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DEVELOPMENT AND USE OF A TAILORED ELECTROLYTE SOLVATION MODEL FOR PREDICTION OF REACTION PATHWAYS IN LITHIUM-SULFUR BATTERIES

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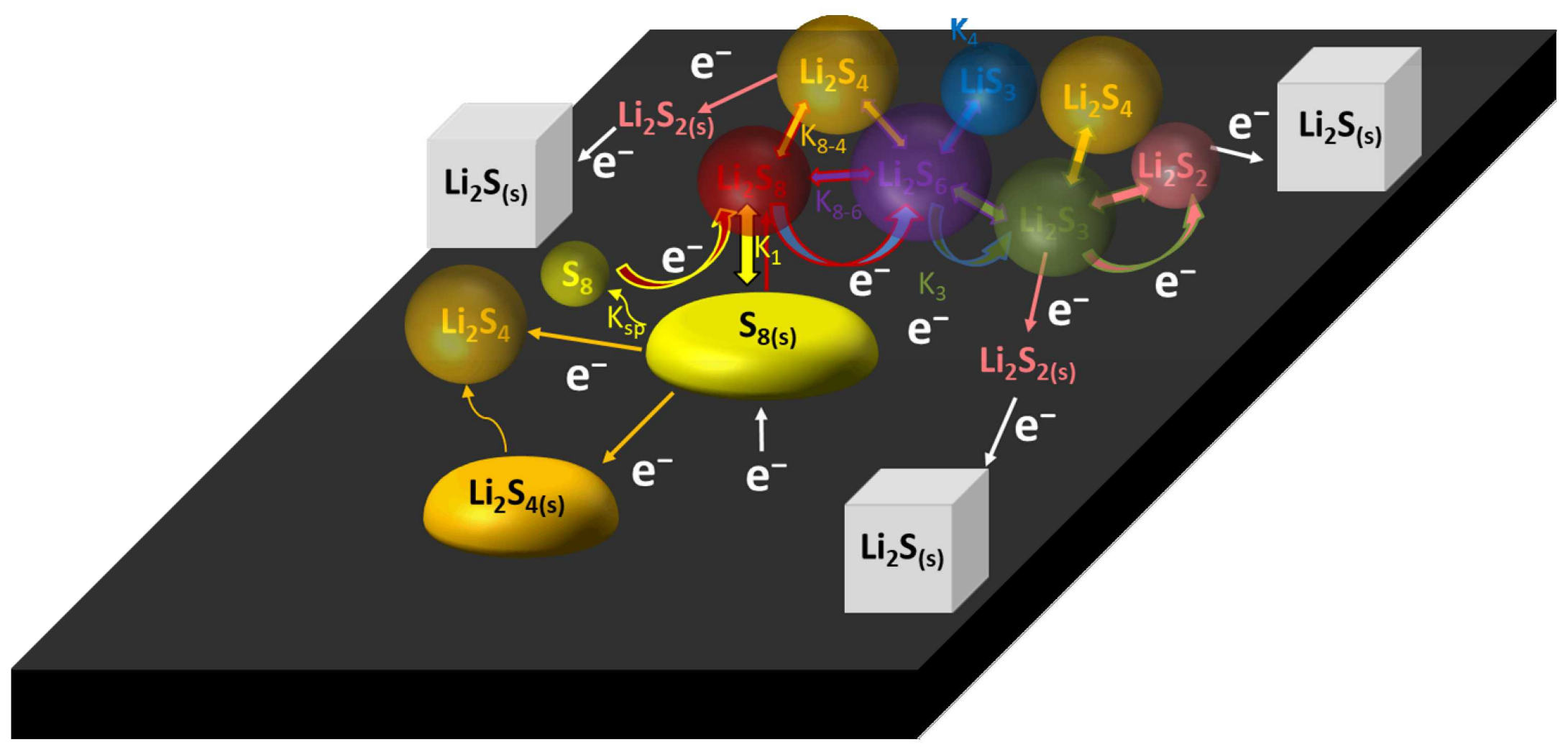
ABSTRACT

Li-S batteries are plagued by parasitic reactions driven by soluble reaction intermediates resulting in stored energy loss and short cycle life. Electrolytes with low solubility limits for these lithium polysulfide (LiPS) intermediates reduce parasitic reactions, improving efficiency and life of cells. Sparingly solvating electrolytes drive sulfur reduction through a solid state pathway, potentially eliminating parasitic losses due to LiPS.[1] Realizing the goal of electrolyte design to enhance cell performance requires a quantitative model of LiPS solubility.

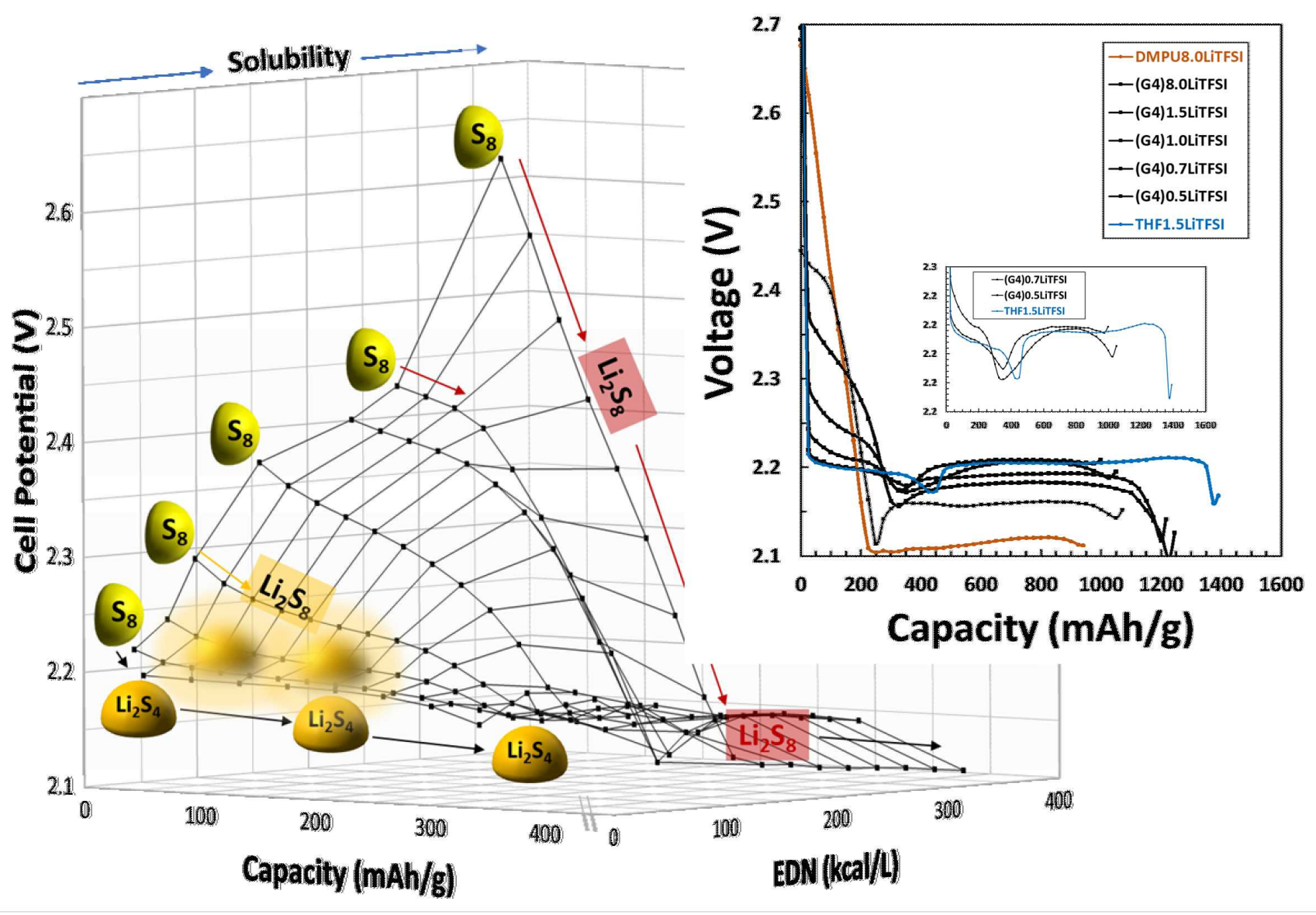
Goals:

- Develop a new electrolyte donor number (EDN) model
- Apply EDN to predict LiPS solubility
- Employ EDN to predict redox reaction pathway



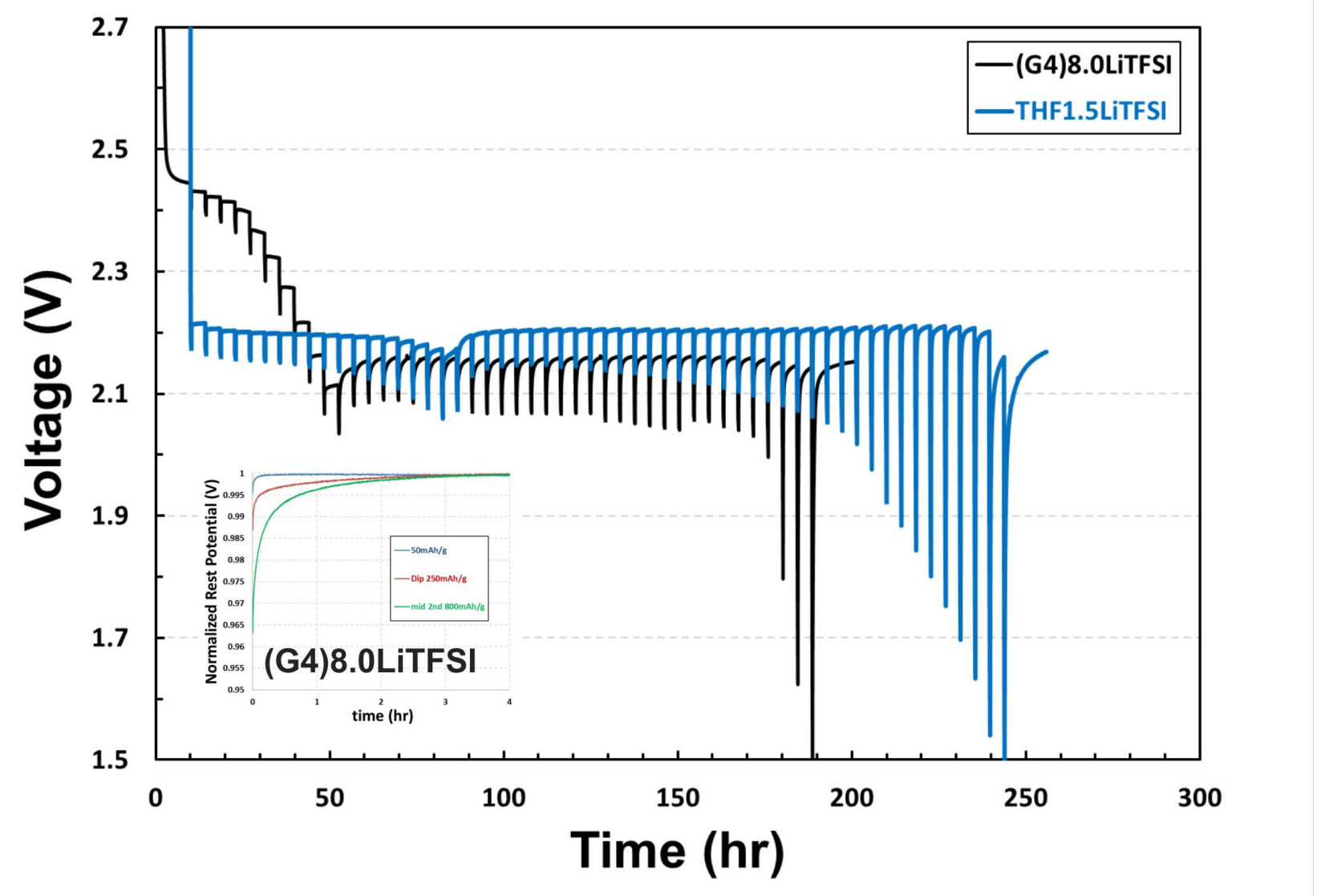
MOTIVATION

- Li-S battery cell performance depends on redox mechanism
- No complete theoretical framework predicts mechanism
- LiPS solubility and speciation governs mechanism
- New model is needed for the solvating properties of electrolytes



METHODS

- Donicity from ^{23}Na NMR
- Coordination ligand population from Raman Spectroscopy
- LiPS solubility from UV/Vis Absorption Spectroscopy
- Mechanism from Galvanostatic Intermittent Titration Technique (GITT)

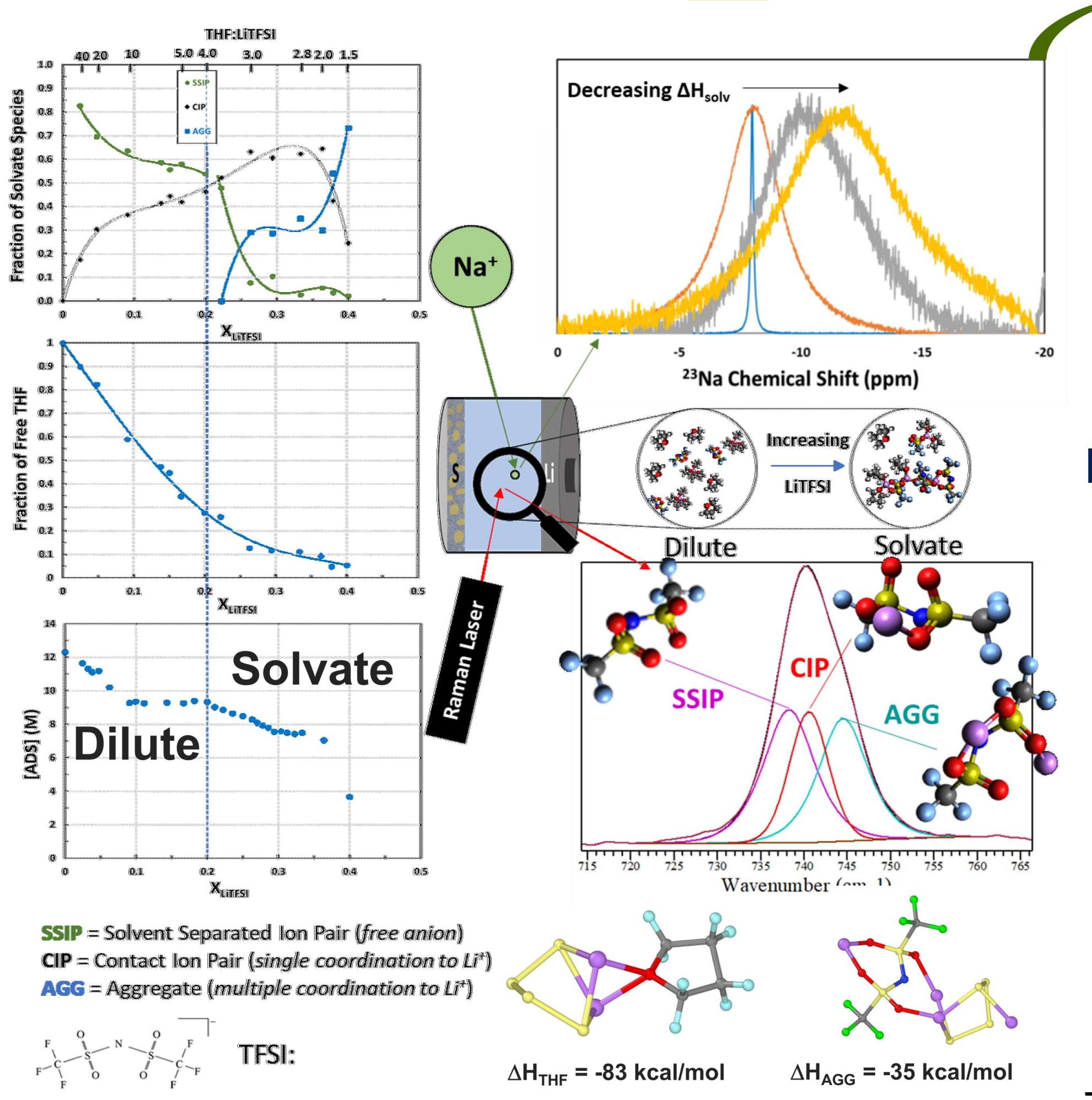


THE ELECTROLYTE DONOR NUMBER MODEL

- Molar enthalpy of solvation (**ΔH_{solv}**): Enthalpy per mole of electron donating site
  - Similar to Gutmann's DN[2], but derived computationally.
- The **Electrolyte Donor Number** (EDN) model:
  - Solvent and anions contribute to overall donicity (**Muli-component**).
  - **[ADS] = Concentration of Available Donor Sites**.
  - Solvation **energy per unit volume (kcal/L)** as key characteristic for [LiPS].

EDN = [ADS]*ΔH$_{solv}$ (kcal/L)

$$^{23}\text{Na-}\Delta H_{Solv} = \frac{\left[\delta_{Na:E(x)} - \delta_{Na:E(x_{low})}\right] * \Delta H_{Solvent} + \left[\delta_{Na:Solv} - \delta_{Na:E(x)}\right] * \Delta H_{AGG}}{\delta_{Na:Solv} - \delta_{Na:E(x_{low})}}$$

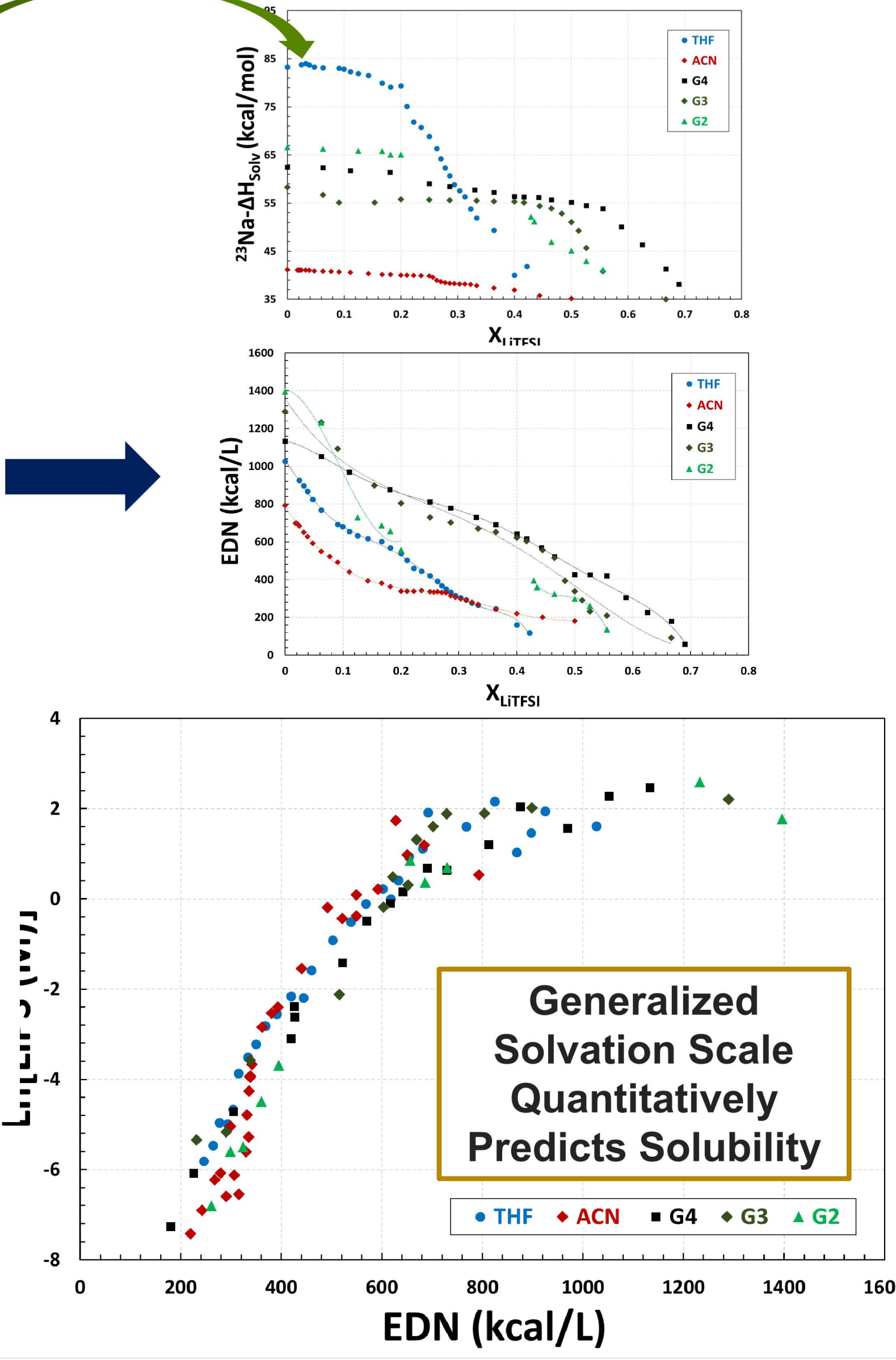


SSIP = Solvent Separated Ion Pair (*free anion*)
CIP = Contact Ion Pair (*single coordination to Li⁺*)
AGG = Aggregate (*multiple coordination to Li⁺*)

$\delta_{Na:E(x)}$ ≡Chemical shift of electrolyte at mole fraction (x)

$\delta_{Na:E(x_{low})}$ ≡ Chemical shift at RT freezing composition

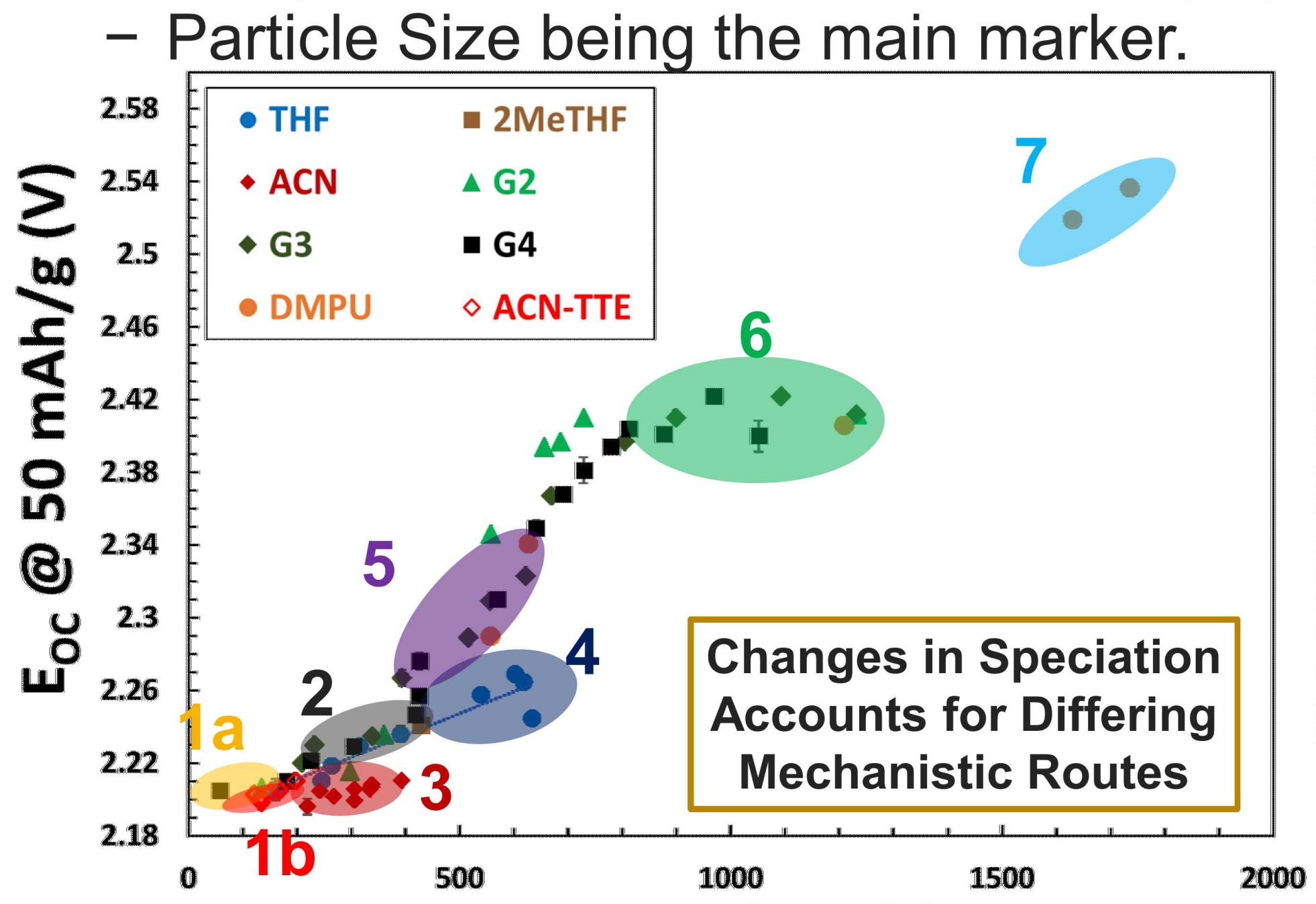
$\delta_{Na:Solv}$ ≡ Chemical shift of pure solvent



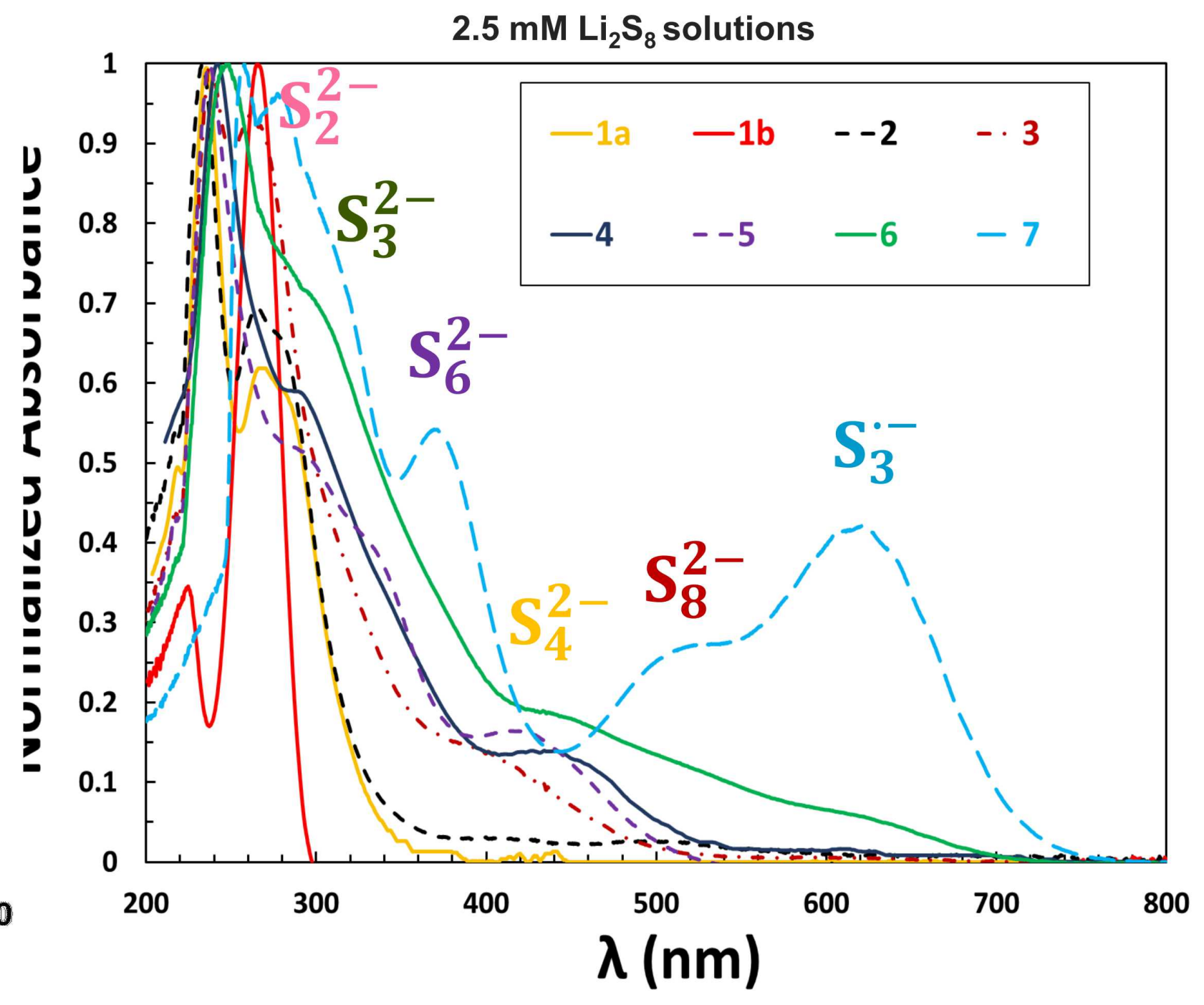
Generalized Solvation Scale Quantitatively Predicts Solubility

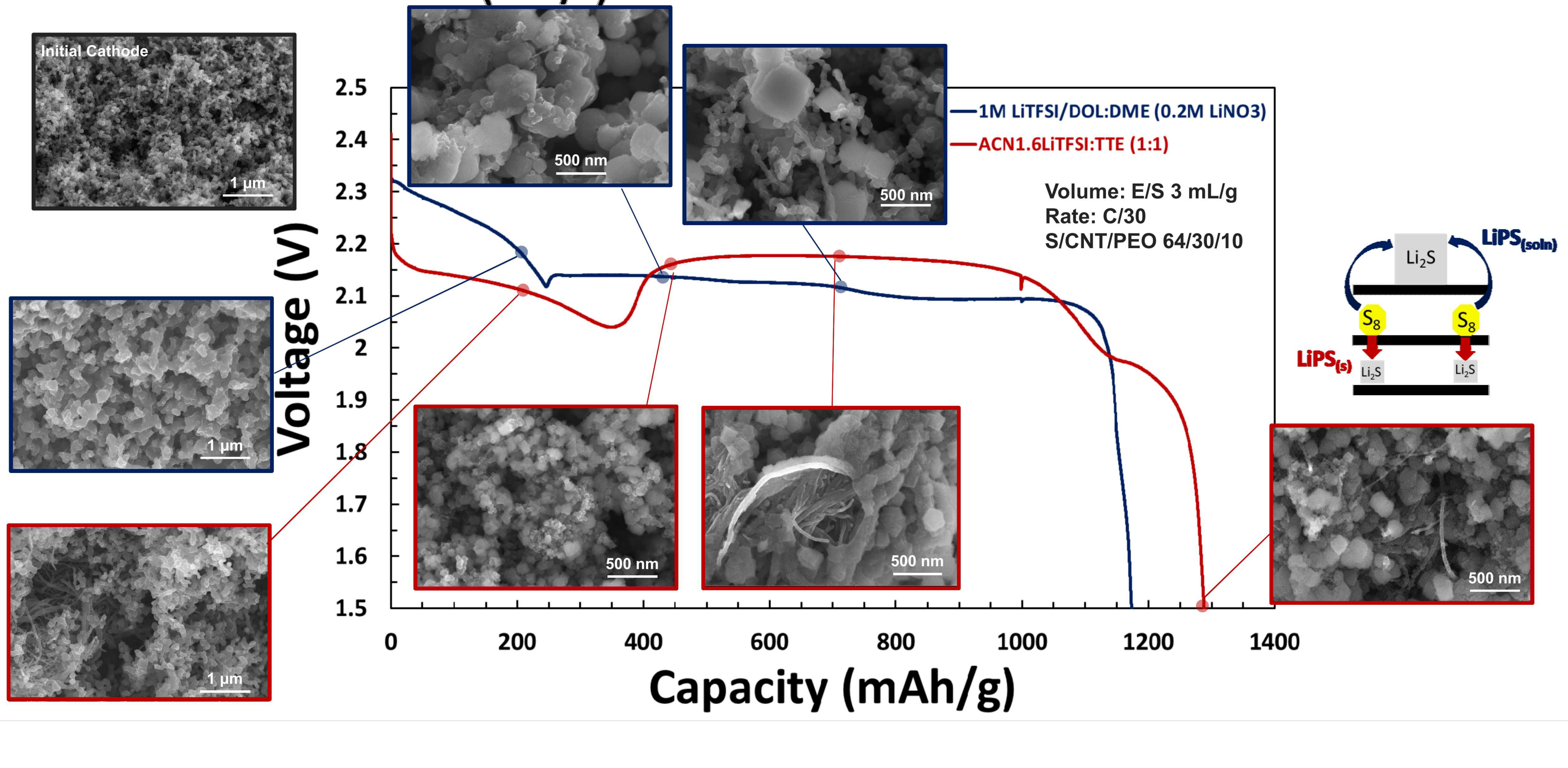
POLYSULFIDE SPECIATION

- UV/Vis absorption and Raman Spectroscopies provide speciation insight.
- Cathode imaging clearly distinguishes mechanistic differences between "dilute" electrolytes and ultra-low LiPS solubility systems.
  - Particle Size being the main marker.



Changes in Speciation Accounts for Differing Mechanistic Routes

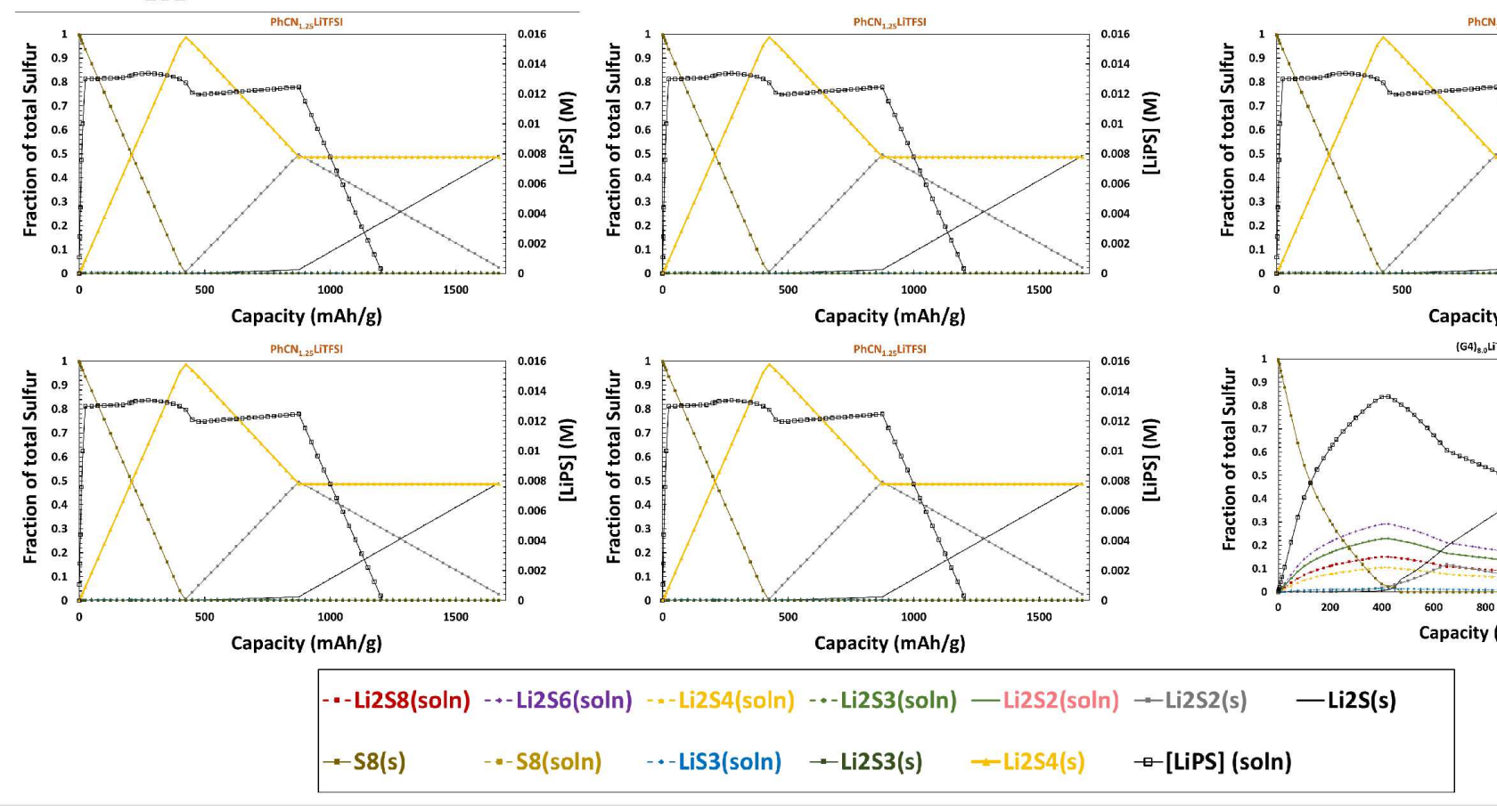




MECHANISM MODELING

- $aS_b + ne^- \rightarrow cS_d \quad (E_i^0)$
- $E = \sum_i \alpha_i \left(E_i^0 - \frac{RT}{nF} Ln \frac{[S_d]^c}{[S_b]^a}\right)$
- $2S_b^{2-} \overset{K_{b\leftrightarrow d}}{\leftrightarrow} S_d^{2-} + \frac{b-d}{8} S_8,\ 2S_b^{2-} \overset{K'_{b\leftrightarrow d}}{\leftrightarrow} S_{b+d}^{2-} + S_{b-d}^{2-},\ S_b^{2-} \overset{K''_{b\leftrightarrow b/2}}{\leftrightarrow} 2S_{b/2}^{\cdot-}$
- $LnK = \frac{nF}{RT}\left(E_R^0 - E_O^0\right)$

EDN and Speciation Provide Key Insight for Thermo-Model



CONCLUSIONS

- An Electrolyte Donor Number (EDN) Model has been developed.
- EDN predicts LiPS solubility in electrolytes
- Redox reaction pathways are predictable with knowledge of EDN and LiPS speciation.
  - Testable hypotheses generated
- We have a path forward for rational electrolyte design.

REFERENCES

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2. Gutmann, V. Electrochimica Acta. **1976**, 21, 661-670
3. Watkins, Narayanan, *et al*. A New Electrolyte Solvation Model for Prediction of Lithium Polysulfide Solubility in Electrolytes for Li-S Batteries. *In preparation*.
4. Watkins *et al*. Revealing the Role of the Electrolyte in Governing Li-S Redox Mechanisms: How a Newly Developed Electrolyte Solvation Scale Predicts Li-S Reaction Routes. *In Preparation*.

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