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JOINT CENTER FOR ENERGY STORAGE RESEARCH

Predicting Lithium Polysulfide Solubility and Reaction Pathway Using a Unique Donicity Scale for Li-S Electrolytes

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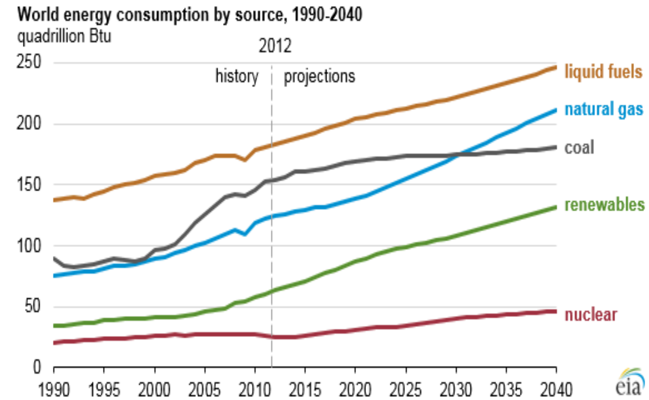
Crucial Need for Better Energy Storage Options

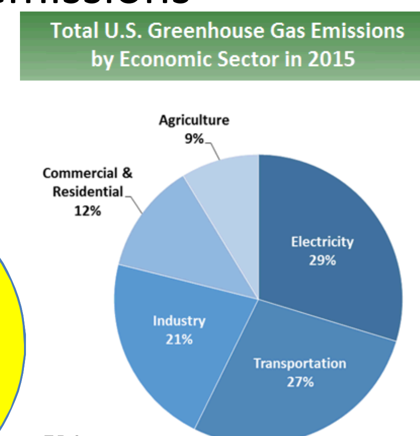
- Increasingly “plugged in” population
  - Creates major strain on the grid.
  - Optimizing renewable infrastructure requires better storage options

Grid Storage



U.S. Energy Information Administration. May 12, 2016 https://www.eia.gov/todayinenergy/detail.php?id=26212

- Fuels used in transportation produce > ¼ of greenhouse gas emissions
  - Batteries have performed better in the market than fuel cells

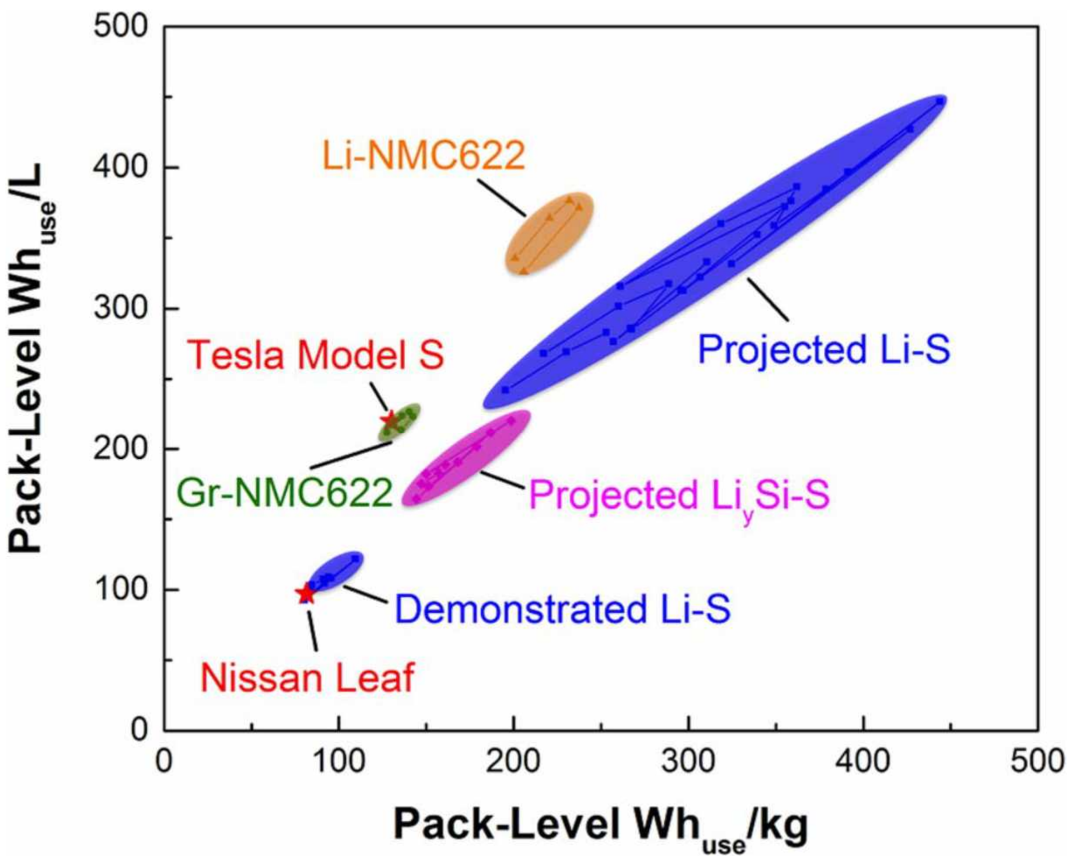


EPA. https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions

https://cleantechnica.com/2016/05/22/tesla-model-3-faq/

Li-S Outcompetes Li-ion

- Theoretical energy density: 2600 Wh/kg (2800 Wh/L)
  - **5x Li-ion**



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

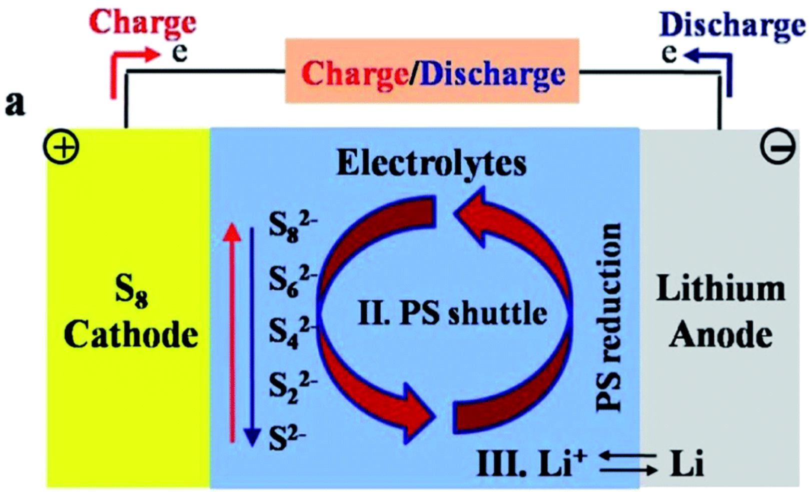
Zephyr UAV (Powered by Sion's Li-S battery)

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

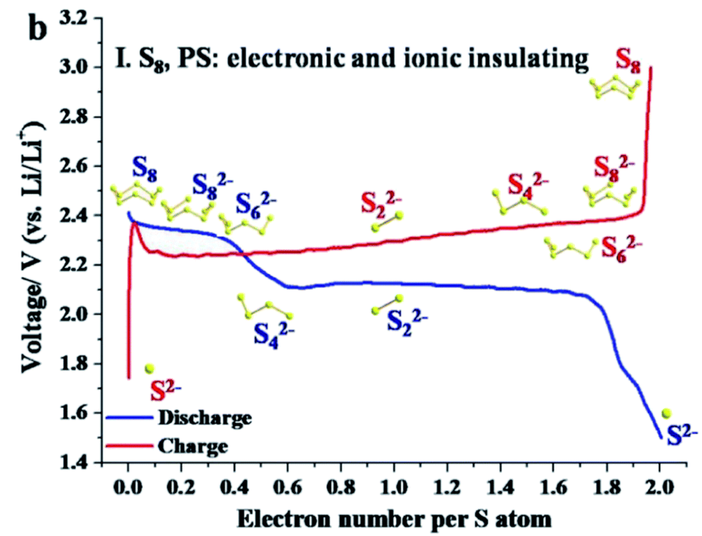
Li-S can extend driving range

Li-S plagued by short cycle life

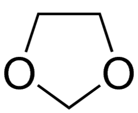
Limits of Standard Li-S Electrolyte



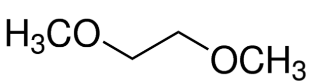
Xu *et al*. J. Mater. Chem. A. **2014**, 47



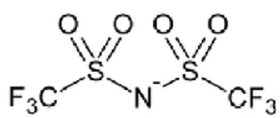
1 M LiTFSI/DOL:DME (3 wt% $LiNO_3$)



1,3 Dioxolane (DOL)



1,2 Dimethoxyethane (DME)



Bis(trifluoromethy lsulfonyl)imide ($TFSI^-$)

Standard electrolyte cannot meet:

- **Energy density targets**
- **Long cycle life demand**

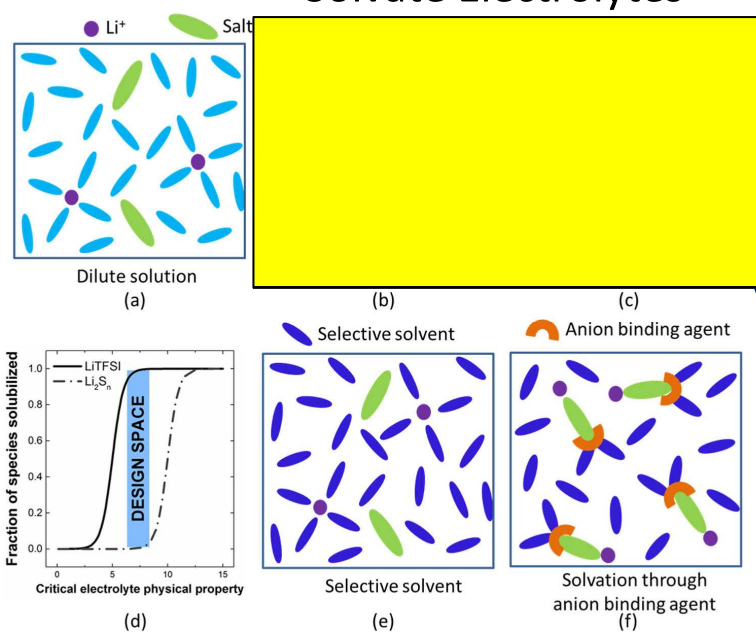
Need new electrolytes

“Sparingly Solvating” Electrolytes

- Low solubility of Lithium Polysulfides (LiPS)
  - Sulfide shuttling is mitigated
- Creating viable Li-S batteries requires management of Li_2S_n precipitation and dissolution reactions.

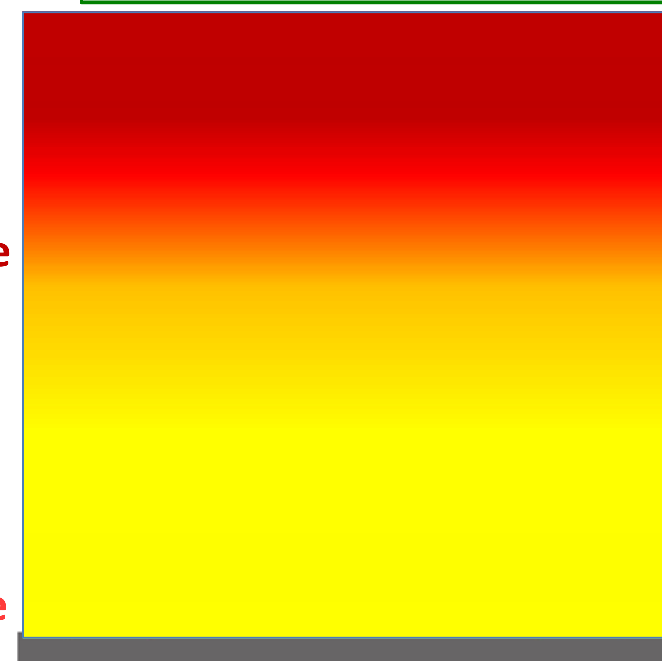
Tuning solubility *must* alter the reaction pathway

Solvate Electrolytes



Dilute Electrolyte

Solvate Electrolyte

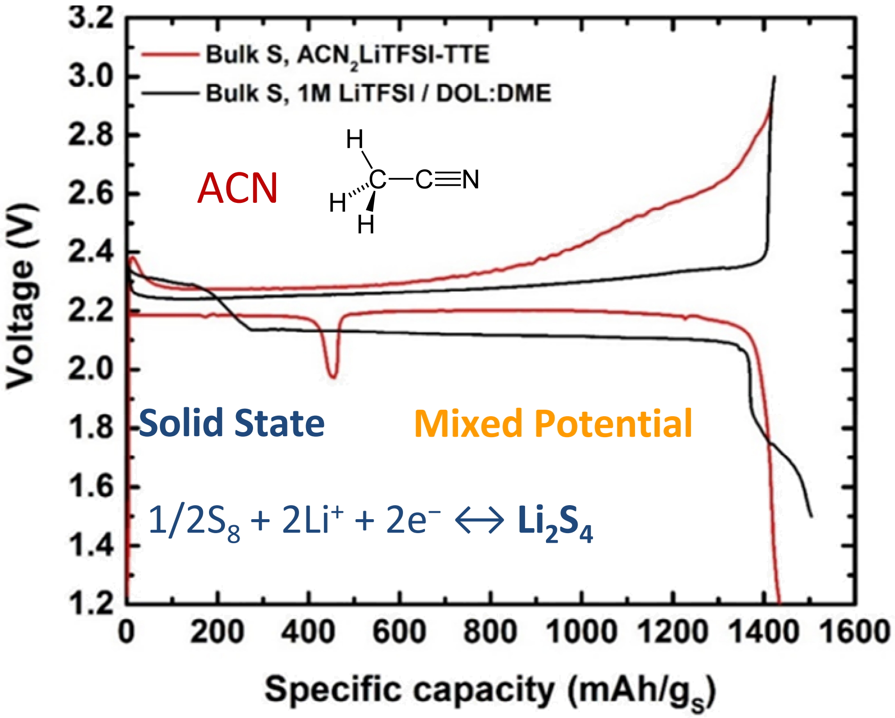


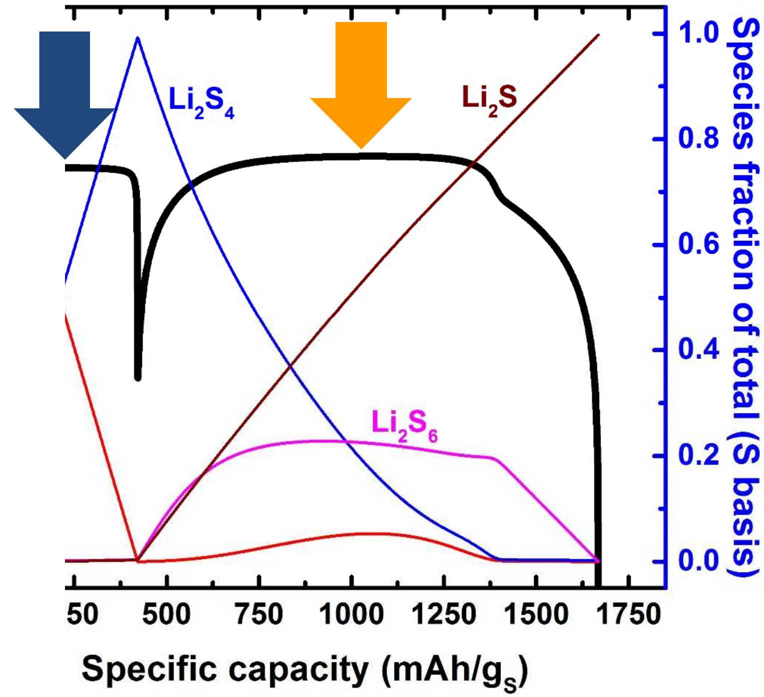
Cheng *et al*. ACS Energy Lett. **2016**, 1, 503−509

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

Demonstrating Altered Redox Pathway

Highly concentrated "solvate" ($AcN_2LiTFSI$) yields a single plateau





Alternative redox pathway drives sulfur reduction as a semi-solid state reaction

Benefit: Potentially regulate Li_2S precipitation to select locations

–Maximizing utilized capacity & rate

Lee and Pang *et al*. ACS Central Sci. **2017**, 3, 605-613.

Building on a Premise

Qualitative → Goal → Quantitative

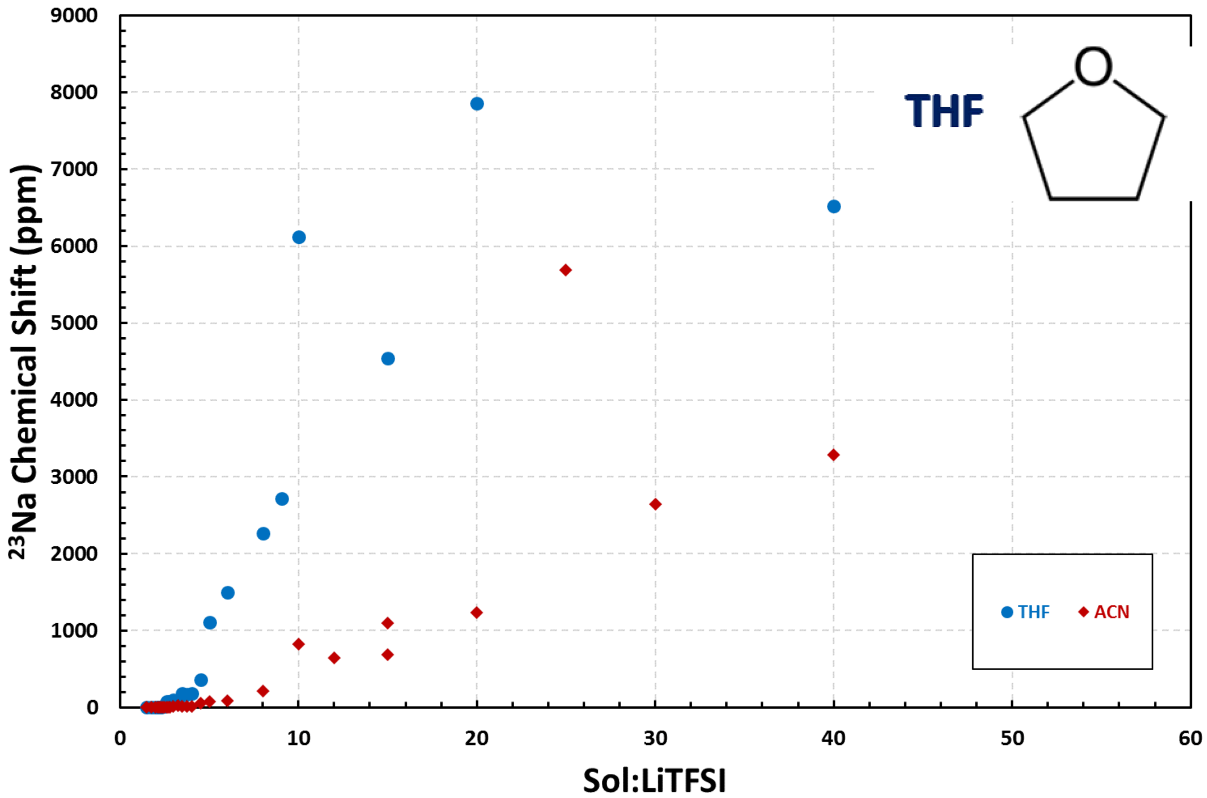
Hypotheses:

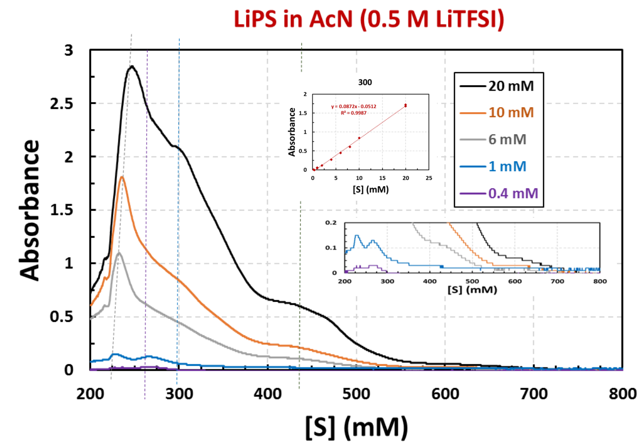
1. Performance is in part driven by reaction pathway.
2. Reaction pathway is controlled by LiPS solubility.
3. LiPS solubility is dictated by an electrolyte's donor strength (DN).

Predictions:

1. A quantitative relationship exists between DN and [LiPS].
2. A quantitative relationship exists between the thermodynamic cell potential and [LiPS], and therefore DN.
3. Performance can be improved by tuning the redox mechanisms within a given cell framework.

Solvent/Salt Ratio Drives Solubility



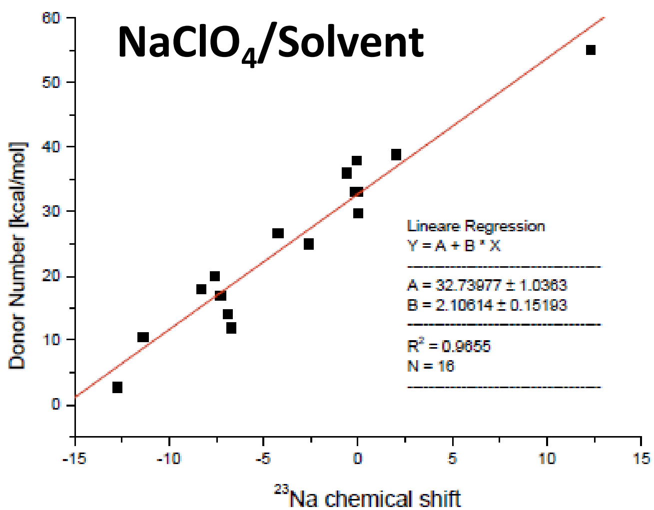


UV/Vis Spectroscopy used to measure solubility

Goal: Create a generalized descriptor for [Li_2S_n] in solvate electrolytes

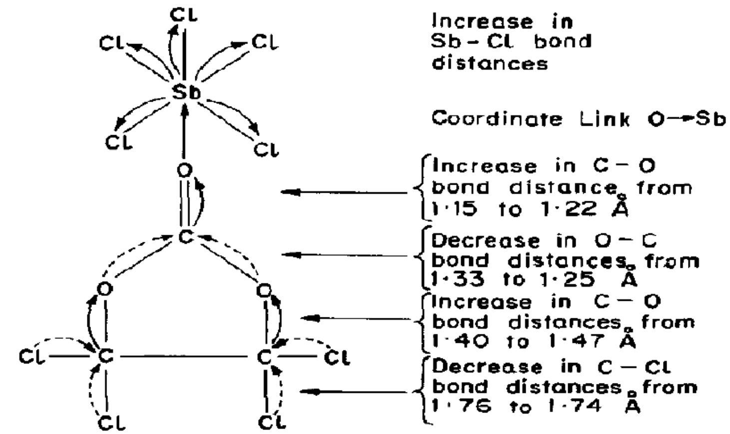
What dictates solubility?

- Hints in the literature that Li_2S_n solubility is related to the solvent's Gutmann **Donor Number***.
  - This has not been explicitly quantified



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

$$\text{DN [kcal/mol]} = 32.7397712308 + 2.1061380895 * \delta_{^{23}\text{Na}} \text{ [ppm]}$$



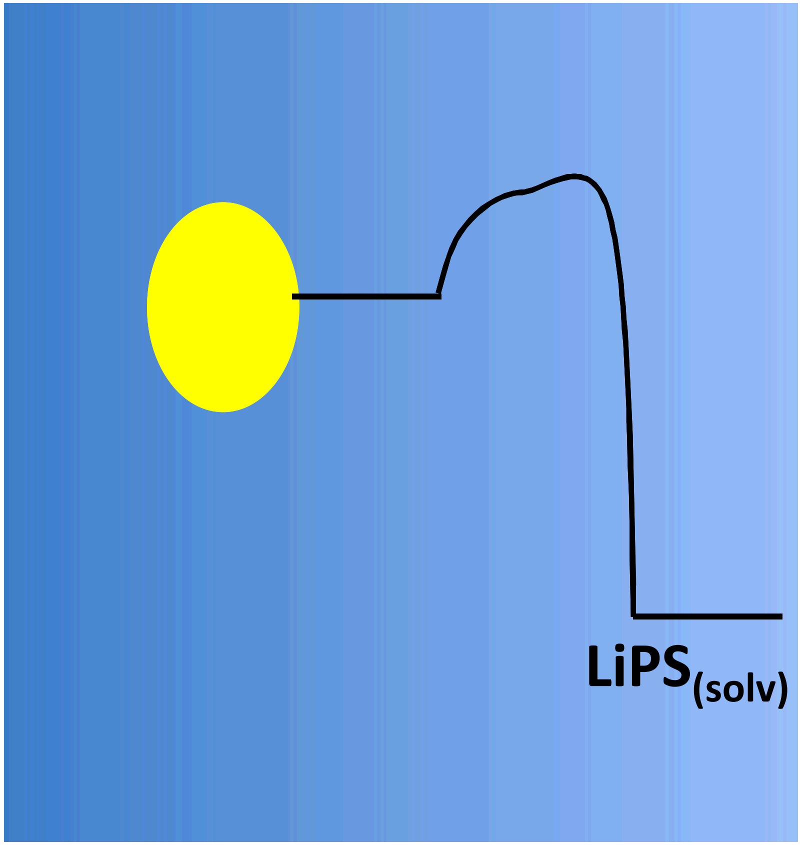
Classic Gutmann Donicity model. A calorimetric measurement gives a ΔH value for the rxn.

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

DN is a measure of a solvating medium's *affinity for a solute*.

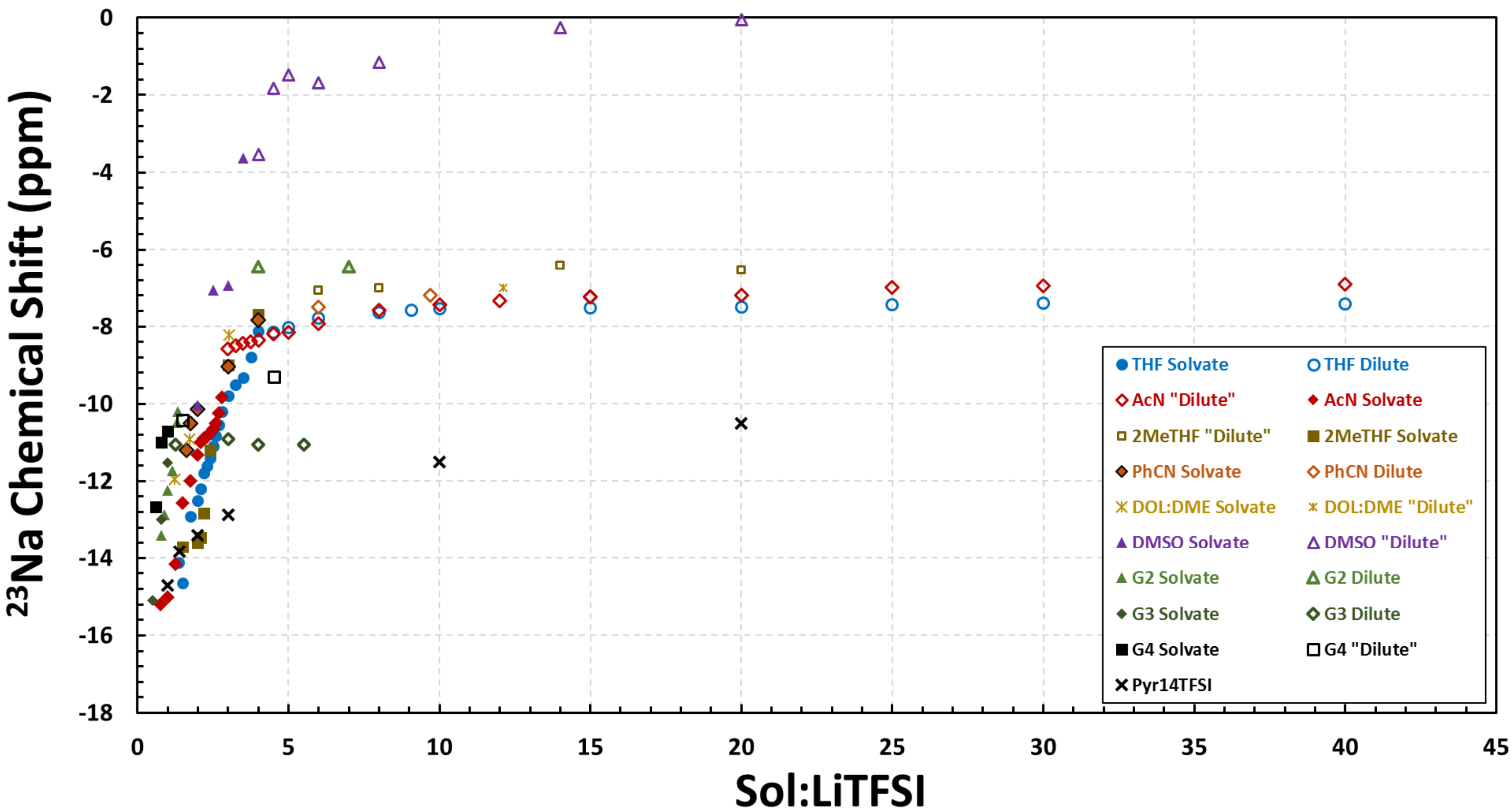
*Rauh *et al*. Chem. J. Inorg. Nucl. Chem. **1977**, 39, 1761-1766

Generalized Donicity



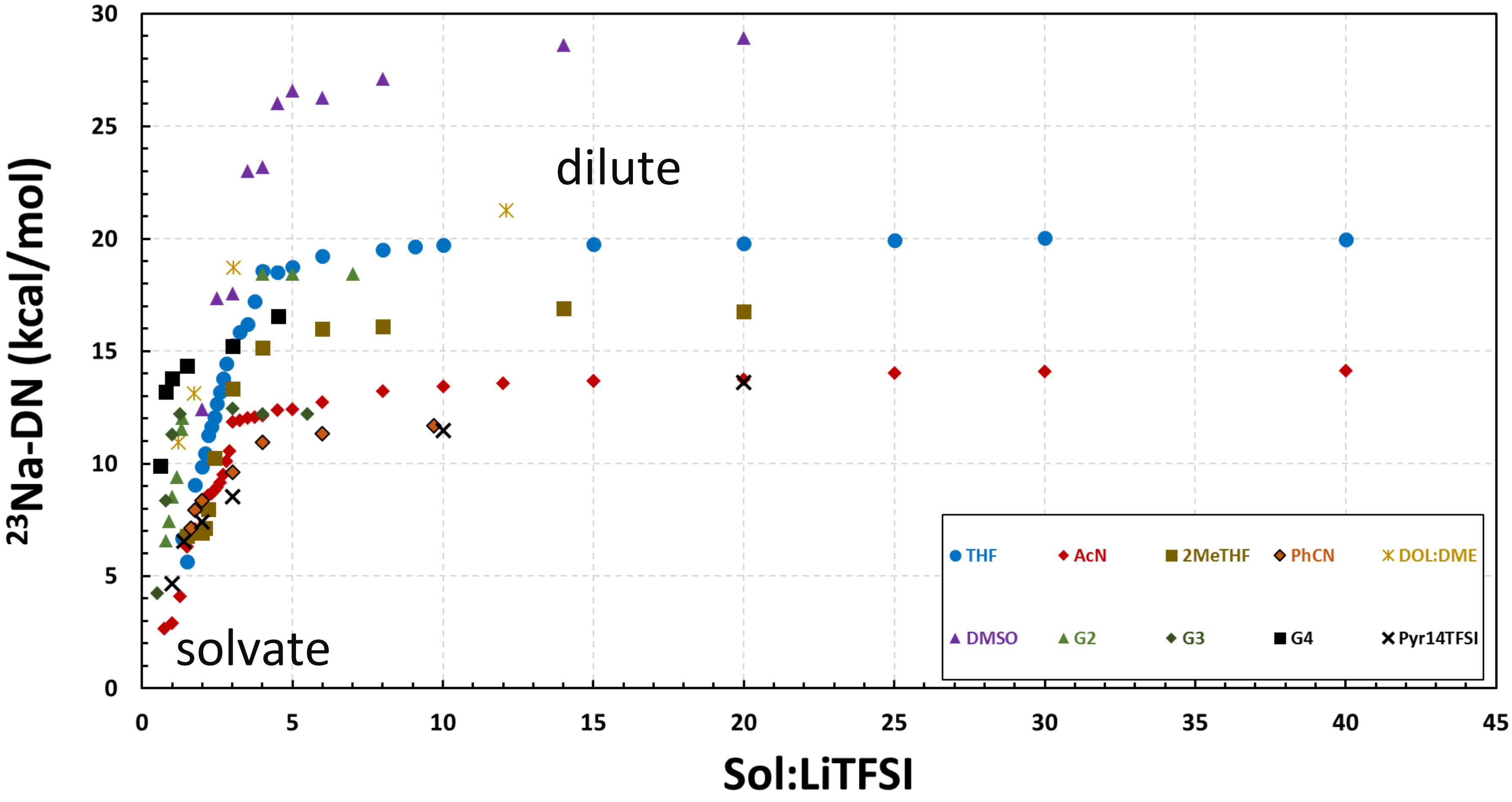
Ideal Case: With DN no other electrolyte information is necessary

Correlating Chemical Shift to DN

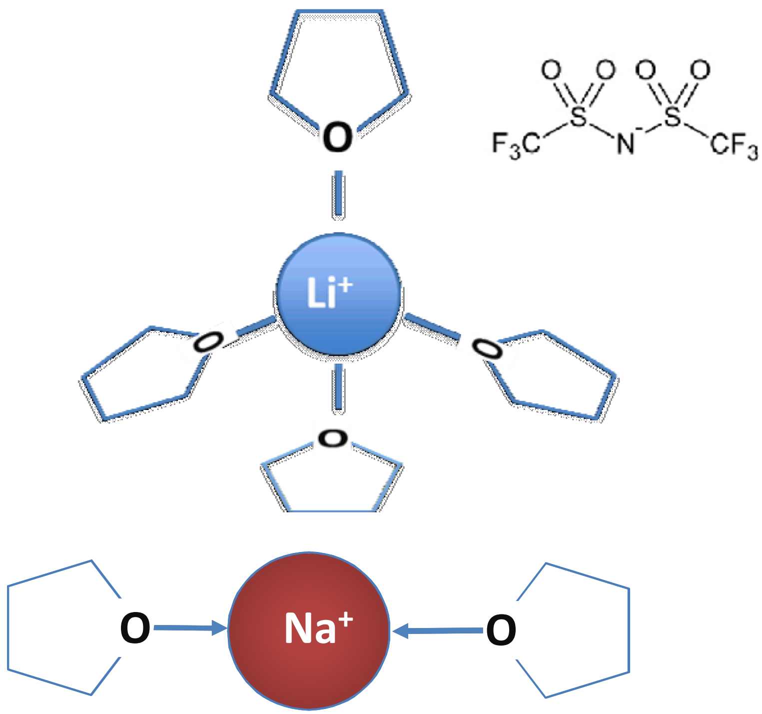


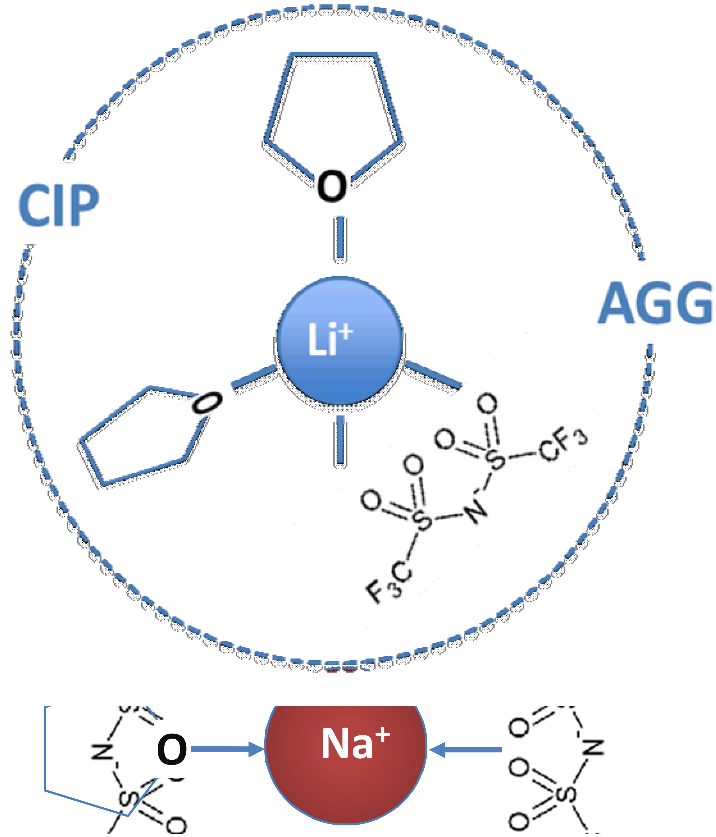
$$^{23}\text{Na-DN} = \left[\frac{\delta_{Na:E} - \delta_{Na:``x=0"}}{\delta_{Na:Sol} - \delta_{Na:``x=0"}}\right] * DN_{Sol}$$

Generalized Electrolyte Donicity Scale



Role of Electrolyte Structure





Dilute regime

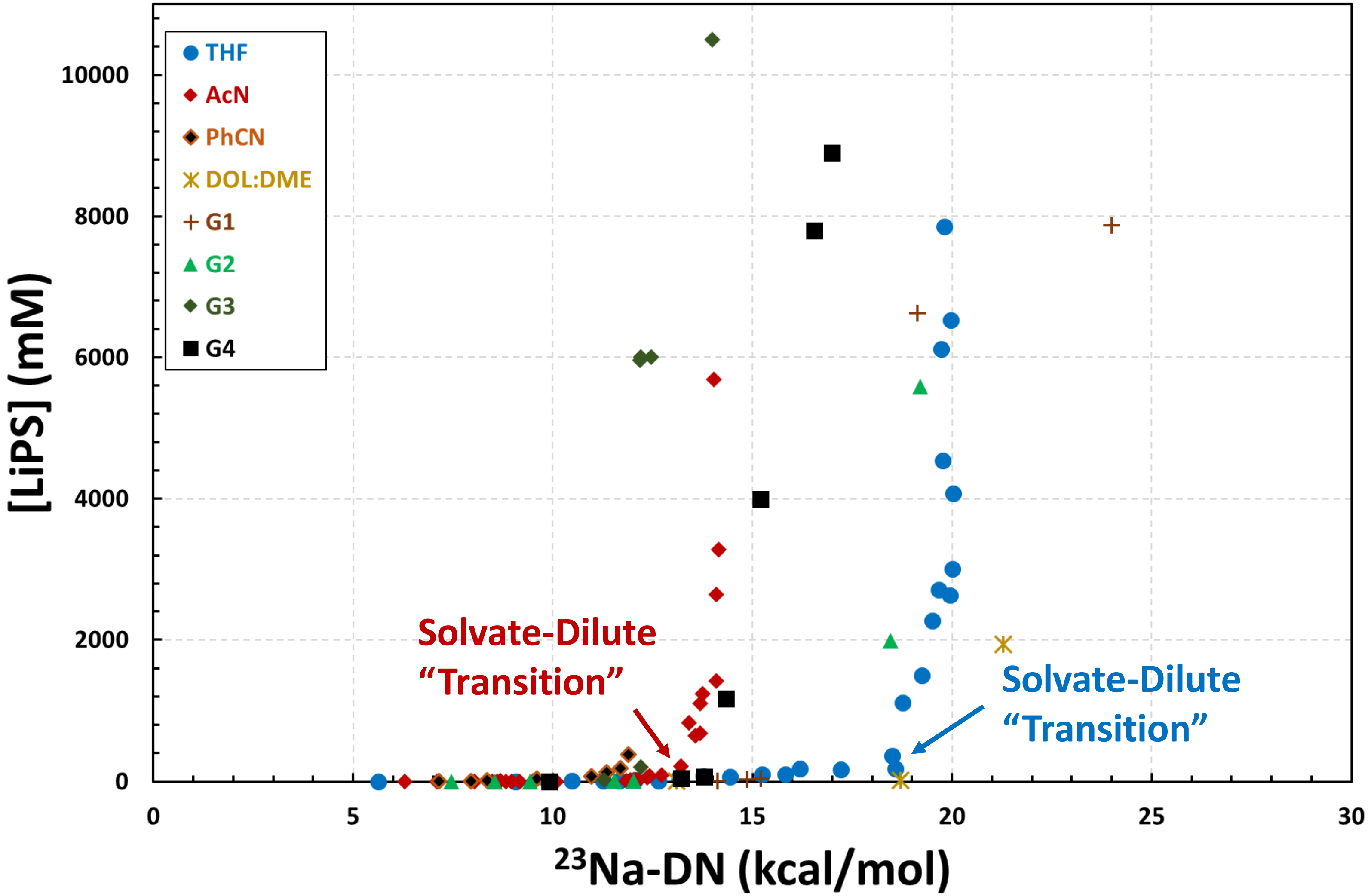
Solvent Dominated

Solvate regime

Anion/CIP/AGG Dominated

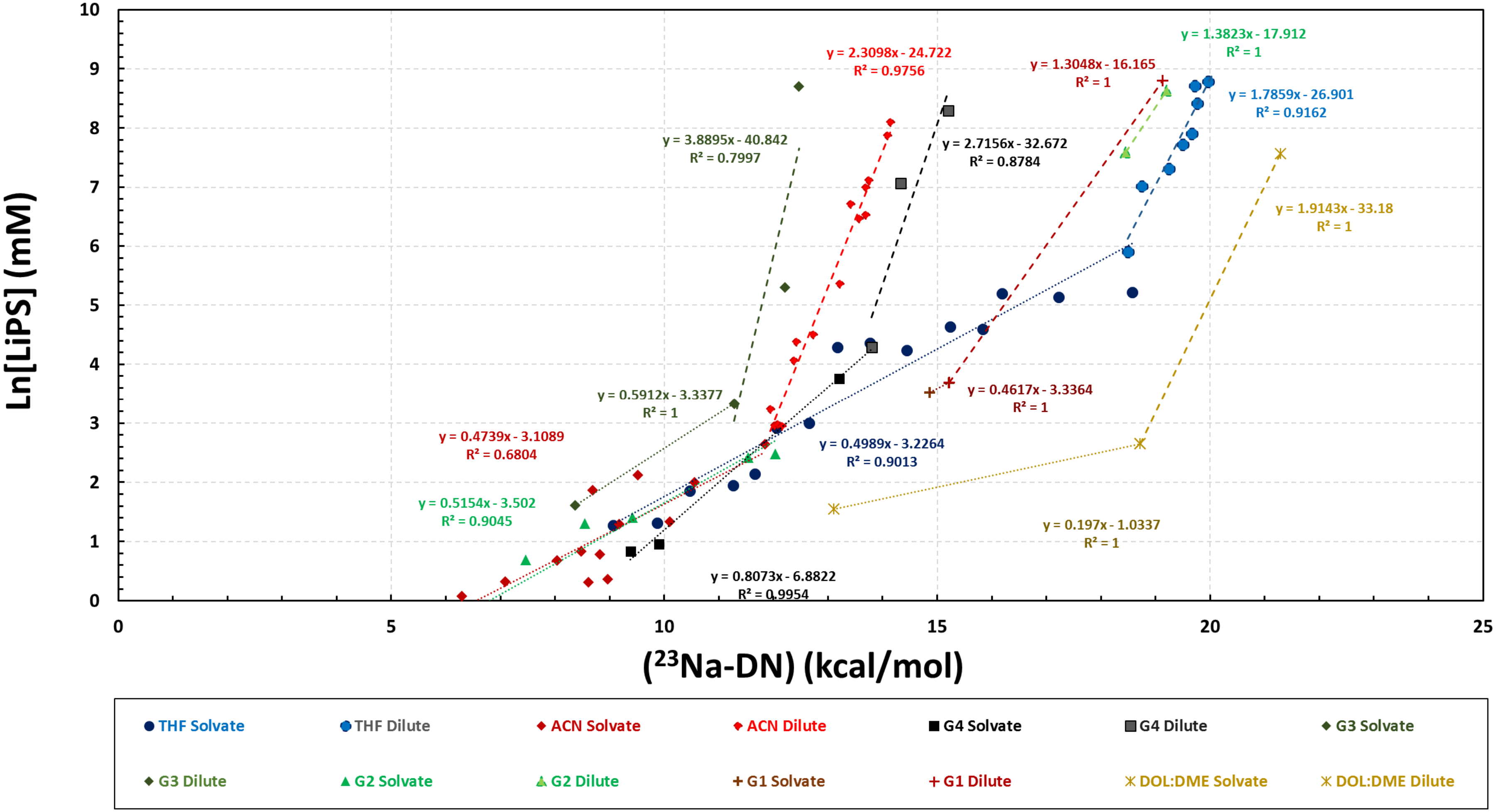
Salt Concentration

Donicity Dictates Solubility

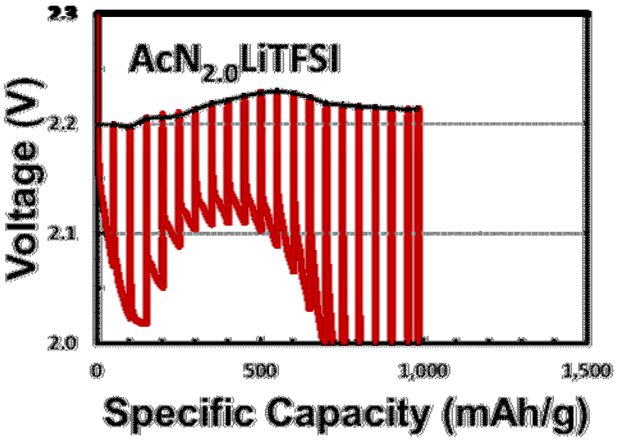


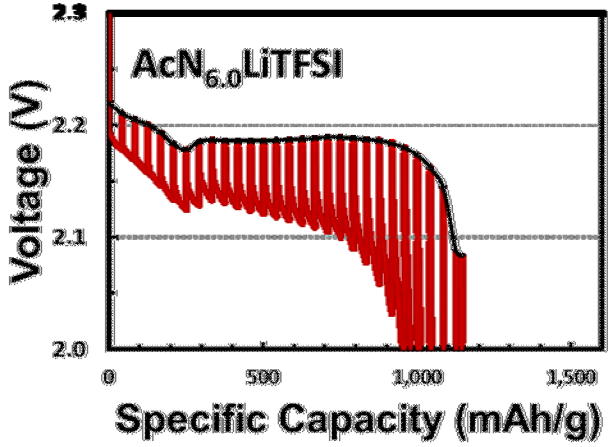
Behavioral change at solvate-dilute transition point

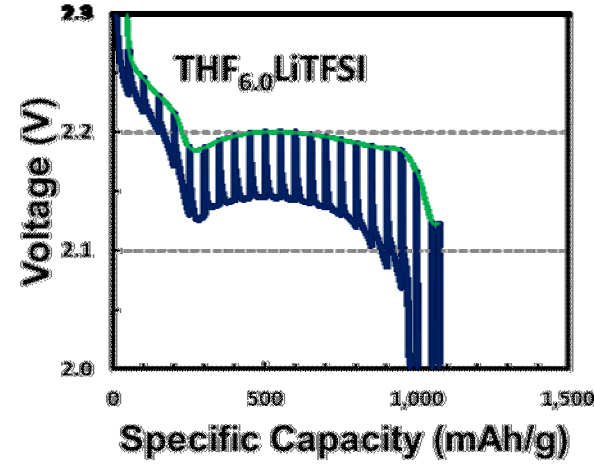
Donicity Dictates Solubility

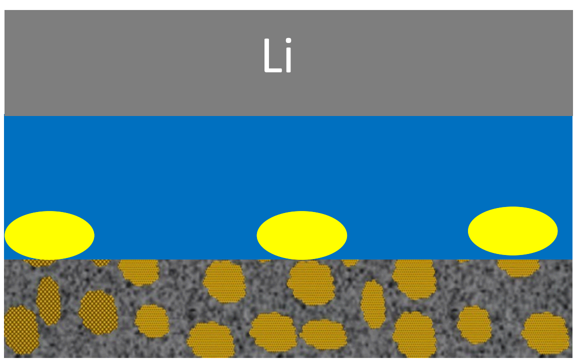


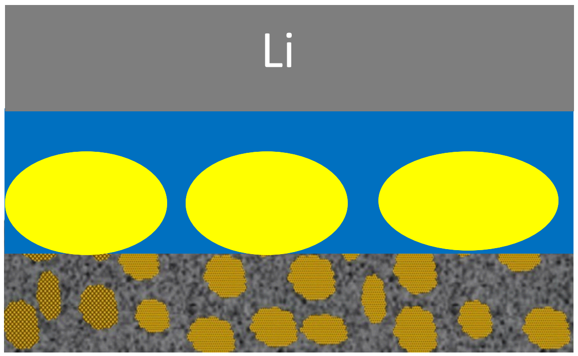
Galvanostatic Intermittent Titration Technique (GITT)

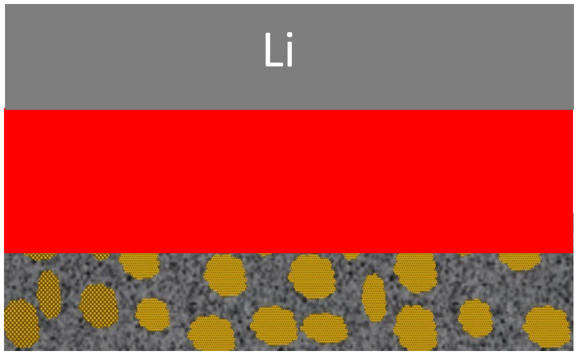




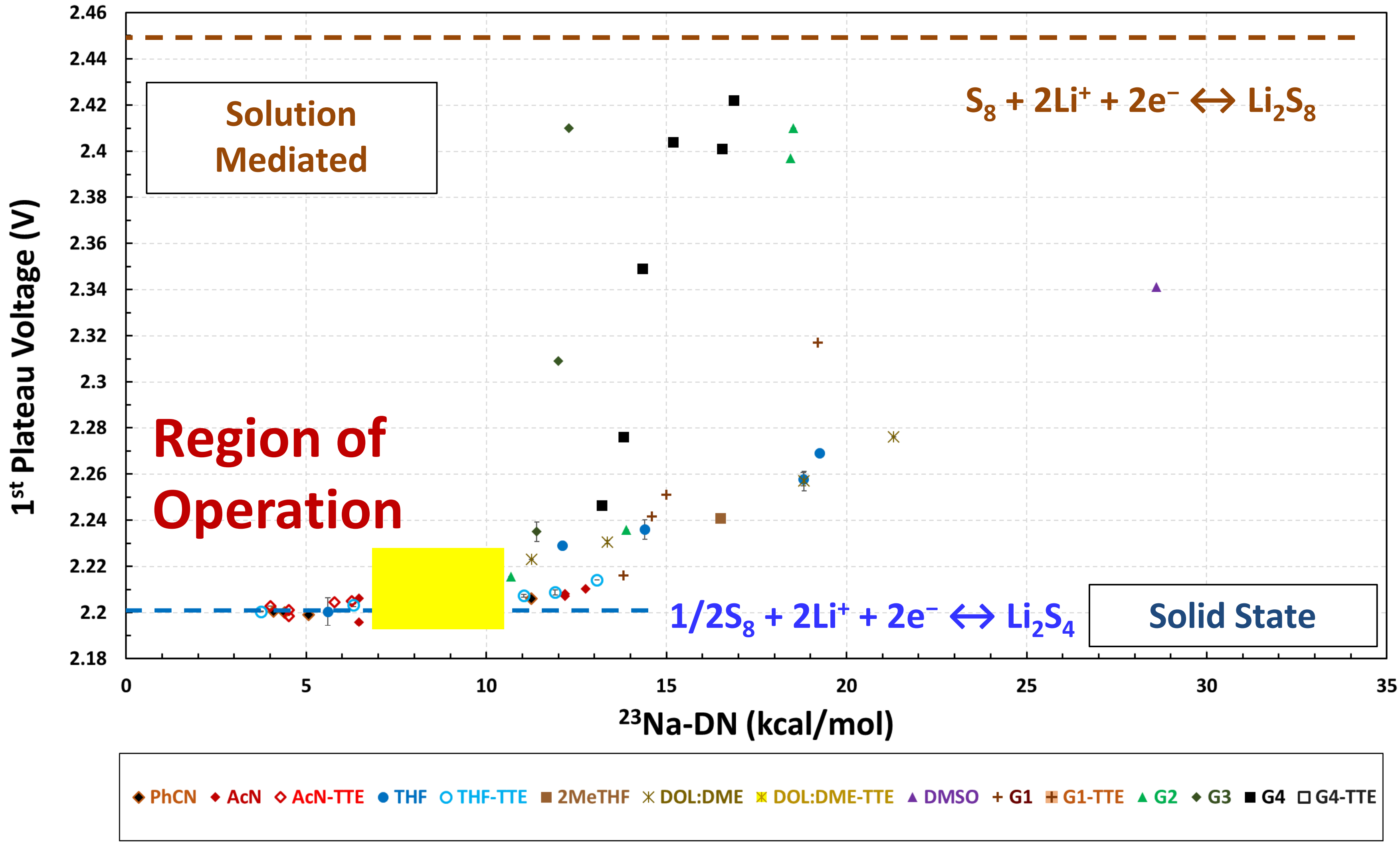








Rxn Pathway is Dictated by Donicity



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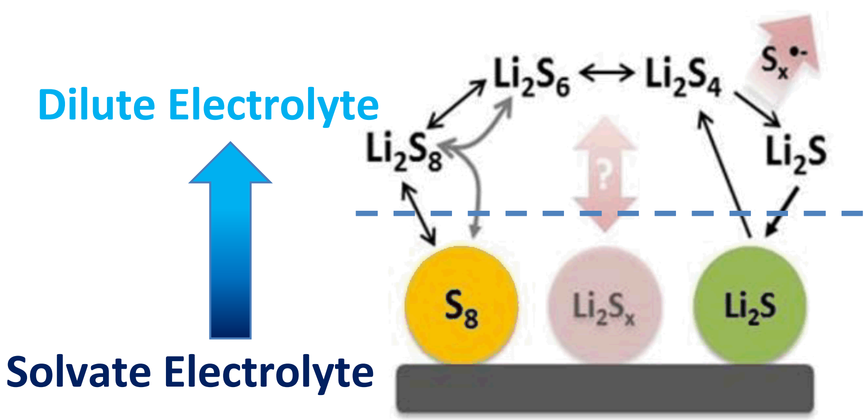
Conclusions and Next Steps

- **Created the generalized descriptor donicity for $[Li_2S_n]$ in solvate electrolytes**
- **Donicity determines $[Li_2S_n]$**
- **Sulfur reduction reaction pathway is dictated by donicity**
- **Identified donicity region in which reaction pathway and kinetics can be balanced**

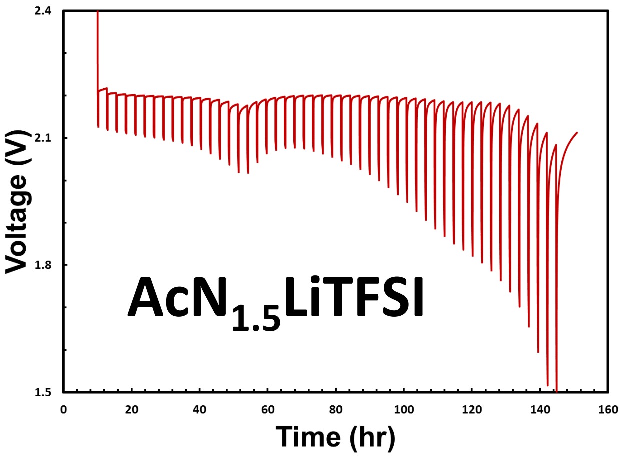
Next…

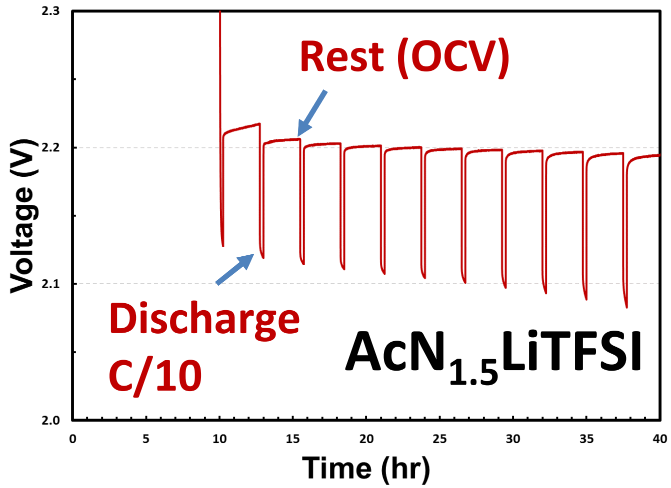
- **Demonstrate use of donicity to control distribution of sulfur to maximize capacity**

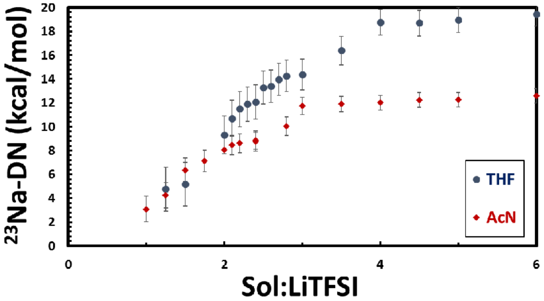


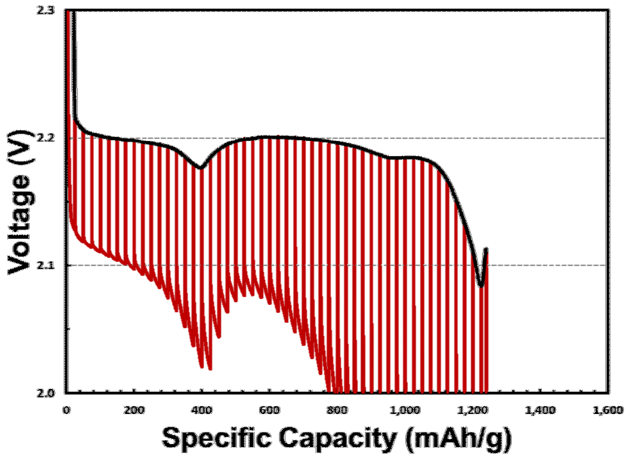
Questions?

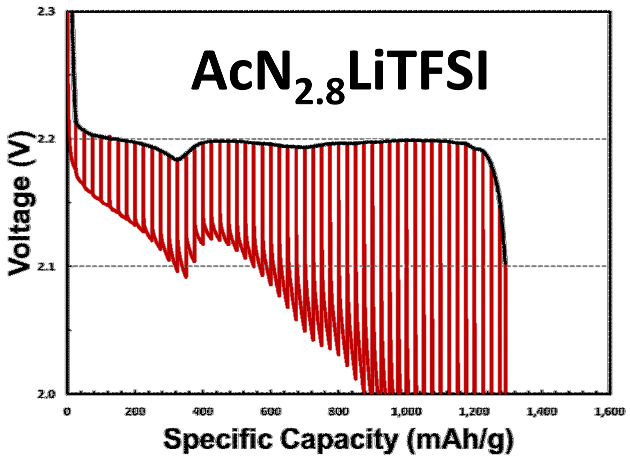
GITT Acetonitrile Series

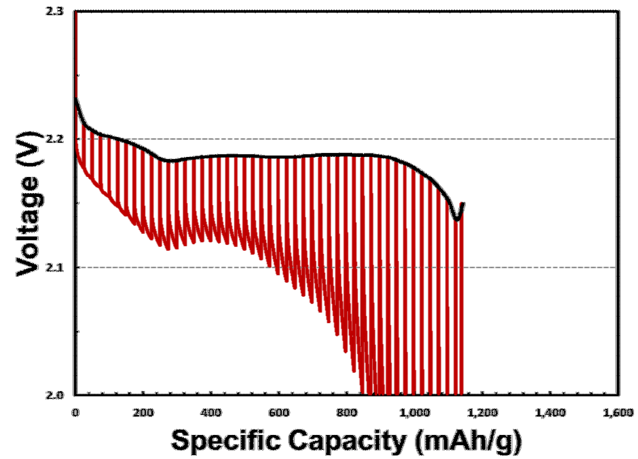












Galvanostatic Intermittent Titration Technique

Other Indirect Measurements

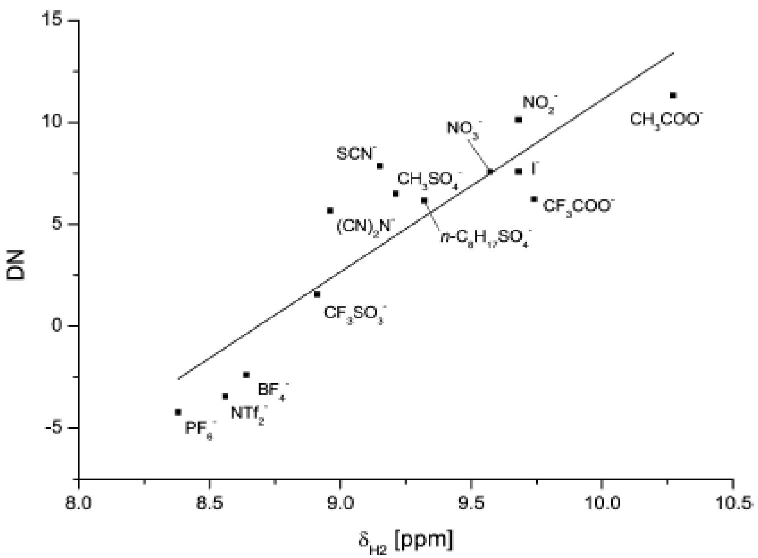
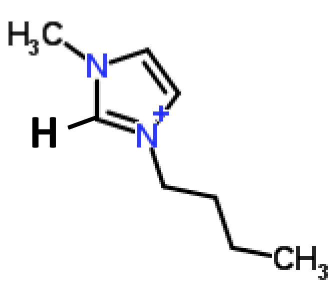
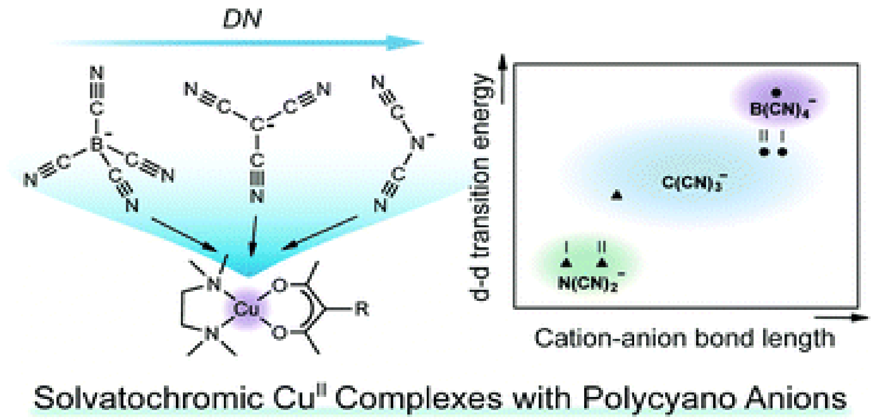


Figure 2. Linear correlation of DN with δ_{H_2} for $[C_4C_1im][X]$, where X is the variation of the anion.

Holzweber et al. Chem. Eur. J. **2013**, 19, 288 – 293.





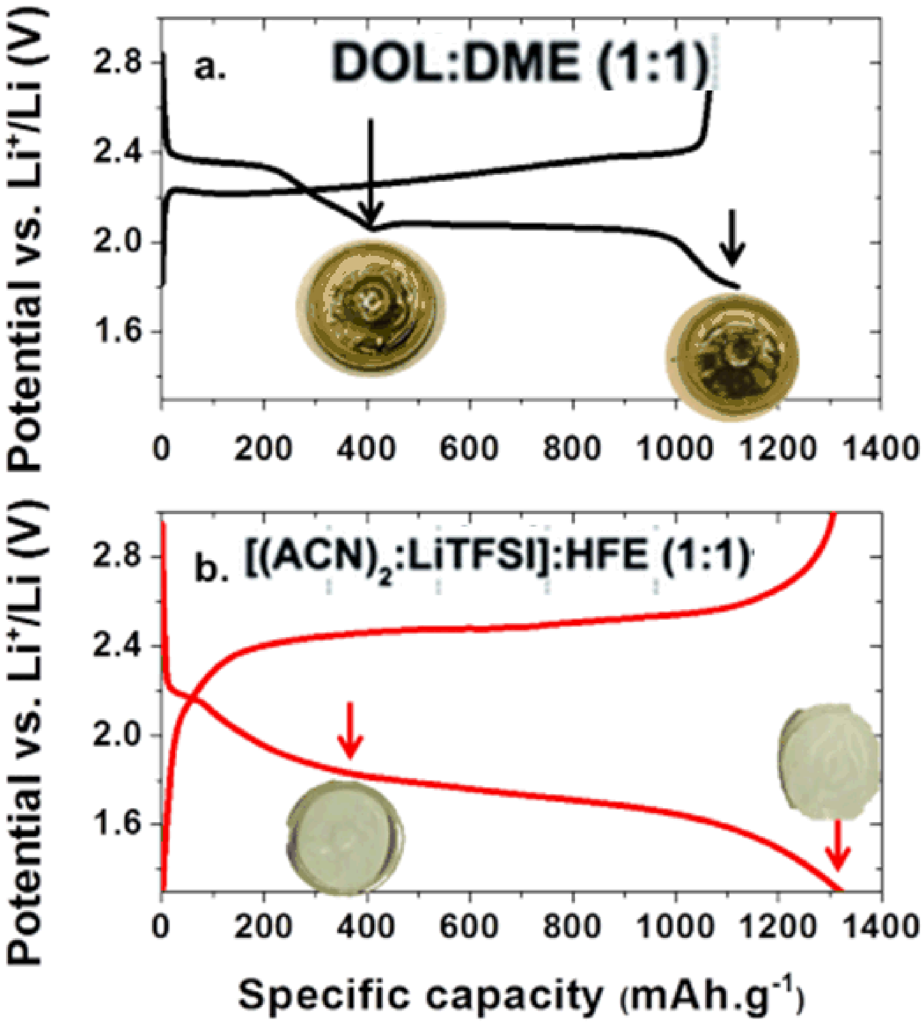
[Cu(X)(acac)(tmen)]

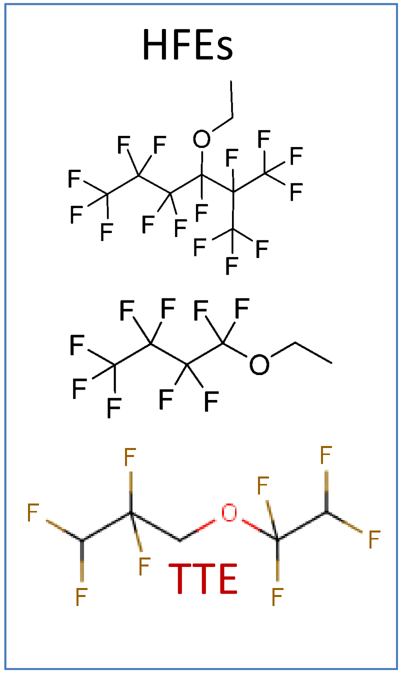
Lan et al. Dalton Trans. **2017**, 46, 5041-5047.

Donor Numbers of Anions in Solution: the Use of Solvatochrornic Lewis Acid-Base Indicators

Linert *et al*. J. Chem. Soc. Dalton Trans. **1993**, 3181–3186.

-Effective DN dependent on DN and AN of solvent, as well as DN of anion





Cuisinier et al. Energy Environ. Sci., 2014, 7, 2697–2705