IPAM: Bridging the Gap: Transitioning from Deterministic to Stochastic Interaction Modeling in Electrochemistry

Incorporating the effect of the EDL in multicomponent electrolytes on electrochemical reactions

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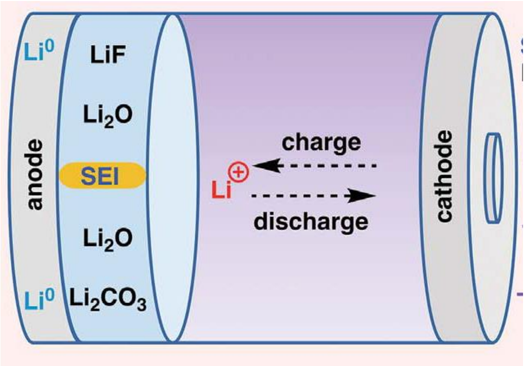
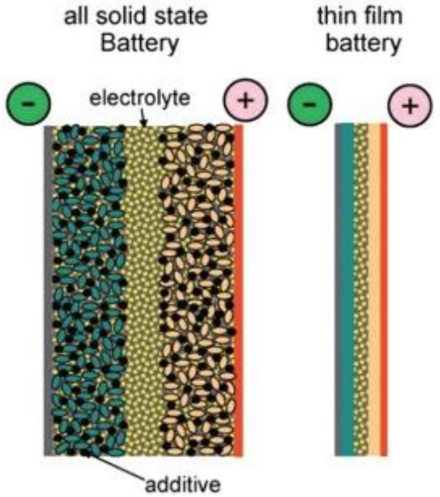
Research: https://vivo.brown.edu/display/yqi27

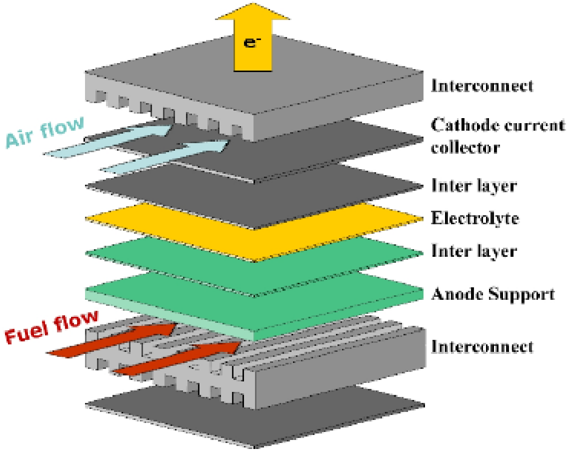
Workshop I: Embracing Stochasticity in Electrochemical Modeling



Batteries

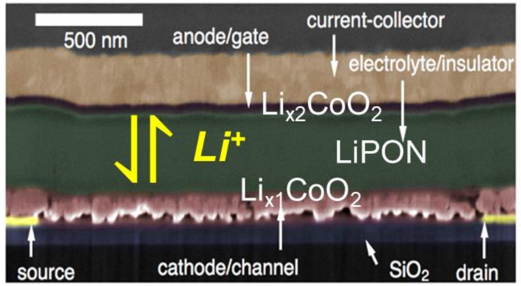


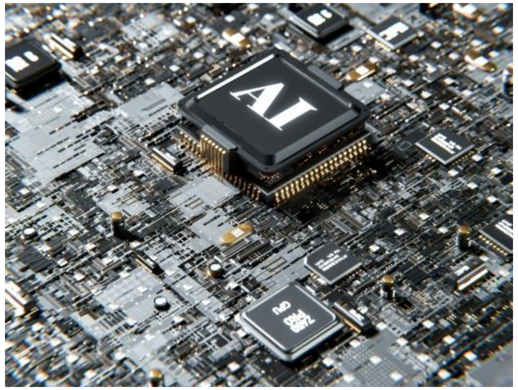
Solid State Batteries



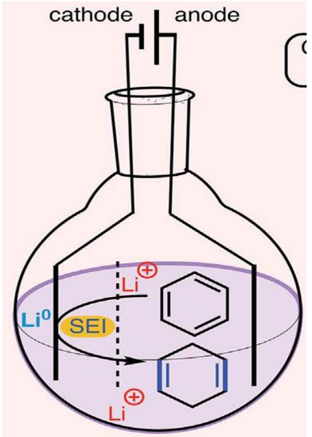
Fuel Cells

First Electrochemical RAM



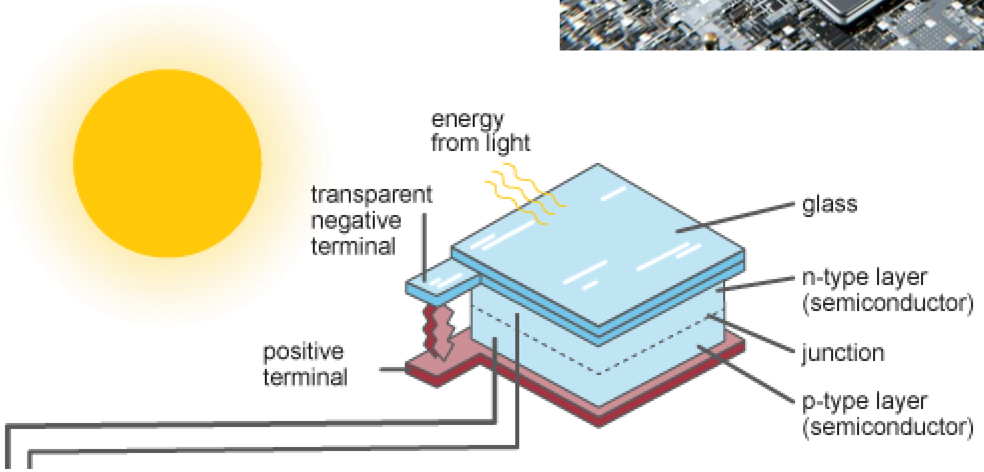


Herbert Kroemer (Nobel Prize 2000):
“The interface is the device”



Electrochemical synthesis

Structural Materials

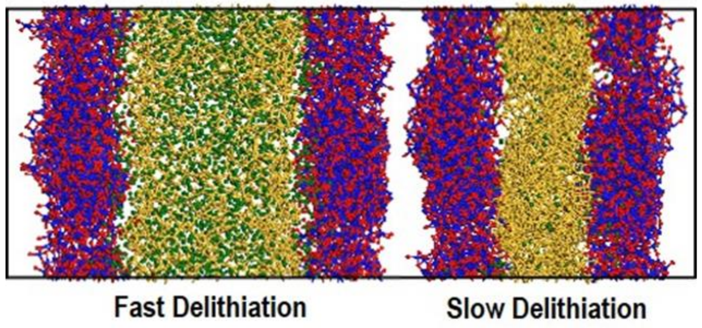


Solar Cells

Coupled Problems at Interfaces

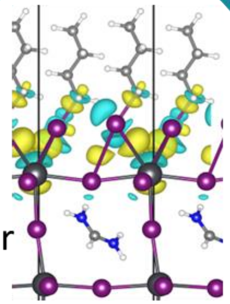
Mechanical

Adhesion



Nano Lett. 2017 Coated Si electrodes

Solar

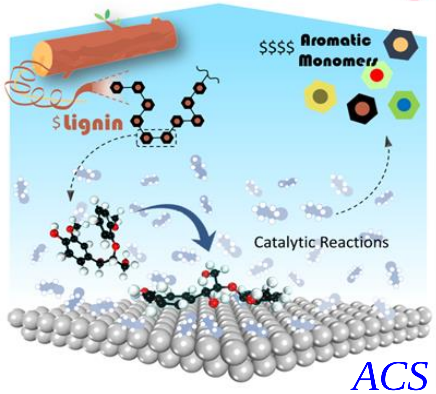


Science 2021

Bonding

Adsorption

Reaction



Catalytic

ACS Sustainable Chem. Eng. 2019

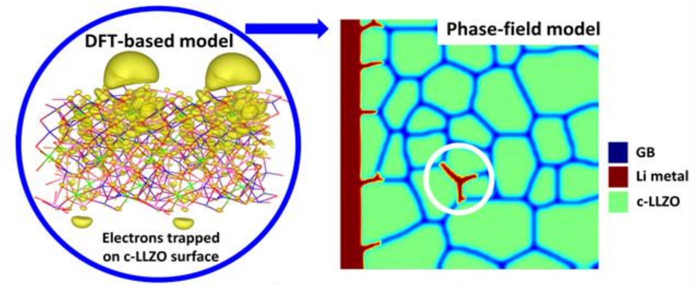
electrochemical synthesis

Stability

Interface

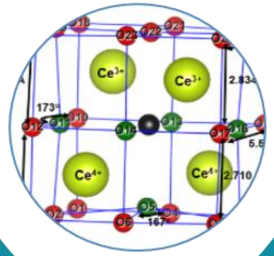
Kinetics

$Li^+ + e^- \leftrightarrow Li^0$



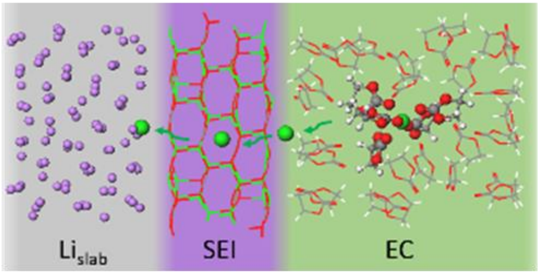
Chem. Mater. 2019 Li/LLZO interface

Defects



SOFC, H_2

$Li^+ + e^- \leftrightarrow Li^0$



Li/SEI/electrolyte Interface

Een. Env. Sci. 2019

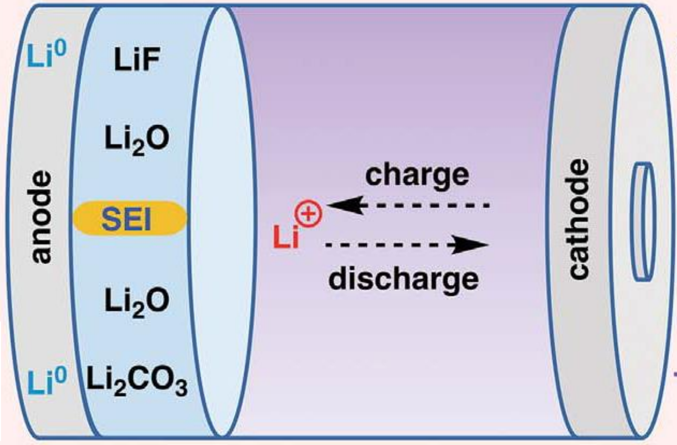
Charge Transfer

Transport

Space Charge Layer

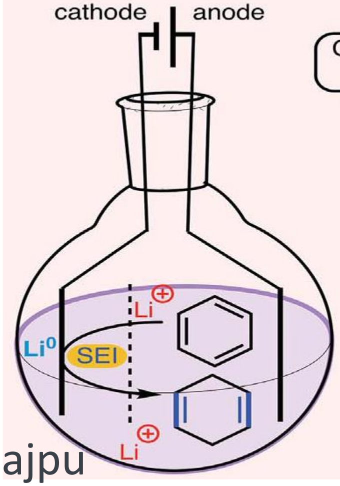
Electrochemical

Multiple electrochemical reactions in a multicomponent electrolyte system



SEI: Solid-Electrolyte Interphase, provides:

- Over-charge protection
- Stability of high potential zone
- Blocks undesirables from reaching the cathode
- Li^0 embedded in the anode



Can the same concept be applied to strongly reducing synthetic electrochemistry?

Synthetic Electroreduction Challenges:

- Unselective reductions
- High overpotentials
- Electrode surface damage
- Electrolyte destruction
- Scalability challenges

Nidhi Rajpu

Peters et al., Science 363, 838–845 (2019).

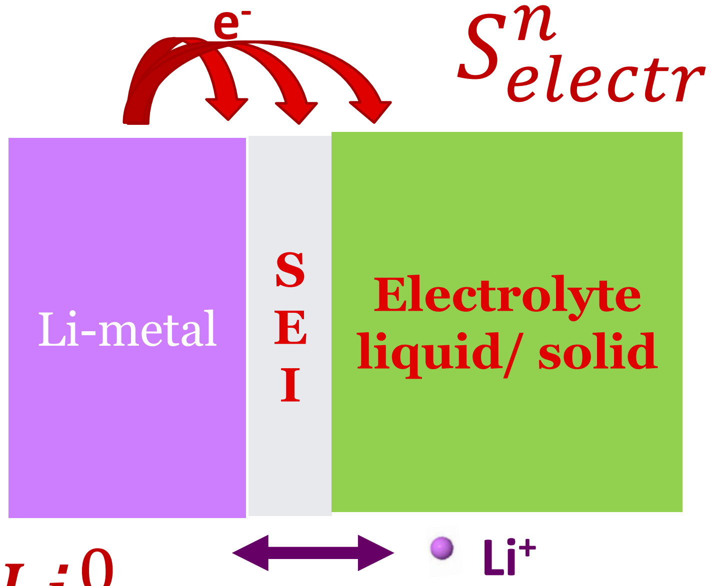
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Center For Synthetic Organic ELECTROCHEMISTRY

• What's in the pot?	**Maybe easier:** organic solvents
• What's at the electrode surface (EDL)?	**Hint:** not just the ions.
• Who gets reduced first, second … ?	**Competitions, selectivity**
• What are the products?	**Surface Layer, Yield**

Li/SEI/electrolyte interfaces and charge transfer reactions

- The Li-metal electrode is negatively charged at electrochemical equilibrium
- The impact of Electrical Double Layer (EDL) on Solid Electrolyte Interphase (SEI) formation
- New EDL models are required for
  - Solid electrolytes (SEI as well)
  - complex electrolytes: Localized high-concentration electrolytes (LHCE)



$$S^{n}_{electrolyte} + e^{-} \rightarrow S^{n-1}$$

Side Reactions
Electrolyte decomposition

Pro: forms a passivation layer
Con: consumes active Li

Li plating / stripping

$$Li^{+} + e^{-} \leftrightarrow Li^{0}$$

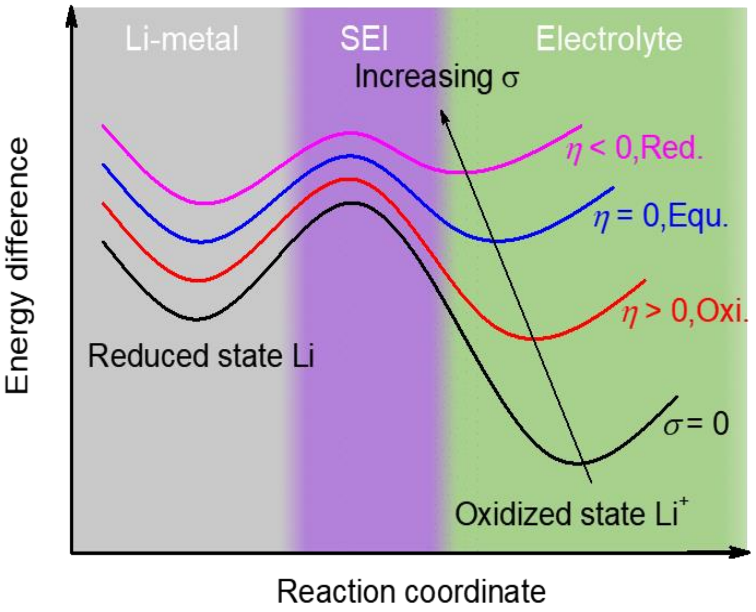
"A Tale of Two Stories" $Li^+ + e^- \leftrightarrow Li^0$

Ref. to lecture by Axel Gross

The Li-metal electrode is negatively charged (ϕ, n_e) during plating/stripping

At electrochemical equilibrium (zero current) for half reaction

$$\Delta G^o + zF\phi^o - RT\ln a_{M^{z+}} = 0$$



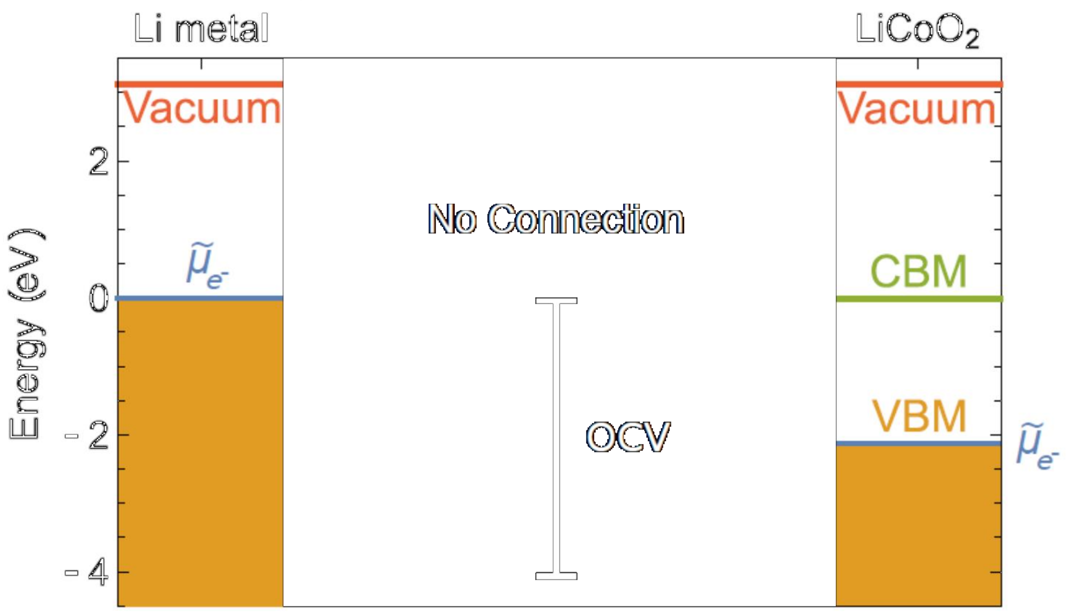
Batteries

Materials

Li and Qi, Energy Environ. Sci., 2019, 12, 1286-1295

At electrochemical equilibrium for full cell

$$\Delta\tilde{\mu}_{Li^+} = \Delta(\mu_{Li} - \tilde{\mu}_{e^-}) = 0$$



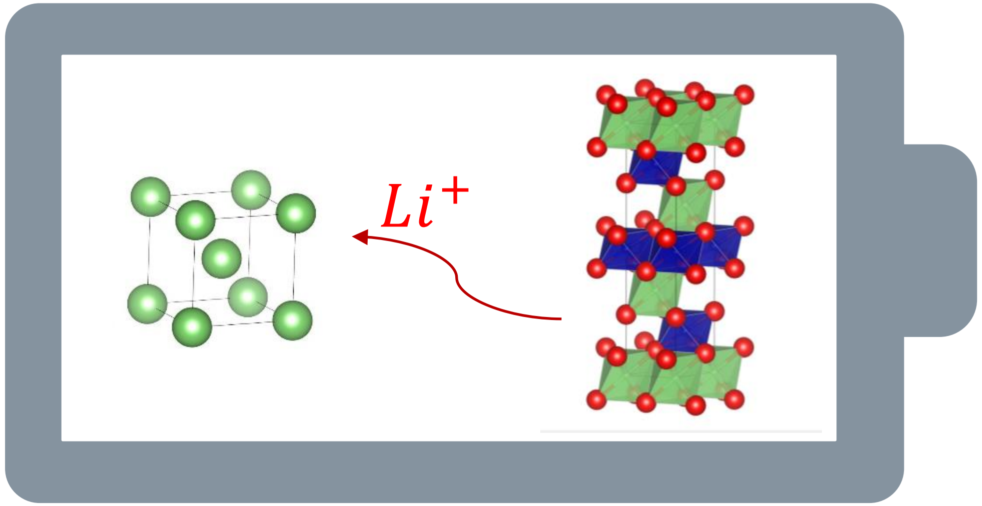
Materials

Swift and Qi, Phys. Rev. Lett. 122, 167701 (2019)

Putting materials into a battery --- ions, electrons, and atoms

The DFT computed Open Circuit Voltage is the different between μ_{Li} at the two electrodes.

$$\mathbf{OCV} = (\mu^{a}_{Li} - \mu^{c}_{Li})/e$$

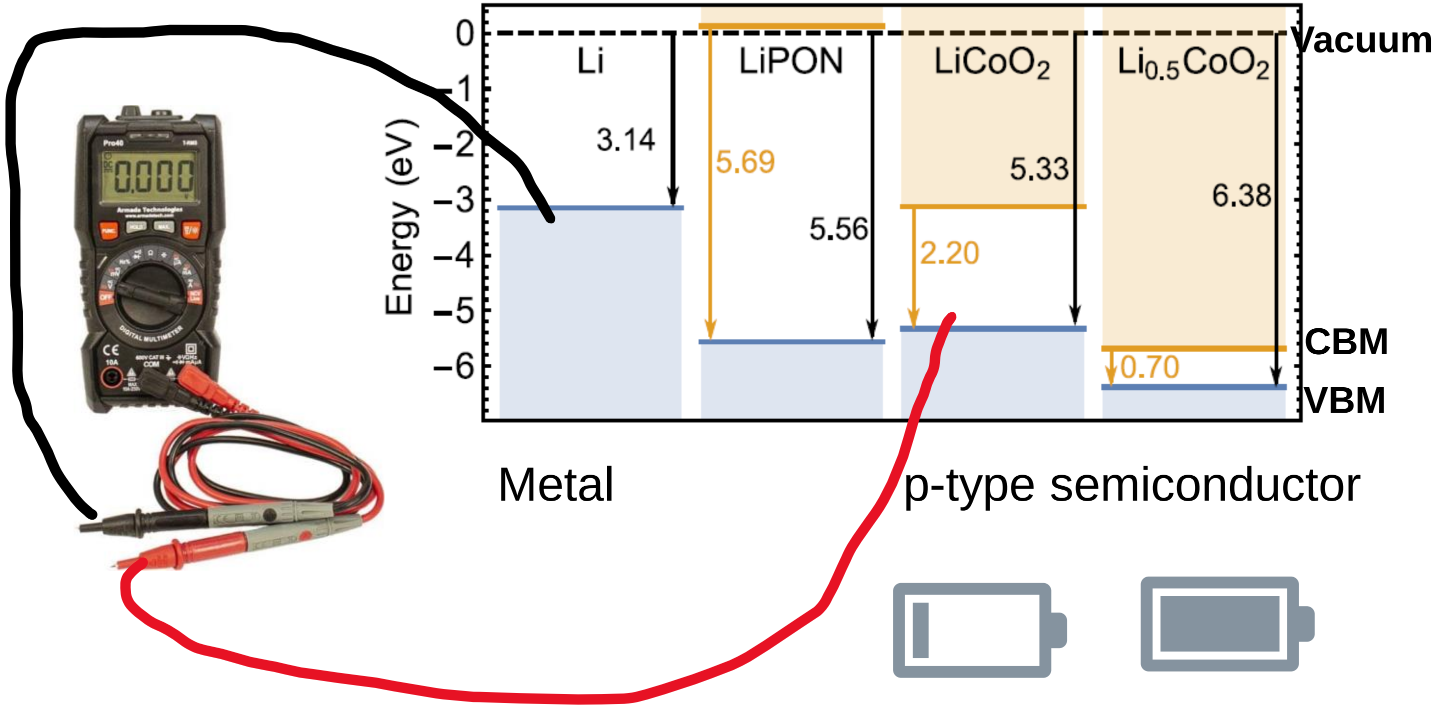


Li $LiCoO_2$

$$\mathbf{OCV} = -\Delta G/nF = 4.02\ \text{V}$$

Measured electrons

DFT computed electronic properties for isolated Materials



Swift and Qi, Phys. Rev. Lett. 122, 167701 (2019)

Putting materials into a battery --- ions, electrons, and atoms

Michael Swift

- Li^+ ions are free to move.
- At open-circuit voltage (OCV) equilibrium, the Li^+ ion electrochemical potential is a constant

$$\Delta\tilde{\mu}_{Li^+} = \Delta\mu_{Li} - \Delta\tilde{\mu}_{e^-} = 0$$

lithium atomic chemical potential

Electron electrochemical potential

The DFT computed OCV is the different between μ_{Li} at the two electrodes.

$$\mathrm{OCV} = (\mu^a_{Li} - \mu^c_{Li})/e$$

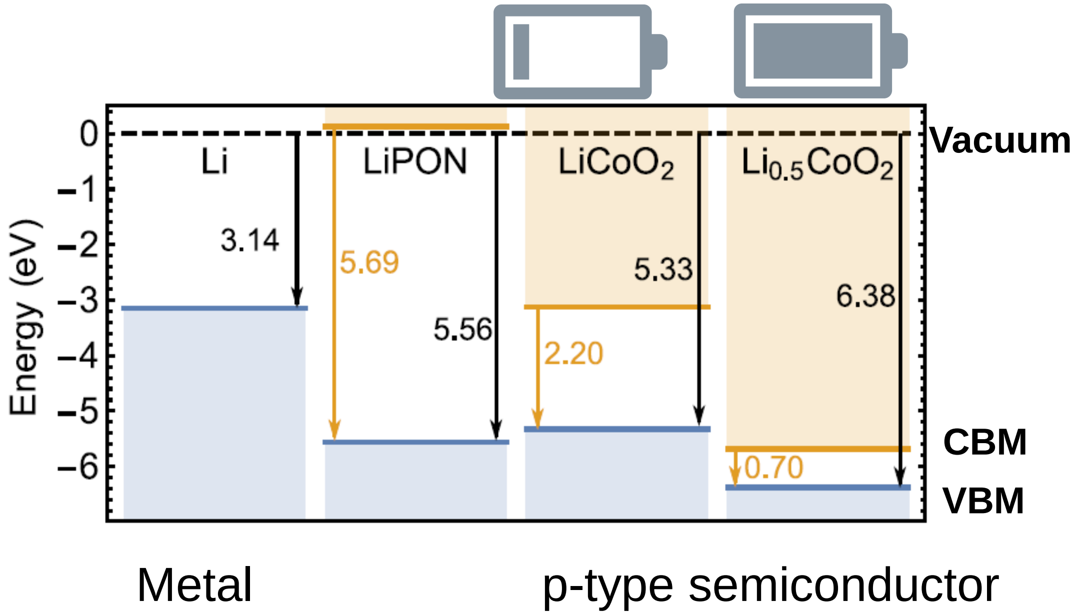
The measured OCV voltage is the difference between $\tilde{\mu}_{e^-}$ in the electrodes.

$$\mathrm{OCV} = (\tilde{\mu}^a_{e^-} - \tilde{\mu}^c_{e^-})/e$$

$\tilde{\mu}_{e^-}$ contains the work function and the electrostatic potential, ϕ

$$\tilde{\mu}_{e^-} = \Phi - e\phi$$

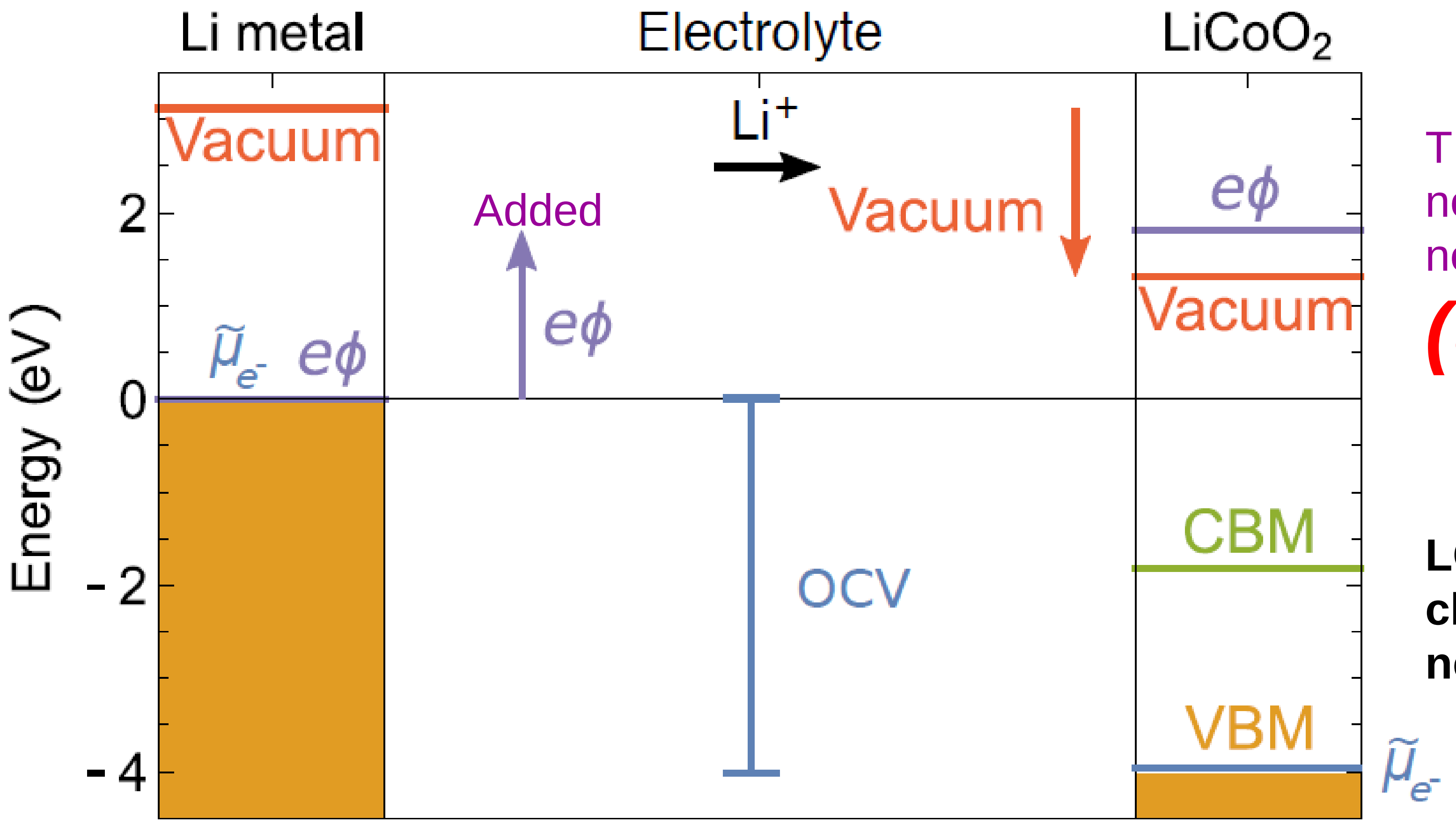
DFT computed work function, no $e\phi$



Swift and Qi, Phys. Rev. Lett. 122, 167701 (2019)

Putting materials into a battery --- ions, electrons, and atoms

$$\Delta\tilde{\mu}_{Li^+} = \Delta\mu_{Li} - \Delta\tilde{\mu}_{e^-} = 0$$



The electrode can not be charge neutral at OCV

$(e\Delta\phi \neq 0)$

LCO is positively charged or Li is negatively charged

DFT computed.

$$\mathbf{OCV} = (\mu^a_{Li} - \mu^c_{Li})/e$$

$$\mathbf{OCV} = (\tilde{\mu}^a_{e^-} - \tilde{\mu}^c_{e^-})/e$$

$$\tilde{\mu}_{e^-} = \Phi - e\phi$$

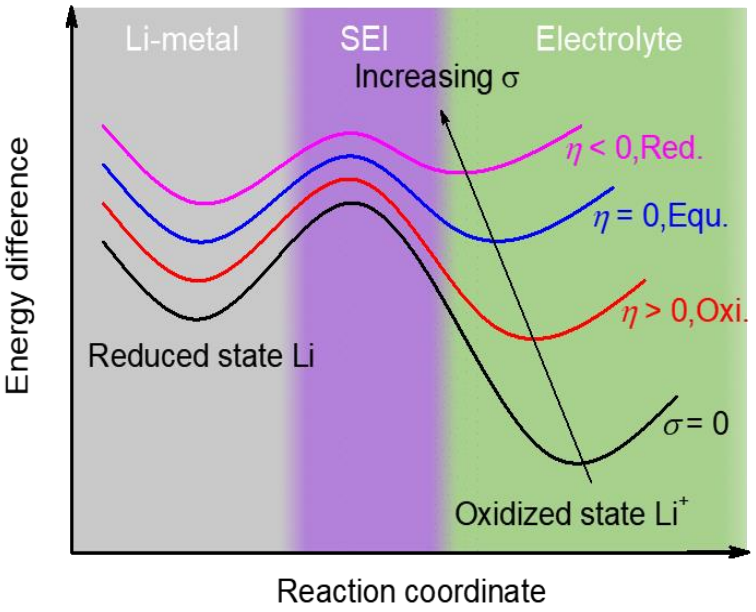
Swift and Qi, Phys. Rev. Lett. 122, 167701 (2019)

"A Tale of Two Stories" $Li^+ + e^- \leftrightarrow Li^0$

Li-metal electrode is negatively charged during plating/stripping

At electrochemical equilibrium (zero current) for half reaction

$$\Delta G^o + zF\phi^o - RT\ln a_{M^{z+}} = 0$$



Batteries

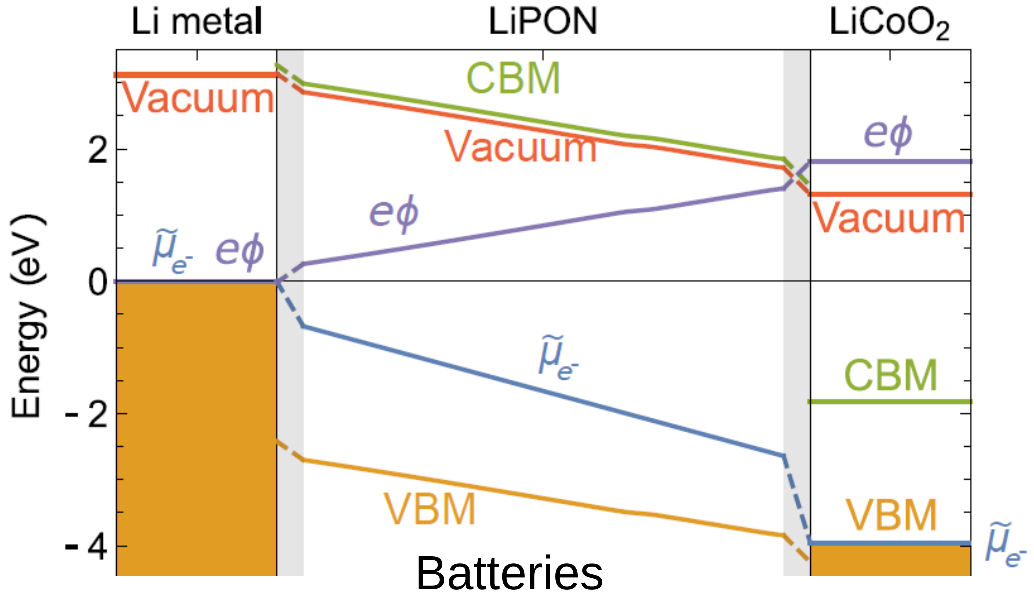
Materials

Li and Qi, Energy Environ. Sci., 2019, 12, 1286-1295

At electrochemical equilibrium for full cells

$$\Delta\tilde{\mu}_{Li^+} = \Delta(\mu_{Li} - \tilde{\mu}_{e^-}) = 0$$

Potential profile (minimum interface)



Batteries

Swift and Qi, Phys. Rev. Lett. 122, 167701 (2019)

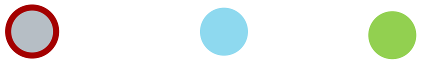
Finding the Electrochemical Equilibrium

Yunsong Li

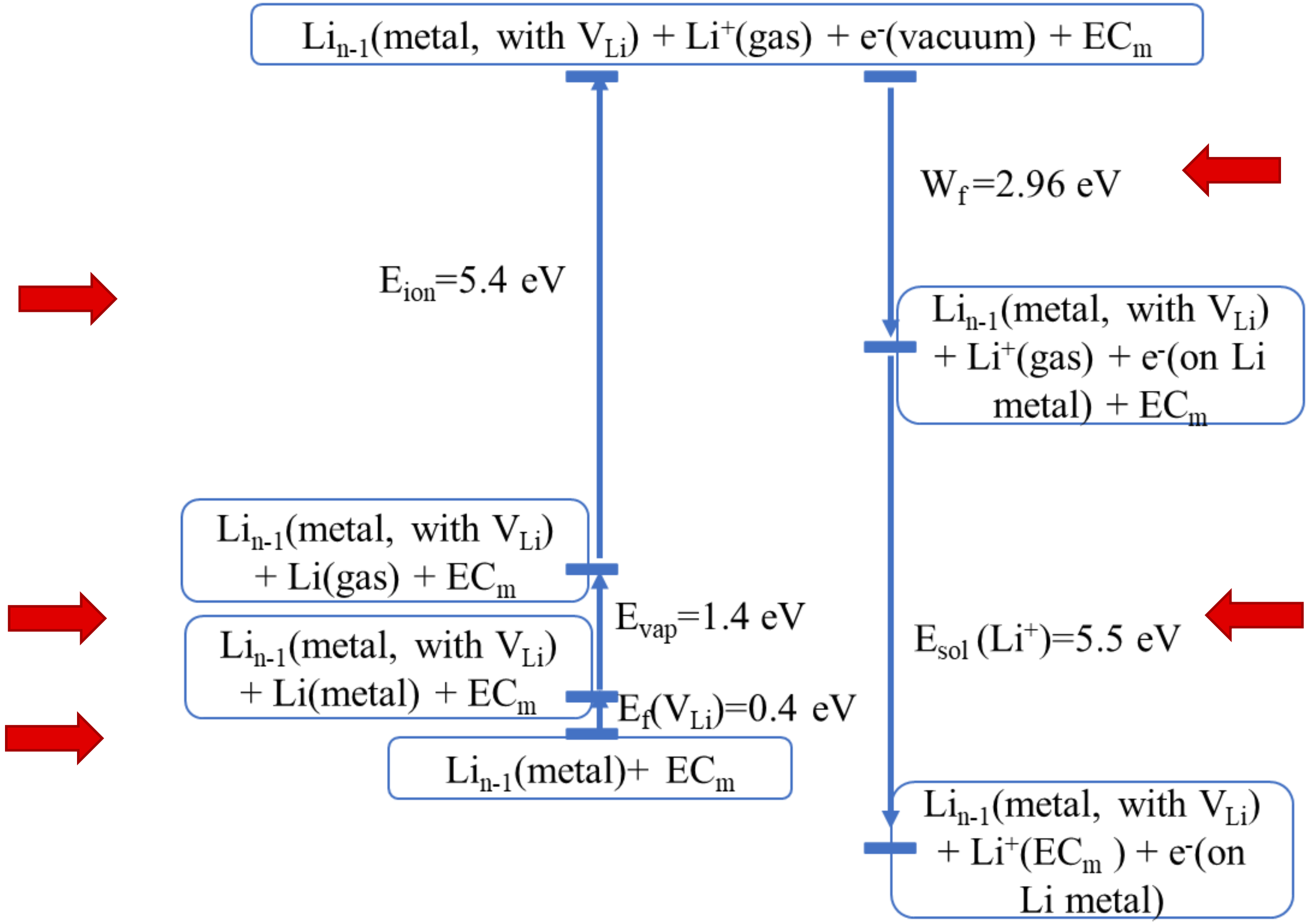
Electrochemical reaction : $Li^{+}(sol) + e^{-} \rightarrow Li^{0}$

$$\Delta G^{o} \approx \Delta U^{o} = \text{oxidized state} - \text{reduced state}$$

$Li^{0}(gas) \rightarrow e^{-} + Li^{+}(gas)$



Modified Born-Haber cycle



Li_{n-1}(metal, with V_{Li}) + Li^{+}(gas) + e^{-}(vacuum) + EC_m

W_f=2.96 eV

E_{ion}=5.4 eV

Li_{n-1}(metal, with V_{Li}) + Li^{+}(gas) + e^{-}(on Li metal) + EC_m

Li_{n-1}(metal, with V_{Li}) + Li(gas) + EC_m

E_{vap}=1.4 eV

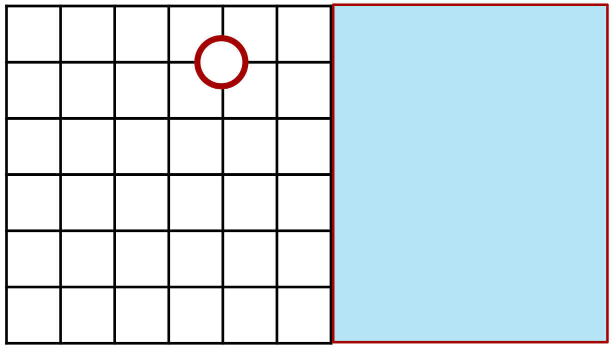
E_{sol} (Li^{+})=5.5 eV

Li_{n-1}(metal, with V_{Li}) + Li(metal) + EC_m

$E_f(V_{Li})$=0.4 eV

Li_{n-1}(metal)+ EC_m

Li_{n-1}(metal, with V_{Li}) + Li^{+}(EC_m) + e^{-}(on Li metal)

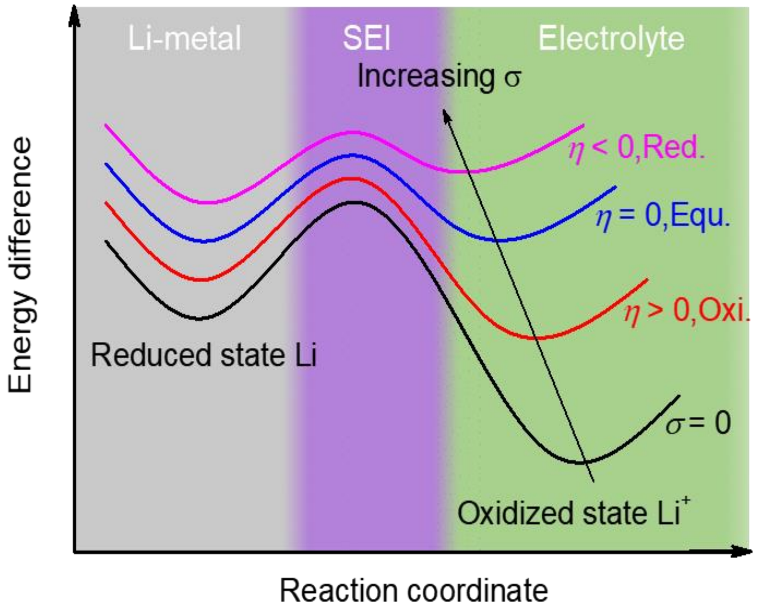


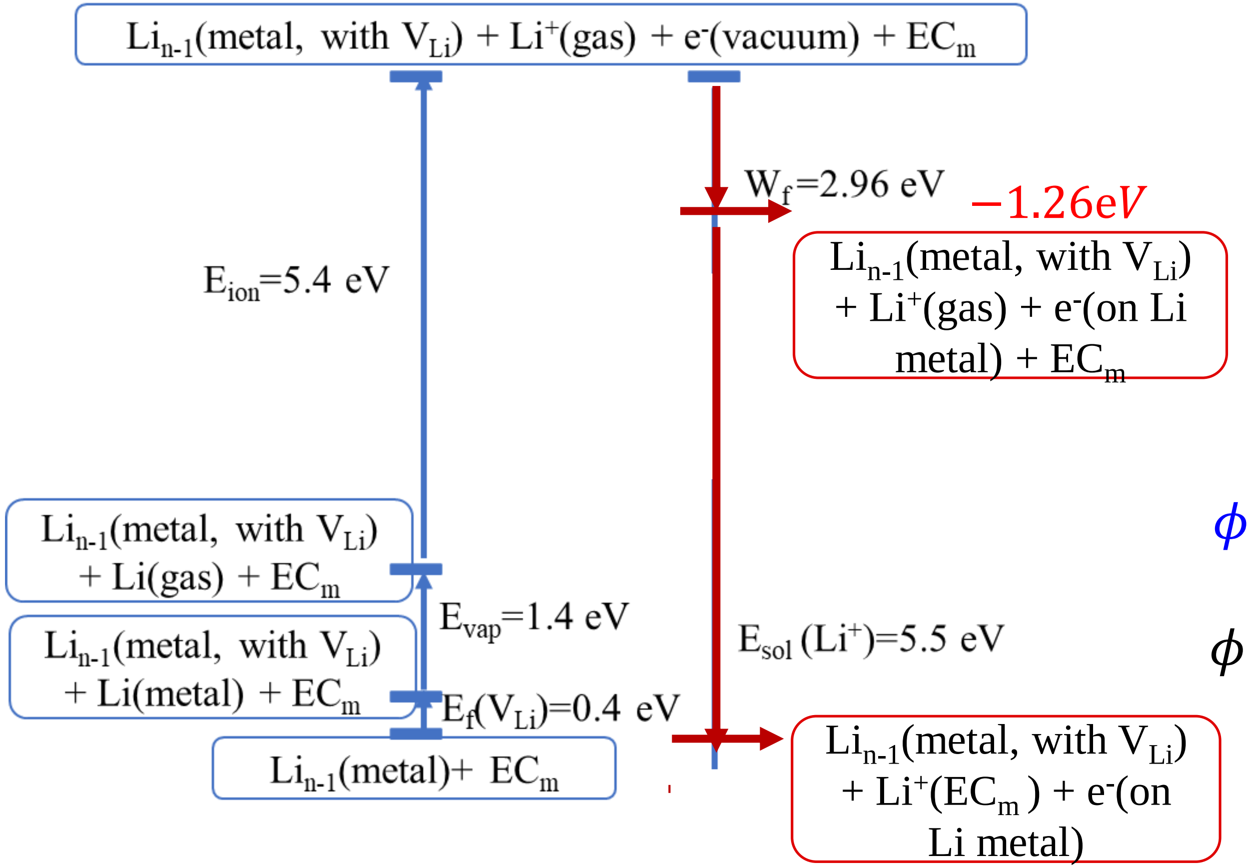
$$\Delta G^{0} = -E_f(V_{Li}) - E_{vap} - E_{ion} + W_f + E_{sol}(Li^{+})$$

Finding the Electrochemical Equilibrium

Electrochemical reaction : $Li^{+}(sol) + e^{-} \rightarrow Li^{0}$

$$\Delta G^{o} \approx \Delta E^{o} = \text{oxidized state} - \text{reduced state}$$





Li_{n-1}(metal, with V_{Li}) + Li^{+}(gas) + e^{-}(vacuum) + EC_m

W_f=2.96 eV

$-1.26eV$

Li_{n-1}(metal, with V_{Li}) + Li^{+}(gas) + e^{-}(on Li metal) + EC_m

E_{ion}=5.4 eV

Li_{n-1}(metal, with V_{Li}) + Li(gas) + EC_m

E_{vap}=1.4 eV

E_{sol} (Li^{+})=5.5 eV

Li_{n-1}(metal, with V_{Li}) + Li(metal) + EC_m

$E_f(V_{Li})$=0.4 eV

Li_{n-1}(metal)+ EC_m

Li_{n-1}(metal, with V_{Li}) + $Li^{+}(EC_m)$ + e^{-}(on Li metal)

$$\phi^{0} = -\frac{\Delta G^{0}}{zF}$$

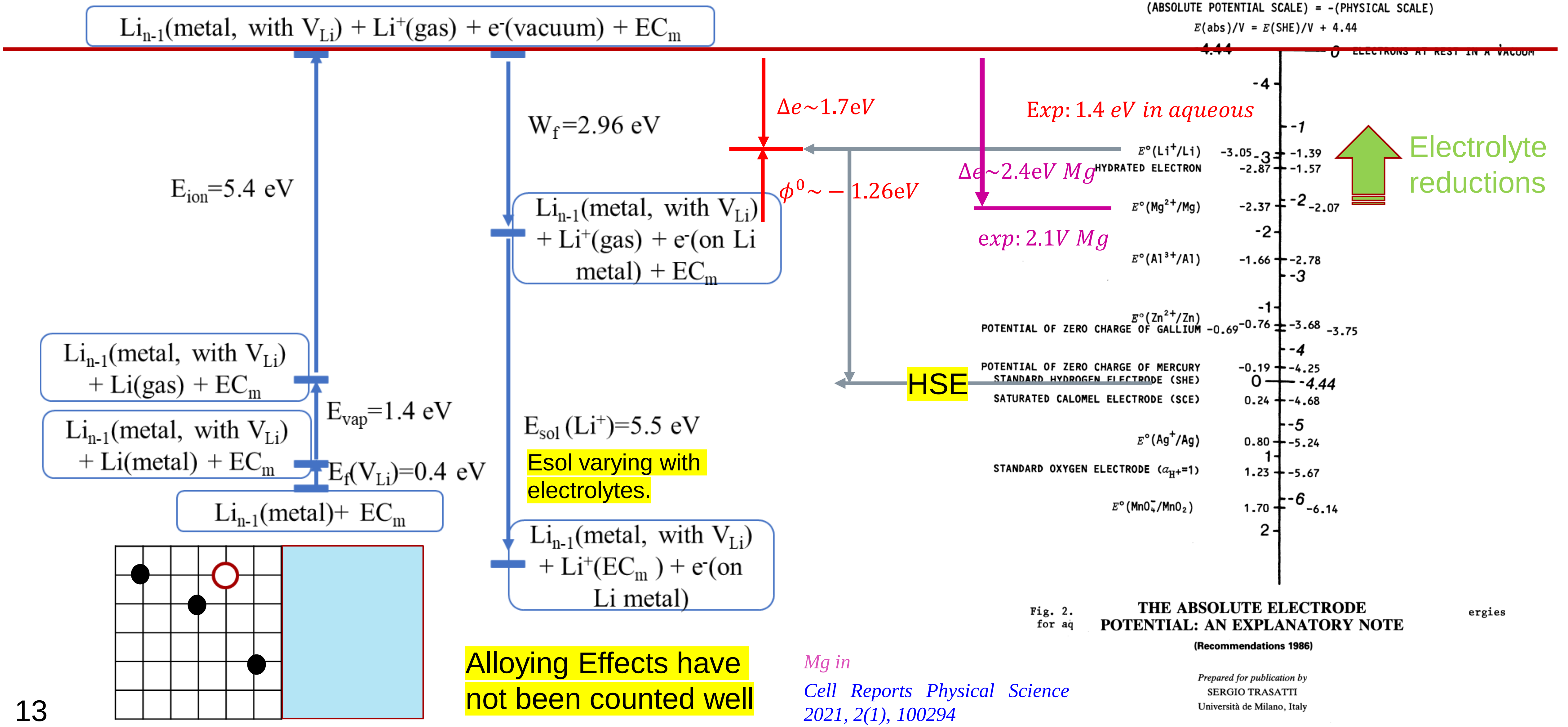
$$\phi^{0} \sim -1.26\ V$$

$$\Delta G^{o} + zF\phi^{o} - RT\ln a_{M^{z+}} = 0$$

$$\Delta G^{0} = -E_f(V_{Li}) - E_{vap} - E_{ion} + W_f + E_{sol}(Li^{+})$$

Varying both electrode (alloying) and electrolytes

e^- in Vacuum (+4.44 vs. SHE, +1.4 vs. Li+/Li in aqueous, +5.07 vs. Fc+/Fc)



Li_{n-1}(metal, with V_{Li}) + Li^+(gas) + e^-(vacuum) + EC_m

E_{ion}=5.4 eV

W_f=2.96 eV

Li_{n-1}(metal, with V_{Li}) + Li^+(gas) + e^-(on Li metal) + EC_m

Li_{n-1}(metal, with V_{Li}) + Li(gas) + EC_m

E_{vap}=1.4 eV

Li_{n-1}(metal, with V_{Li}) + Li(metal) + EC_m

$E_f(V_{Li})$=0.4 eV

Li_{n-1}(metal)+ EC_m

E_{sol} (Li^+)=5.5 eV

Esol varying with electrolytes.

Li_{n-1}(metal, with V_{Li}) + Li^+(EC_m) + e^-(on Li metal)

$\Delta e \sim 1.7eV$

$\phi^0 \sim -1.26eV$

$Exp: 1.4\ eV\ in\ aqueous$

$\Delta e \sim 2.4eV\ Mg$

$exp: 2.1V\ Mg$

HSE

Electrolyte reductions

THE ABSOLUTE ELECTRODE POTENTIAL: AN EXPLANATORY NOTE

(Recommendations 1986)

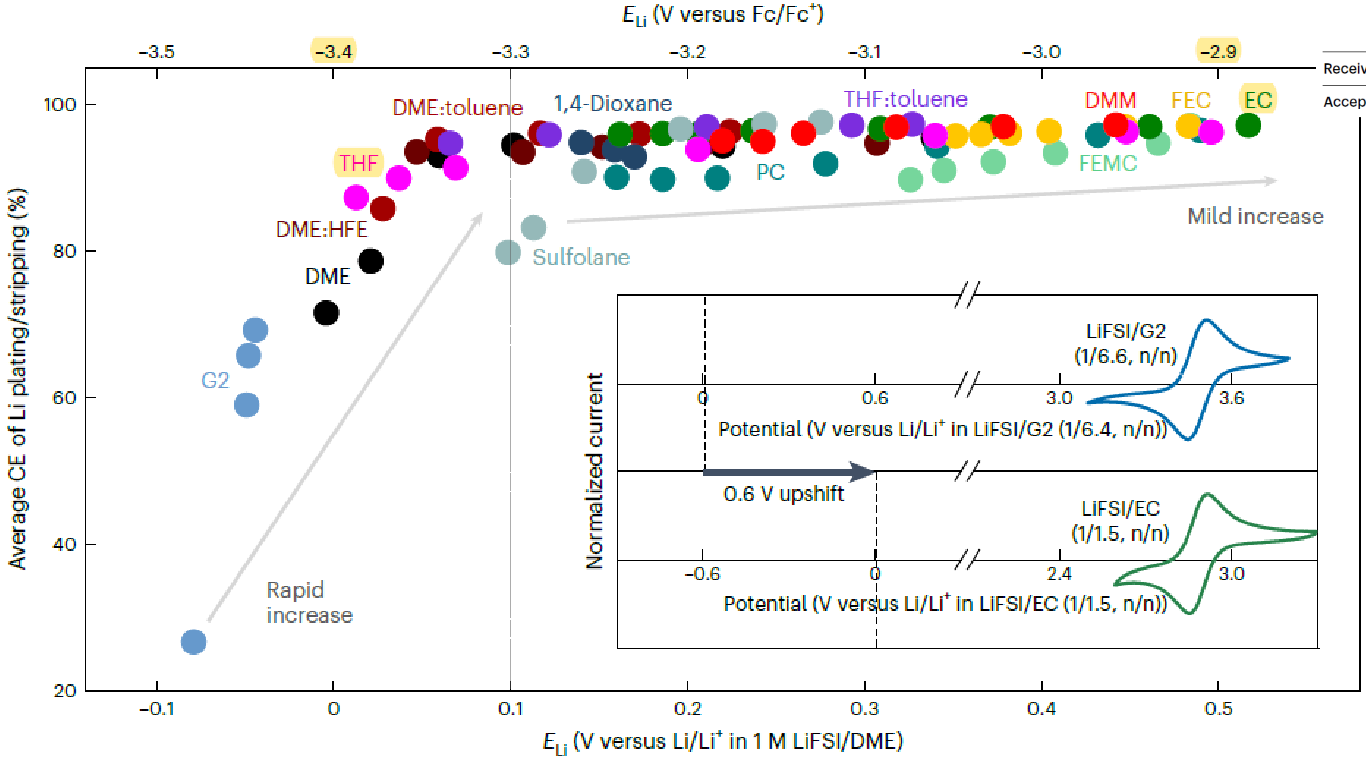
Prepared for publication by
SERGIO TRASATTI
Università de Milano, Italy

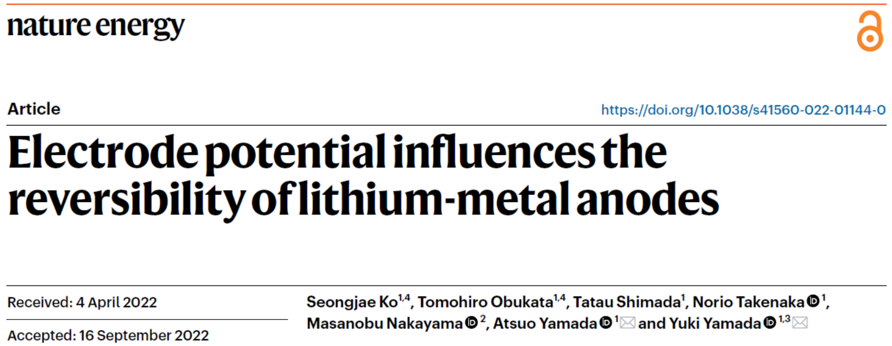
Alloying Effects have not been counted well

Mg in

Cell Reports Physical Science 2021, 2(1), 100294

The intertwined two charge transfer reactions




nature energy

Article https://doi.org/10.1038/s41560-022-01144-0

Electrode potential influences the reversibility of lithium-metal anodes

Received: 4 April 2022

Accepted: 16 September 2022

Seongjae Ko[1,4], Tomohiro Obukata[1,4], Tatau Shimada[1], Norio Takenaka[1], Masanobu Nakayama[2], Atsuo Yamada[1] and Yuki Yamada[1,3]

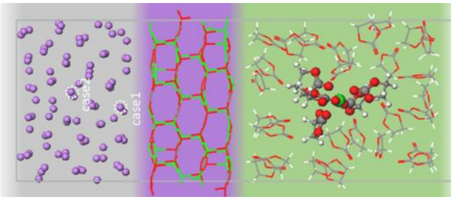
Li-deposition voltage is electrolyte dependent

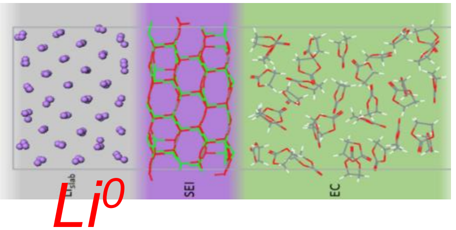
→ electric potential (surface charge) impacts SEI formation and CE.

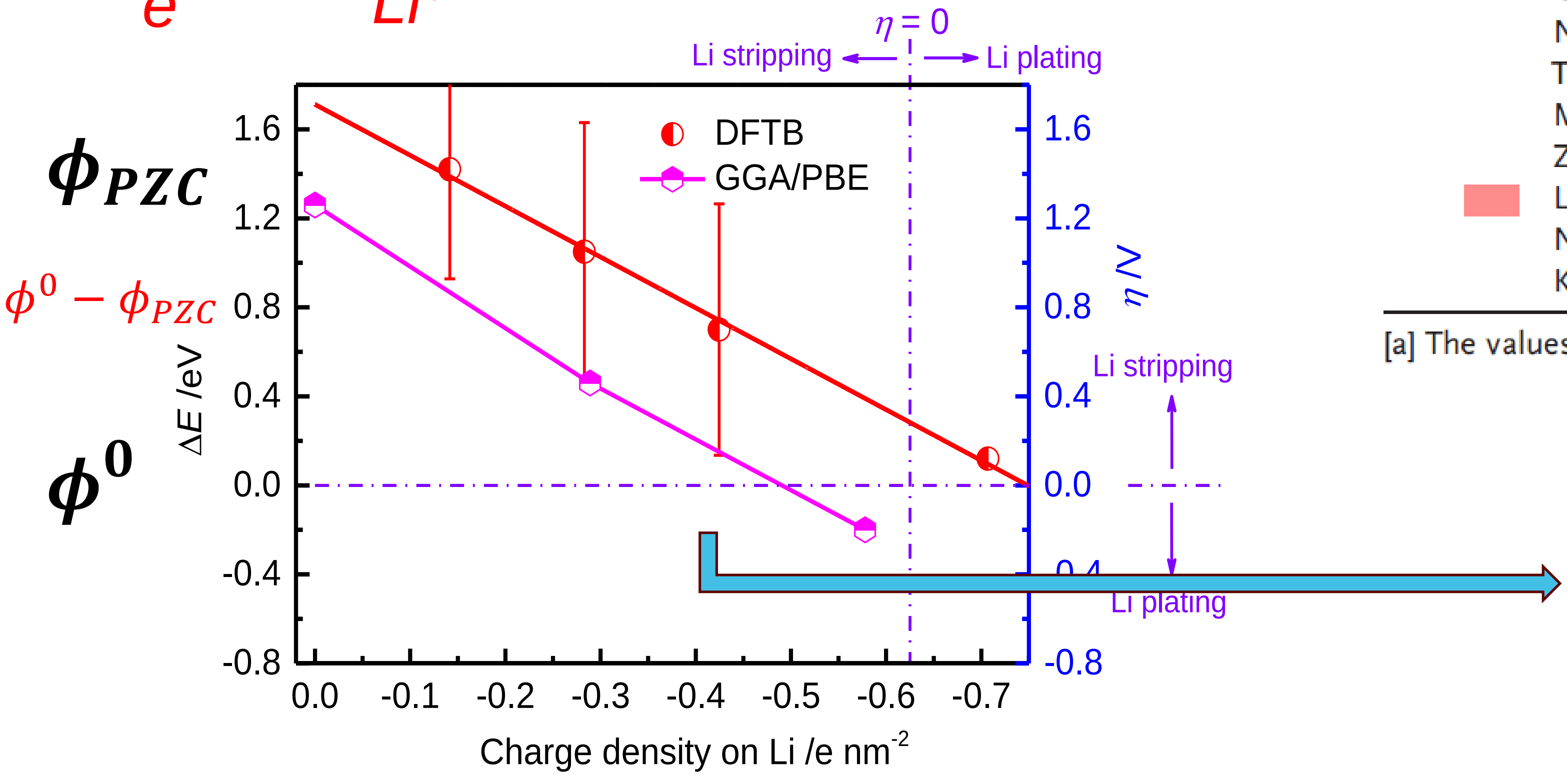
Finding the Equilibrium State when Li^0/Li^+ is at 0 Volt

Electrochemical reaction

$$Li^+(sol) + e^- \rightarrow Li^0$$







Li and Qi, Energy Environ. Sci., 2019, 12, 1286-1295

E. Santos and W. Schmickler, Angew. Chem. Int. Ed. 2021, 60, 5876

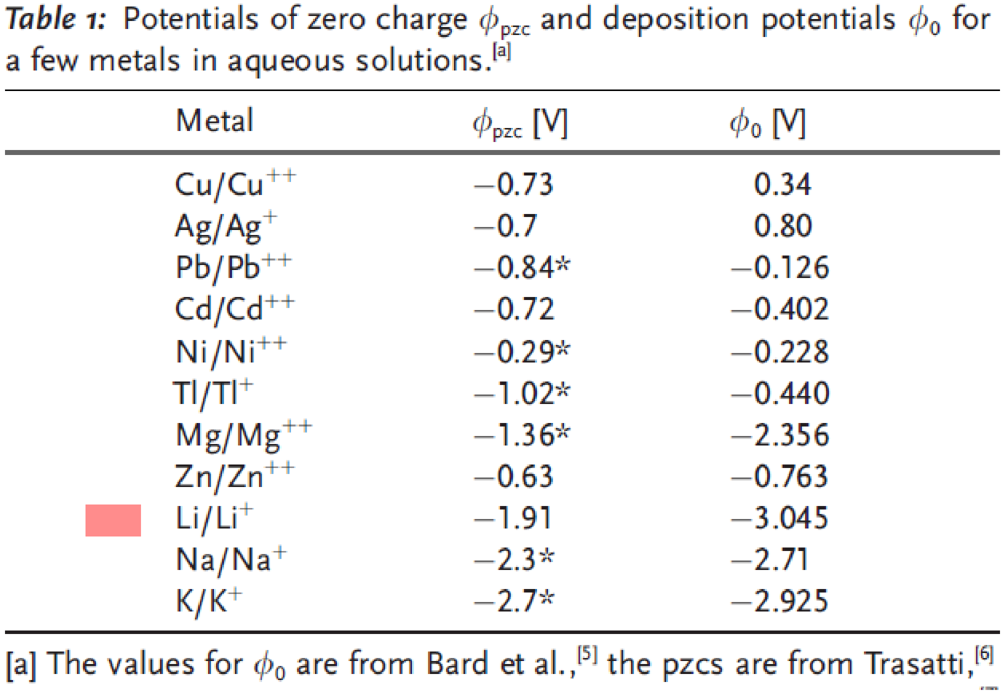
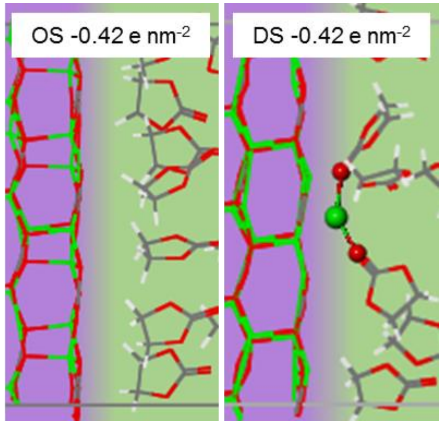


Table 1: Potentials of zero charge ϕ_{pzc} and deposition potentials ϕ_0 for a few metals in aqueous solutions.[a]

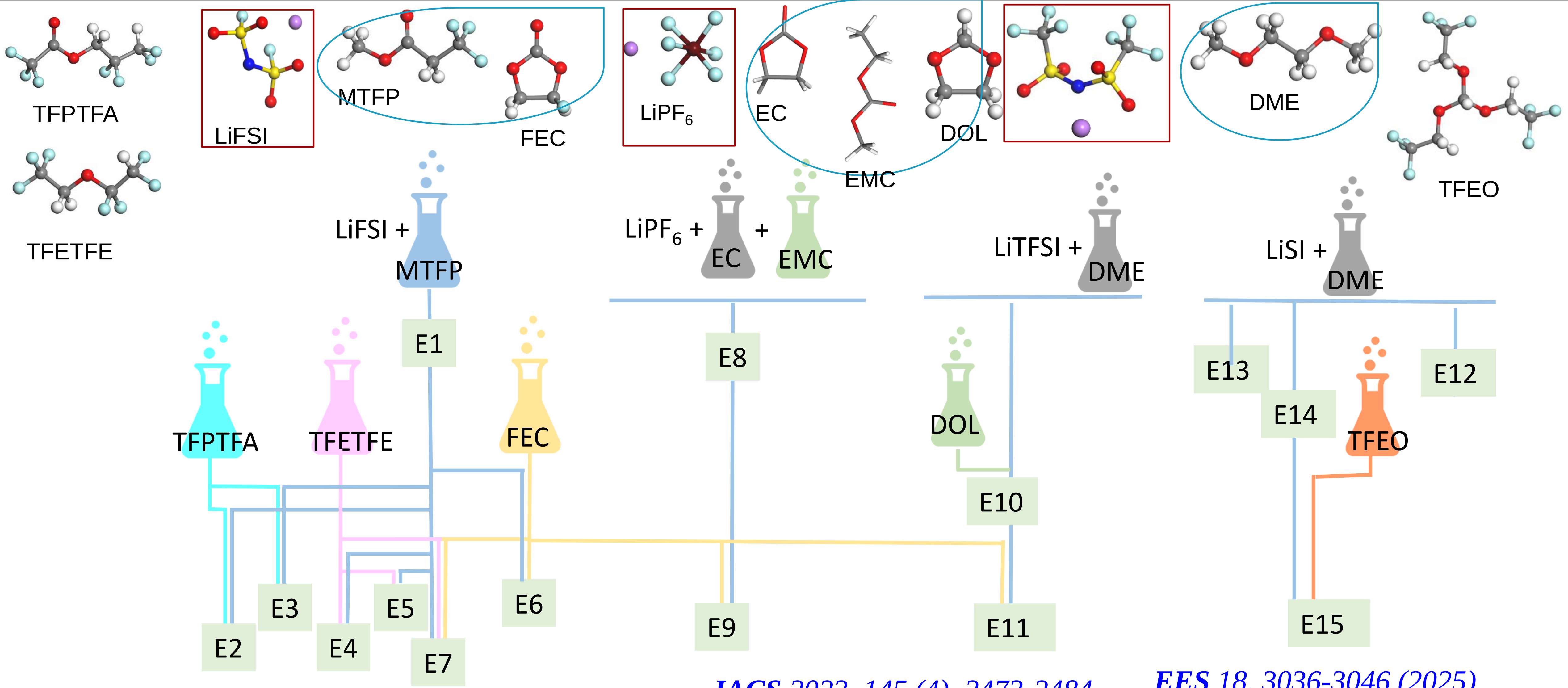
Metal	ϕ_{pzc} [V]	ϕ_0 [V]
Cu/Cu^{++}	−0.73	0.34
Ag/Ag^+	−0.7	0.80
Pb/Pb^{++}	−0.84*	−0.126
Cd/Cd^{++}	−0.72	−0.402
Ni/Ni^{++}	−0.29*	−0.228
Tl/Tl^+	−1.02*	−0.440
Mg/Mg^{++}	−1.36*	−2.356
Zn/Zn^{++}	−0.63	−0.763
🟥 Li/Li^+	−1.91	−3.045
Na/Na^+	−2.3*	−2.71
K/K^+	−2.7*	−2.925

[a] The values for ϕ_0 are from Bard et al.,[5] the pzcs are from Trasatti,[6]



Electrolyte Design: Chemical, Composition, Structure

Ref. to Lecture by Nidhi Rajput



J. Phys. Chem. *Lett.* 14, 7718−7731 (2023)

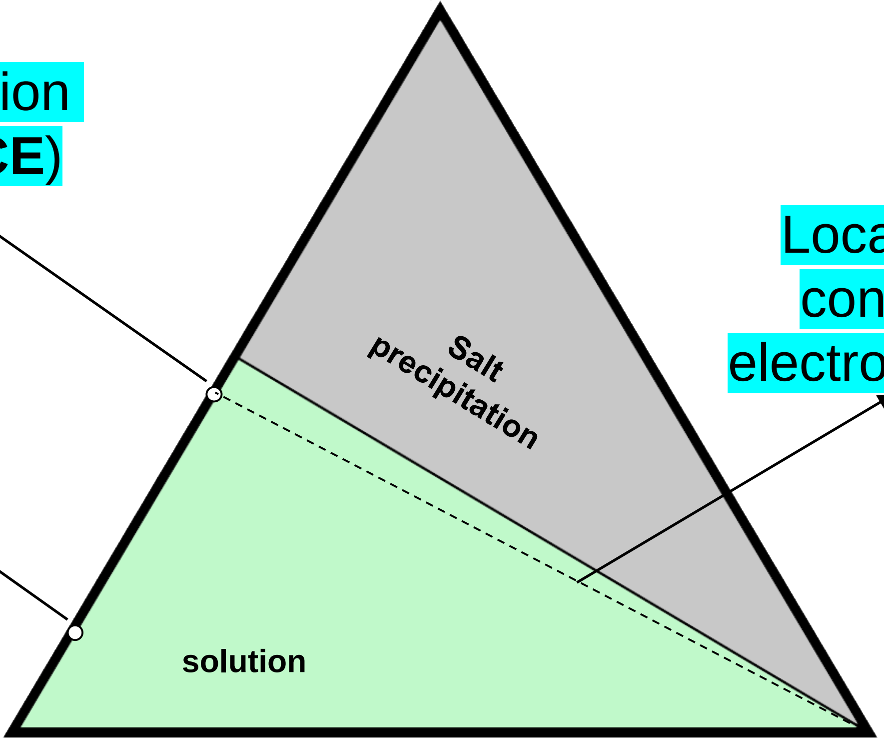
… …

JACS *2023, 145 (4), 2473-2484*

EES *18, 3036-3046 (2025)*

Nature Mat. *22, 1531–1539 (2023)*

Large Design Space (chemistry, composition, structure) of electrolytes



Salt: $LiPF_6$, LiTFSI, LiFSI

High-concentration electrolytes (**HCE**)

Low-concentration electrolytes (**LCE**) e.g. 1M

Localized high-concentration electrolytes (**LHCE**)

Solvent:
Carbonate based: EC, EMC
Ether based: DOL, DME, MFTP
Fluorinated: e.g. FEC …

Diluent is introduced to form LHCE:

TFEO, TFPTFA, TFETFE

Co-design of Electrode and Electrolyte

(e.g. what worked for the graphite electrode doesn’t work for the Li-metal electrode)

Challenges for next-generation electrolytes for high energy electrode (e.g. Li, Na, Zn, Mg, ….)

SEI; Ion conductivity, viscosity, wettability, cost, safety, …

DFT ⇌ MD → Phase Field for temporal and spatial SEI Evolution

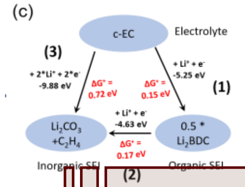
Energy Environ. Sci., (2025)
18, 7541-7554

Kinetics

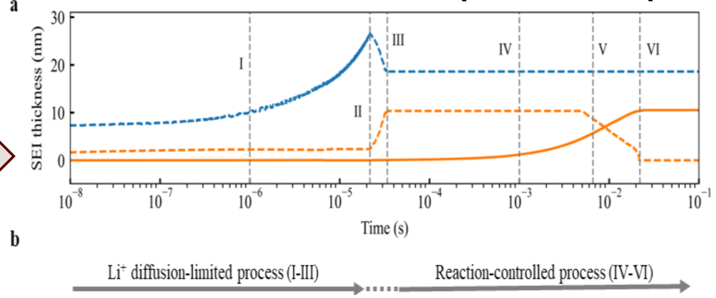
Marcus's Theory, Reaction kinetics

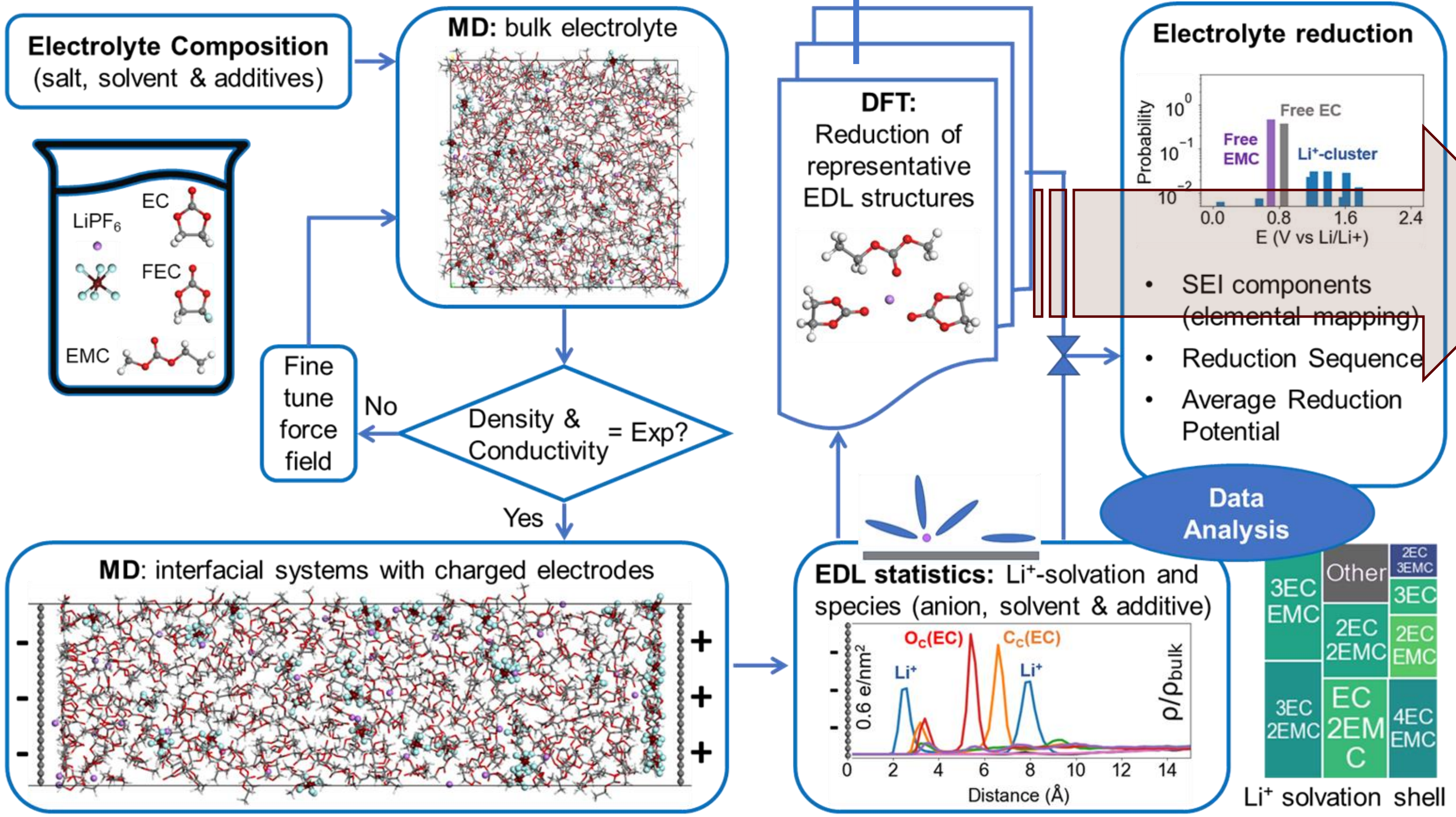
Simplification

Phase Field Modeling



SEI thickness and composition (time)





Electrolyte Composition (salt, solvent & additives)

MD: bulk electrolyte

DFT: Reduction of representative EDL structures

Electrolyte reduction

- SEI components (elemental mapping)
- Reduction Sequence
- Average Reduction Potential

Fine tune force field

Density & Conductivity = Exp?

No

Yes

MD: interfacial systems with charged electrodes

EDL statistics: Li⁺-solvation and species (anion, solvent & additive)

Data Analysis

Li⁺ solvation shell

EC as an idealized electrolyte

Focused on
Thermodynamics
Equilibrium assumption

Validate the model in LCE:
- two types of solvents
- Role of FEC additives

LHCE
- Micelle-like structures
- Composition

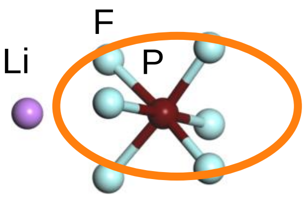
Reduction of Realistic Electrolytes within the EDL

Qisheng Wu

- What’s the electrolyte structure near the charged interface (within the electrical double layer)?
- How do they decompose and contribute to the beneficial LiF phase? (an electronically passivating layer)

Salt: 1M

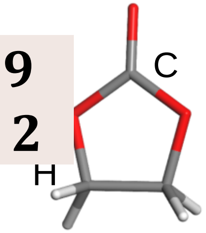
LiPF$_6$



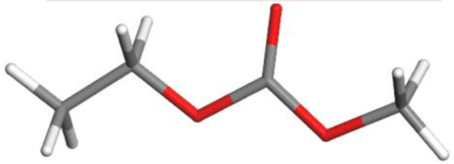
Solvent: EC:EMC=3:7

(Strong solvent)

$$\varepsilon_r(EC) = 89$$
$$\varepsilon_r(EMC) = 2$$



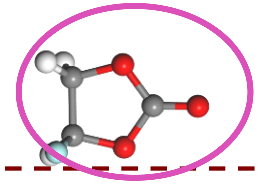
EC (ethylene carbonate)



EMC (Ethyl methyl carbonate)

Additive: <~ 10%

FEC

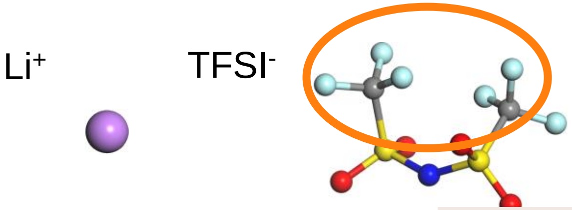


For Graphite Electrode

$$\varepsilon_r(FEC) = 79.7$$

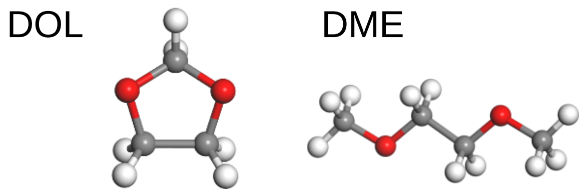
● Li ● N ● O ● F
● S ● C ● H ● P

Salt: 1M



Solvent: DOL:DME = 6:1

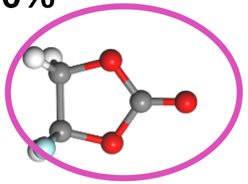
(weak solvent)



Relative permittivity
$$\varepsilon_r(DOL, DME) = 7$$

Additive: <~10%

FEC

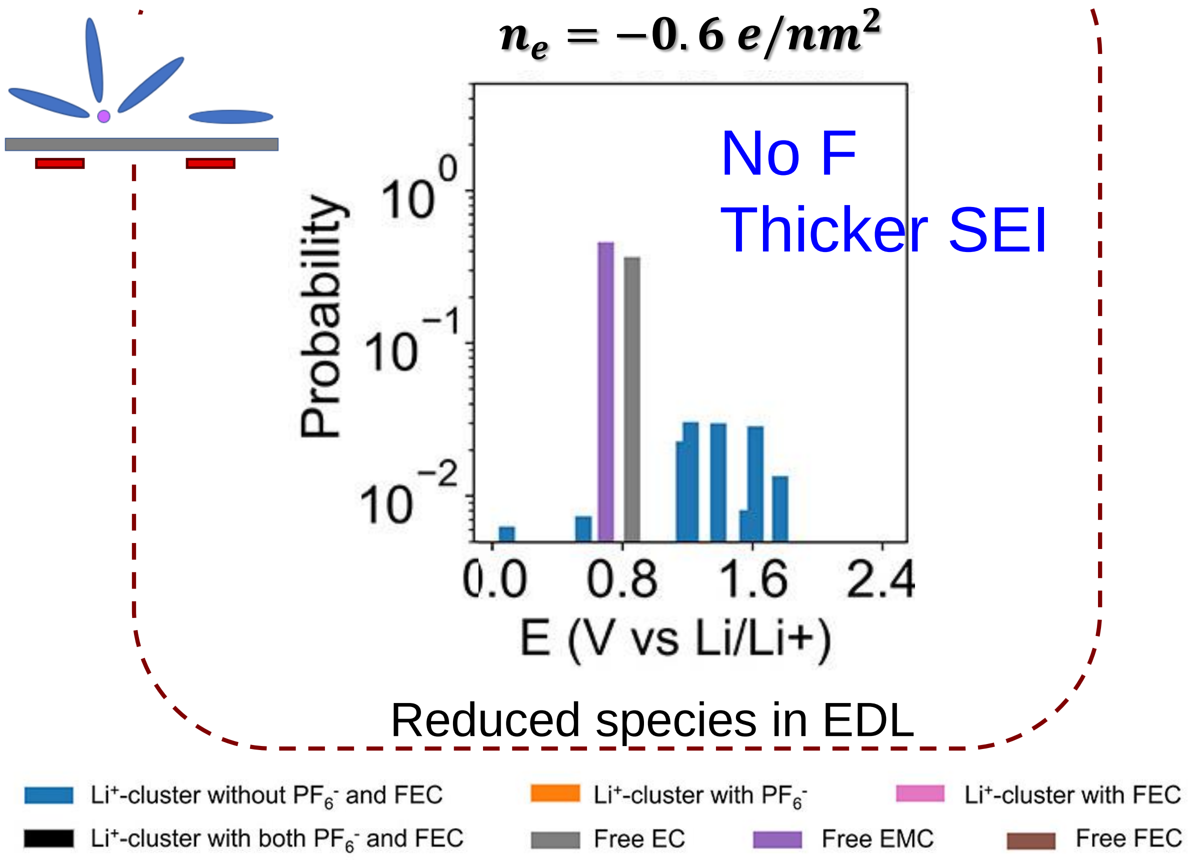


For Li-metal Electrode

Reduction of Realistic Electrolytes within the EDL

- What's the electrolyte structure near the charged interface (within the electrical double layer)?
- How do they decompose and contribute to the beneficial LiF phase?

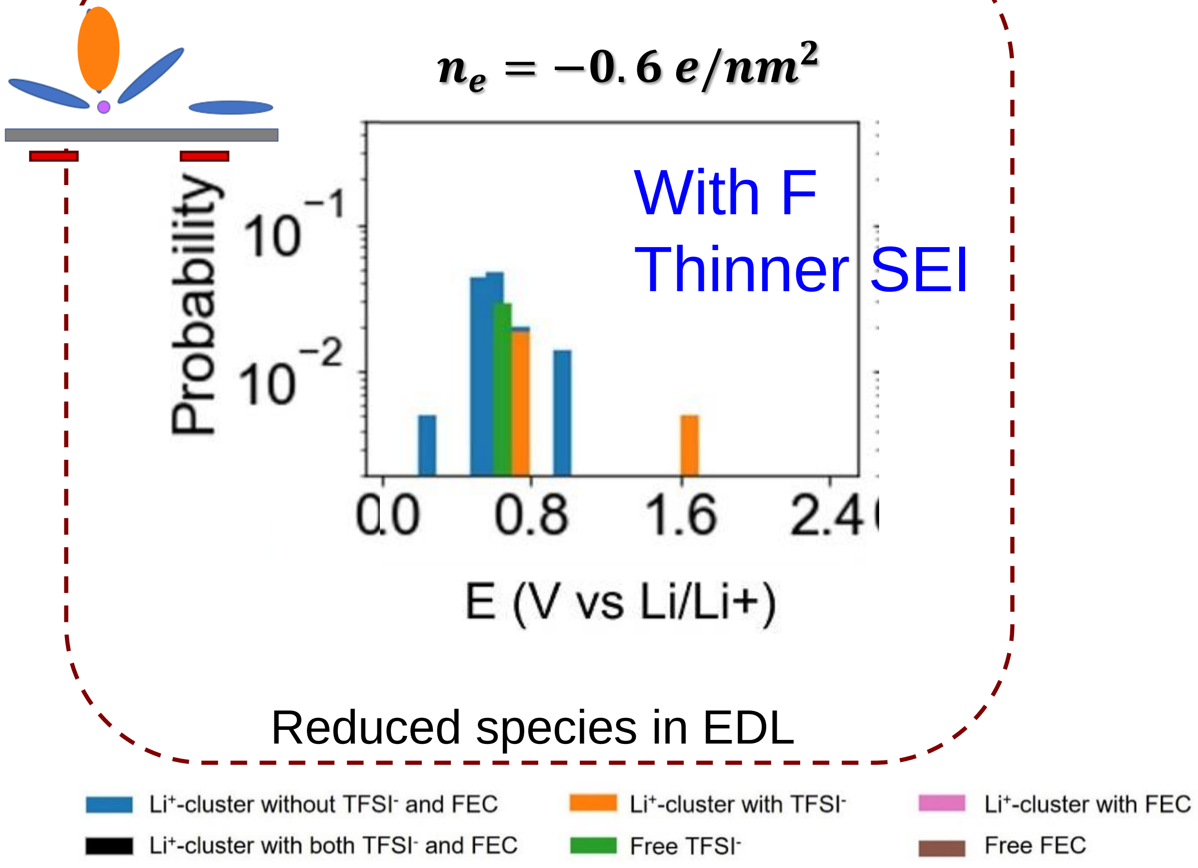
1M $LiPF_6$ in EC:EMC at 20C
stronger solvent, Well-solvated ions


$n_e = -0.6\ e/nm^2$

No F
Thicker SEI

Reduced species in EDL

1M LiTFSI in DOL:DME at 20C
Weak solvent, ions pairs


$n_e = -0.6\ e/nm^2$

With F
Thinner SEI

Reduced species in EDL

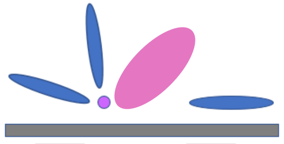
Reduction of Realistic Electrolytes within the EDL

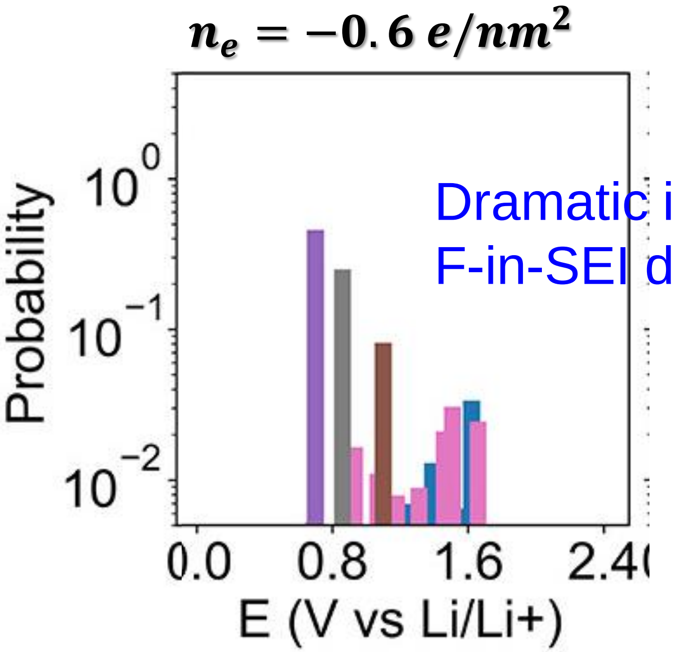
- What's the electrolyte structure near the charged interface (within the electrical double layer)?
- How do they decompose and contribute to the beneficial LiF phase?

1M $LiPF_6$ in EC:EMC at 20C
stronger solvent, Well-solvated ions

Add FEC

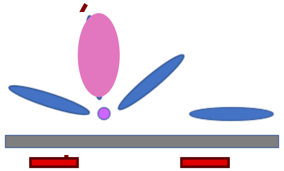
1M LiTFSI in DOL:DME at 20C
Weak solvent, ions pairs

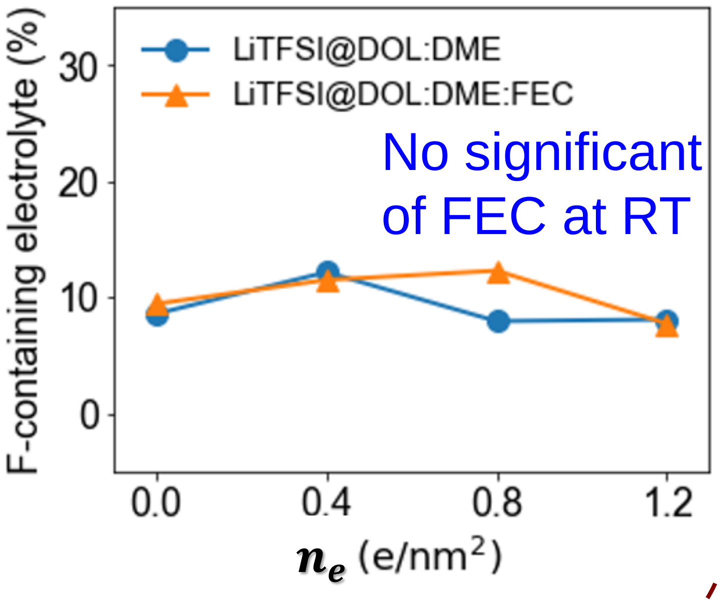




Dramatic increase of F-in-SEI due to FEC

Reduced species in EDL





No significant impact of FEC at RT

Reduced species in EDL

Sensitive to temperature

No F
Need to add FEC

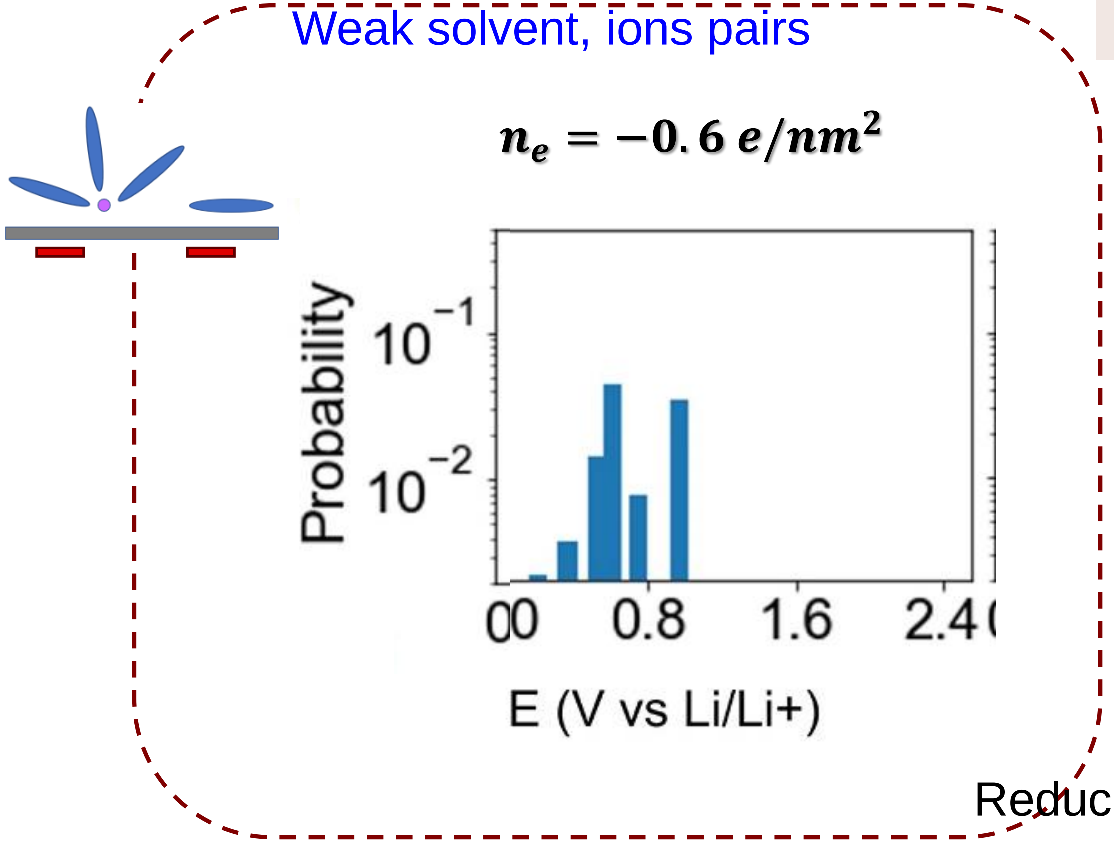
$$1/\kappa = \left(\frac{\varepsilon\varepsilon_0 kT}{2z^2e^2n^0}\right)^{1/2}$$

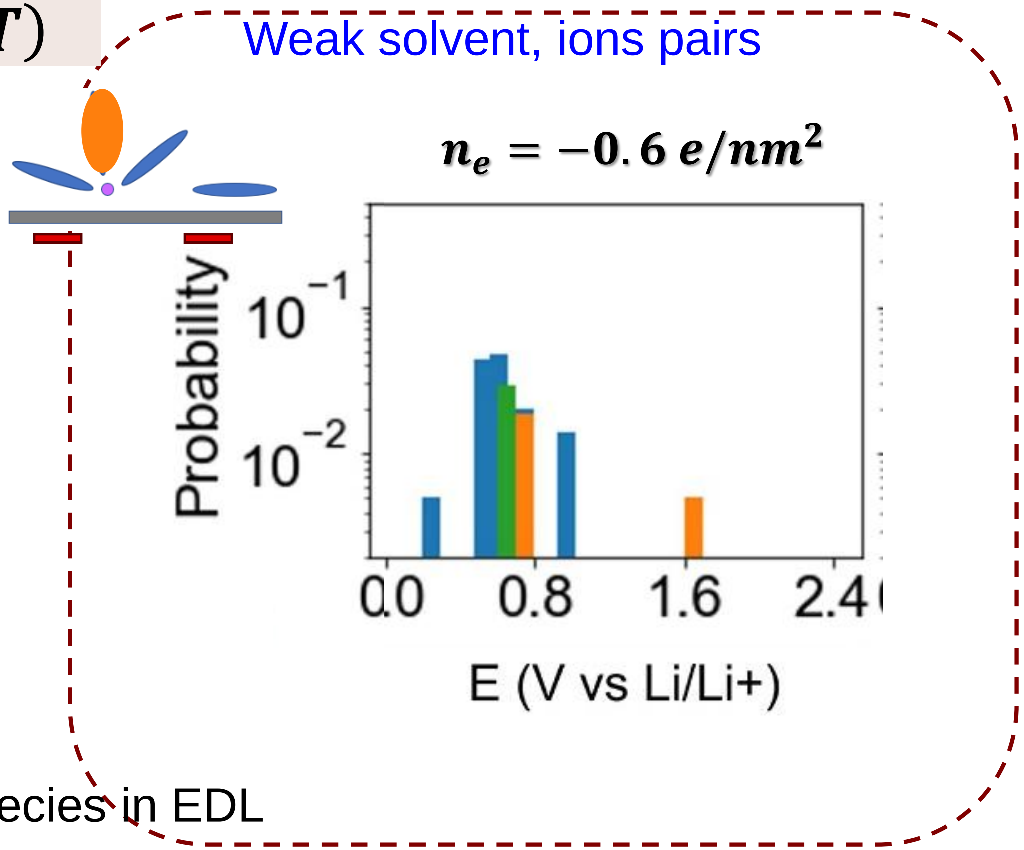
With F
No impact from FEC

1M LiTFSI in DOL:DME at -40C
Weak solvent, ions pairs

$\boldsymbol{\varepsilon_r(T)}$

1M LiTFSI in DOL:DME at 20C
Weak solvent, ions pairs





Reduced species in EDL

🟦 Li⁺-cluster without TFSI⁻ and FEC
⬛ Li⁺-cluster with both TFSI⁻ and FEC
🟧 Li⁺-cluster with TFSI⁻
🟩 Free TFSI⁻
🟪 Li⁺-cluster with FEC
🟫 Free FEC

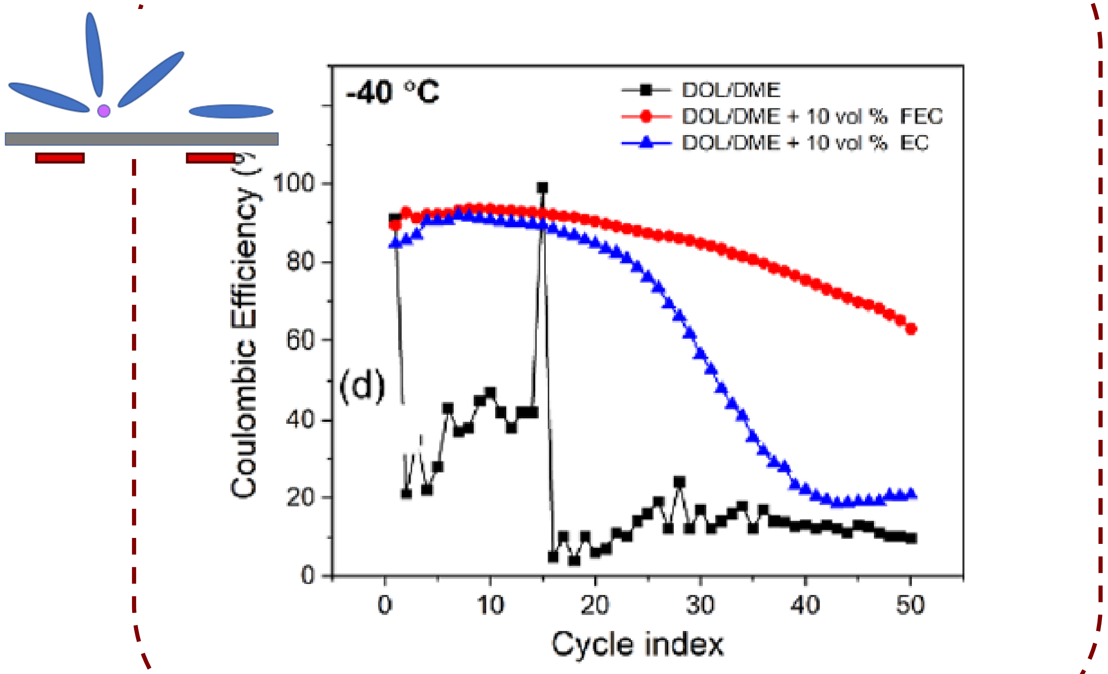
Sensitive to temperature

No F
Need to add FEC

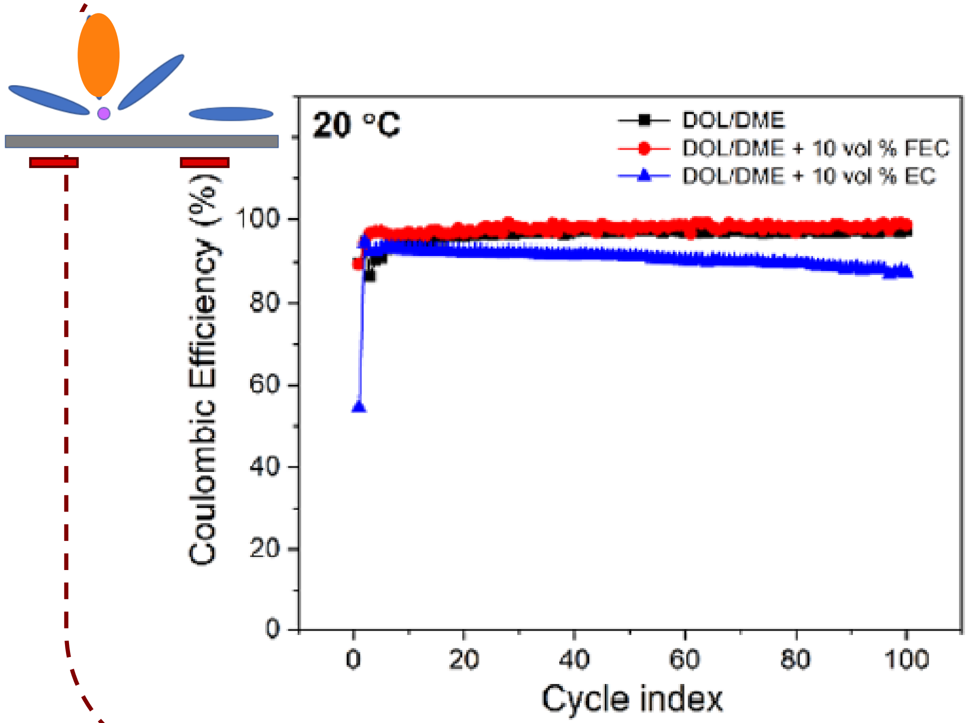
- This is consistent with the trend given by XPS measurement for F, C and O content in SEI

With F
No impact from FEC

1M LiTFSI in DOL:DME at -40C
Weak solvent, ions pairs



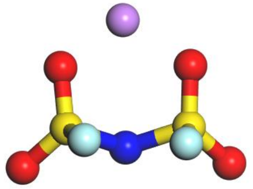
1M LiTFSI in DOL:DME at 20C
Weak solvent, ions pairs



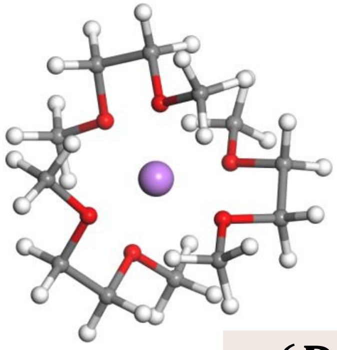
AC Thenuwara, … Y. Qi, M.T. McDowell, ***ACS Energy Lett.*** *2020, 5, 2411−2420*
Q. Wu, M.T. McDowell, Yue Qi, ***JACS*** *2023, 145 (4), 2473-2484*

high-concentration and localized high-concentration electrolytes (LHCE)

● Li ● N ● O ● F ● S ● C ● H

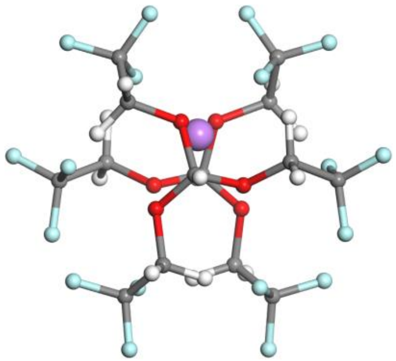


Li^+ - FSI^-



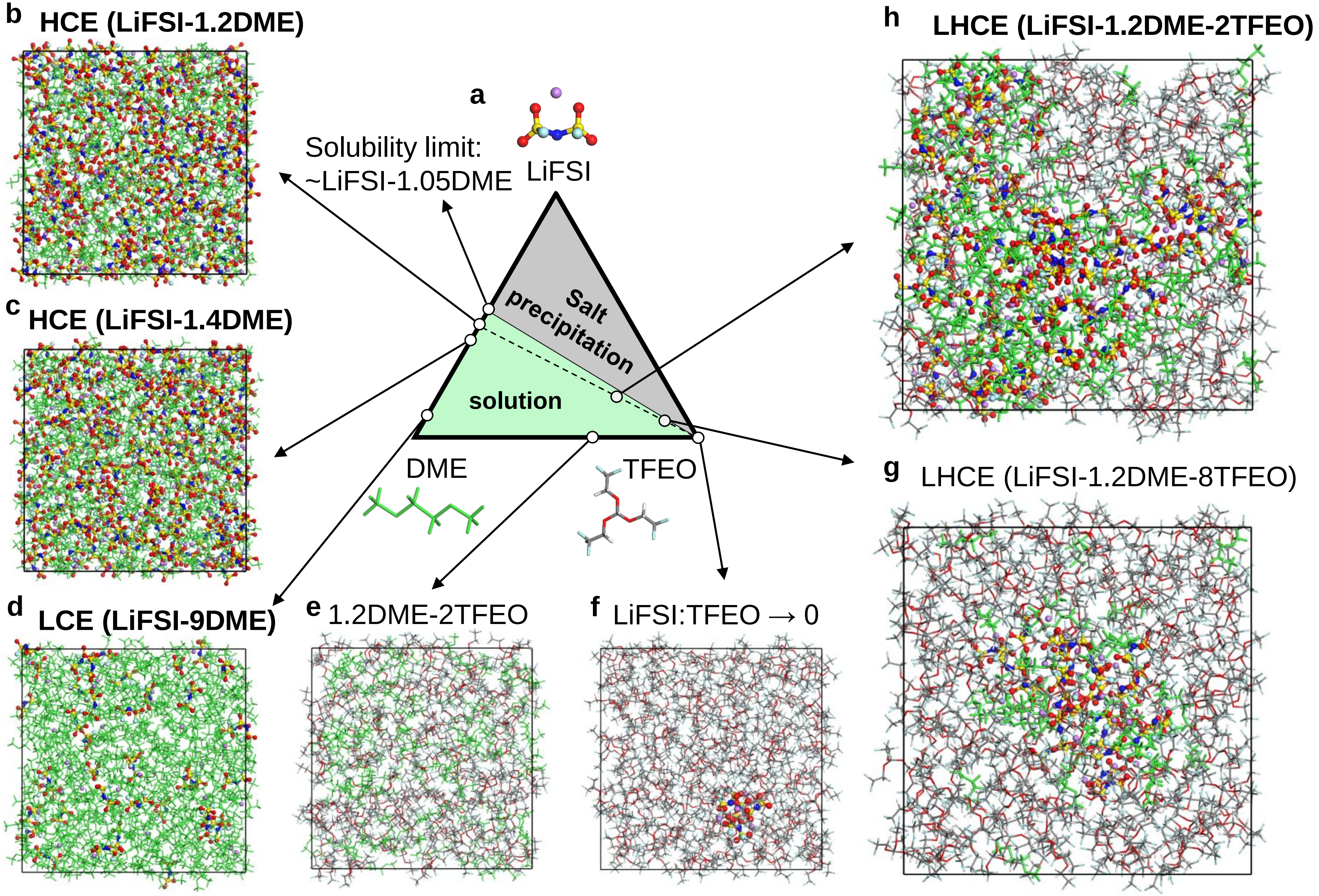
Li^+ - 3DME

$\varepsilon_r(DME) = 7.2$



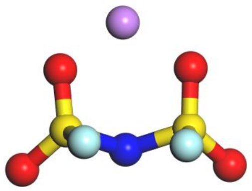
Li^+ - 2TFEO

$\varepsilon_r(TFEO) = 7.1$

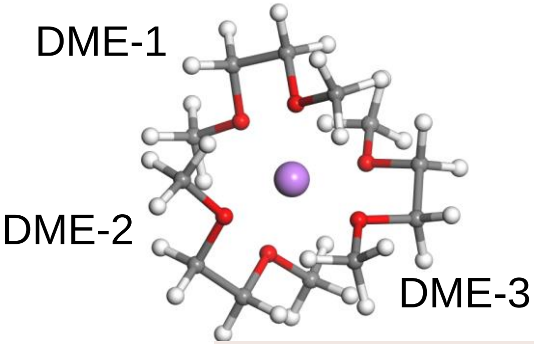


What makes DME a solvent ($\varepsilon_r = 7.2$) but not TFEO ($\varepsilon_r = 7.1$)?

Li$^+$ - FSI$^-$



Li$^+$ - 3DME



$\boldsymbol{\varepsilon_r(DME) = 7.2}$

Li$^+$ - 2TFEO

TFEO-1

TFEO-2

What makes DME a solvent (ε_r = 7.2) but not TFEO (ε_r = 7.1)?

$\boldsymbol{\varepsilon_r(TFEO) = 7.1}$

● Li ● N ● O ● F ● S ● C ● H

- The formation of different solvation shells, which are mainly driven by steric and electronic effects.
- As a result, DME has much stronger solvating ability than TFEO despite their similar dielectric constant (~7.0) [1,2]

DFT-calculated binding energies

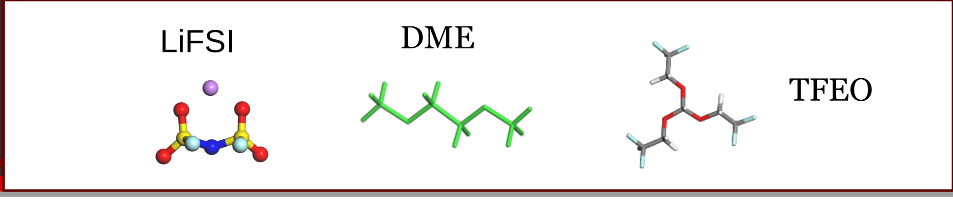
Li$^+$ - FSI$^-$	**6.07 eV**
Li$^+$ - TFEO	2.00 eV
Li$^+$ - 2TFEO	**2.89 eV**

Li$^+$ - DME	2.81 eV
Li$^+$ - 2DME	4.50 eV
Li$^+$ - 3DME	**5.39 eV**

Gaussian 09 code; M06-2X // 6-31+G**; SMD

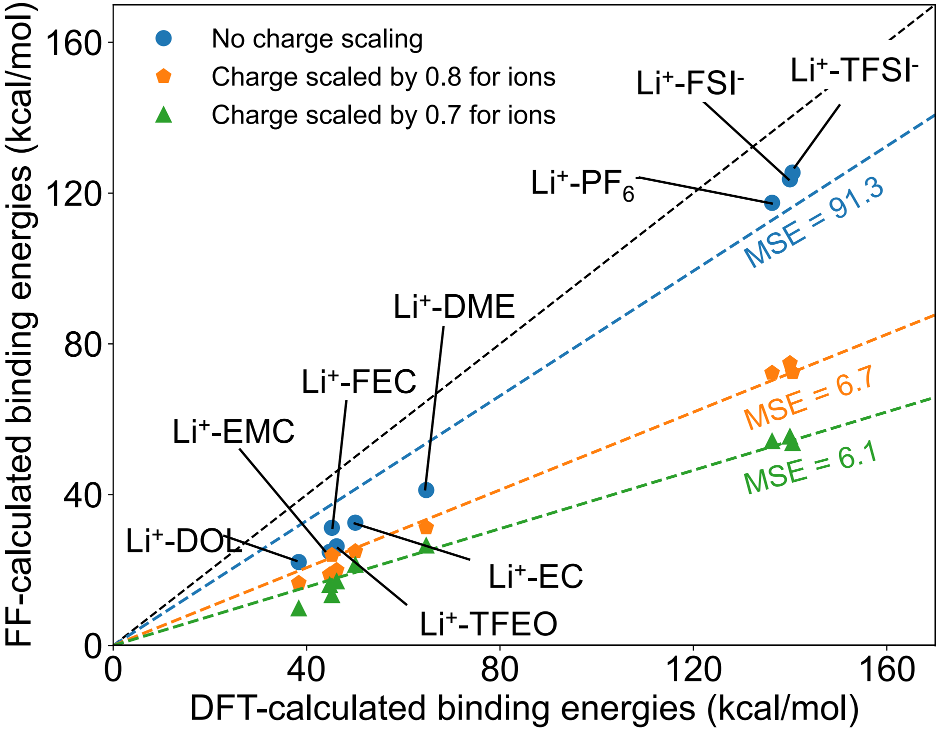
[1] Journal of Solution Chemistry 25, 1163-1173 (1996)
[2] Cao, X., Zhang, J.-G. & Xu, W. Electrolyte for Stable Cycling of Rechareable Aklali Metal and Alkali Ion Batteries. United States patent (2019).

Computational Details



Calibrate the COMPASS III force field;
Charge scale of 0.7 for salt

- Well describe electronic polarization and Li$^+$ transport
- Well describe aggregation between Li$^+$ and anions

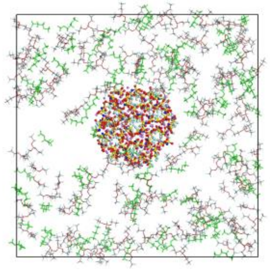


Qisheng Wu, et al. *JACS,* 145, 2473 (2023)

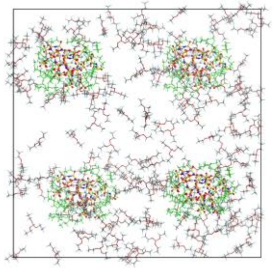
Dassault Systèmes BIOVIA, Materials Studio, 2020; Mol. Simul. 2020, 0 (0), 1–12; JCP, 1984, 81, 511–519; JCP, 1984, 81, 3684–3690.

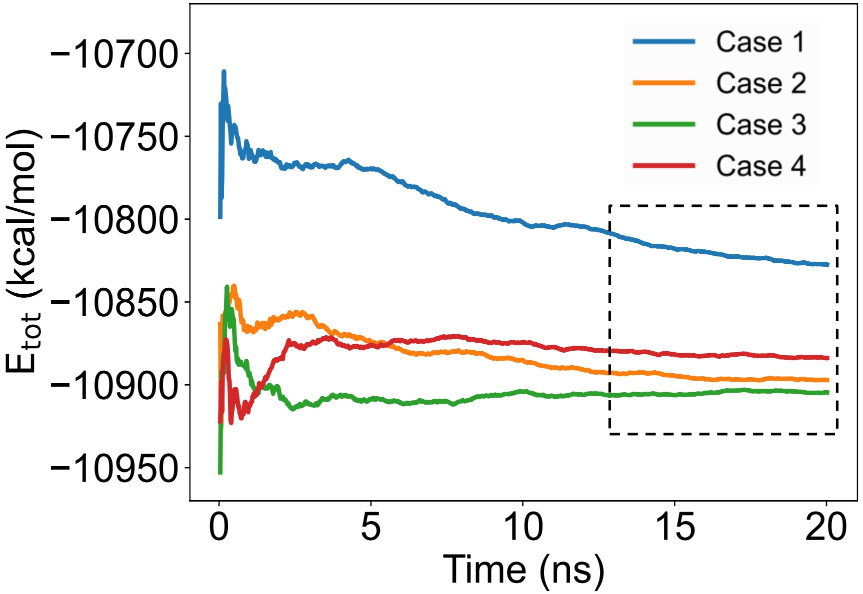
MD simulations with different initial structures to find heterogeneous structures.

Case 1: one large cluster

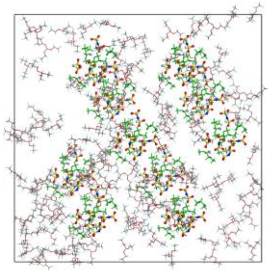


Case 2: smaller clusters

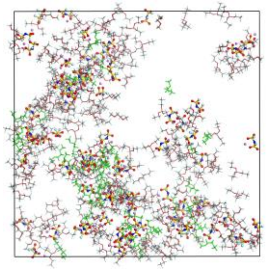




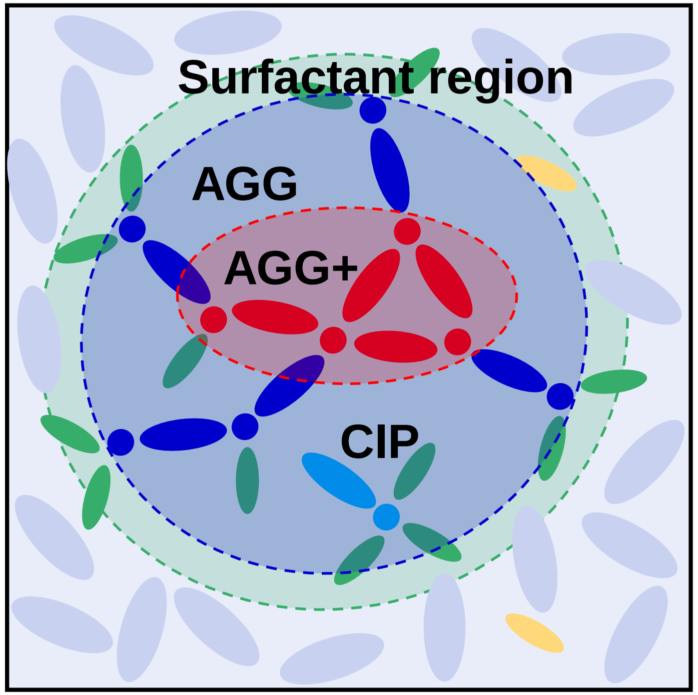
Case 3: small clusters



Case 4: randomly packed



A Unified Model for LHCE: a micelle-like structures

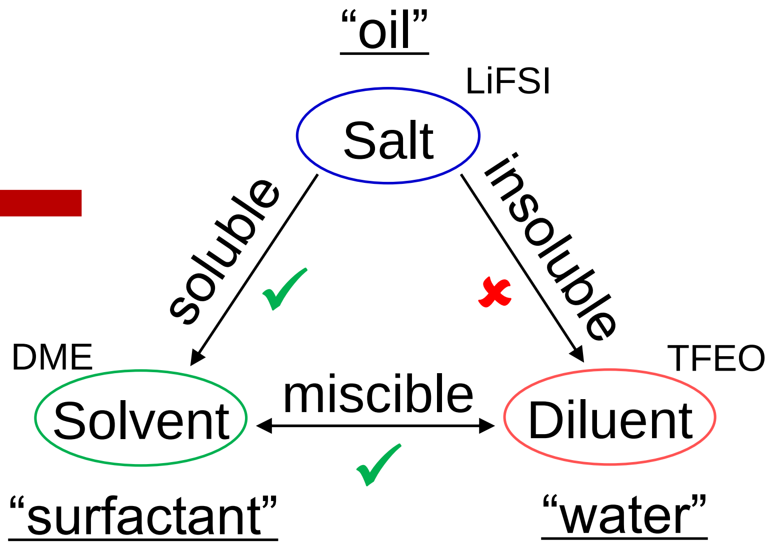


⬭ diluent ⬭ Free solvent

⬭ Li⁺ coordinated solvent

● CIP ● Aggregates (AGG)

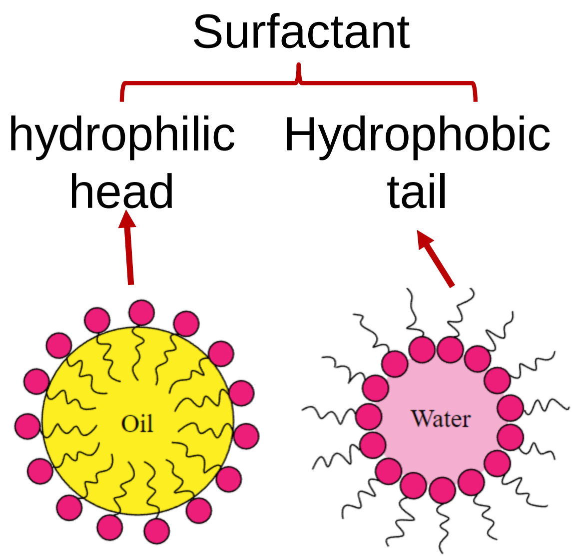
● higher coordinated aggregates (AGG+)



- Solvent acts like surfactant and forms a surfactant region
- Solvent can completely enter both salt and diluent phase
- Stable heterogenous structures
- Local salt concentration gets higher with a gradient
- A critical concentration is needed to form micelles

Micelle in microemulsion

Trans. Faraday Soc. 9, 99 (1913)



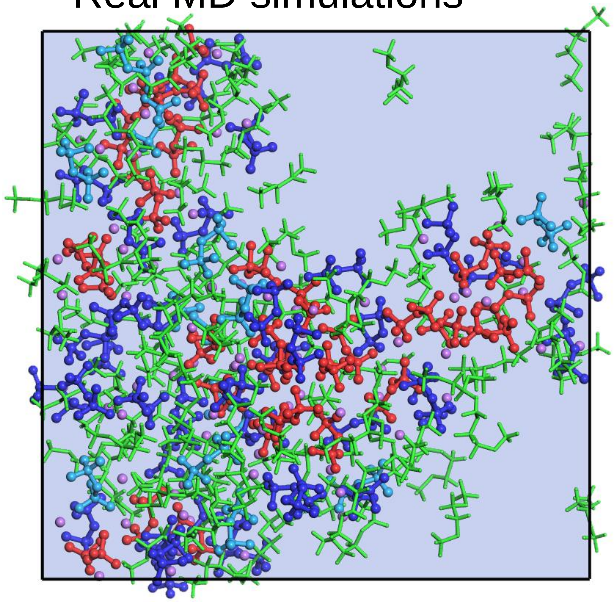
https://www.chegg.com/learn/topic/function-of-micelle

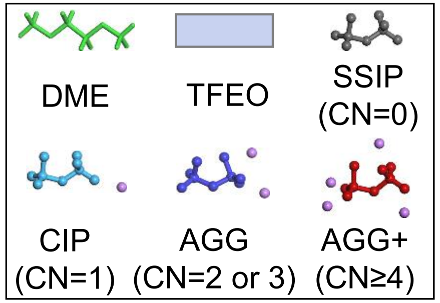
Nature Mat. 22, 1531–1539 (2023)

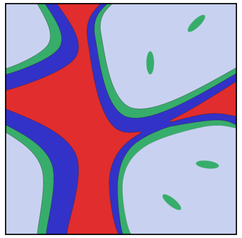
LHCE get more localized through micelle-like structures

- Solvent forms surfactant region and even enters diluent phase, giving higher local concentration
- Salt concentration gradient forms, with higher value at center of the clusters

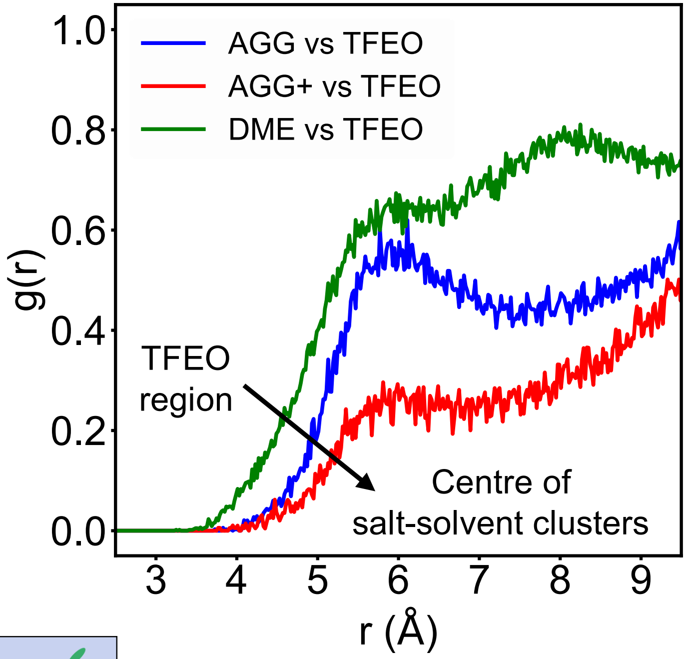
Real MD simulations

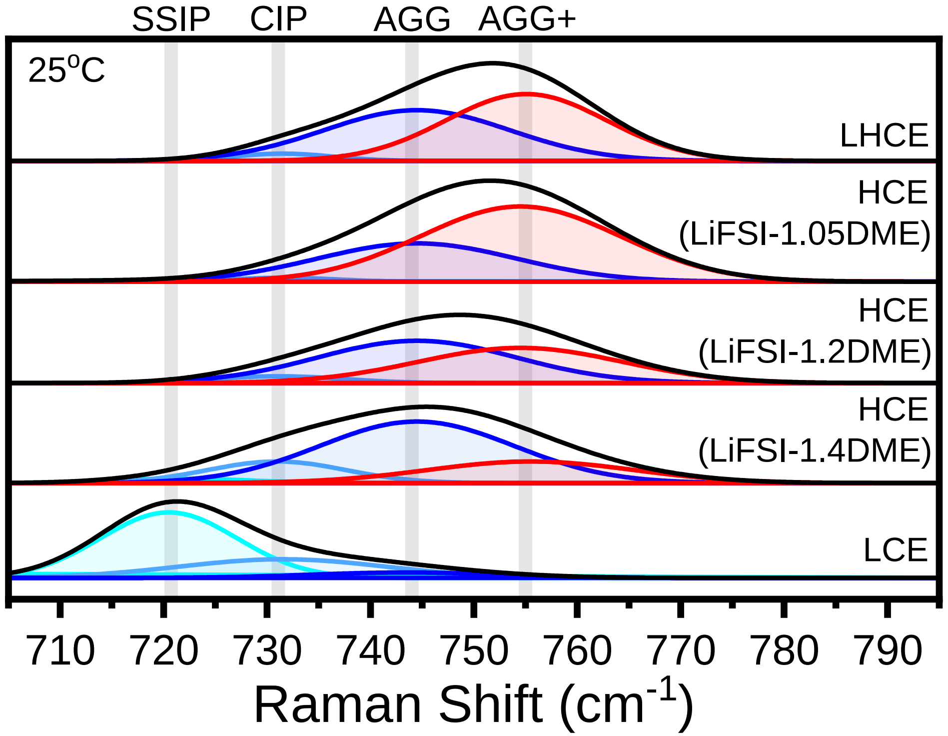






Radial distribution function





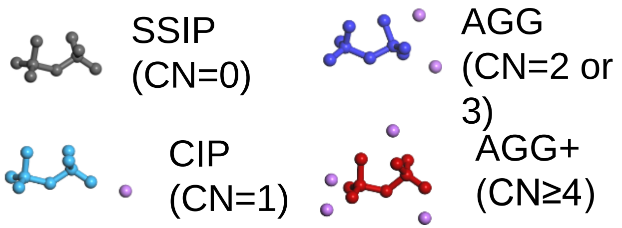
- Salt-solvent clusters in LHCE are transformed to show higher Li^+-anion coordination than that in HCE counterpart.

Nature Mat. 22, 1531–1539 (2023)

Electrolytes with homogenous vs heterogeneous structures

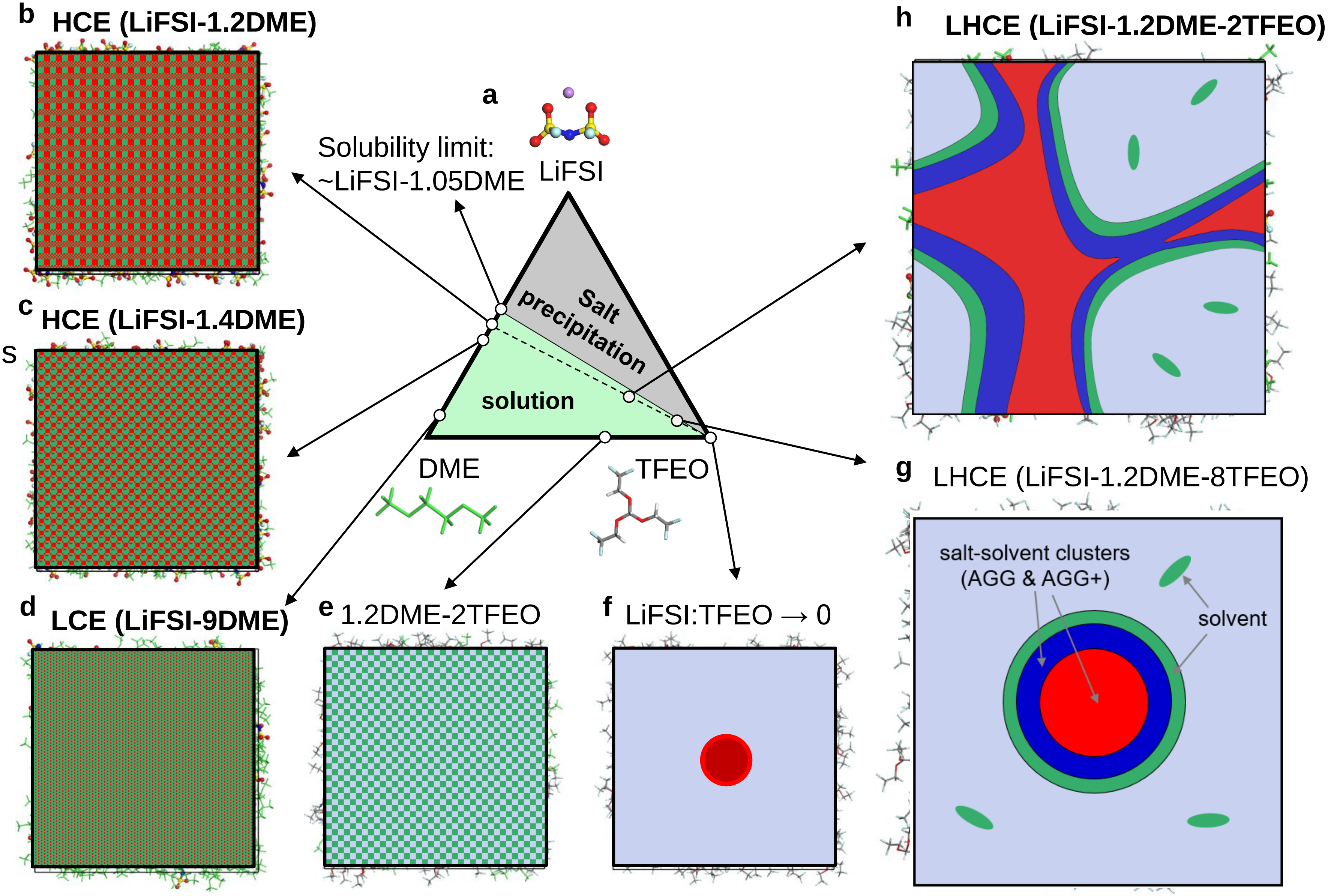
It was found that LHCE shows higher coordination between Li$^+$ and salt anion (FSI$^-$) than its HCE counterpart

SSIP: solvent-separated ion pair
CIP: contact ion pair
AGG: aggregates
AGG+: higher coordinated aggregates

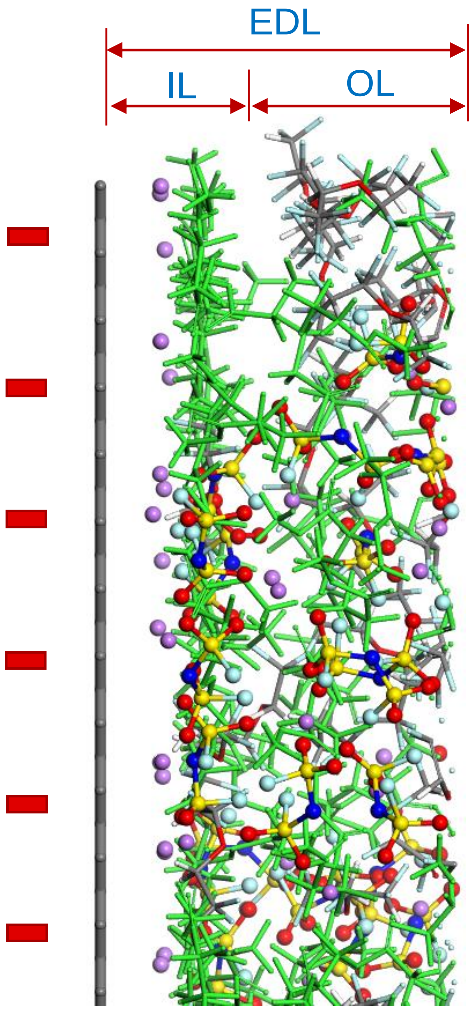


Quantitative Analysis shows:

- LCE: mainly SSIP & CIP;
- HCE: mainly CIP & AGG
- LHCE: mainly AGG & AGG+

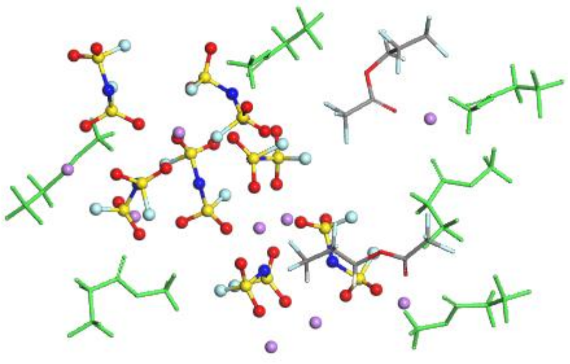


EDL Structures of Complex Electrolytes

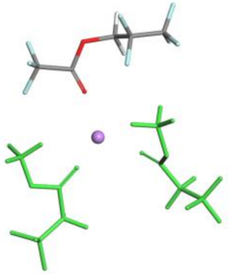


EDL: Electric Double Layer; 0-13 Å from negative electrode based on charge screening length
IL: Inner Adsorbed Layer (0-5 Å)
OL: Outer Diffuse Layer (5-13 Å)

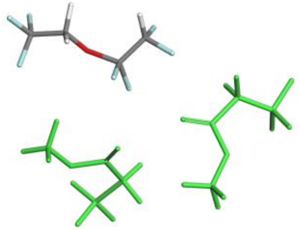
Heterogeneity of the EDL structure of LHCE/LMCE
3 Different clusters observed
Counting all the CN numbers



Salt-Solvent-(some Diluent) clusters



Li-Solvent-Diluent solvation shells



Solvent-Diluent mixture phase

Stern Model should be used to describe EDL of HCE/LHCEs

EDL of LHCE is heterogeneous → form heterogenous LiF nanograins

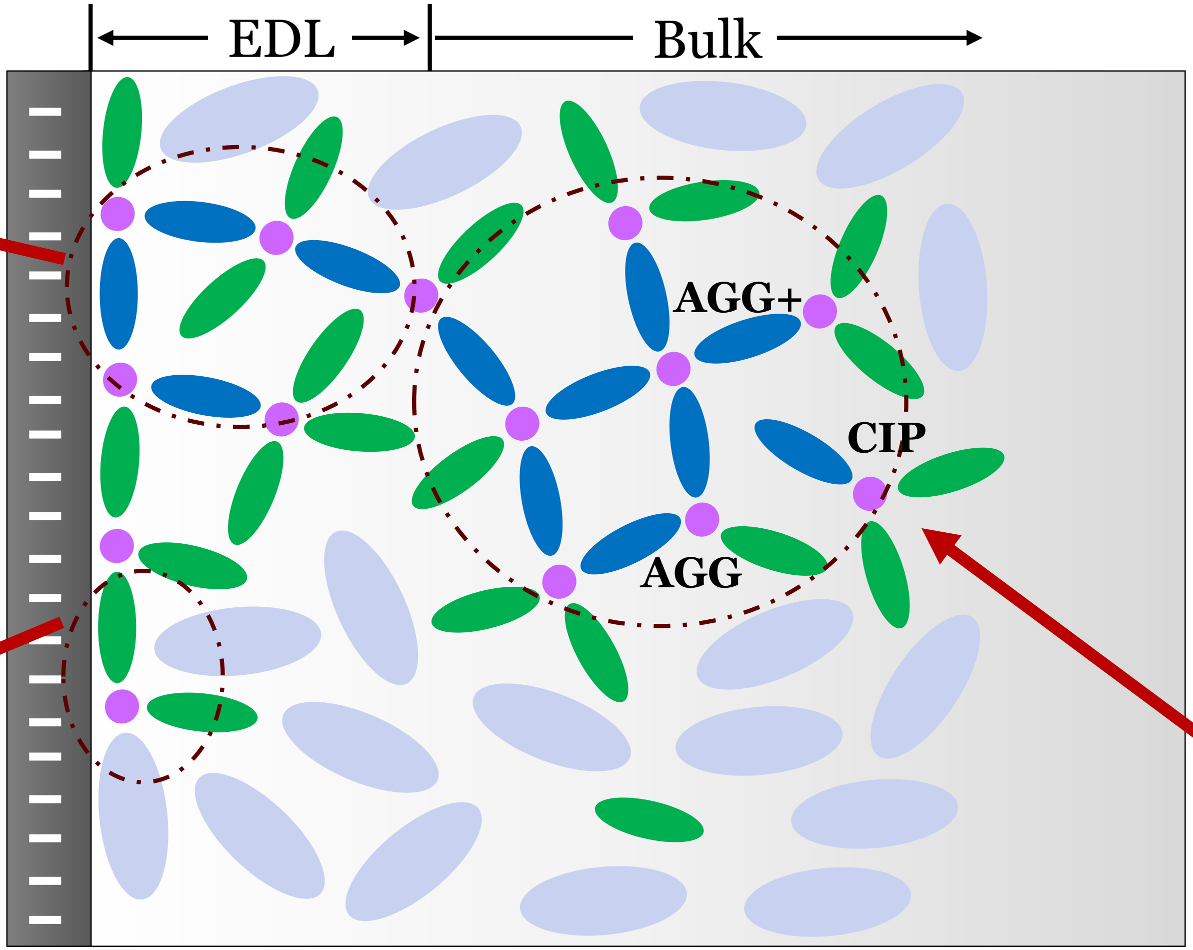
Salt-solvent clusters

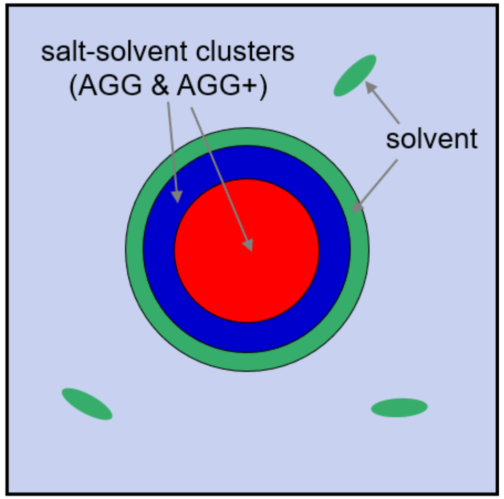
Ion-abundant region

Anode (charging)

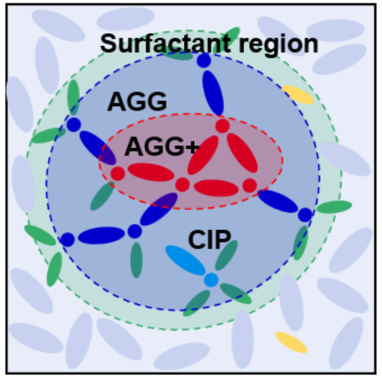
Li$^+$ coordinates to solvent, and possibly with diluent

Ion-deficient region





Bulk phase of LHCE



● Li$^+$ ion

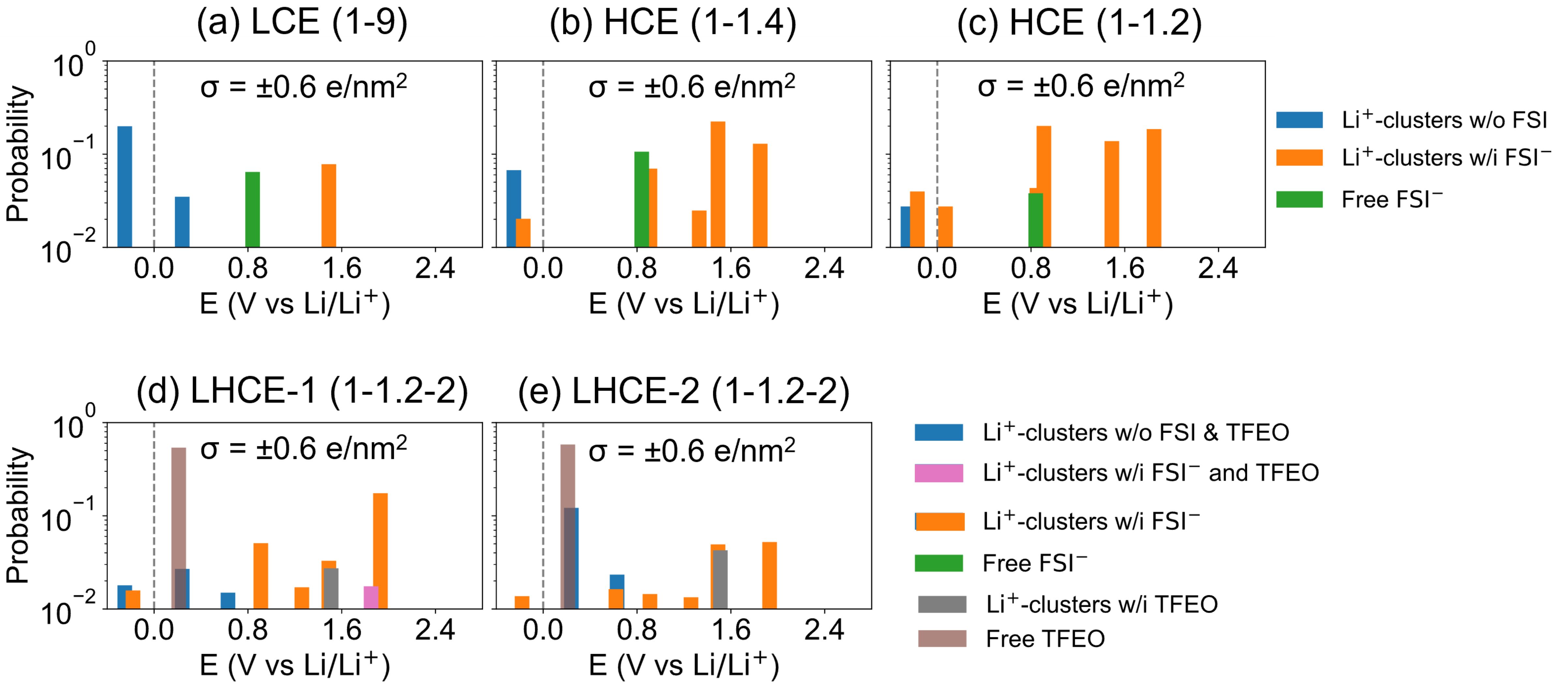
● anion

● solvent

● diluent

Wu and Qi, Energy Environ. Sci., 18, 3036-3046 (2025)

Applying MD-DFT-data model to Heterogeneous Electrolytes



Wu and Qi, Energy Environ. Sci., 2025, 18, 3036-3046

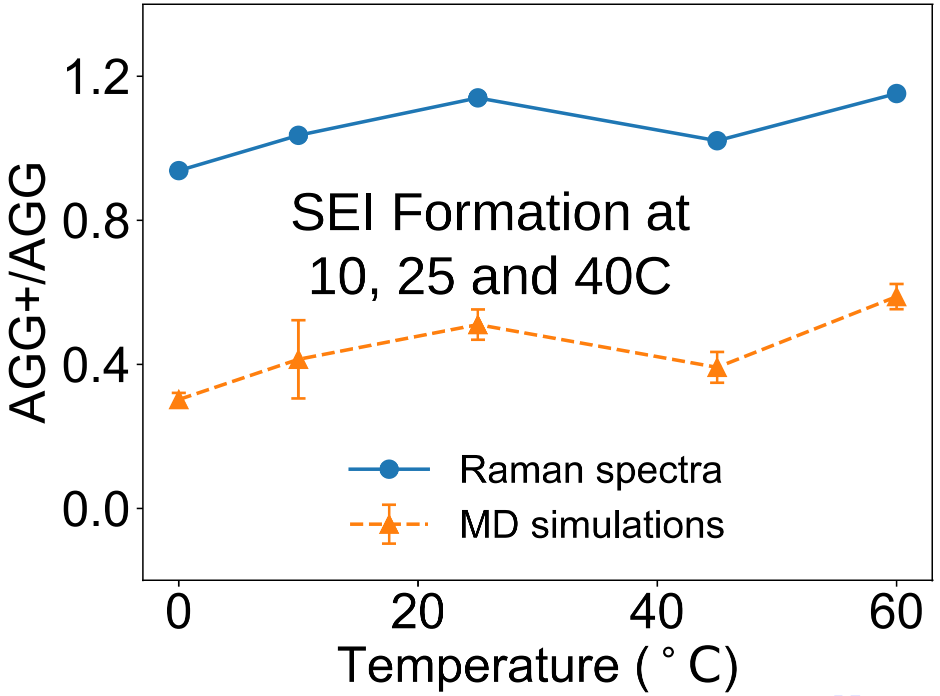
Use T to push local salt concentration even higher, benefits SEI

Competition of salt-solvent solubility and solvent-diluent miscibility

- More DME enters the TFEO region with T ↑, AGG+ ↑
- DME dissolves more LiFSI salt with T↑, AGG+ ↓

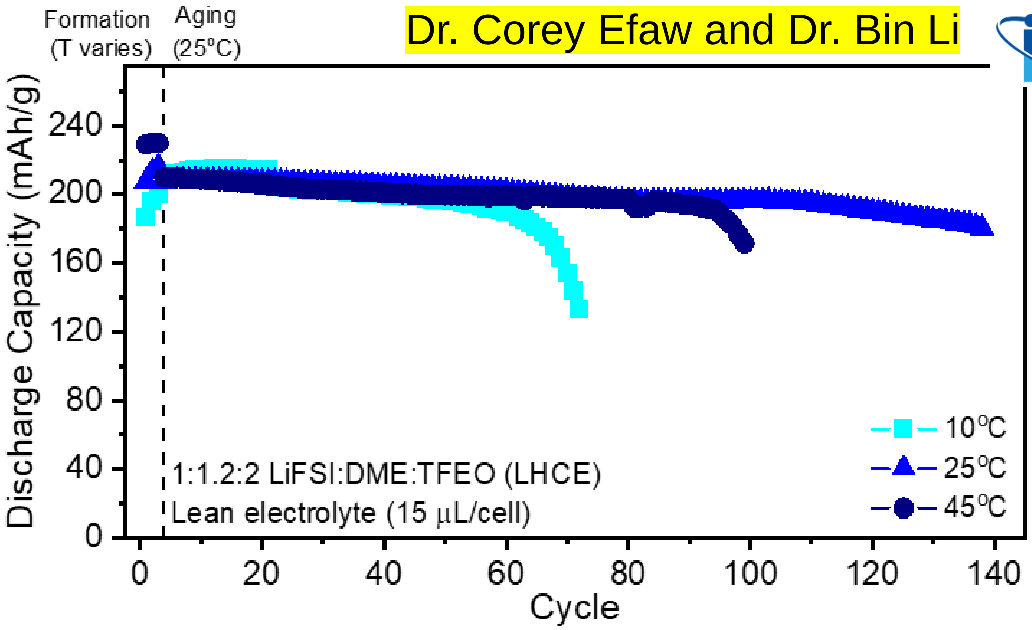
The two competing effects give a higher AGG+/AGG ratio at 25 ° C compared to those at 10 and 45 ° C

LHCE(LiFSI-1.2DME-2TFEO)



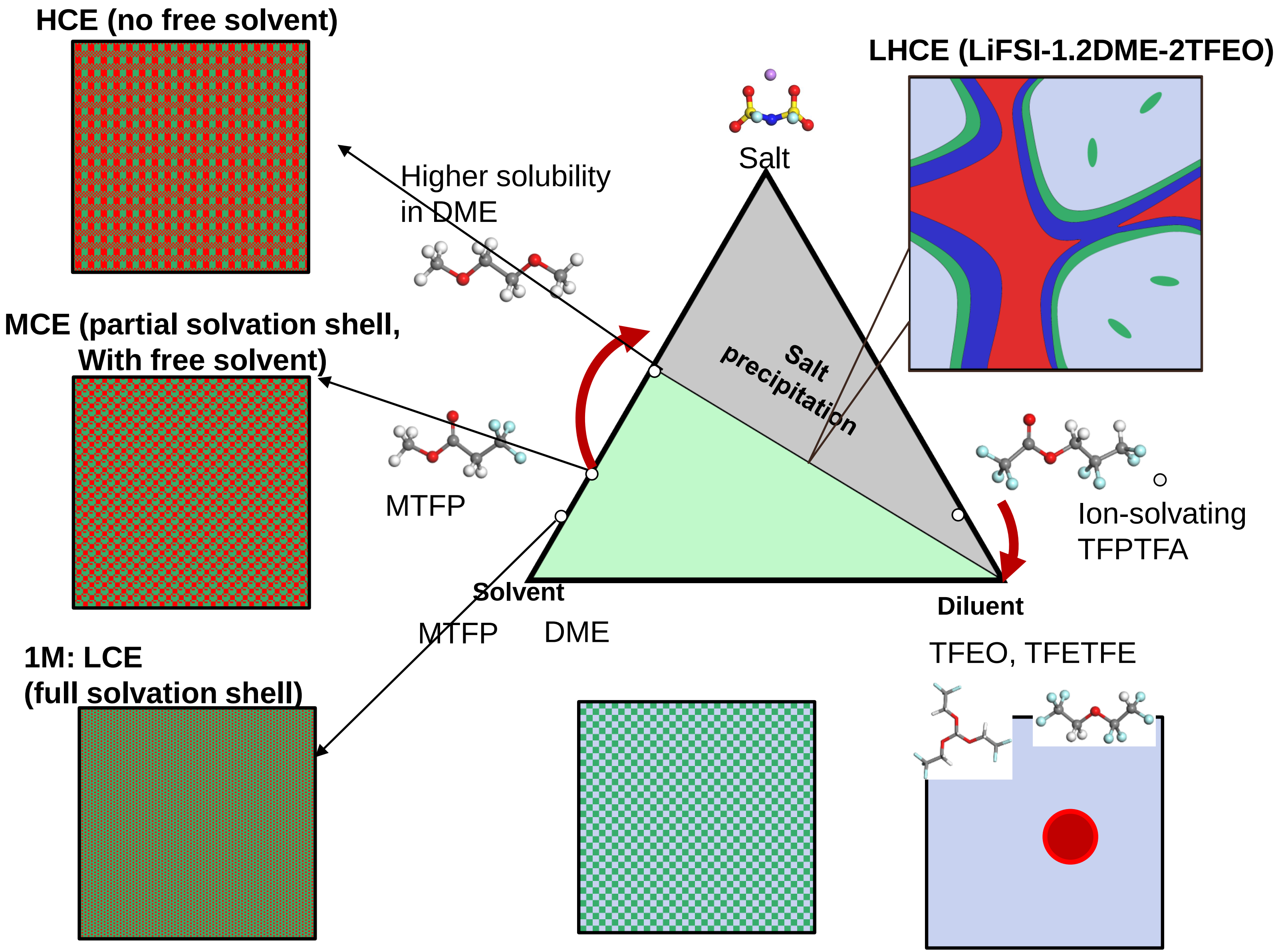
After SEI formation, cycling at 25 ° C

Dr. Corey Efaw and Dr. Bin Li



Nature Mat. 22, 1531–1539 (2023)

Tuning chemistry, composition - structures – properties



HCE (no free solvent)

MCE (partial solvation shell, With free solvent)

1M: LCE (full solvation shell)

Higher solubility in DME

MTFP

Salt

Salt precipitation

Solvent

MTFP DME

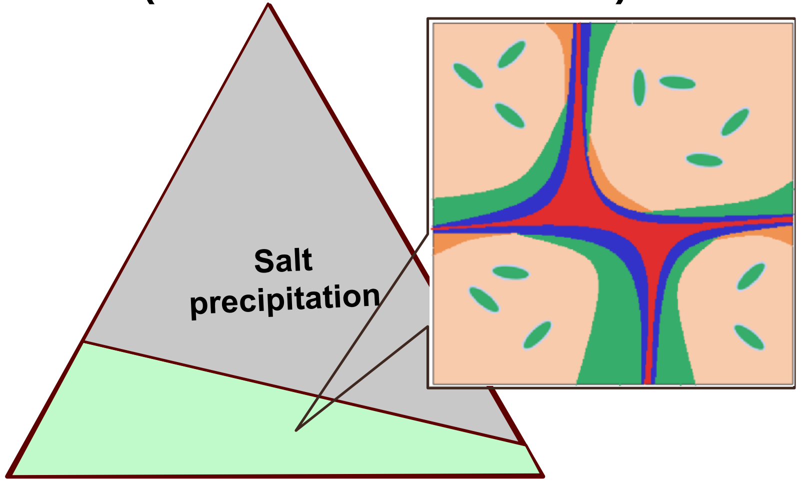
Diluent

TFEO, TFETFE

Ion-solvating TFPTFA

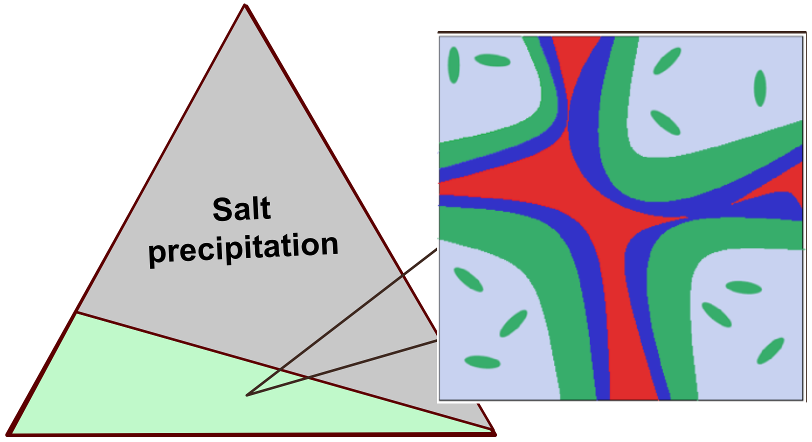
LHCE (LiFSI-1.2DME-2TFEO)

LMCE (LiFSI-3.2MTFP-1.6TFPTFA)



Salt precipitation

LMCE (LiFSI-3.2MTFP-1.6TFETFE)

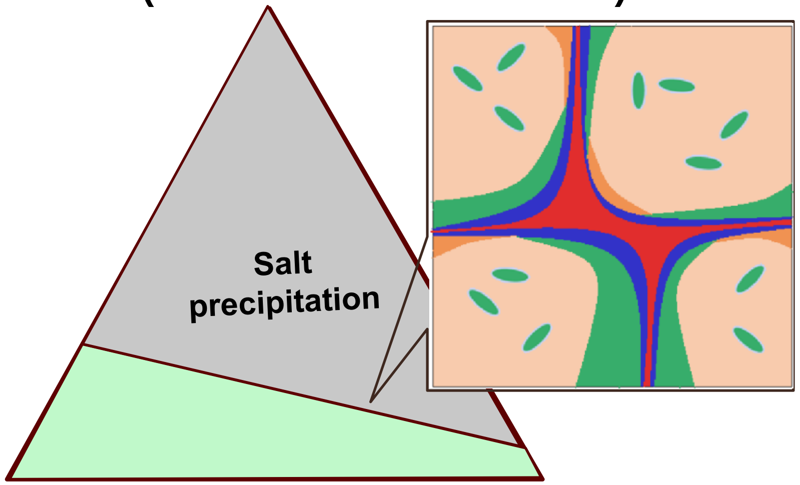


Salt precipitation

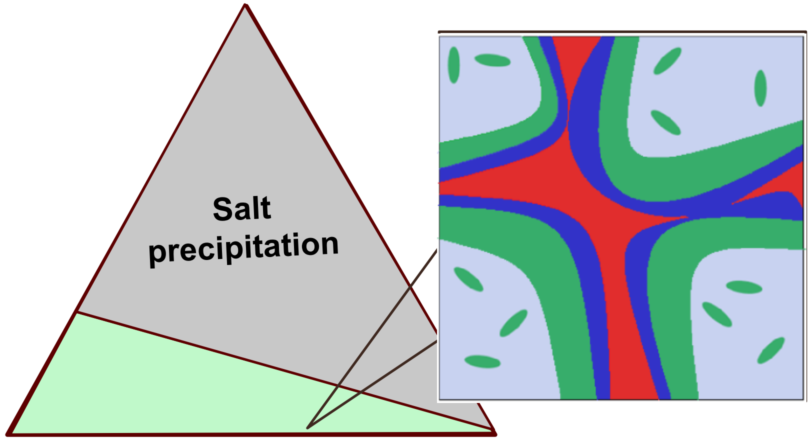
Tuning chemistry, composition - structures – properties

Md Jamil Hossain

LMCE (LiFSI-3.2MTFP-1.6TFPTFA)



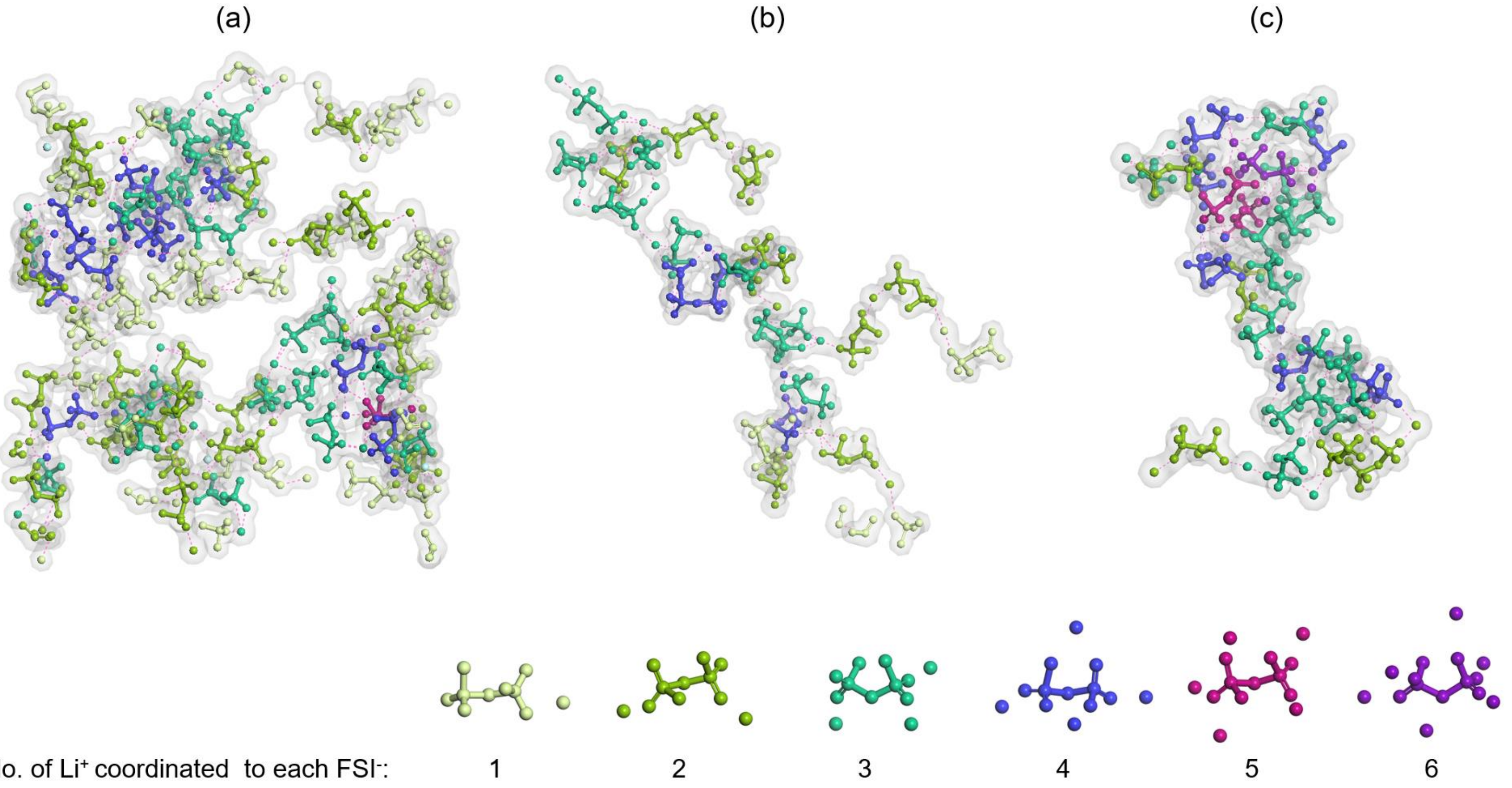
LMCE (LiFSI-3.2MTFP-1.6TFETFE)



Solubility of
LiFSI in MTFP is ~2.25M
Lower ion-to-solvent ratio
MCE (LiFSI-3.2MTFP)

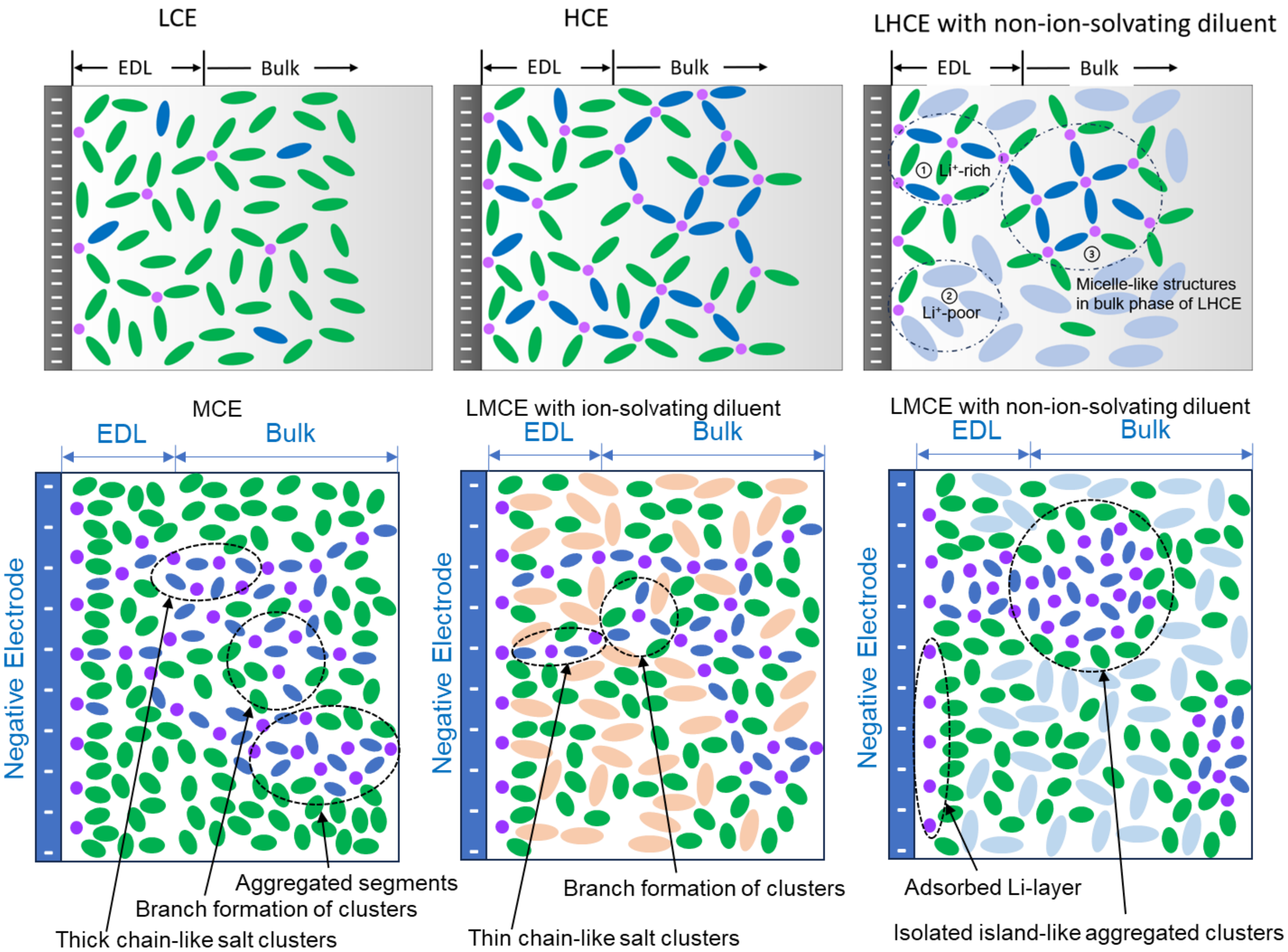
LMCE
(LiFSI-3.2MTFP-1.6TFPTFA)
TFPTFA enters solvation shell

LMCE
(LiFSI-3.2MTFP-1.6TFETFE)
TFETFE has no solubility



In collaboration with Esther S. Takeuchi

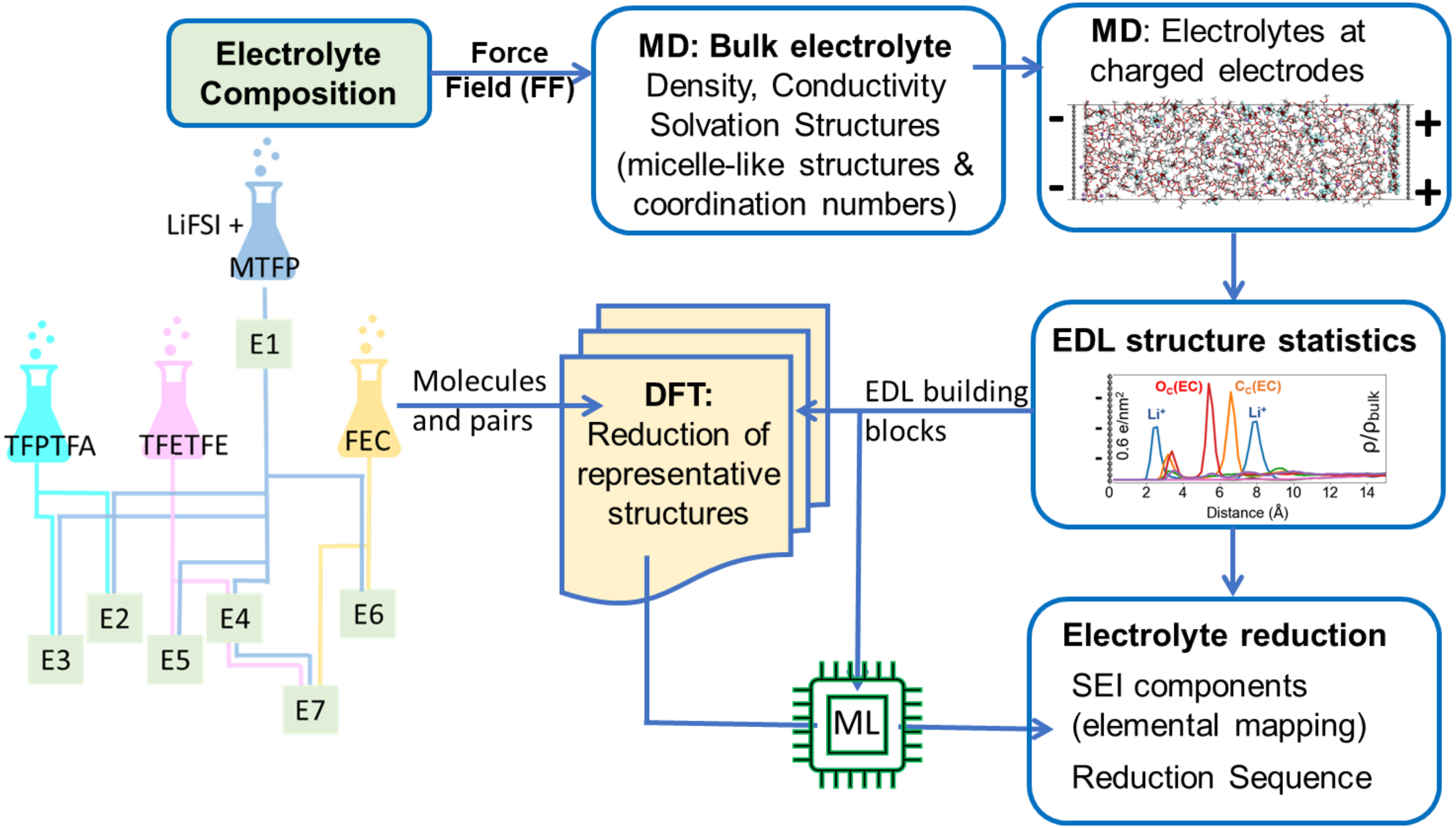
Schematics of EDL structures of electrolytes



LHCE (LiFSI-1.2DME-2TFEO)

LMCE
(LiFSI-3.2MTFP-1.6TFETFE)

Modified workflow



Electrolyte Composition

Force Field (FF)

MD: Bulk electrolyte
Density, Conductivity
Solvation Structures
(micelle-like structures & coordination numbers)

MD: Electrolytes at charged electrodes

EDL structure statistics

Molecules and pairs

DFT: Reduction of representative structures

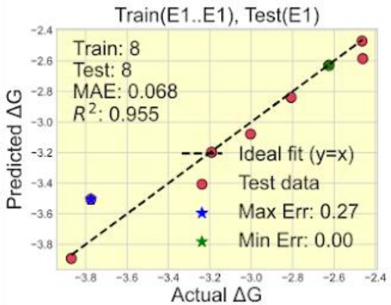
EDL building blocks

Electrolyte reduction
SEI components (elemental mapping)
Reduction Sequence

Trained the Reduction Potentials in the EDL

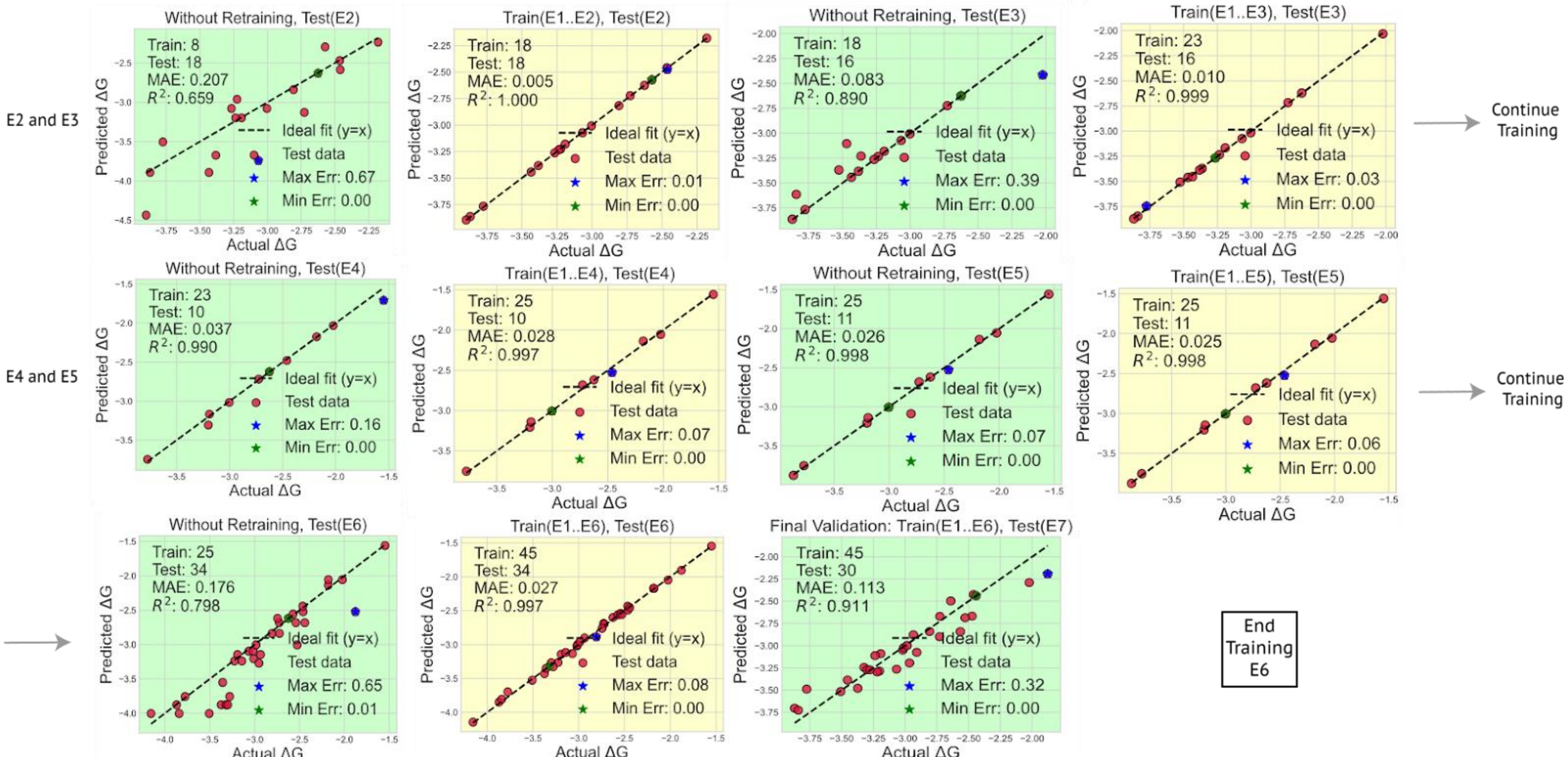
- Better performance is seen using linear regression as a starting point in the Gradient Boosting Regressor
- Show new species in the EDL
- No need to train N! combinations

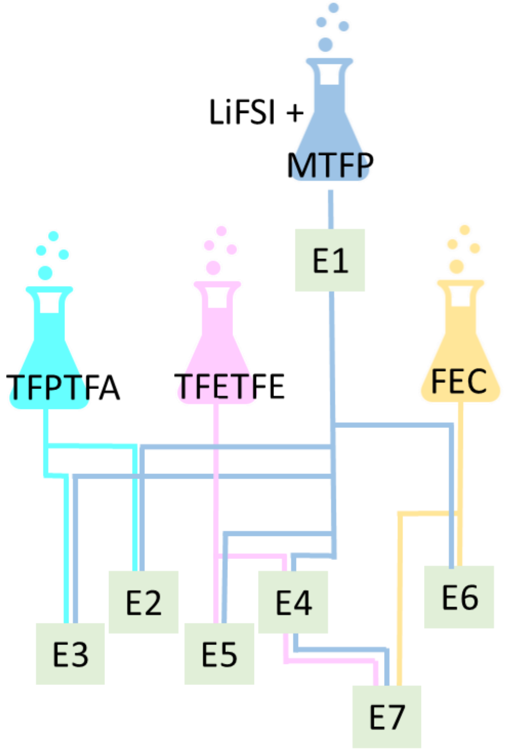
Start Training E1



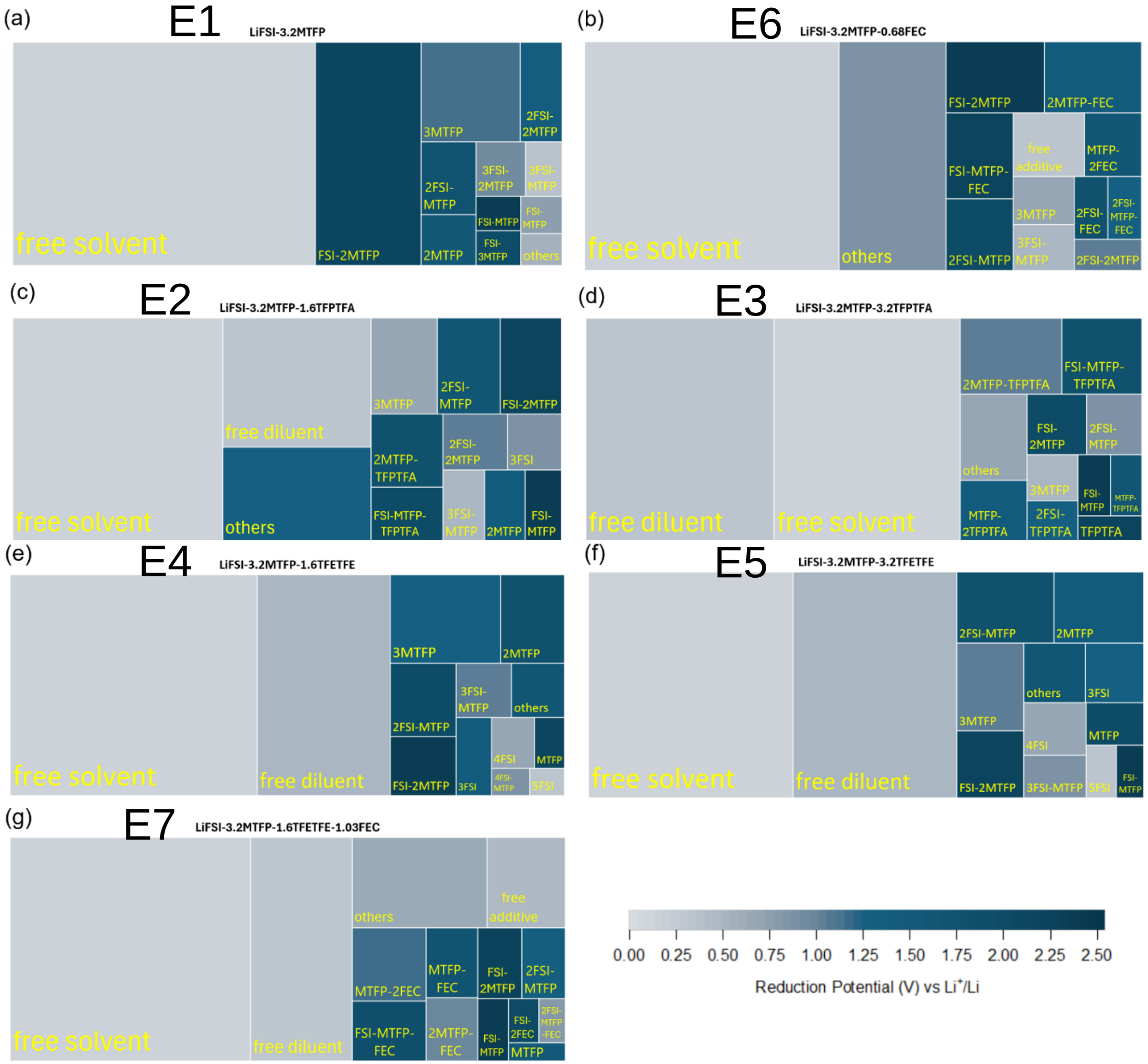
Continue Training

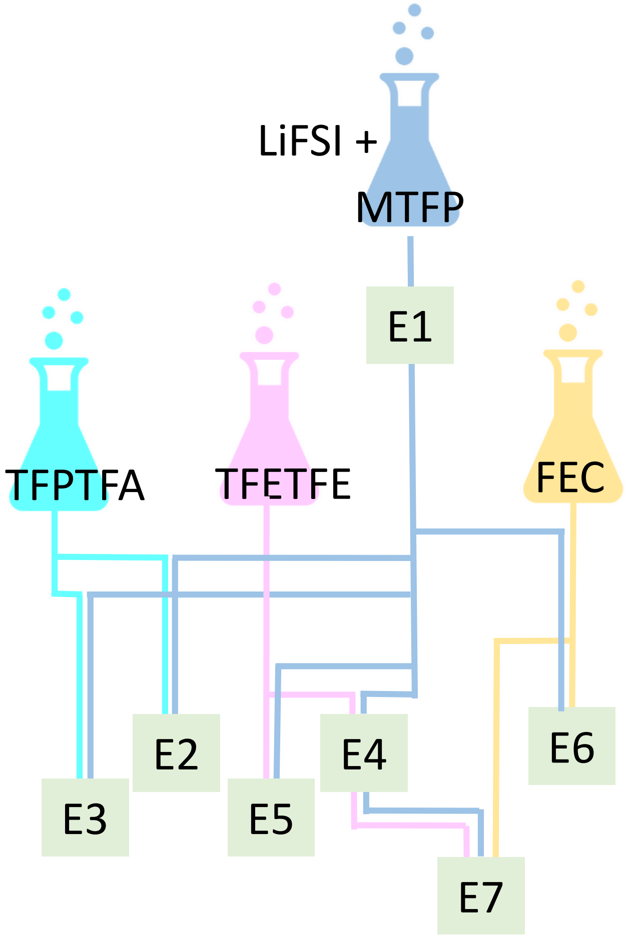
Tilas Kabengele





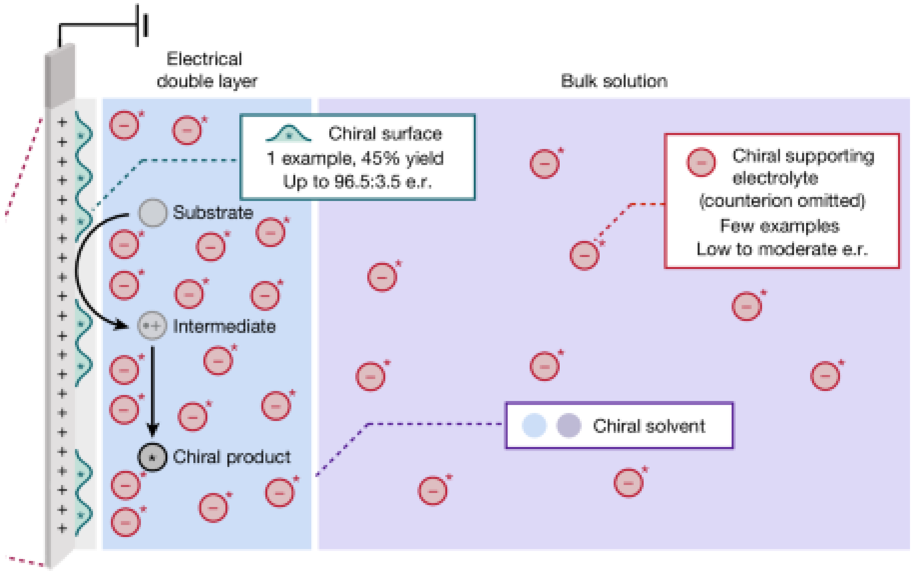
Adding FEC doesn’t always increase LiF

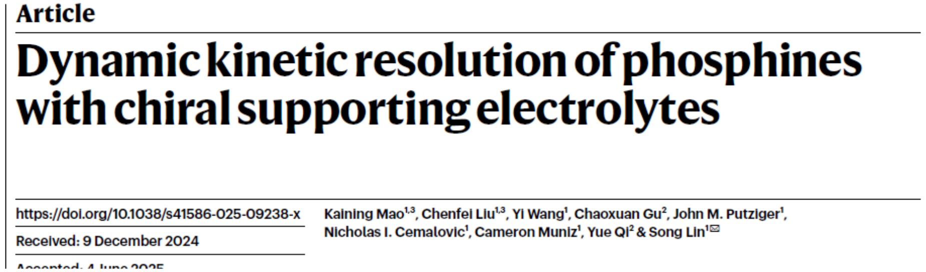




Take advantage of the EDL for reactions

$$\text{Reaction Rate} = [\text{concentration}]\ k(T)$$

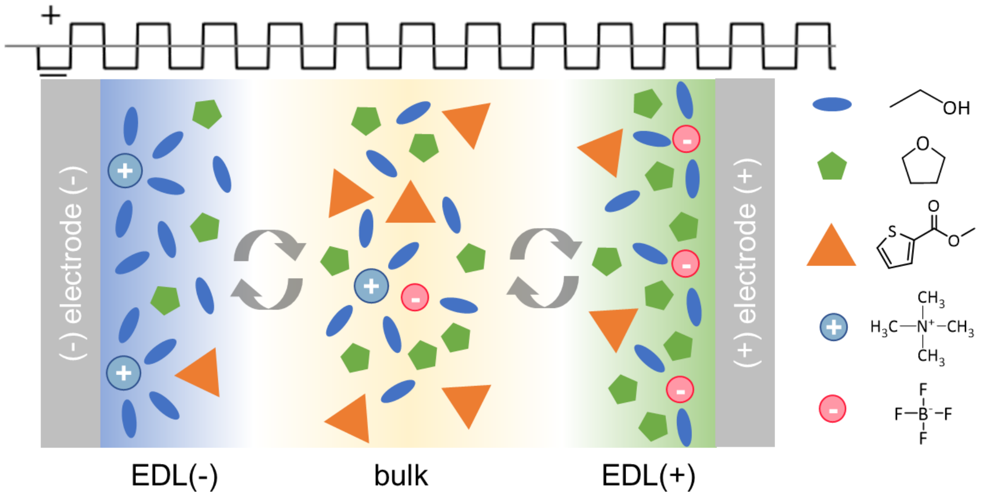



Article

Dynamic kinetic resolution of phosphines with chiral supporting electrolytes

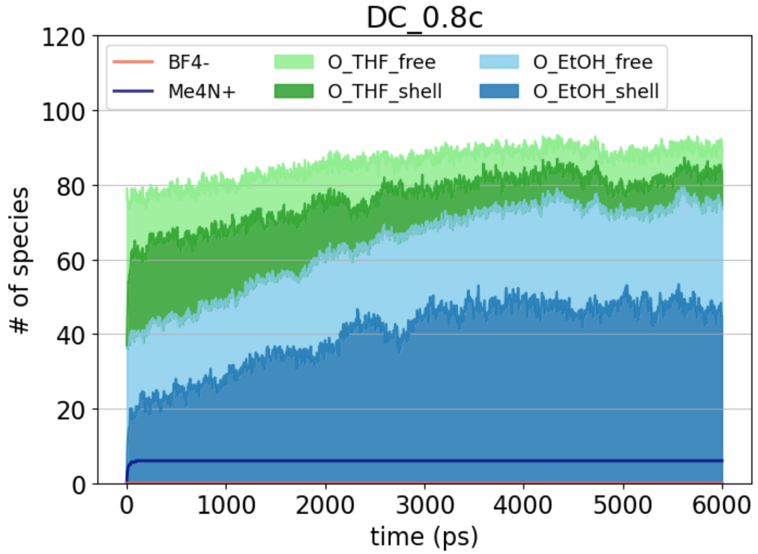
https://doi.org/10.1038/s41586-025-09238-x
Received: 9 December 2024
Accepted: 4 June 2025

Kaining Mao[1,3], Chenfei Liu[1,3], Yi Wang[1], Chaoxuan Gu[2], John M. Putziger[1], Nicholas I. Cemalovic[1], Cameron Muniz[1], Yue Qi[2] & Song Lin[1]✉



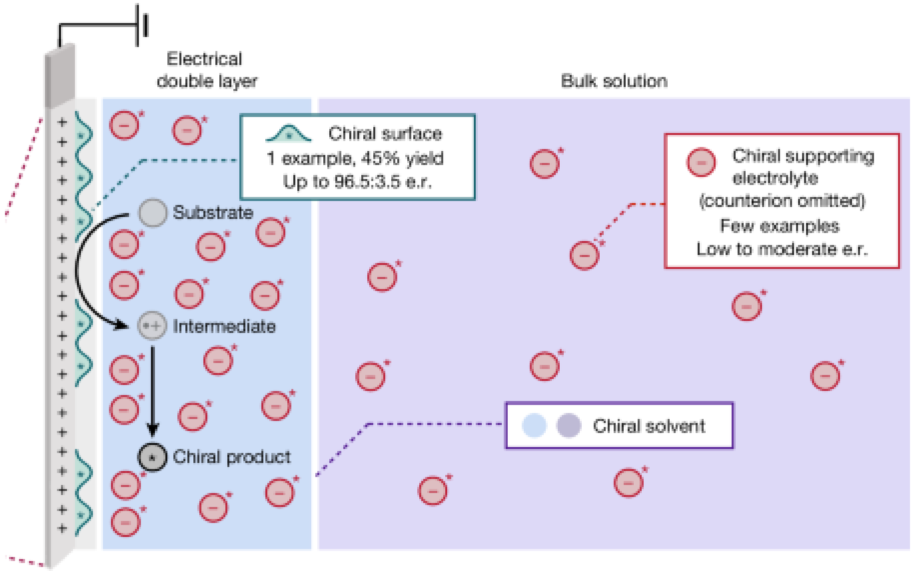
AC indirectly disturbs charge-neutral species due to their interaction with ions

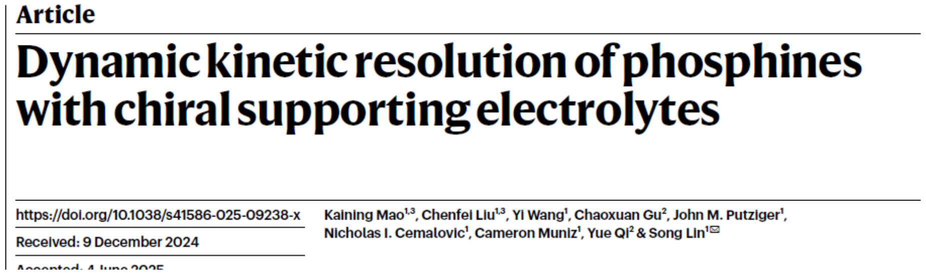
Example: Thiophene Birch-type reduction, EtOH-THF co-solvent



Take advantage of the EDL for reactions

Reaction Rate = [concentration] $k(T)$





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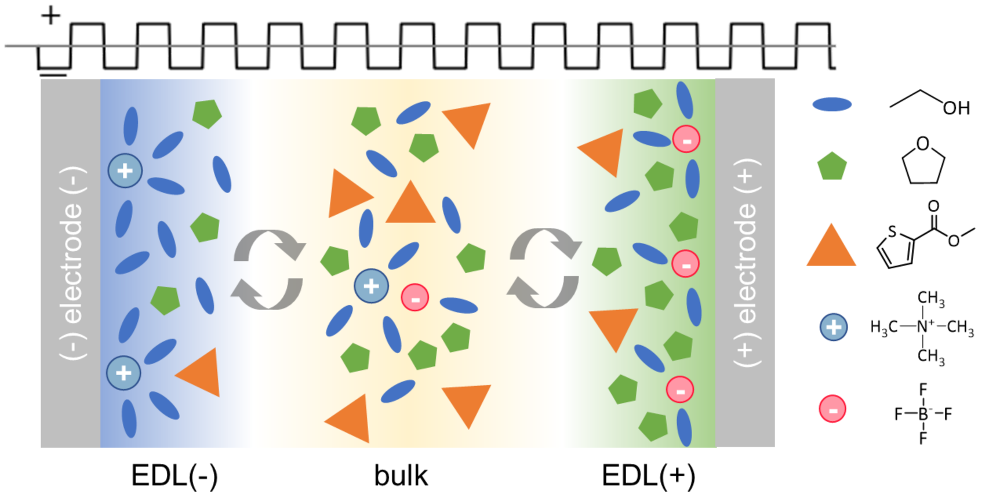

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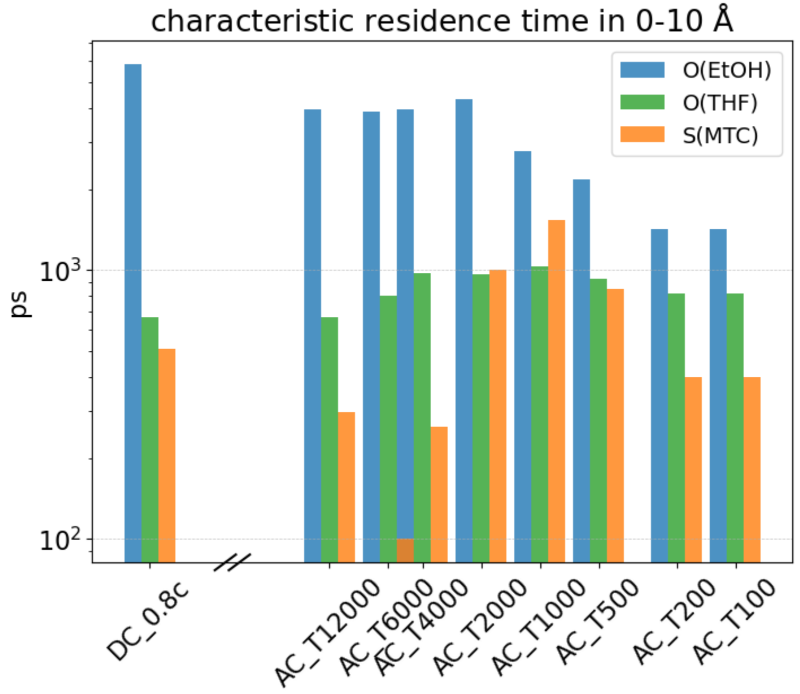
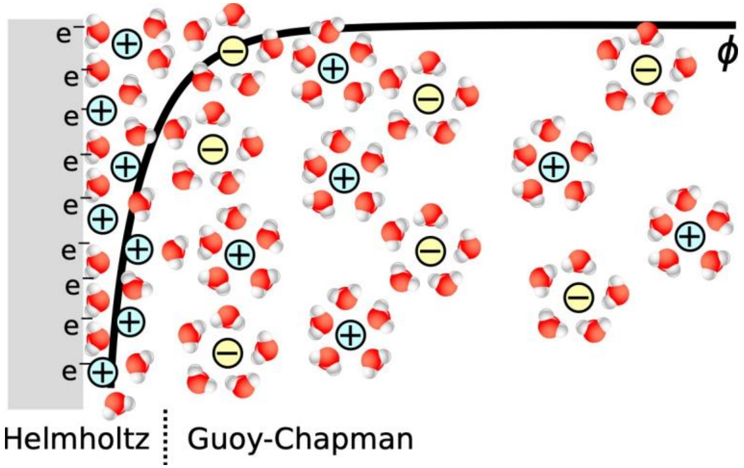
Example: Thiophene Birch-type reduction, EtOH-THF co-solvent



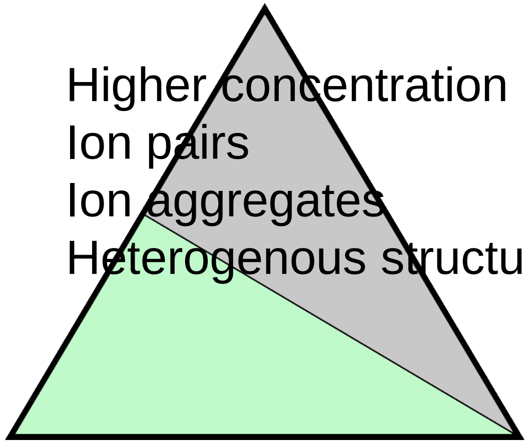
Challenges I: EDL models for non-ideal and complex electrolytes

Complex Electrolyte EDL

Liquid EDL, dilute electrolyte, well-solvated ions



typical liquid electrolyte with a 1 M solution has an ion density of $6\text{x}10^{20}$ cm^{-3}.

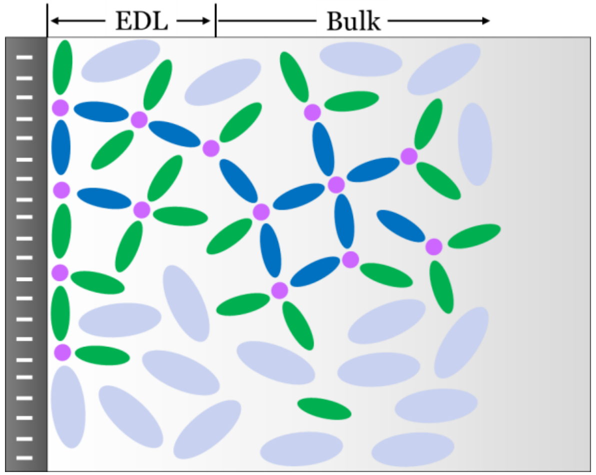


Salt

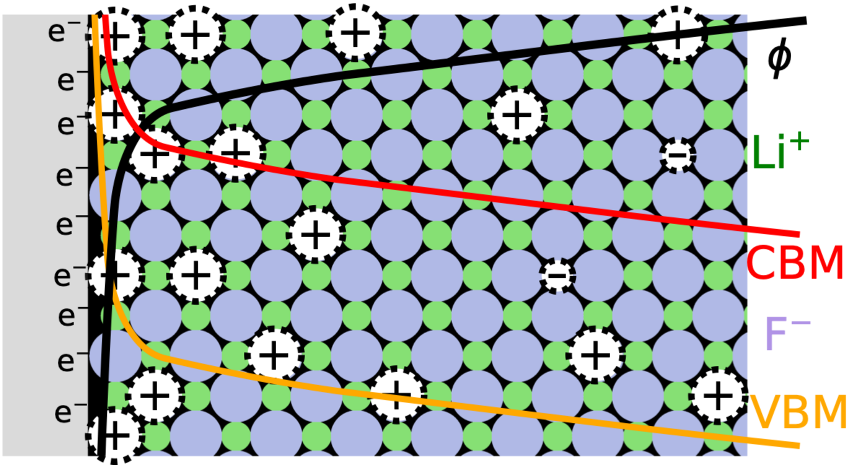
Higher concentration
Ion pairs
Ion aggregates
Heterogenous structures

Solvent

Diluent



Solid EDL

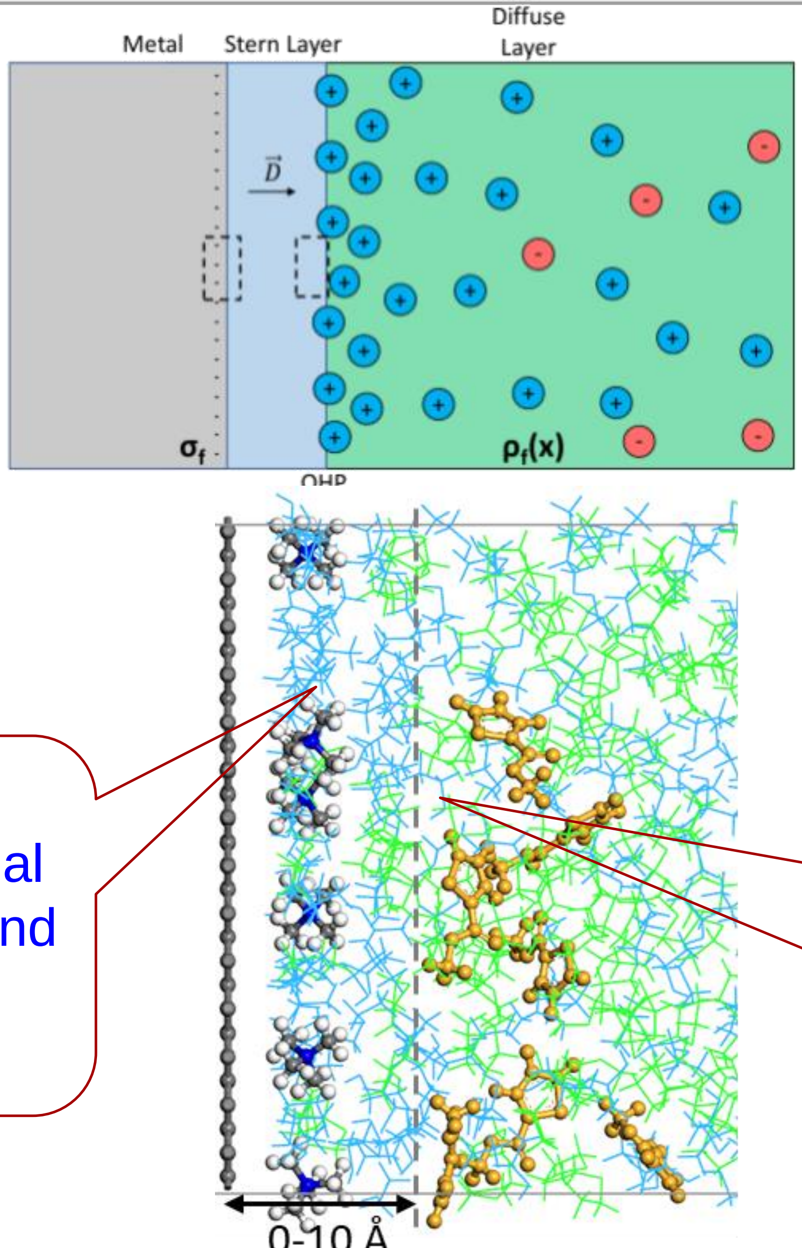


LiF has a Li^+ density of $6\text{x}10^{22}$ cm^{-3}, but a lithium vacancy concentration of $3\text{x}10^{6}$ cm^{-3}

Swift, Swift, Qi,
Nature Computational Science
(2021) 1, 212–220

How to couple the effect of EDL on Reactions

Postdoc position opening



$$\phi_{bulk} = 0\ V$$

The charge and potential on the EDL structures and dynamics.

The chemical composition in the EDL (charged, not charged) is different from the bulk. This is an important input for QM calculations

Acknowledgment

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Chaoxuan Gu (Brown)

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Hui (Clarrie) Xiong (Boise State)
Corey M Efaw, Eric Dufek (INL)
Yugang Zhang, Xiao-Qing Yang, David C Bock (BNL)
Xia Cao, Wu Xu, Ji-Guang Zhang, Jie Xiao, Jun Liu (PNNL)
Amy Marschilok, Esther Takeuchi (StonyBrook)

CSOE:
Shelley Minteer, Song Lin, Long Lou, Henry White, Kim See,
Matthew Neurock, Kevin Moeller …

2020

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