INL/CON-23-72780-Revision-0

Localized High-Concentration Electrolytes Get More Localized

May 2023

Corey Michael Efaw, Qisheng Wu, Ningshengjie Gao, Haoyu Min Zhu, Kevin L Gering, Hui Claire Xiong, Eric J Dufek, Bin Li

Changing the World's Energy Future

Idaho National Laboratory

INL is a U.S. Department of Energy National Laboratory operated by Battelle Energy Alliance, LLC

INL/CON-23-72780-Revision-0

Localized High-Concentration Electrolytes Get More Localized

Corey Michael Efaw, Qisheng Wu, Ningshengjie Gao, Haoyu Min Zhu, Kevin L Gering, Hui Claire Xiong, Eric J Dufek, Bin Li

May 2023

Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

Understanding Solvation Structures of Localized High-Concentration Electrolytes Used for Li-Metal Batteries

243rd ECS, A01-0437

May 31st, 2023

Corey Efaw
Postdoctoral Fellow, INL

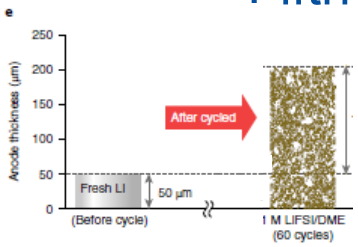
Bin Li & Eric Dufek
Mentors, INL

Idaho National Laboratory

Background and Motivation of Binary Electrolyte

Low-Concentration Electrolyte (LCE)

- Solvent separated ion pairs – free cation/anion
- Contact ion pairs – single Li^+-FSI^- coordination
- Solvent-driven SEI formation – organic-rich
- Heterogeneous, porous, & unstable SEI

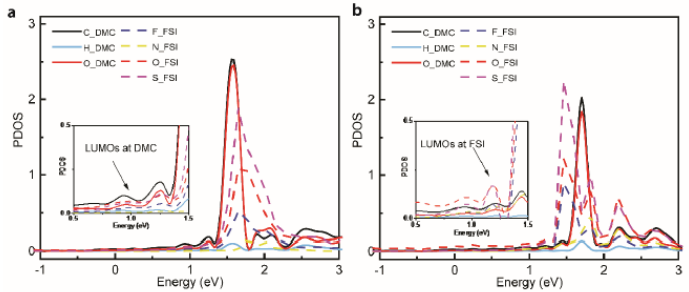


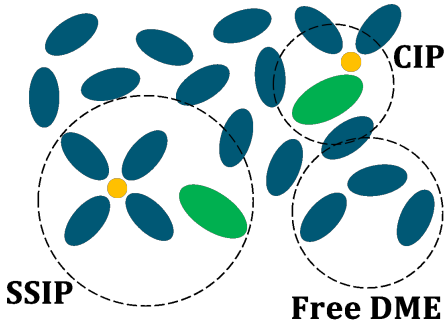
X. Cao et al, *Nature Energy* **4**, 796 (2019).

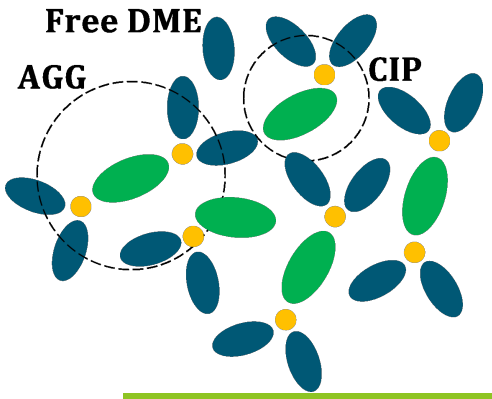
High-Concentration Electrolyte (HCE)

- Aggregate clusters – multiple Li^+-FSI^- coordination
- Salt-driven SEI formation – inorganic-rich
- High cost, high viscosity & poor ionic conductivity

S. Chen et al, *Adv. Mater.* **30**, 1706102 (2018).





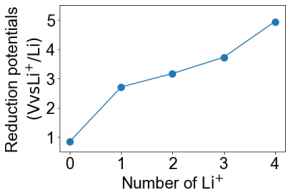


X. Cao et al, *Nature Energy* **4**, 796 (2019).

Background and Motivation – Solvation Structure of Ternary Electrolyte

Localized High-Concentration Electrolyte (LHCE)

- Diluent – reduced viscosity, improved thermal and high-voltage stability
  - Click to edit text
- Steric effect & non-interacting with salts
  - Second level
- Aggregate cluster – multiple Li^+-FSI^- coordination
  - Third level
- Increased SEI uniformity (monolithic)
  - Fourth level
- Salt-derived formation – inorganic-rich (e.g., LiF, Li_2O)
  - Fifth level



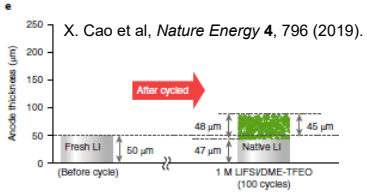
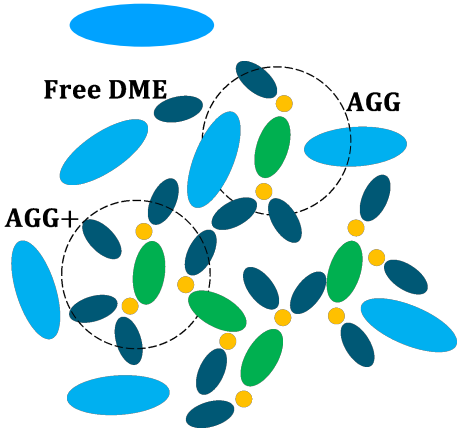


Table 1 | Physical properties of TFEO and conventional solvents

Compound	DFT calculation		Boiling point (°C)	Viscosity at 30 °C (cP)
	HOMO (eV)	LUMO (eV)		
EC	−8.47	−0.28	243	1.90 (at 40 °C)[24]
EMC	−8.14	−0.07	107	0.65[24]
DME	−7.19	−0.18	85	0.46[24]
TFEO	−9.06	−0.63	143	0.43

LUMO, lowest unoccupied molecular orbital.



Electrolyte

LiFSI/DMC-BTFE (0.51:1.1:2.2 by mol)
LiFSI/TEP-BTFE (0.75:1:3 by mol.)

LiFSI/EC-EMC-BTFE (0.51:0.22:0.88:2 by mol.) + 0.15 M LiDFOB
LiFSI/TMS-TTE (1:3:3 by mol.)

LiFSI/DME-TTE (1:1.2:3 by mol.)

LiFSI/DME-TFEO (1:1.2:1 by mol.)
LiFSI/DME-TFEO (1:1.2:2 by mol.)
LiFSI/DME-TFEO (1:1.2:3 by mol.)
LiFSI/DMC-TTE (1:2.2:3 by mol.)
LiFSI/DMC-VC-TTE (1:2:0.2:3 by mol.)
LiFSI/DMC-EC-TTE (1:2:0.2:3 by mol.)

LiFSI/TEP-EC-BTFE (1:1:0.33:4 by mol.)
LiFSI/TEP-BTFE (1:1.33:4 by mol.)
LiFSI/TEP-BTFE (1:1.33:4 by mol.) + 0.12 wt.% FEC
1.8 M LiFSI/EC-EMC-BTFE (0.3:0.7:2 by mol.) + 5 wt.% FEC

How do salt ions accumulate differently when a diluent is included?

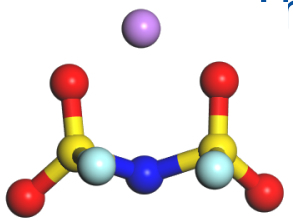
How do we decide our LHCE components and proportions?

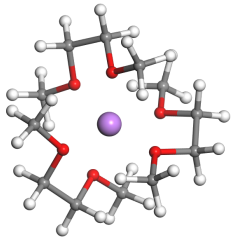
Background and Motivation – Electrolyte Properties

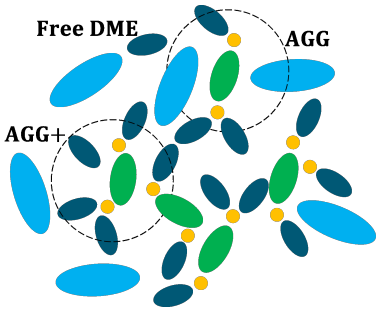
- Multiscale understanding of electrolyte

Atomic & Molecular Interactions

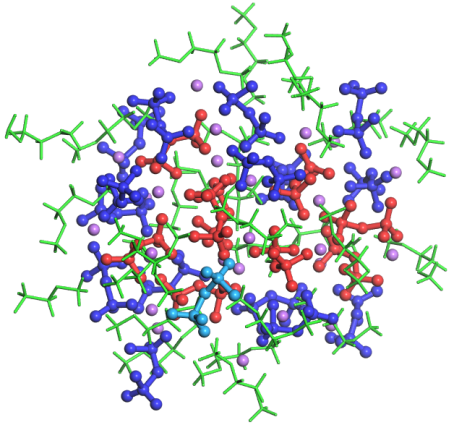
- Click to edit text
  - Second level
    - Third level
      - Fourth le
        - Fifth

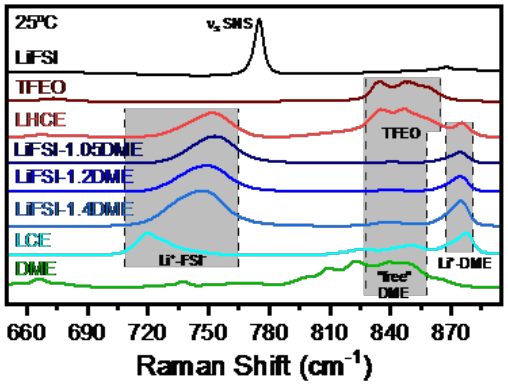




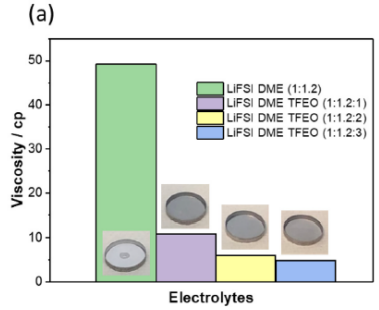


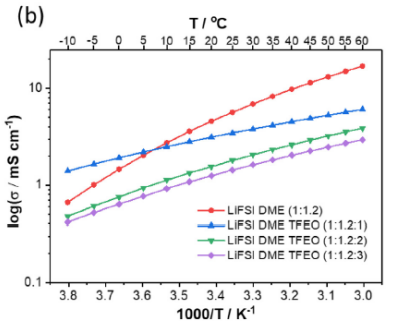
Solvation Structure Stability & Distribution





Macroscale Properties





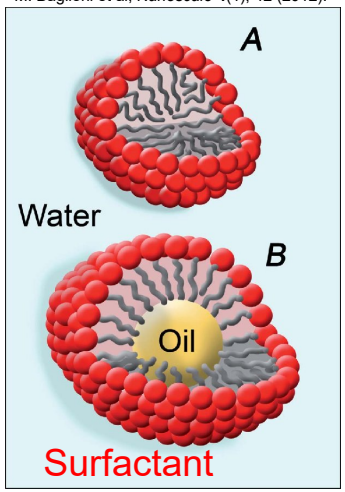
X. Cao et al, *Nature Energy* **4**, 796 (2019).

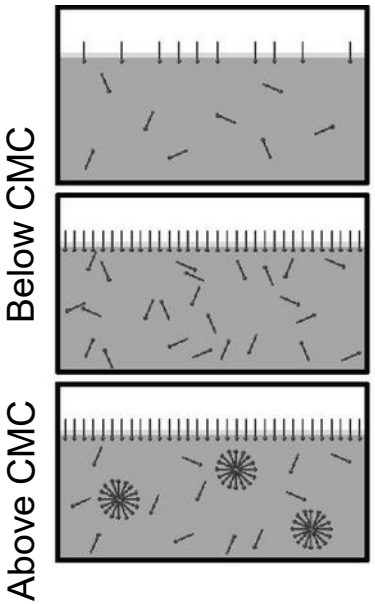
C.M. Efaw, Q. Wu et al, submitted to *Nature Materials*.

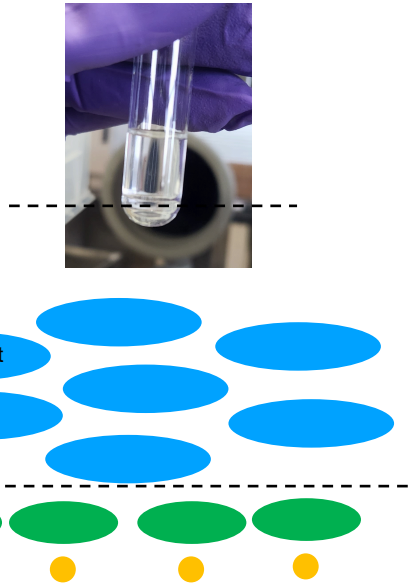
Background and Motivation – Micelle Structure

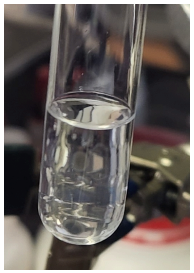
- **Micelle structure** – arrangement of molecules in a 3-D spherical form
  - Surfactant permits mixture of otherwise immiscible components
    - Click to edit text
- **Critical micelle concentration (CMC)** – “break” point of micelle structures being maintained, based upon concentration of surfactant
    - Second level
      - Third level
- Apply this to an LHCE’s solvation structure – “micelle-like” structure
        - Fourth level
          - Fifth level

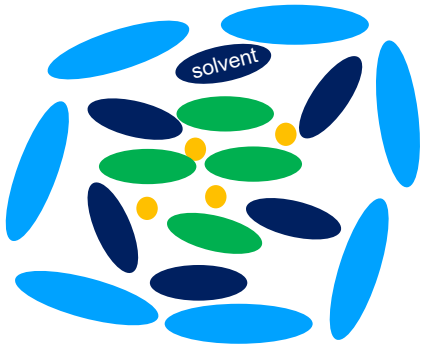
M. Baglioni et al, *Nanoscale* **4**(1), 42 (2012).





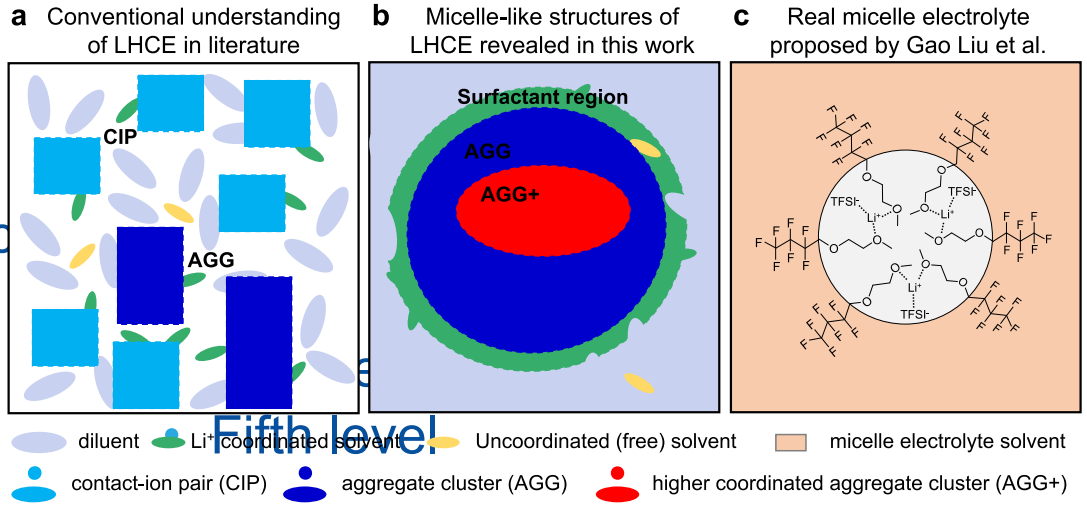


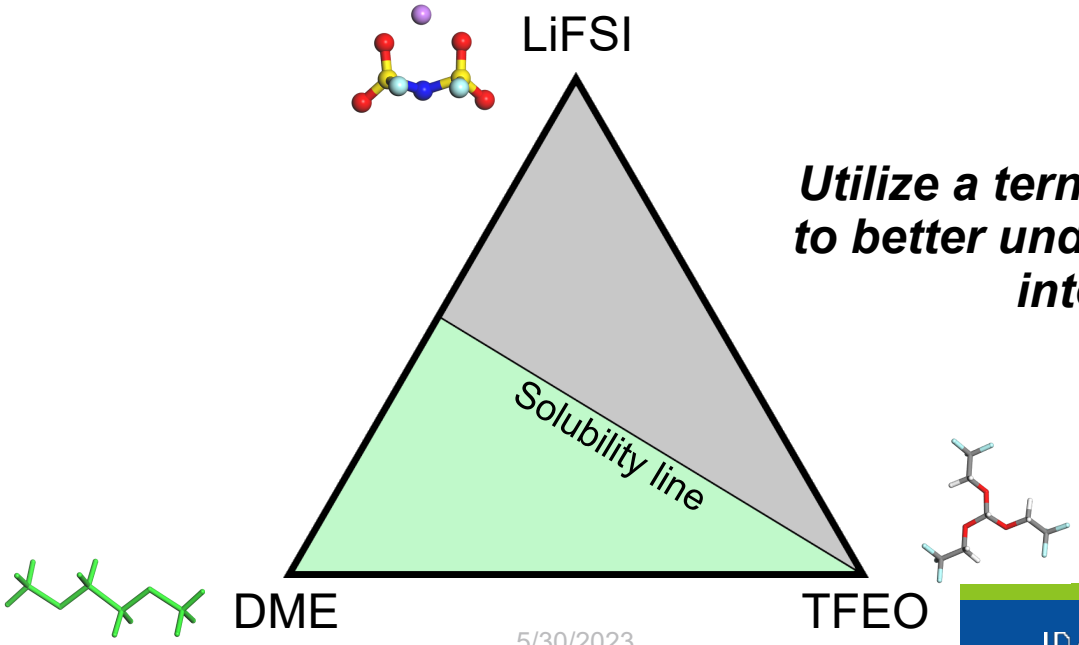




Background and Motivation – Micelle-like” Structure

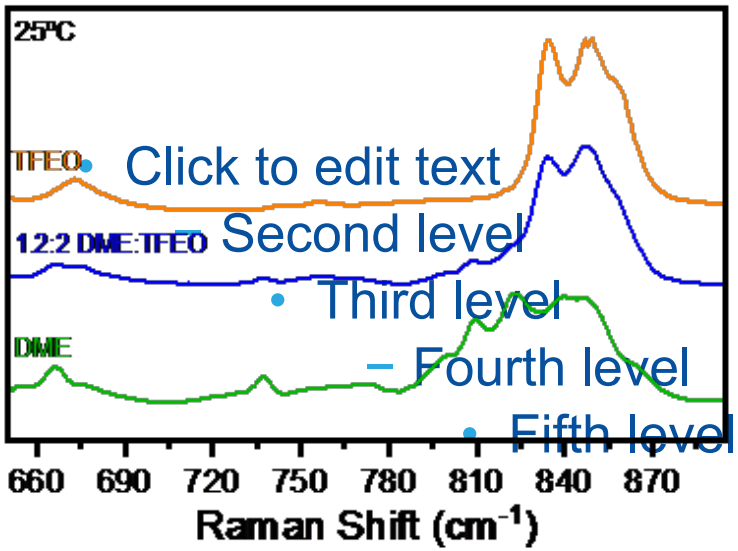
- Click to
  - Sec
    - Fifth level!





Utilize a ternary phase diagram to better understand electrolyte interactions

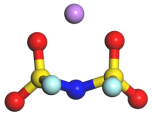
Bicarbonate Electrolyte Mixtures



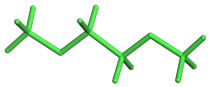
- Click to edit text
  - Second level
    - Third level
      - Fourth level
        - Fifth level

- ***Immiscibility between LiFSI & TFEO***
- ***Miscibility between DME & TFEO***
- ***TFEO dominates mixed solvent Raman spectra***

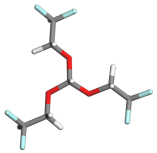
LiFSI

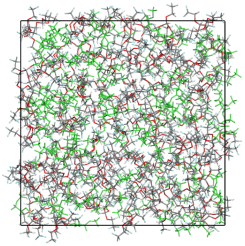


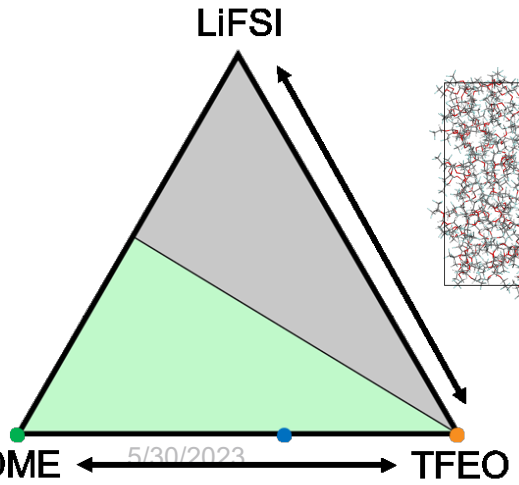
DME

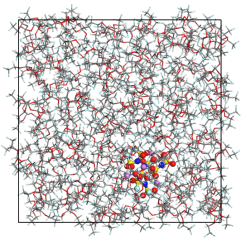


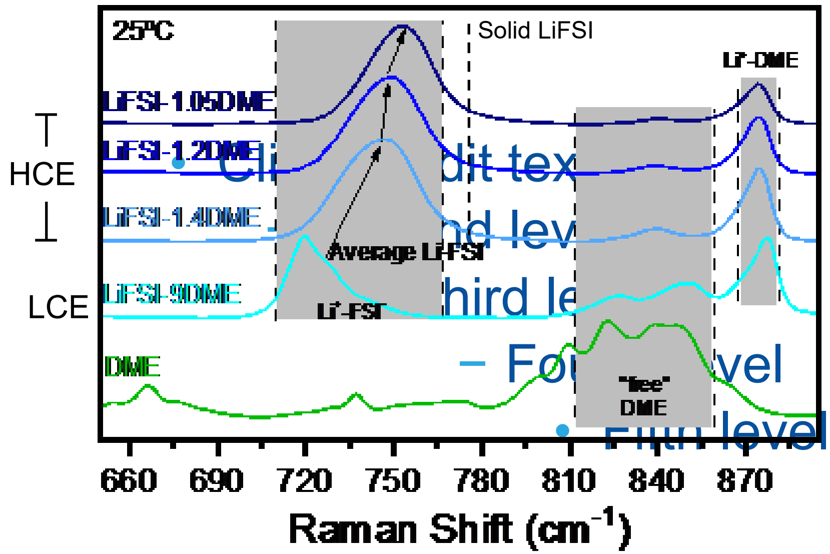
TFEO

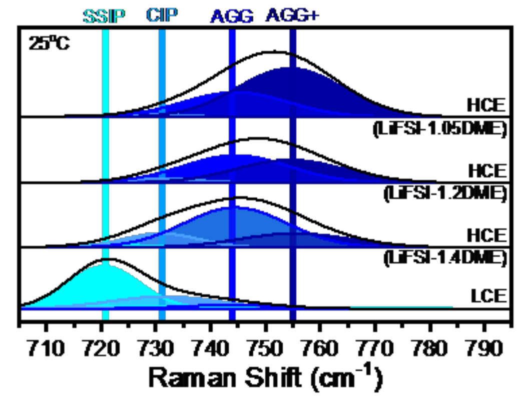


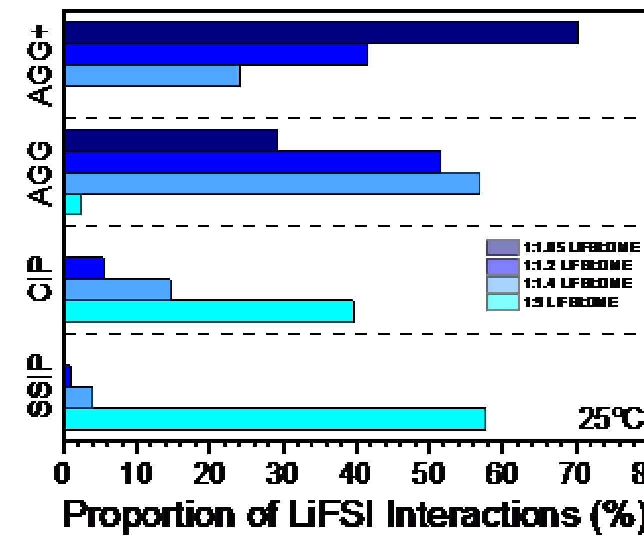


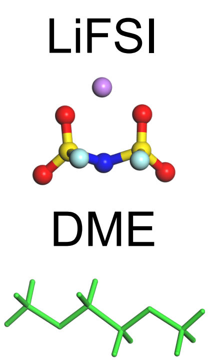


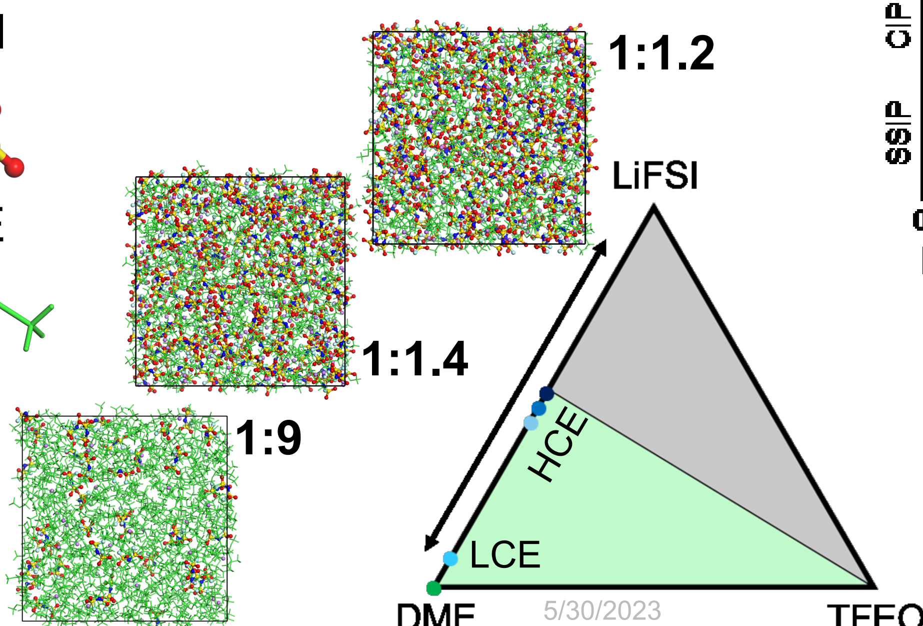






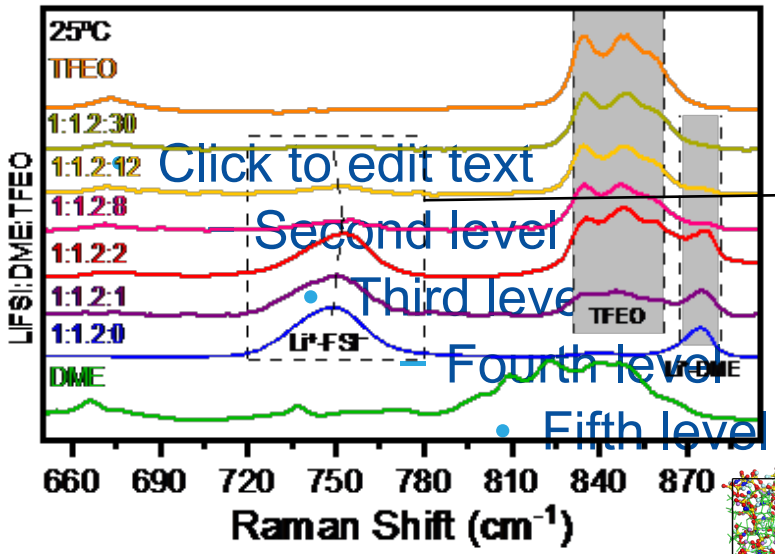




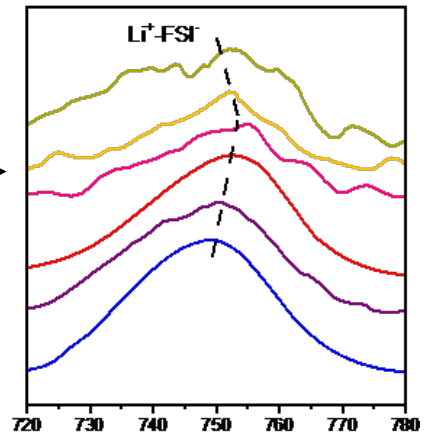


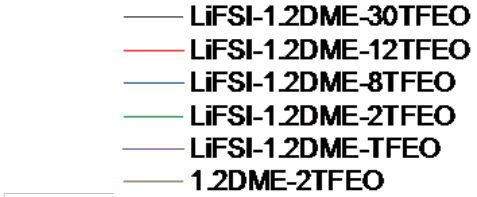
Add more LiFSI…get greater aggregation, with uniform distribution

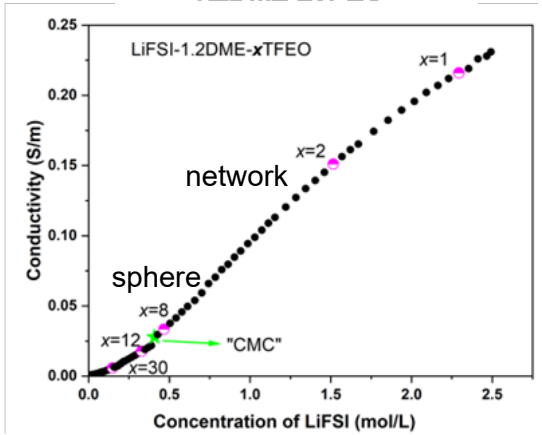
Click to edit Master title style

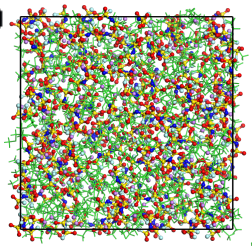


Click to edit text
- Second level
- Third level
- Fourth level
- Fifth level



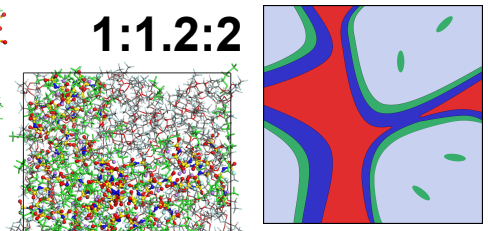


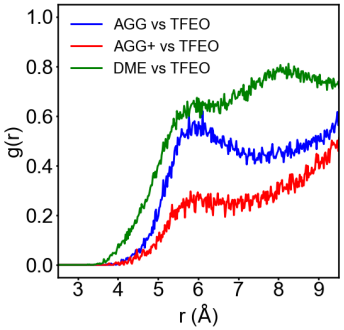




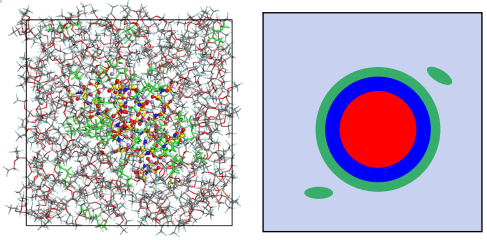
1:1.2:0

1:1.2:2

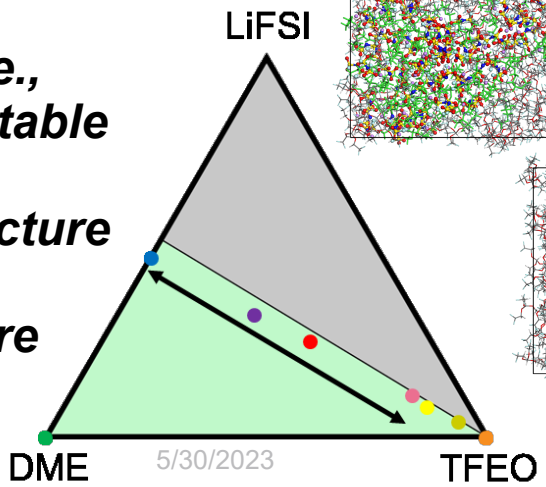




1:1.2:8

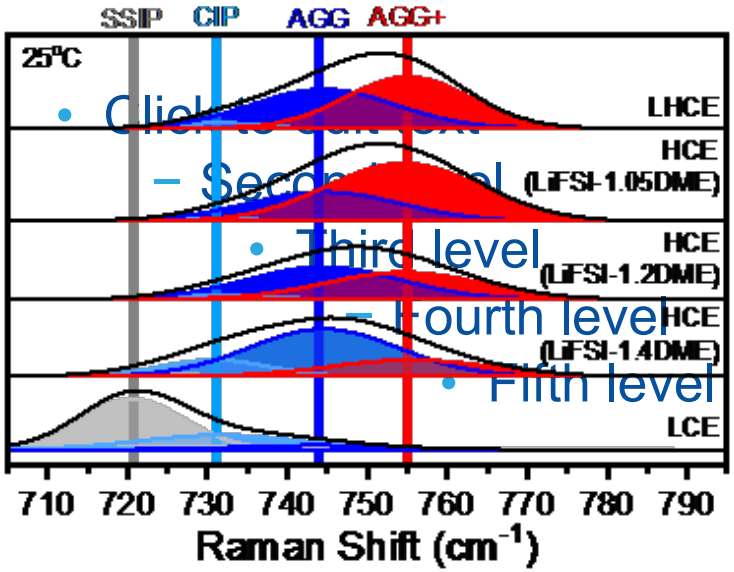


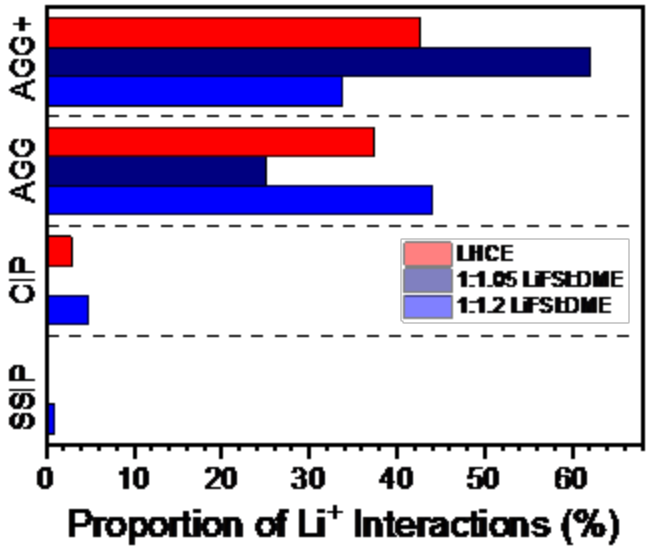
- *"CMC" seen between 12<x<8*
- *After CMC is met, an interconnected network (i.e., micelle-like) can become stable rather than a sphere*
- *Gradient, "core-shell" structure observed*
- *Size of micelle-like structure determined by SAXS*



Click to edit Master text

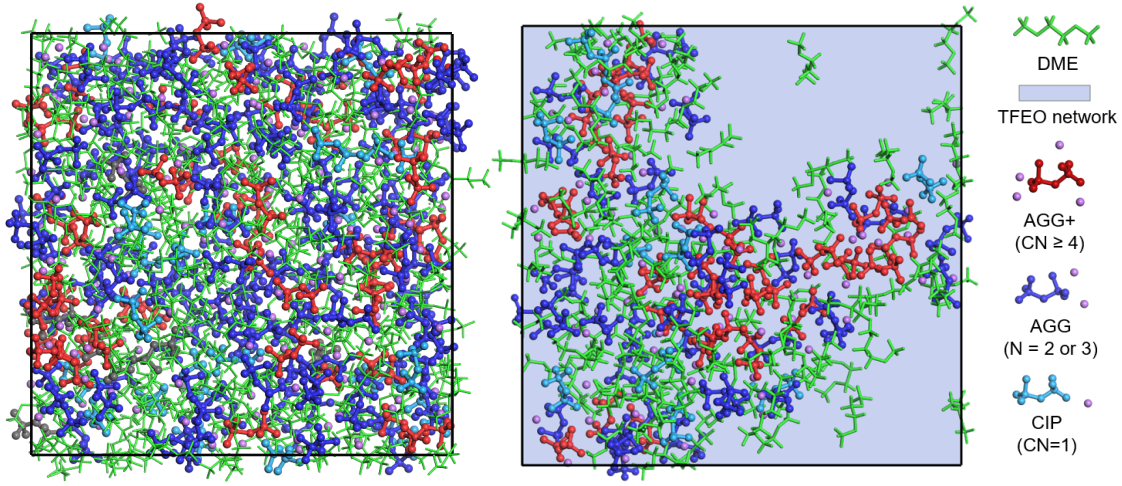
- Click to edit Master text
  - Second level
    - Third level
      - Fourth level
        - Fifth level

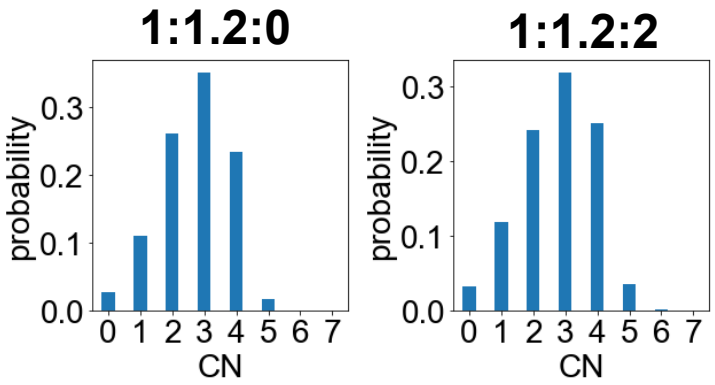




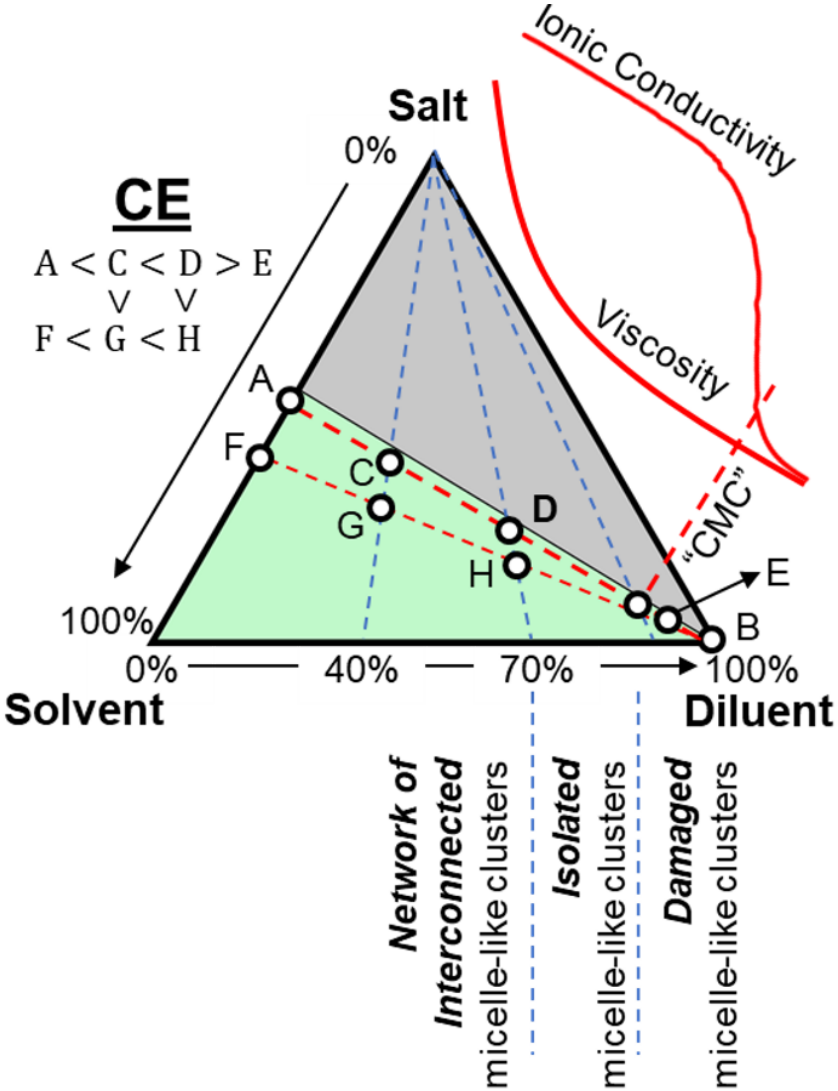
Extend "localization" vs. binary LiFSI-DME system

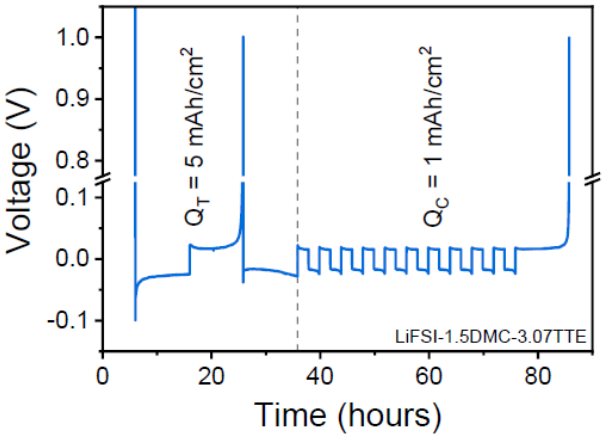
1:1.2:0 **1:1.2:2**





Design Criteria for LHCEs





- ***Identify the "CMC" breakpoint to determine the best mixture of salt-solvent-diluent***
- ***Determined performance with Cu\|Li Coulombic Efficiency tests***
- ***Start to determine design criteria of LHCEs***

Perspective & Ongoing Work

- New insights into the structure & properties of LHCEs
  - Interactions at molecular, structural, & macroscale
    - Bicontinuous structure proposed
- Inspire rational optimization of LHCEs to improve cell capabilities
  - Decision matrix of what kinds & how much components to include in LHCEs
  - Observe impact of other parameters (e.g., T) for improved formation protocols & application-based electrolytes
- We need more insight into electrolyte properties & interactions
  - Correlation and expansion of experiments with models
  - Different applications need different electrolyte properties
    - How can we extend microscale improvements while maintaining functional macroscale properties??
  - Impacts of electric field on properties, interfacial mechanisms

Click to edit Master title

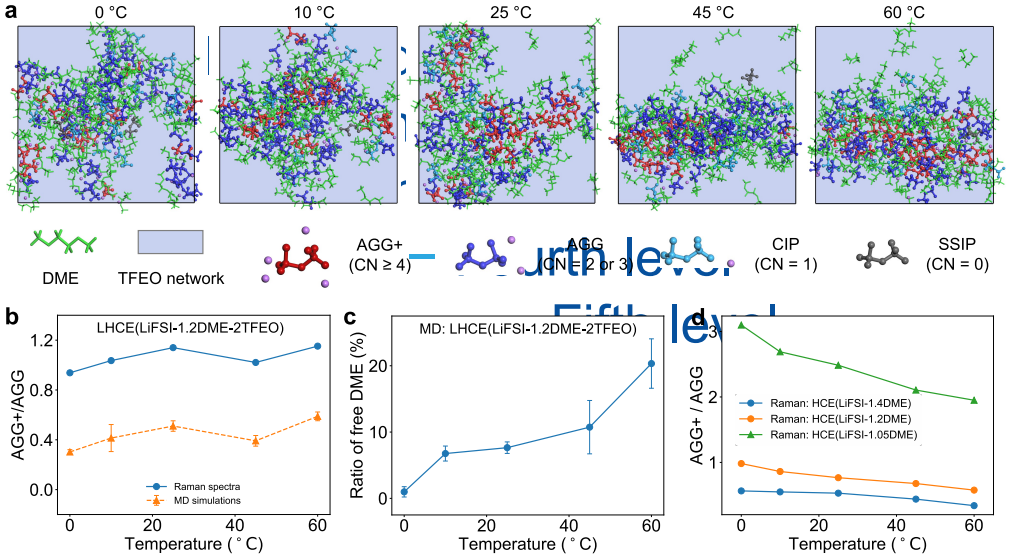
- Research has been supported by the Vehicle Technologies Office (VTO) of the U.S. Department of Energy (DOE) through the Advance Battery Materials Research Program (Battery500 Consortium), contract nos. DE-AC07-05ID14517 & DE-AC05-76RLO1830
- NASA grant no. 80NSSC21M0107
- National Synchrotron Light Source II & SMI beamline (12-ID) under DOE OSF contract no. DE-SC0012704
- **DOE VTO**: Tien Duong, Dave Howell and Patricia Smith for support and guidance
- **INL**: Ning Gao, Kevin Gering, Eric J. Dufek, Bin Li*, Yuxiao Lin, Gorakh M. Pawar, Boryann Liaw,
- **Brown University**: *Qisheng Wu*, Yue Qi
- **UW & PNNL**: Wu Xu, Ji-Guang Zhang, Jie Xiao, Jun Liu, Xia Cao
- **Boise State University**: Min Zhou, Michael F. Hurley, Claire Xiong, Elton Graugnard, J.D. Hues, Jake Soares, Nicholas Bulloss, Paul H. Davis
- **BNL**: Yugang Zhang, Enyuan Hu, Xiao-Qing Yang, Sha Tan

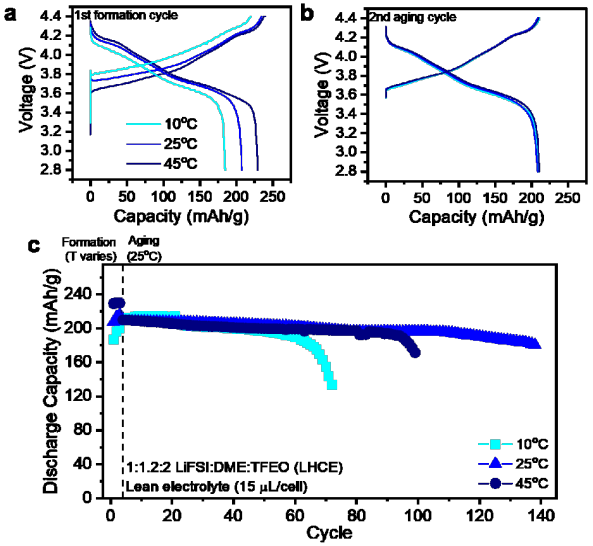
Click to edit Master title

- Click to edit text
  - Second level
    - Third level
      - Fourth level
        - Fifth level

Questions?

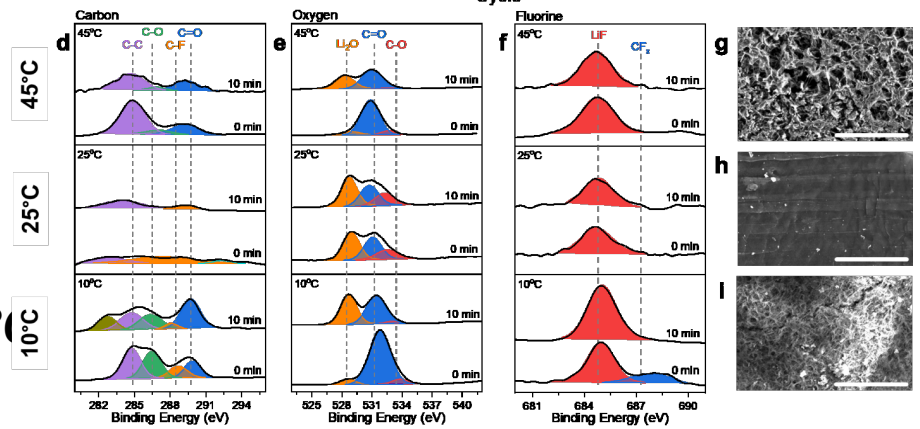
Effects of Temperature on Solvation





- ***Salt is solvated more with increasing temperature***
- ***DME-TFEO miscibility increase with temperature***
- ***"Goldilocks phenomena" is found amongst the comingling effects at 25°C***
- ***Outside "optimal" temperature range, external effects play a greater role***

Correlation between increased aggregation with performance & make-up of SEI



Click to edit Master title style – same temperature effects!

- Click to e
  - Secc
    -

a

Salt-solvent clusters	Ratio
SSIP	0.0 %
CIP	1.7 %
AGG	53.1 %
AGG+	45.2 %
AGG+/AGG	0.85

b