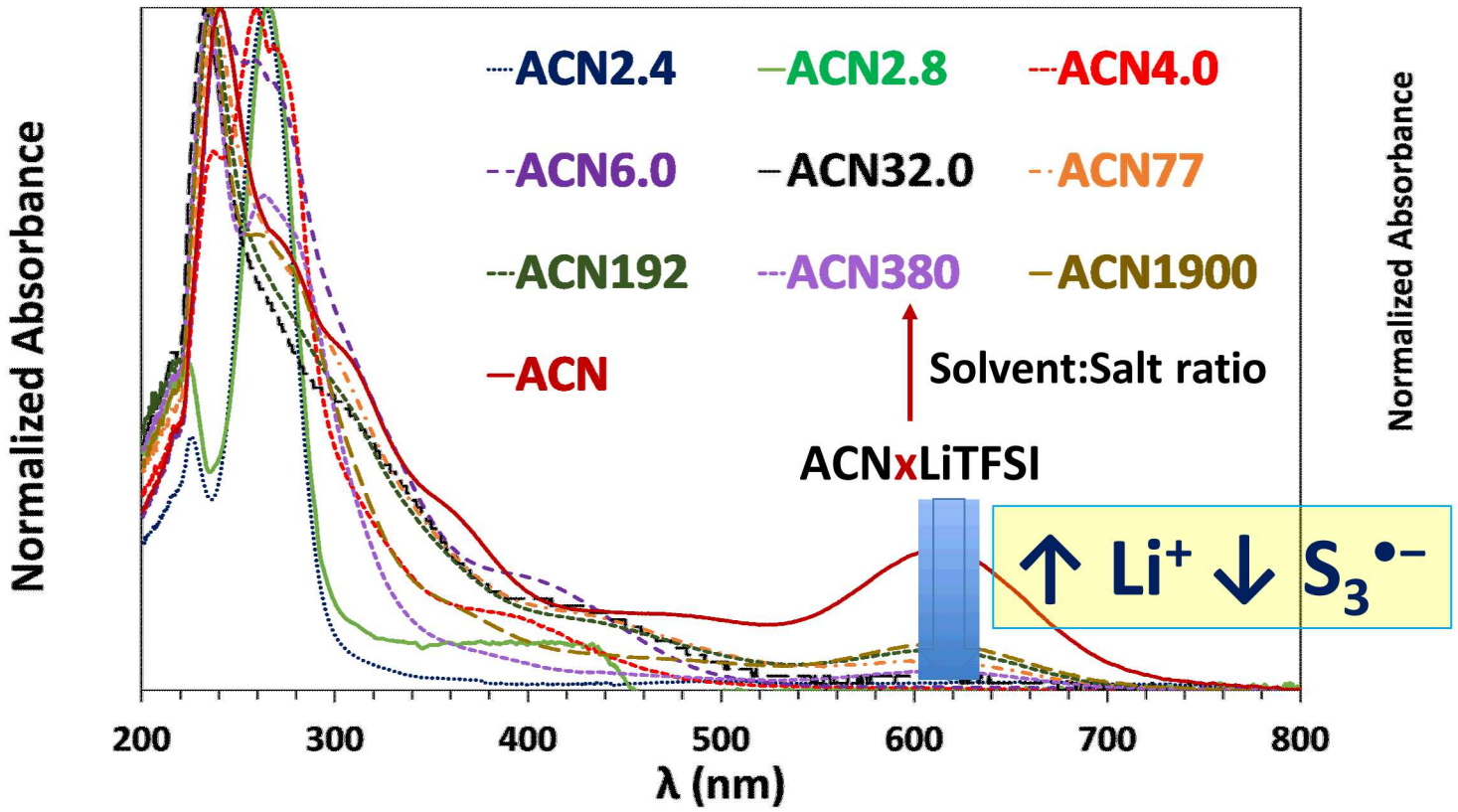
↓ $S_3^{\bullet-}$ Mg^{2+} > Li^+

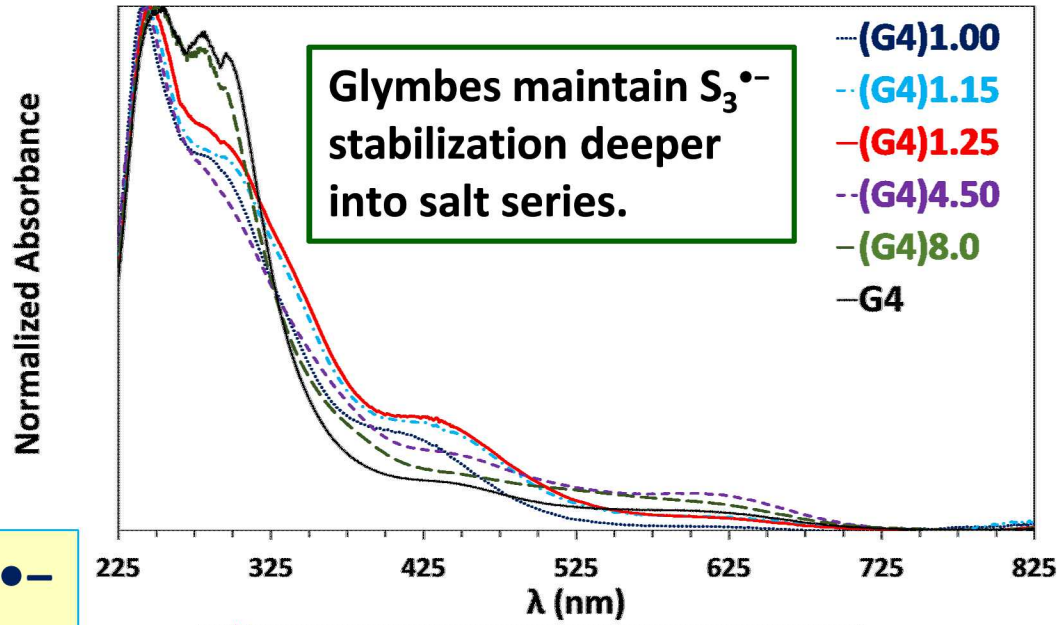
Effect varies by solvent

He *et al.* J. Electrochem. Soc., **2018**, 165 (16) A4027-A4033

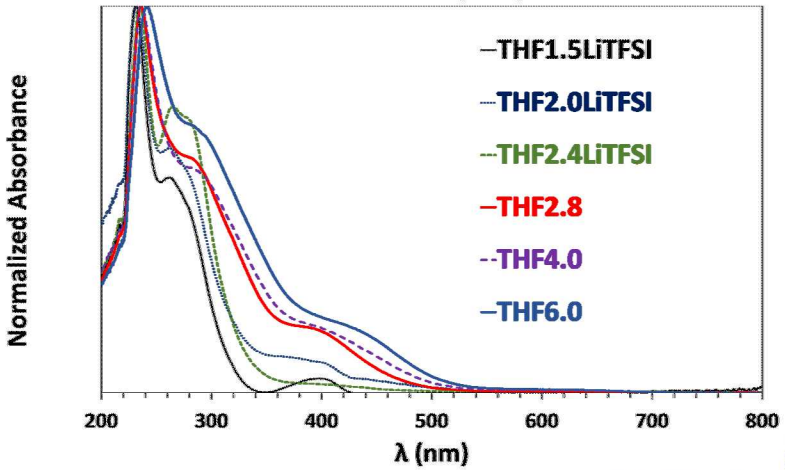
Bieker *et al.* J. Phys. Chem. C **2018**, 122, 21770−21783

Increasing [Li^+] Destabilizes $S_3^{\bullet-}$ Due to Decrease in Permittivity and/or "Hard Acid" Interaction

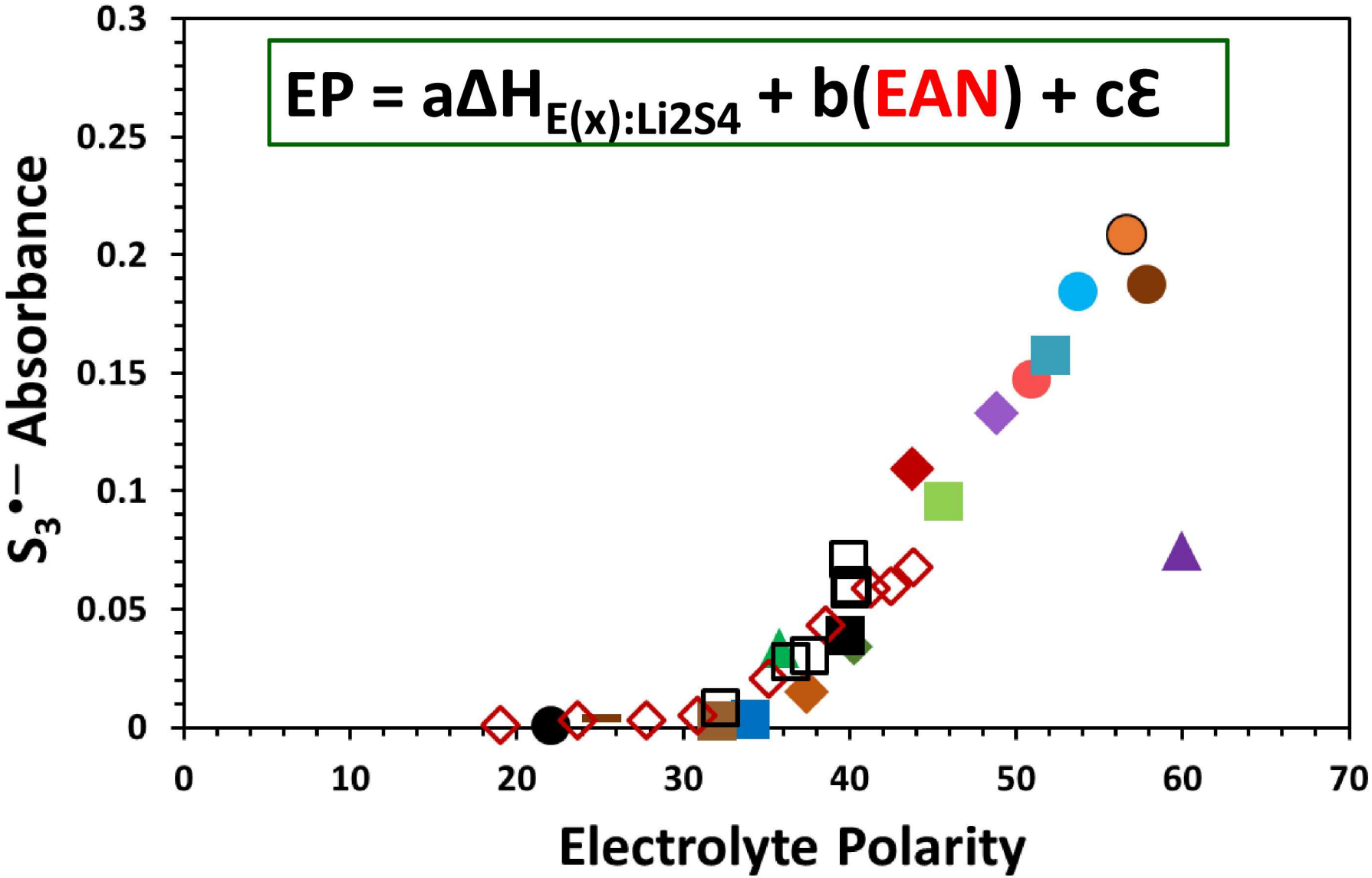




Some solvents never show $S_3^{\bullet-}$



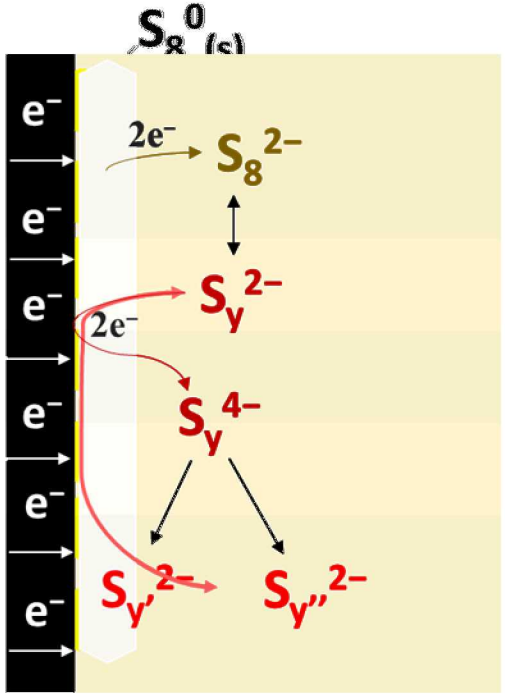
Speciation Described by Function of $\Delta H_{E(x):Li2S4}$, EAN, and Ɛ

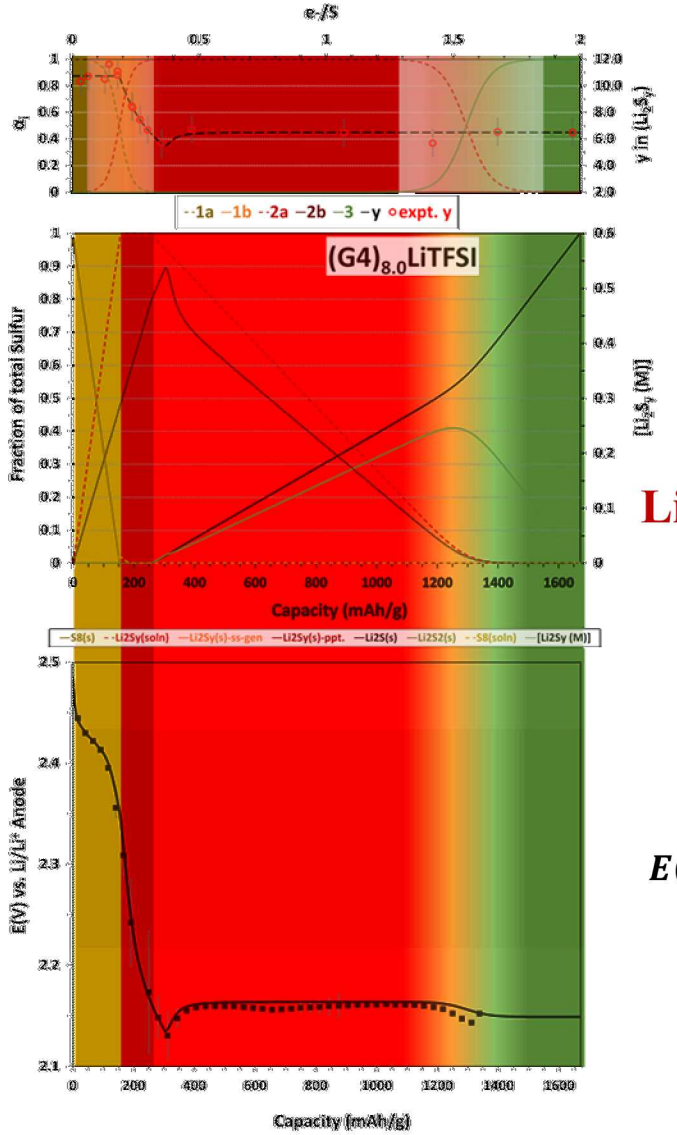


Discharge Mechanism Divided into 3 or 4 Regions

Region 1 (Consumption of $S_8^0{}_{(s)}$):

$$\frac{y}{8}S_8^0 + 2Li^+ + 2e^- \rightarrow Li_2S_y$$





Region 2 (PS Speciation Transition):

$$y(Q) = Q_{Theory}/Q$$

Region 3 (Formation of $Li_2S_{(s)}$ and/or $Li_2S_{2(s)}$):

$$Li_2S_y + 2Li^+ + 2e^- \rightarrow XLi_2S_{(s)} + ZLi_2S_{2(s)} + (2 - X - Z)Li_2Sy'$$

y' = minimum y

$$E(Q) = \sum_{i,Q} \alpha_{i,Q} E_i^0 - \frac{RT}{F} \sum_{i,Q} \frac{\alpha_{i,Q}}{n_i} \left\{ Ln\left(\frac{[Li_2S_y]_Q}{[S_8^0]_Q^{y/8}} \right) + Ln\left(\frac{1}{[Li_2S_y]_Q} \right) \right\}$$

$$\alpha_{i,Q} = \frac{L}{1 + e^{-k(Q-Q_o)}}$$

Fraction of echem described by logistic function

Acknowledgements

B. Narrayanan, L. Curtiss, C.-W. Lee, L. Chen,
K.C. Lau, M. Balasubramanian, K. Gallagher

Argonne NATIONAL LABORATORY

Q. Pang, A. Shyamsunder, L.F. Naza

UNIVERSITY OF WATERLOO

H.-L. Wu, M. Shin, K. See, A. Gewirth

B. Perdue, N. Hahn

Sandia National Laboratories

Questions?

Thermodynamics Governed by Nernst Equation

$$E(Q) = \sum_{i,Q} \alpha_{i,Q} E_i^0 - \frac{RT}{F} \sum_{i,Q} \frac{\alpha_{i,Q}}{n_i} \left\{ Ln\left(\frac{\left[Li_2S_y\right]_Q}{\left[S_8^0\right]_Q^{\,y/8}} \right) + Ln\left(\frac{1}{\left[Li_2S_y\right]_Q} \right) \right\}$$

Fraction of echem described by logistic function

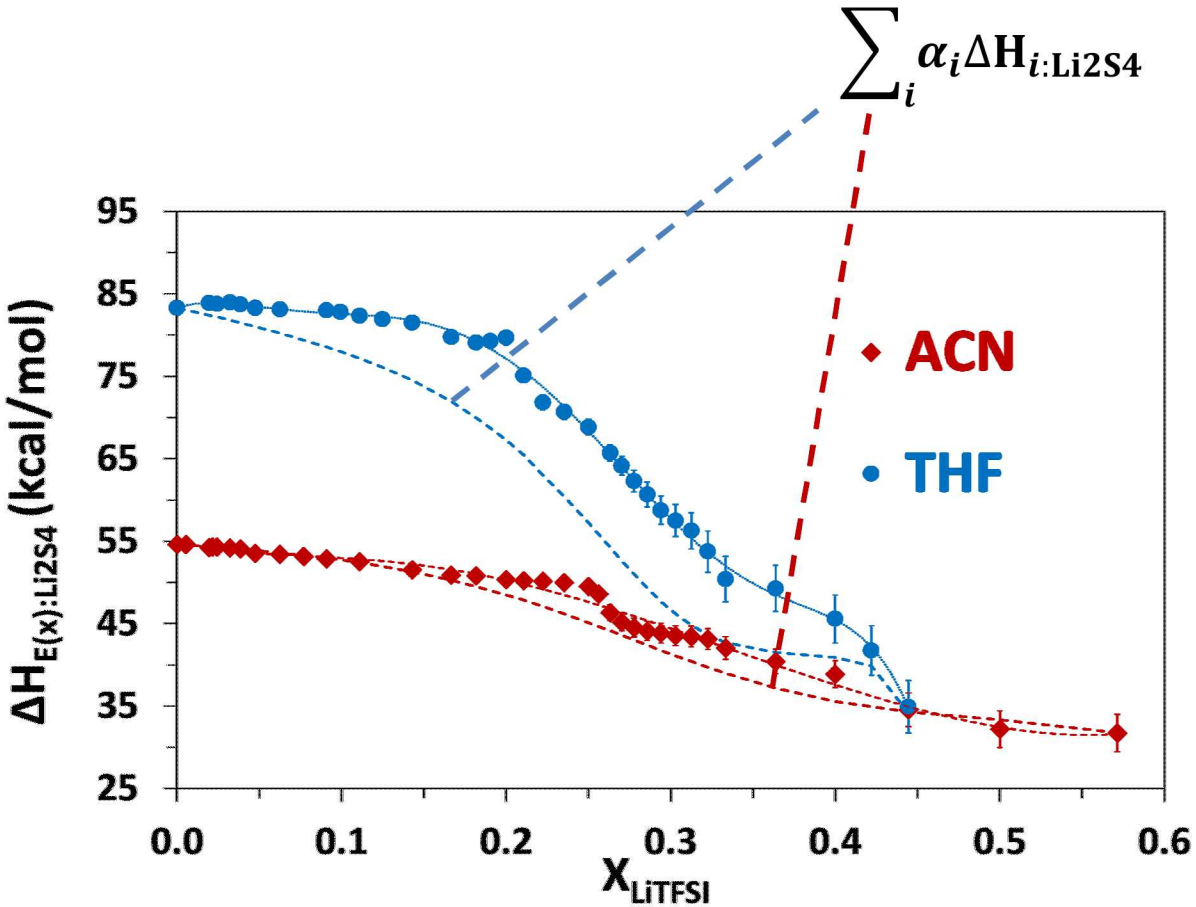
$$\alpha_{i,Q} = \frac{L}{1 + e^{-k(Q-Q_o)}}$$

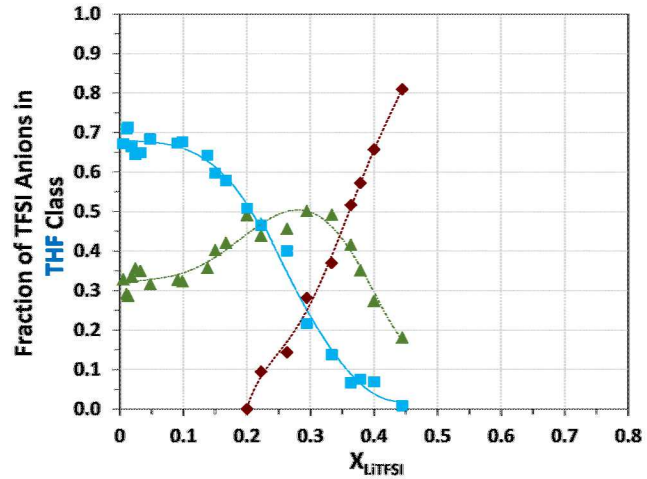
$$[S_{PS}]_Q = \int_0^{Q_{dep}} \frac{Q * 3600 \left(\frac{S}{hr}\right) * y(Q)}{\left(\frac{E}{S}\right) F} ; 0 \leq Q \ll Q_{sdepl}$$

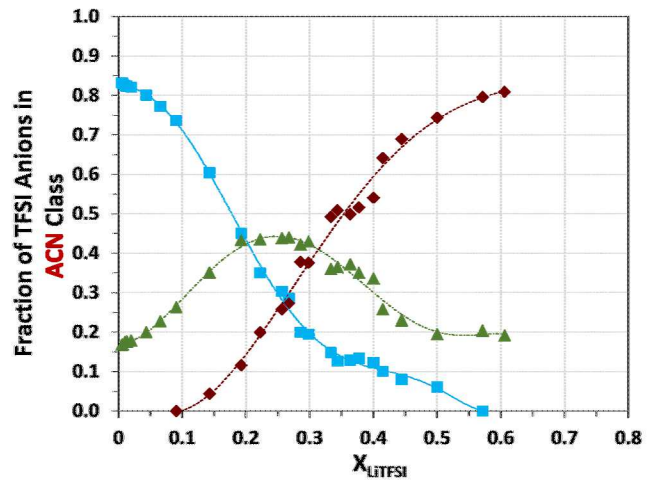
$$[S_{PS}]_Q = [S_{PS}]_{sat} ; Q_{sdepl} \leq Q < Q_{Li_2S_{y(s)}-depl}$$

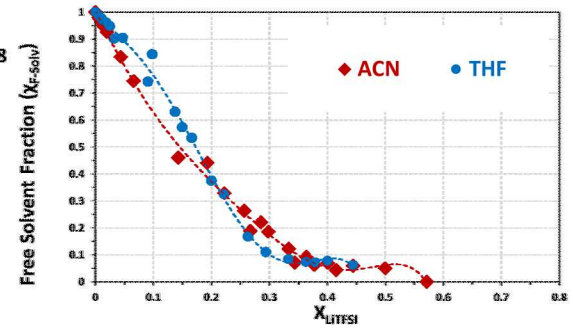
$$[S_{PS}]_Q \equiv \int_{Q_{Li_2S_{y(s)}-depl}}^{Q_j} \left\{ [S_{PS}]_{sat} - \alpha_2(Q) \left(\frac{Q * 3600 \left(\frac{S}{hr}\right) * 8}{\left(\frac{E}{S}\right) \left[16 - \frac{16}{y} - 8\left(\frac{Z}{Z+X}\right)\right] F} \right) \right\} dQ ; Q_{[S_{PS}]max} \leq Q < Q_{Theory}$$

δ_{Na} Measures Emergent Properties (Relative ΔH) Not Predicted by a Linear Combination of $\Delta H_{Solv:Li2S4}$

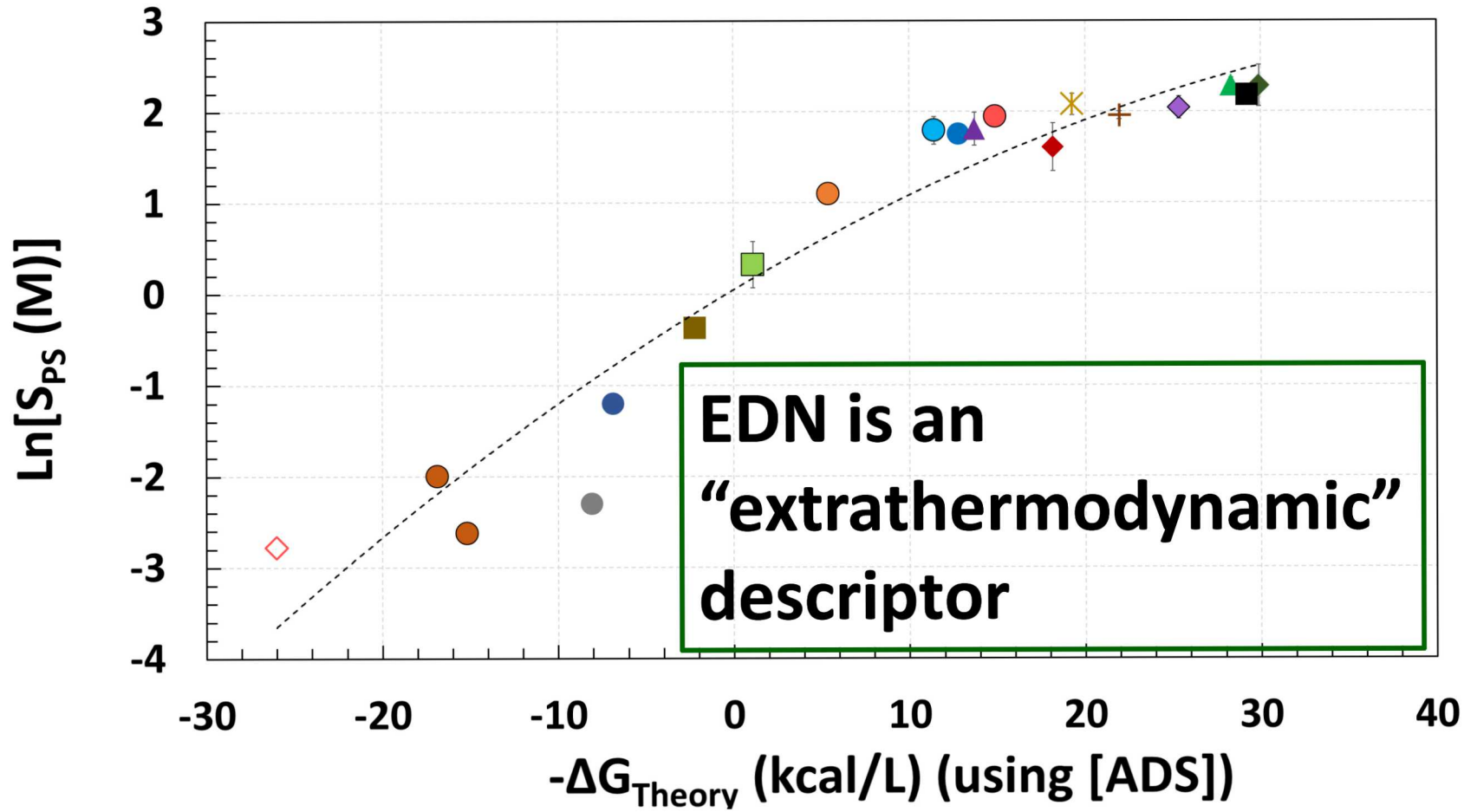




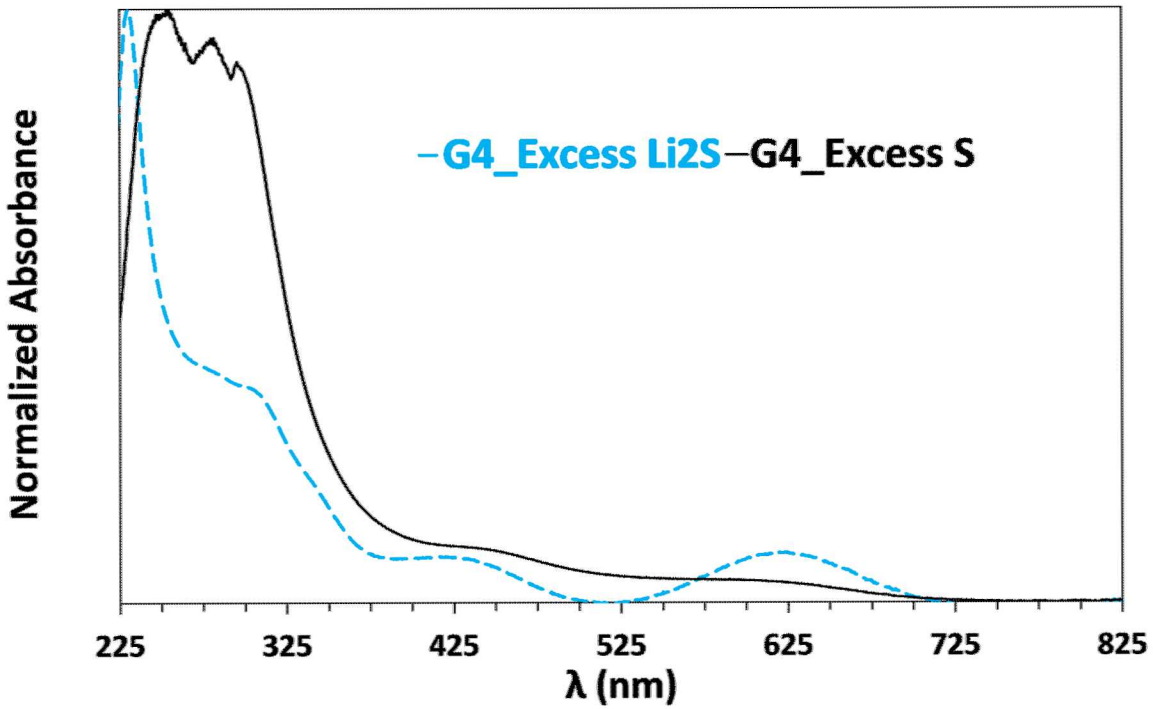


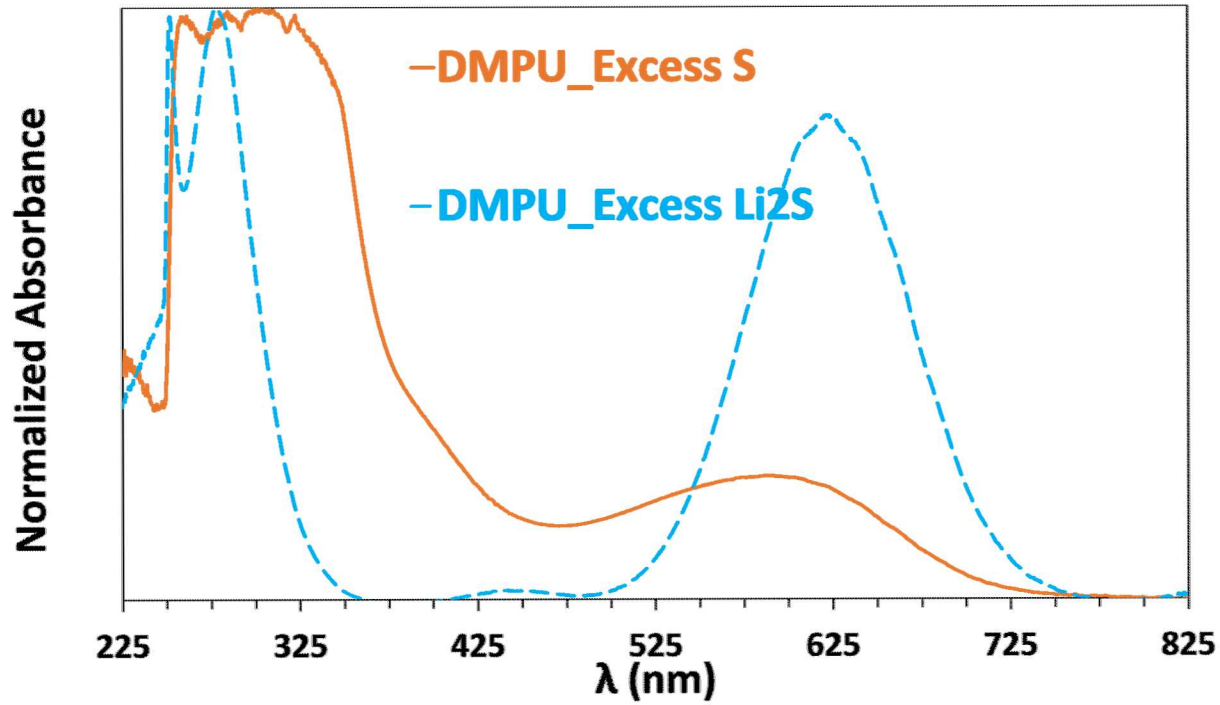


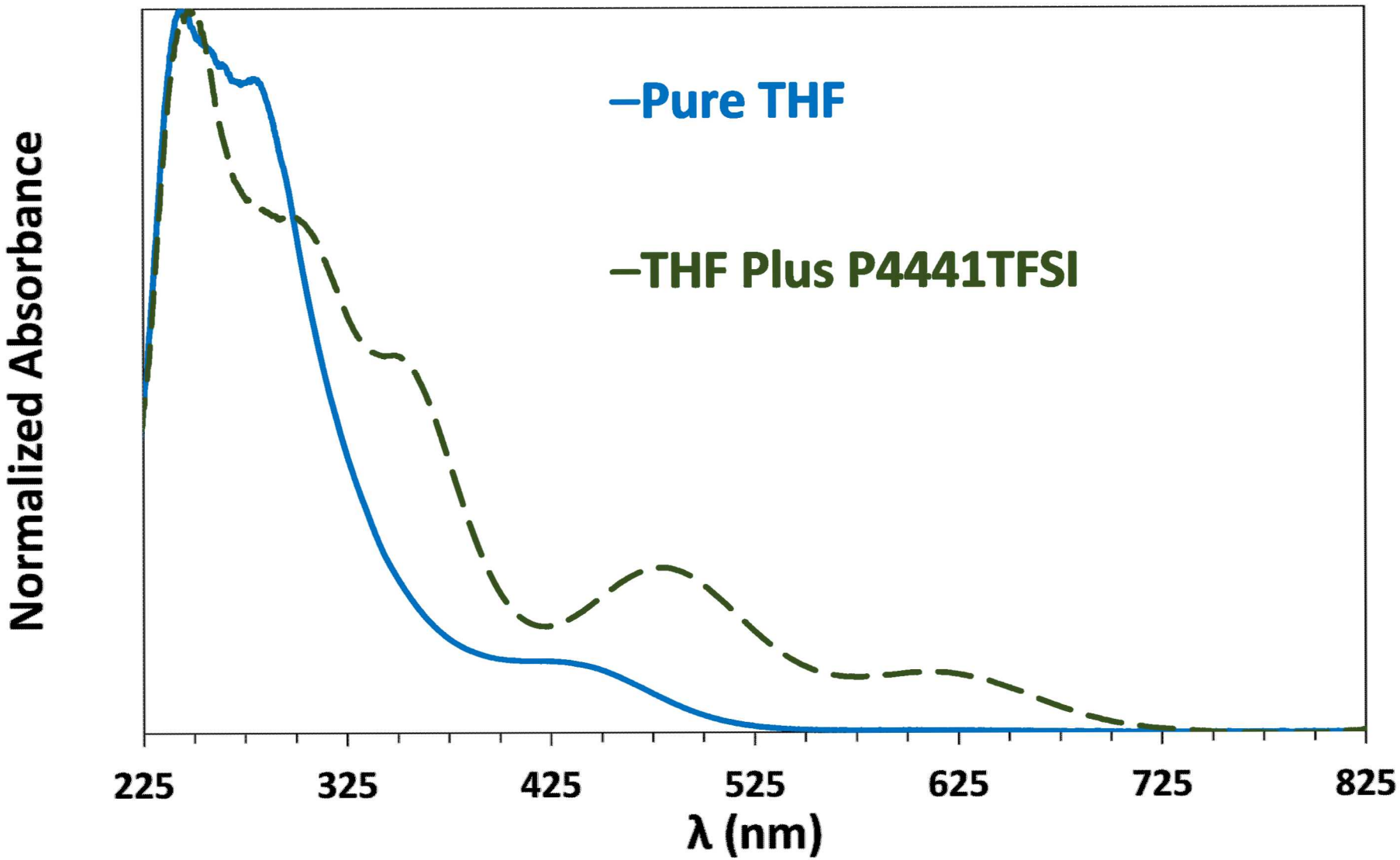
Solubility vs. EDN Resembles Trend vs. Theoretical ΔG (volumetric)



Speciation Dependent on Place in Discharge

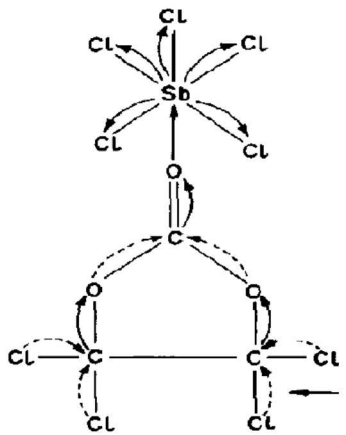





–Pure THF
–THF Plus P4441TFSI
Normalized Absorbance
225
325
425
525
625
725
825
λ (nm)

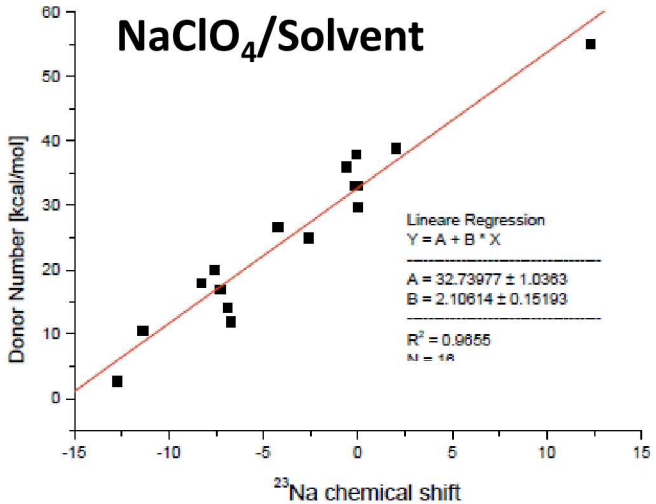
Electron Pair Donation (EPD) Strength Has Been a Suggested Descriptor for Solubility

- Suggestions in the literature that LiPS solubility is related to the solvent's Gutmann **Donor Number (DN)***.
  - This has not been explicitly quantified



Gutmann, V. Electrochimica Acta. 1976, 21, 661-670

Classic Gutmann Donicity model. A calorimetric measurement gives a ΔH value for the ***complex formation with $SbCl_5$***.



Schmeisser et al. Chem. Eur. J. 2012, 18, 10969 – 10982

$\sigma_{p\text{-}23Na}$ = -270 ppm >> $\sigma_{d\text{-}23Na}$ = +9.7 ppm

$\sigma_{d\text{-}7Li} \approx \sigma_{p\text{-}7Li}$

*Rauh *et al*. Chem. J. Inorg. Nucl. Chem. **1977**, 39, 1761-1766