Superconcentrated Electrolytes

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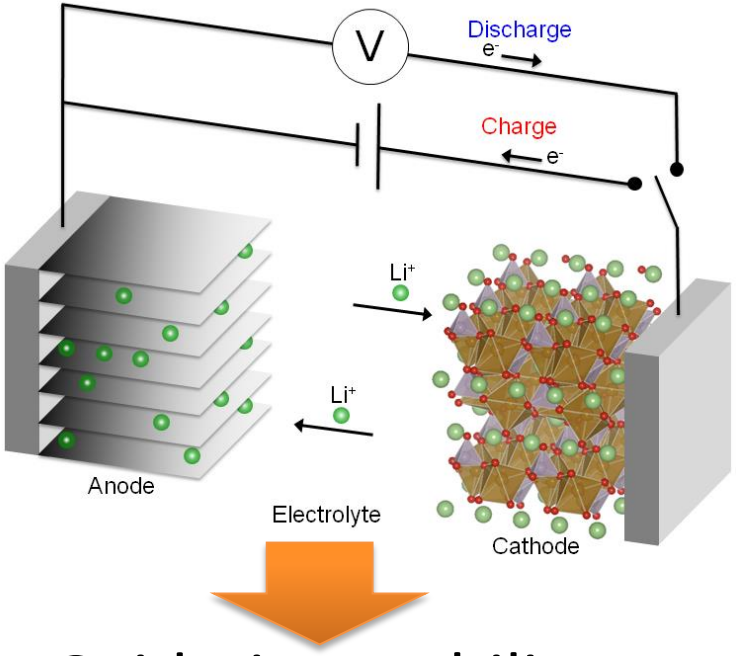
NIMS

Toward better batteries

Electrolyte is a key

Sophistication

- Fast charge
- High safety



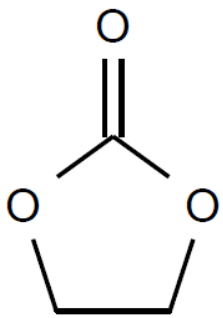
Electrode diversification

- Oxygen
- Sulfur
- 5 V class

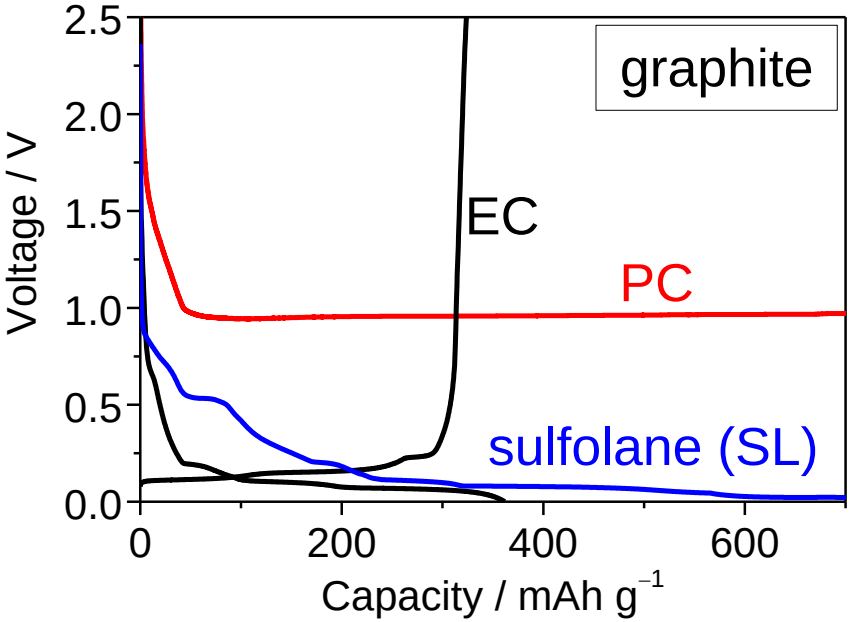
- Oxidation stability
- Radical attack stability
- Li_2S_m dissolution block
- Non-flammability
- Fast Li^+ transport etc.

Solvent limitation by anode

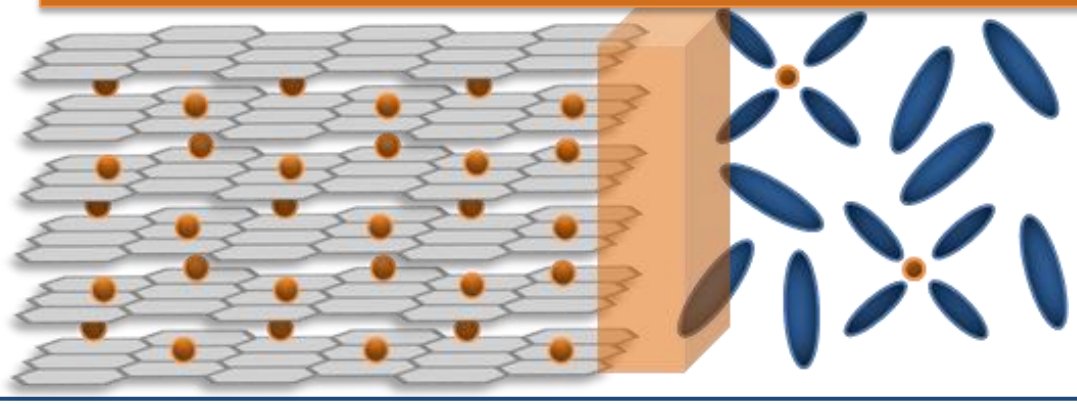
EC is essential



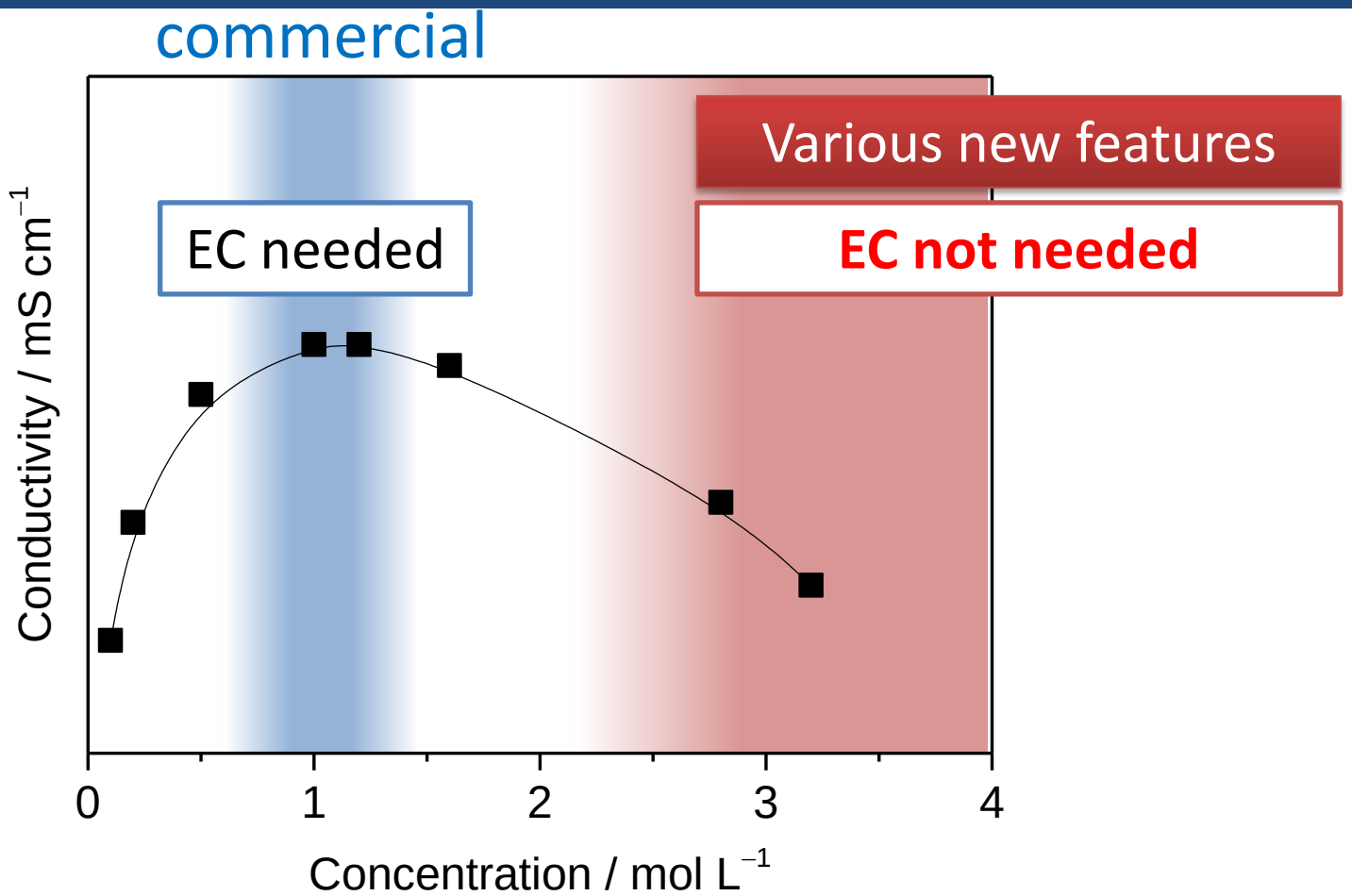
Ethylene carbonate (EC)



EC decomposition & SEI formation



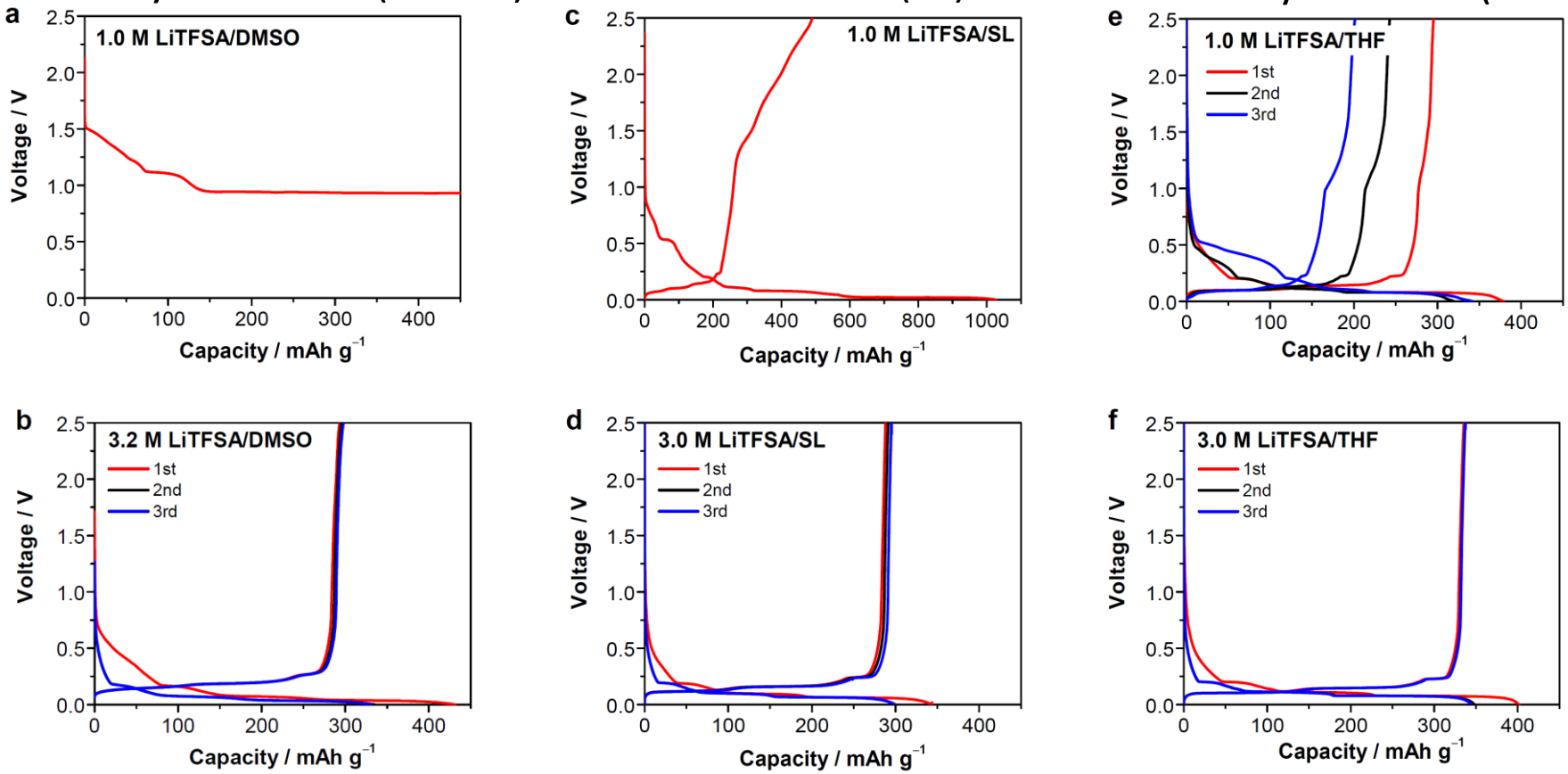
Highly concentrated electrolyte



W. R. McKinnon et al., ***J. Electrochem. Soc.***, 132, 364 (1985).
S. K. Jeong et al., ***Electrochem. Solid-State Lett.*** 6, A13 (2003).
T. M. Pappenfus et al., ***J. Electrochem. Soc.***, 151, A209 (2004).
Y. Yamada et al., ***J. Phys. Chem. C***, 114, 11680 (2010).
K. Yoshida et al., ***J. Am. Chem. Soc.***, 133, 13121 (2011).
L. Suo et al., ***Nat. Commun.***, 4, 1 (2013).
Y. Yamada et al., ***Chem Commun.***, 49, 11194 (2013).
D.W. McOwen et al., ***Energy Environ. Sci.***, 7, 416 (2014).
Y. Yamada et al., ***ACS Appl. Mater. Interfaces***, 6, 10892 (2014).
Y. Yamada et al., ***J. Am. Chem. Soc.***, 136, 5039 (2014).

EC-free graphite anode reaction

Dimethyl sulfoxide (DMSO) | Sulfolane (SL) | Tetrahydrofuran (THF)



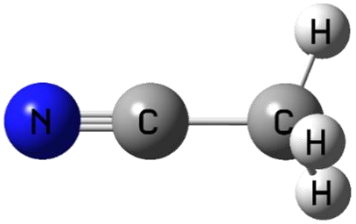
Superconcentrated electrolytes universalize graphite anode reaction.

Diversity of electrolyte design

New material beyond EC

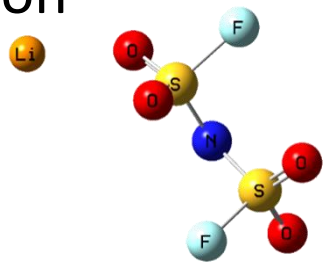
Acetonitrile (AN)

◎ high oxidation stability
◎ excellent ionic transport
× low reduction stability



Amide salt (LiTFSA, LiFSA)

◎ high stability
◎ high dissociation
× Al corrosion



Topic

- ◆ Enhanced reduction stability
- ◆ Suppression of Al corrosion
- ◆ Fast reaction

Topic

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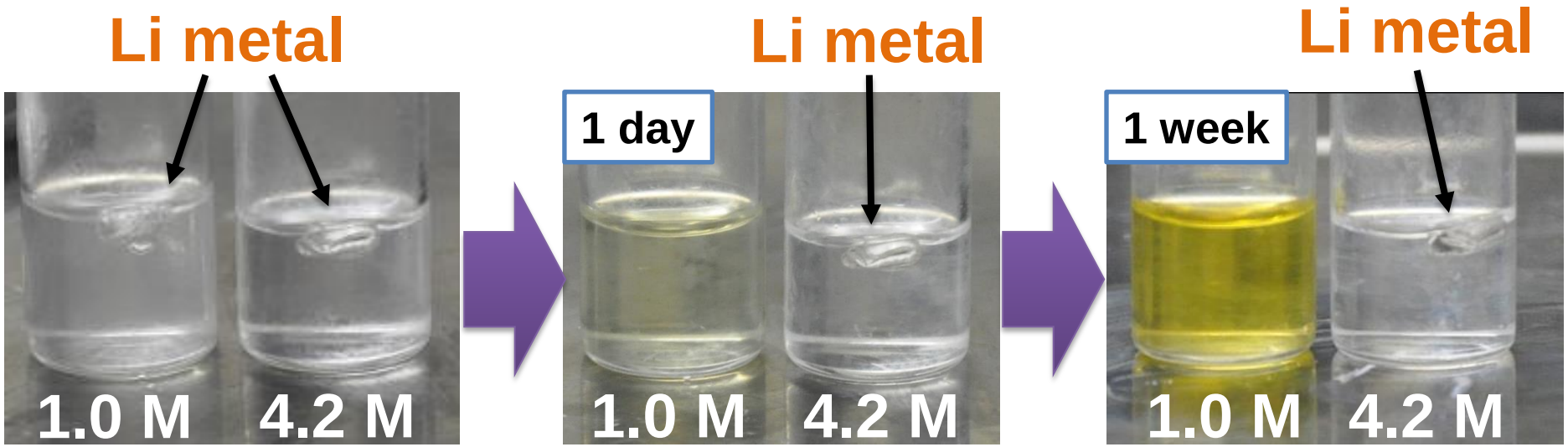
Enhanced reduction stability

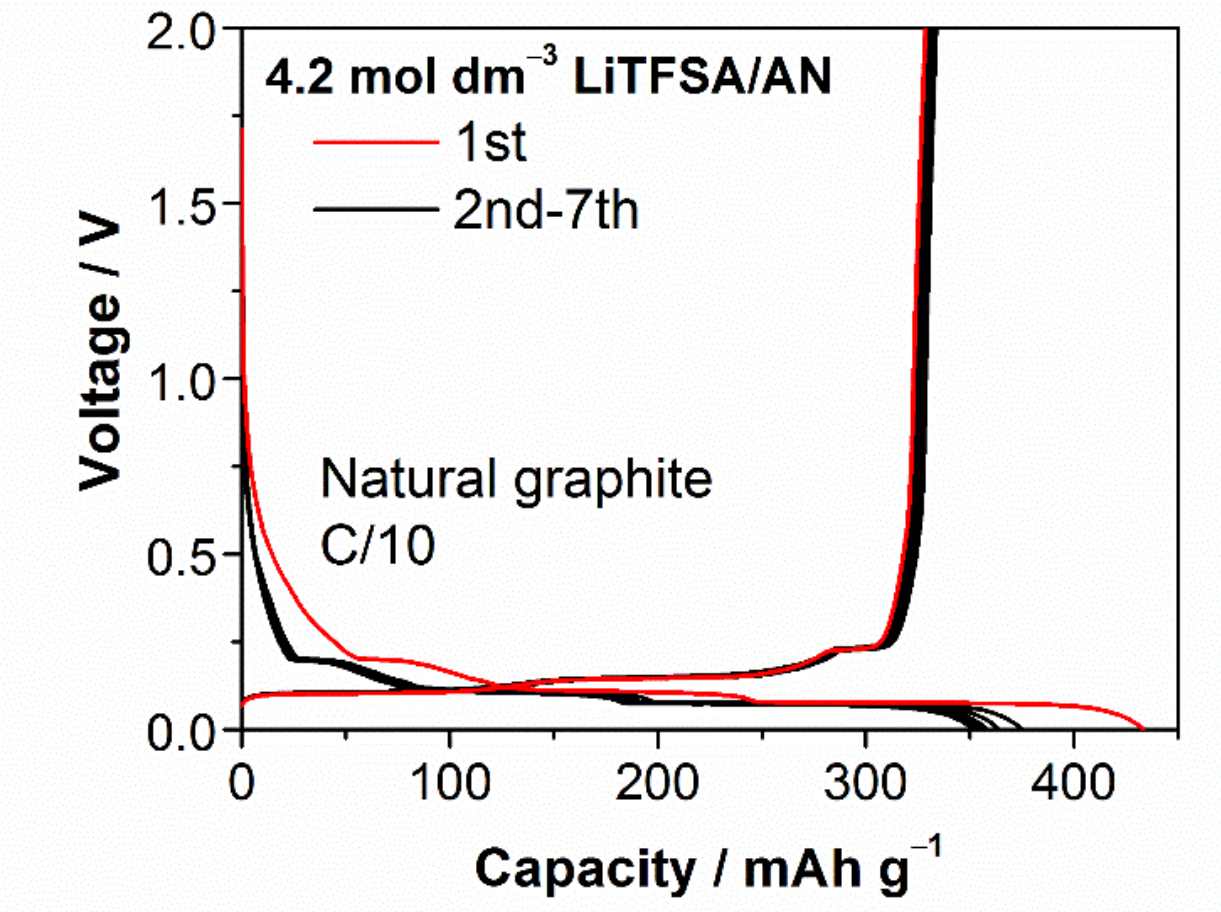
LiTFSA/acetonitrile (AN)



$$CH_3CN + 2Li \rightarrow CH_3^- + CN^- + 2Li^+$$

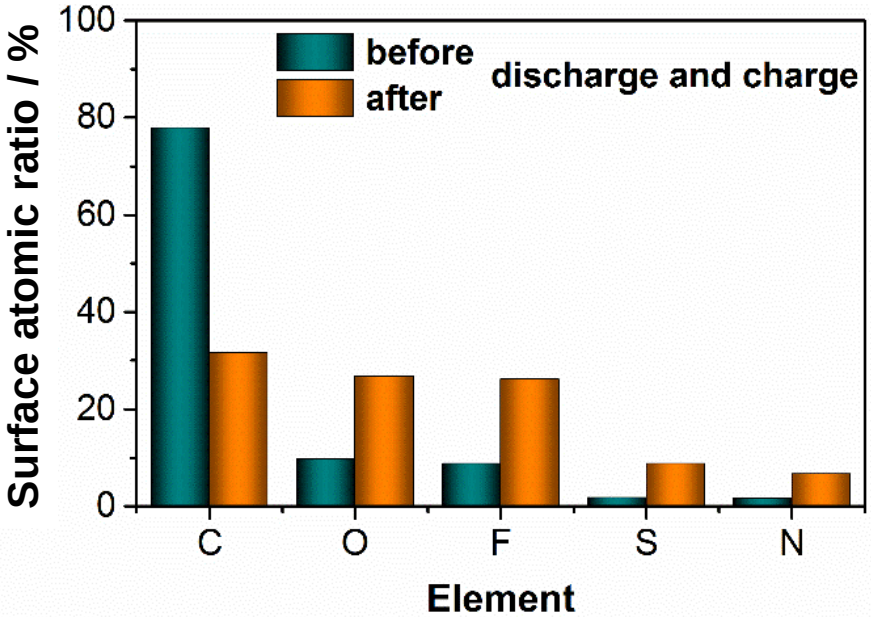
Y. Yamada et al., ***J. Am. Chem. Soc.***, 136, 5039 (2014).

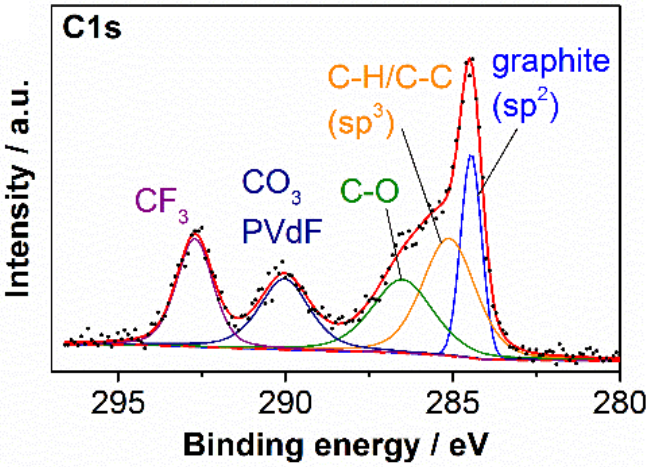
Stable cycling of graphite half cell

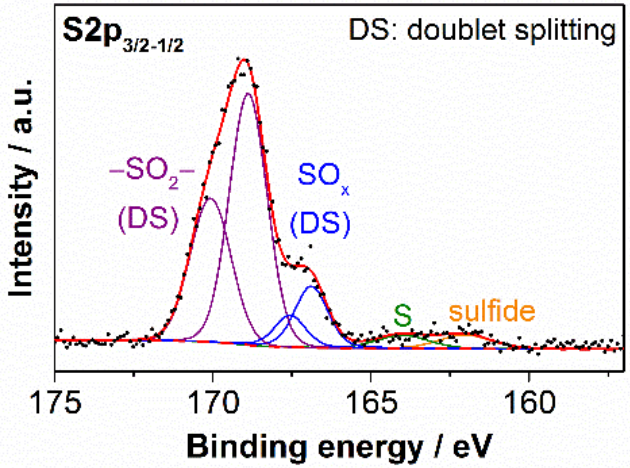


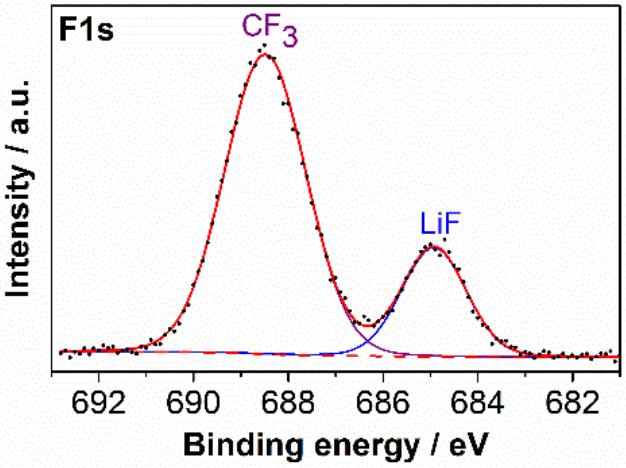
Y. Yamada et al., ***J. Am. Chem. Soc.***, 136, 5039 (2014).

Li salt-based SEI on graphite

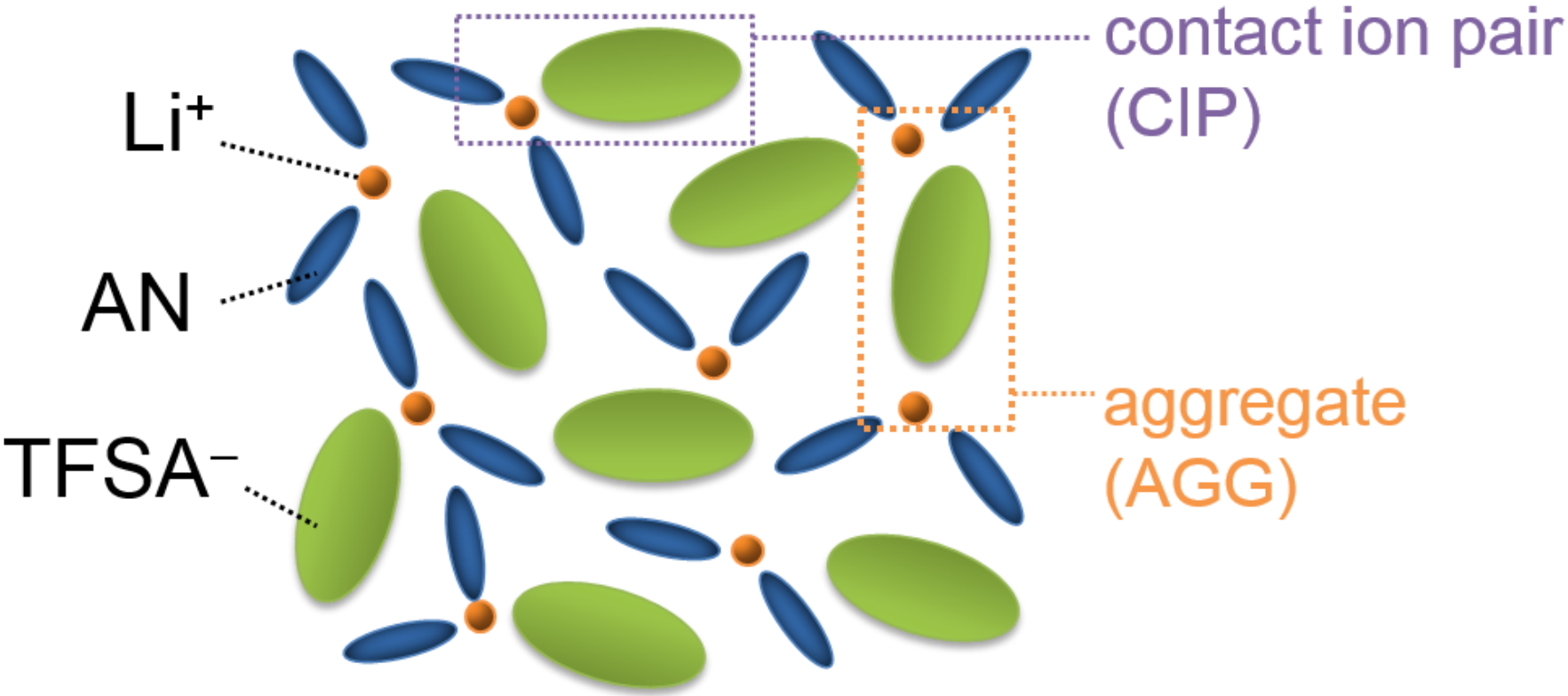








Solution structure of LiTFSA/AN

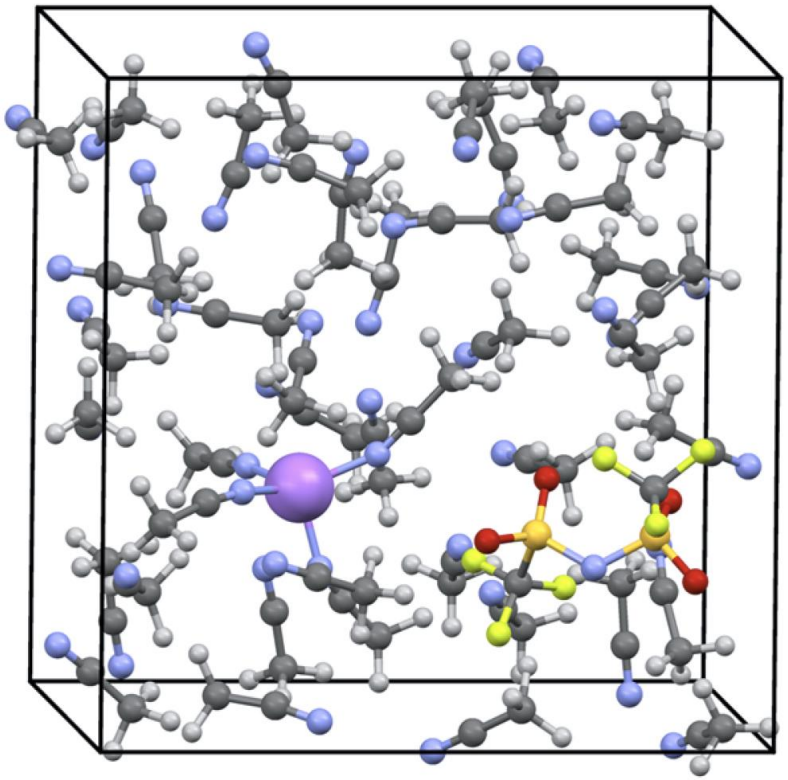


- All solvents coordinating to Li^+
- All anions coordinating to Li^+

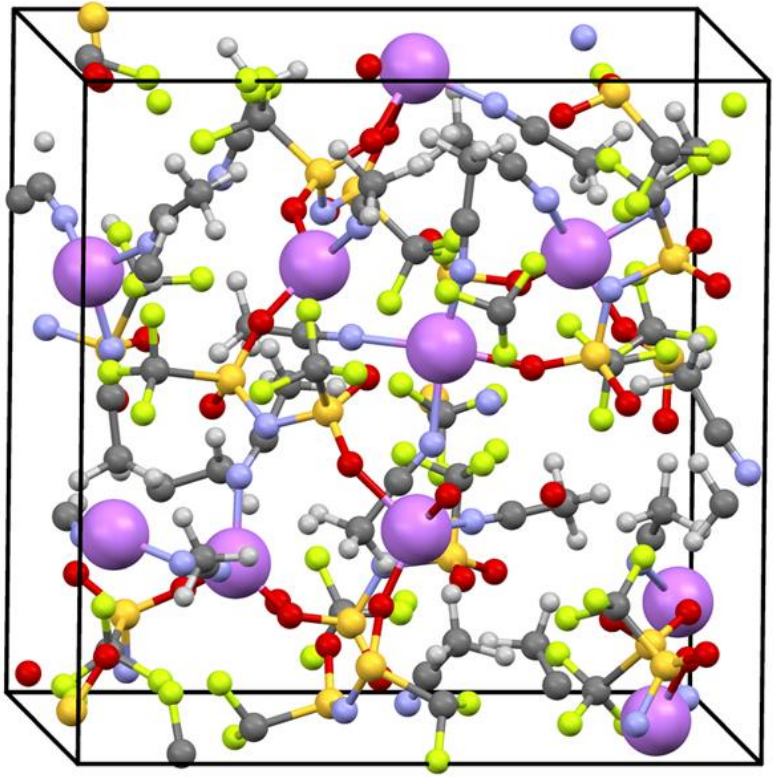
Why is Li salt-based SEI formed?

First-principle DFT-MD

Dilute (0.4 mol/L)
(1-LiTFSA, 43-AN)



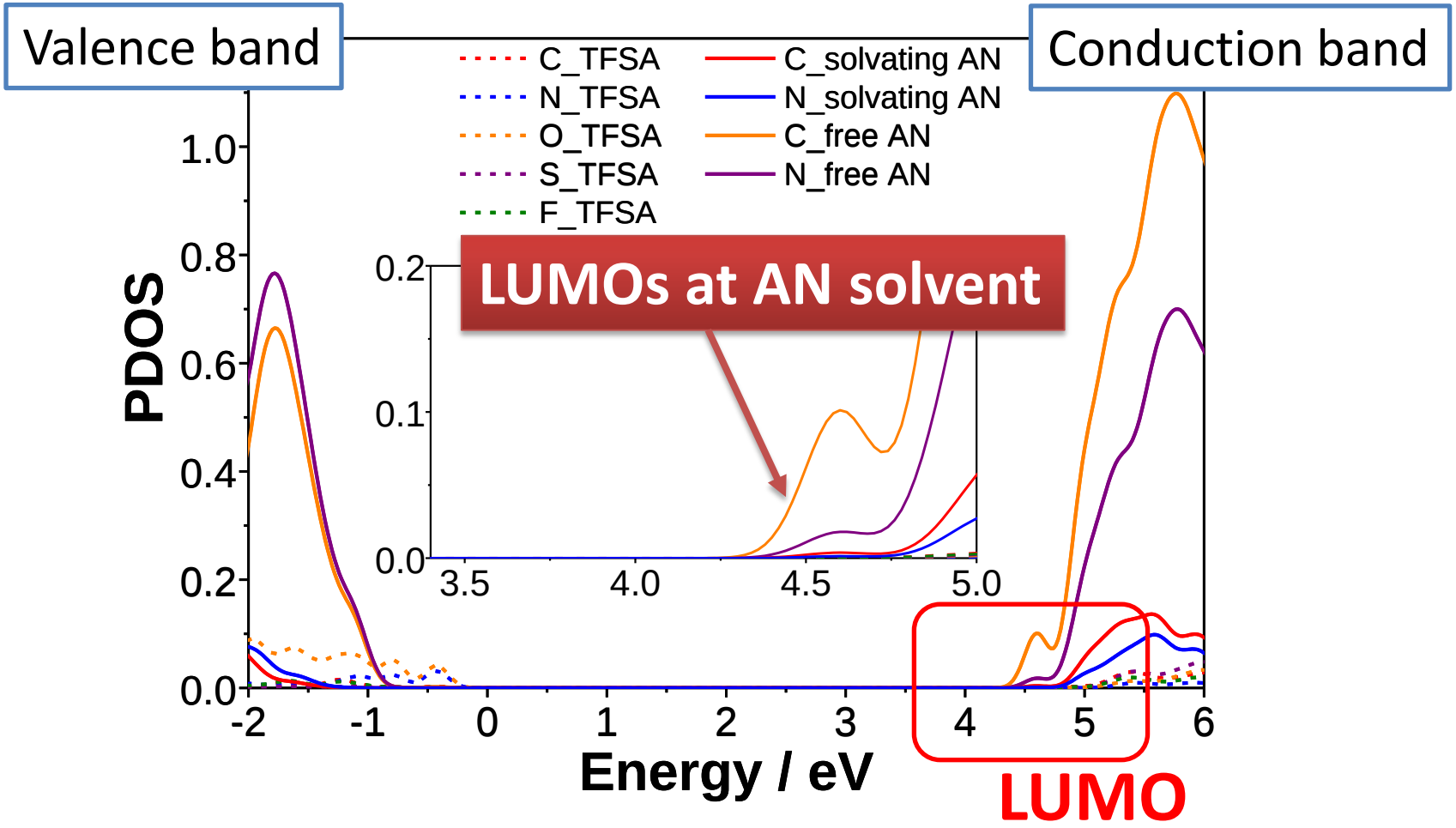
Concentrated (4.2 mol/L)
(10-LiTFSA, 20-AN)



CPMD PBE

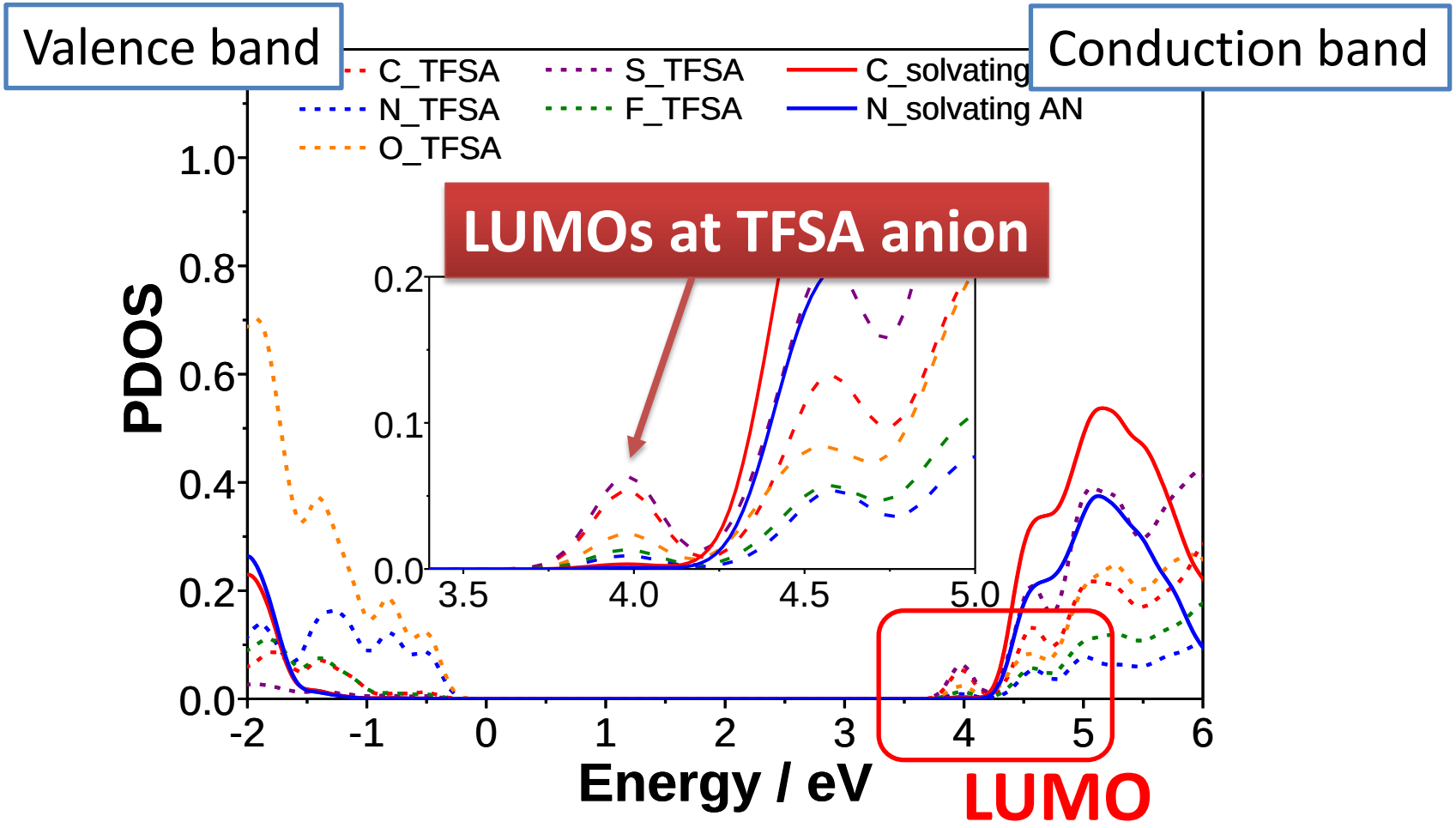
Electronic structure of dilute solution

Solvent should be reduced



Electronic structure of concentrated solution

Anions should be reduced

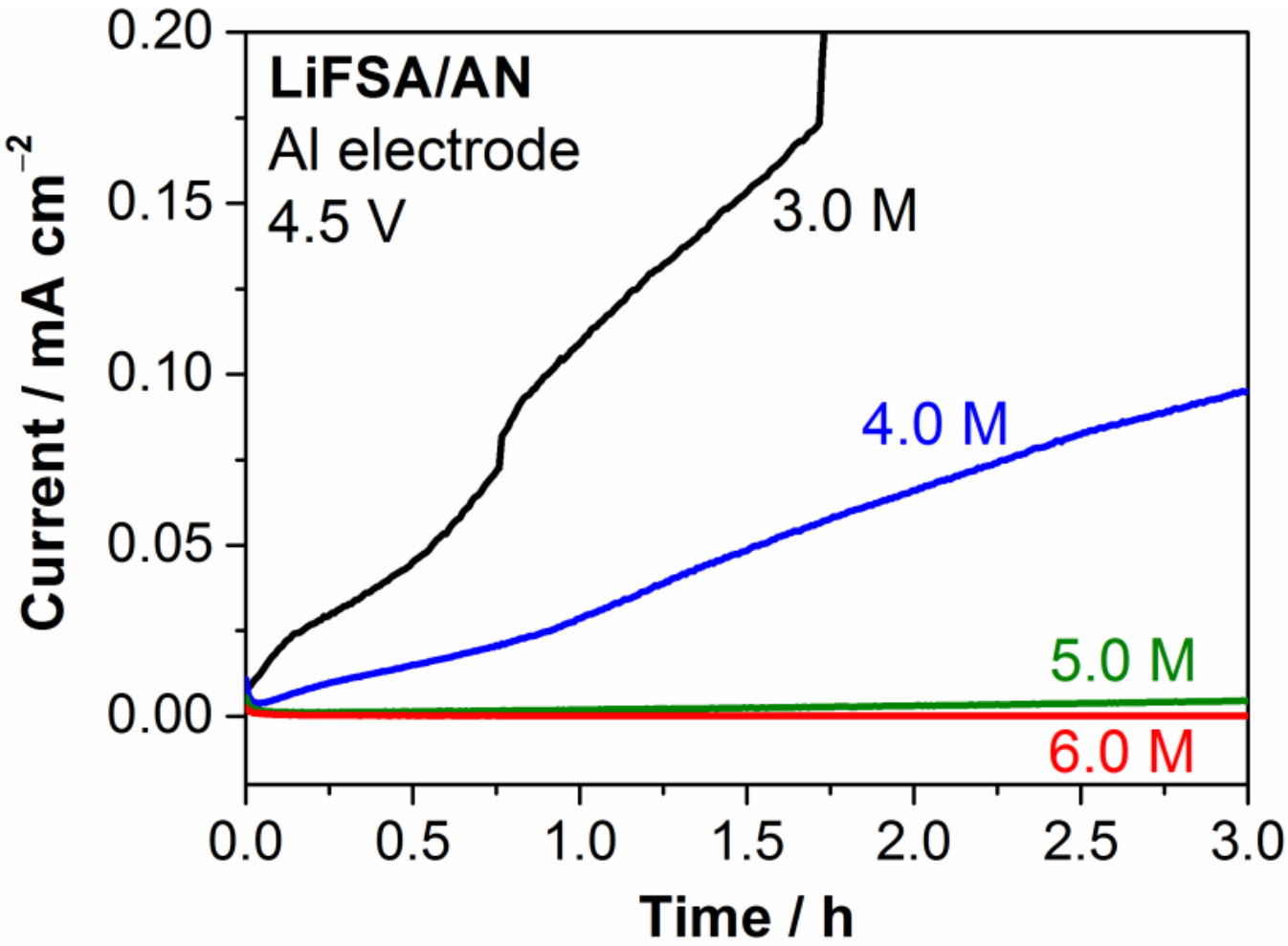


Topic

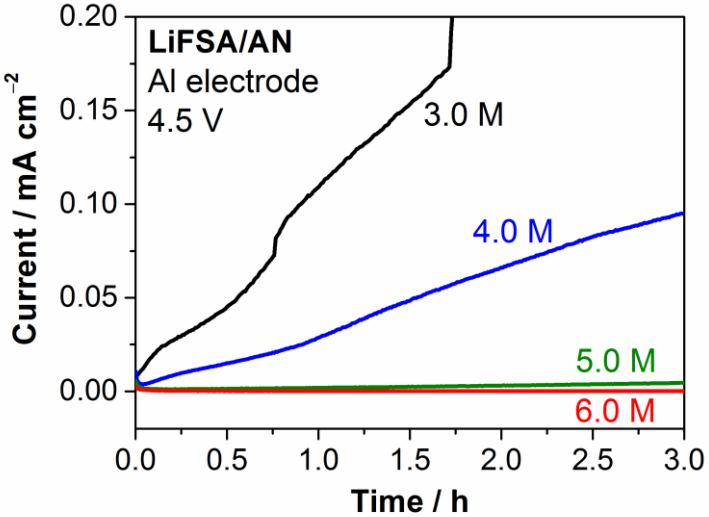
- Enhanced reduction stability
- Suppression of Al corrosion
- Fast reaction

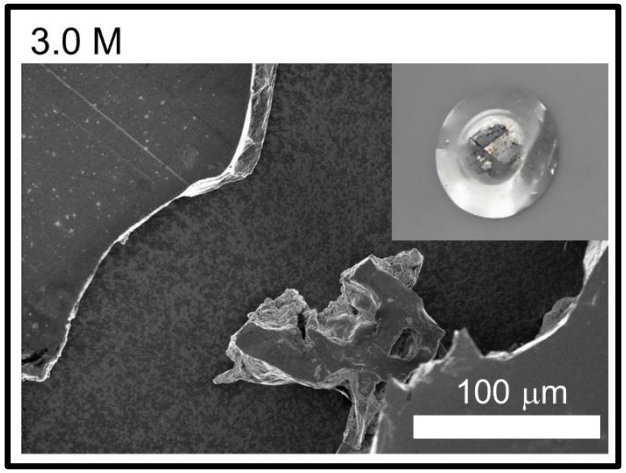
Oxidation stability at Al electrode

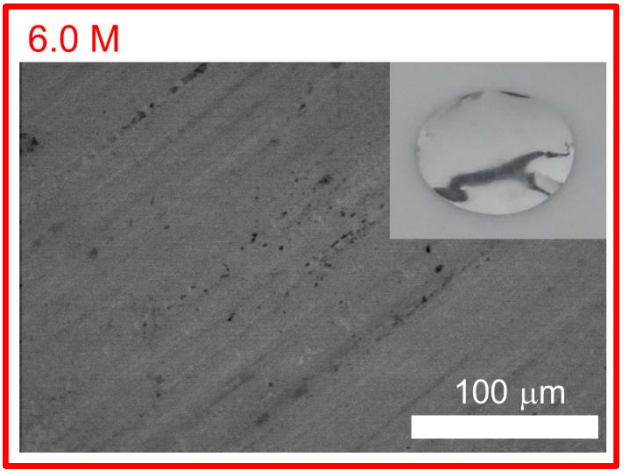
Higher stability at higher concentrations

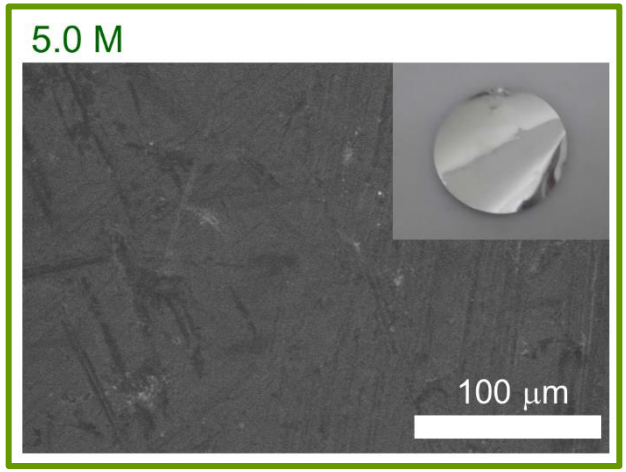


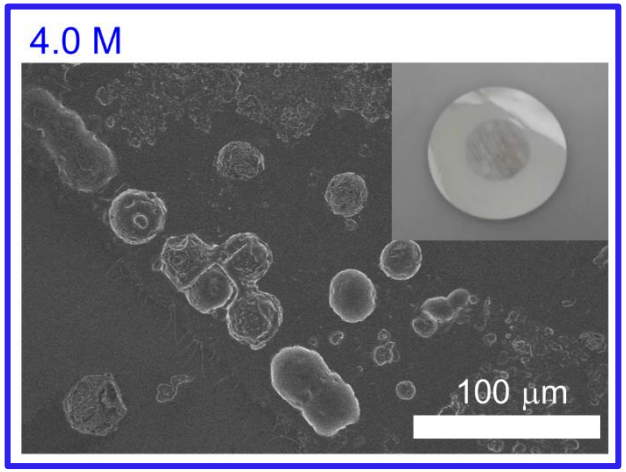
Suppression of Al corrosion





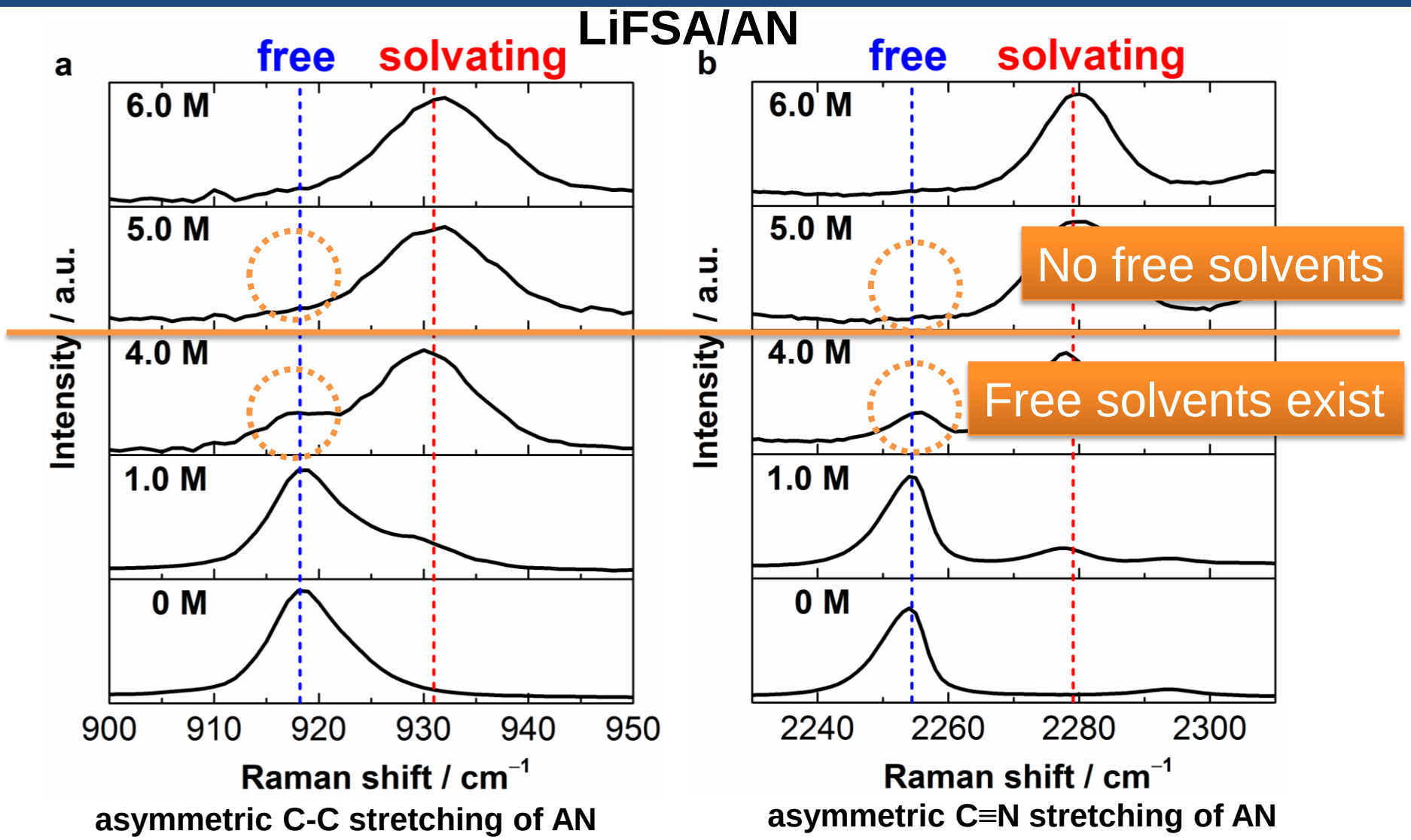






Striking difference between 4.0 M and 5.0 M

Free solvent disappears over 5 M



Theoretical evidence (DFT-MD)

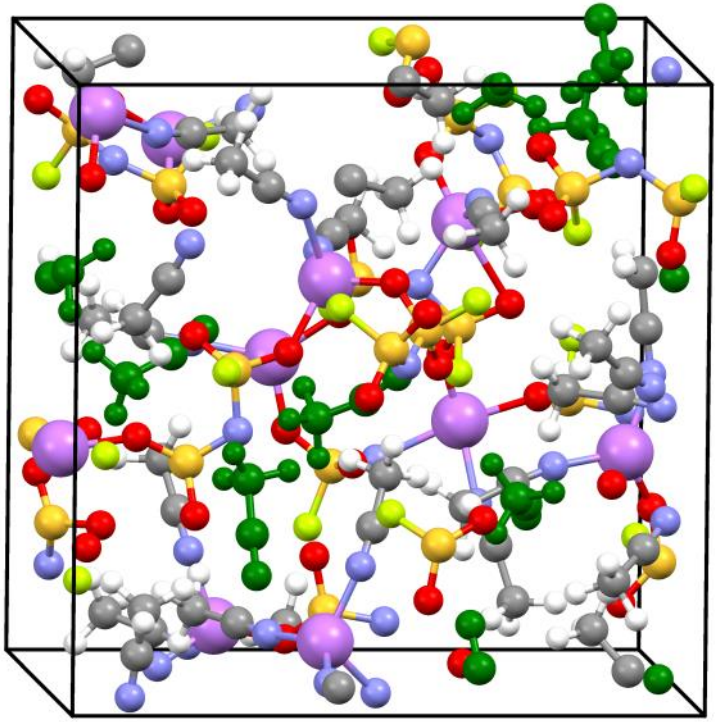
4.0 M $LiN(SO_2F)_2$/AN

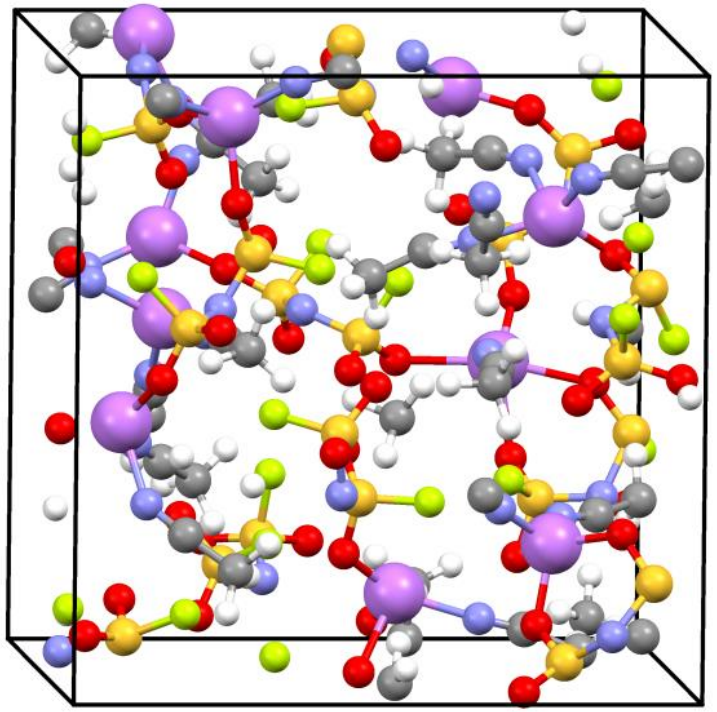
- 10-LiFSA
- 30-AN

5.0 M $LiN(SO_2F)_2$/AN

- 10-LiFSA
- 20-AN

Dark green: free solvent

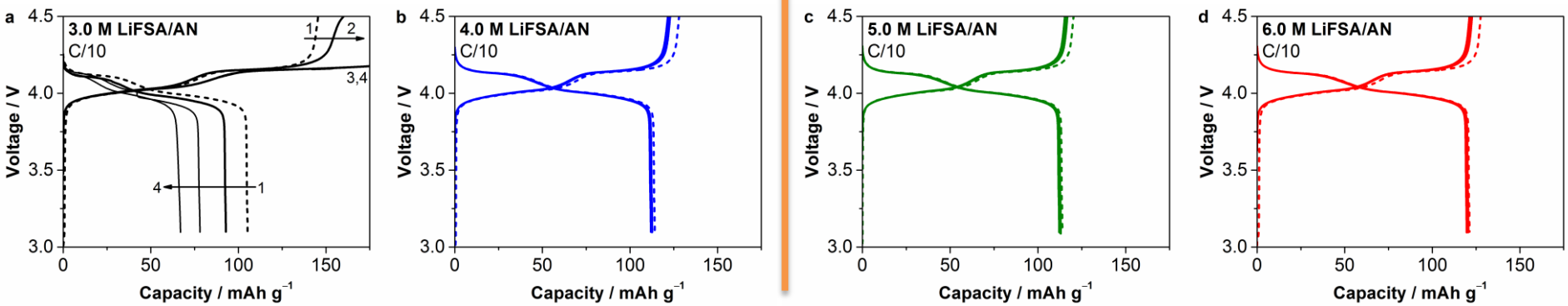


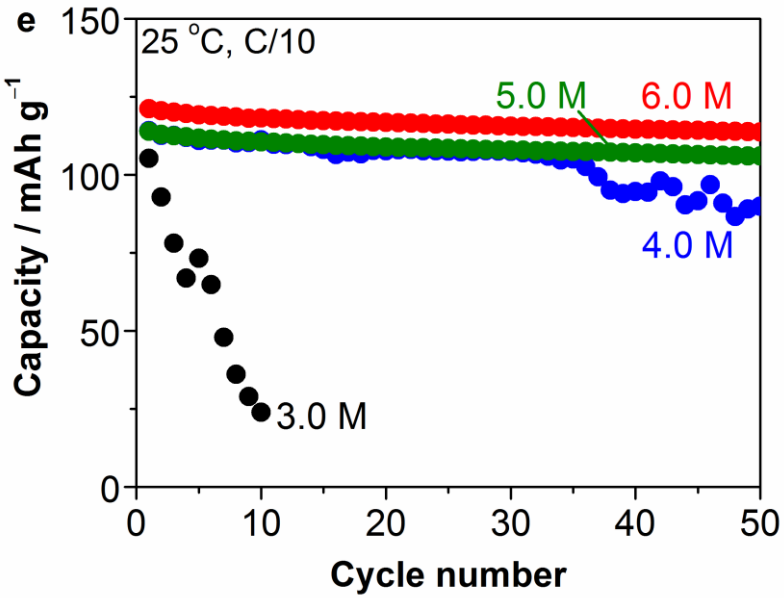


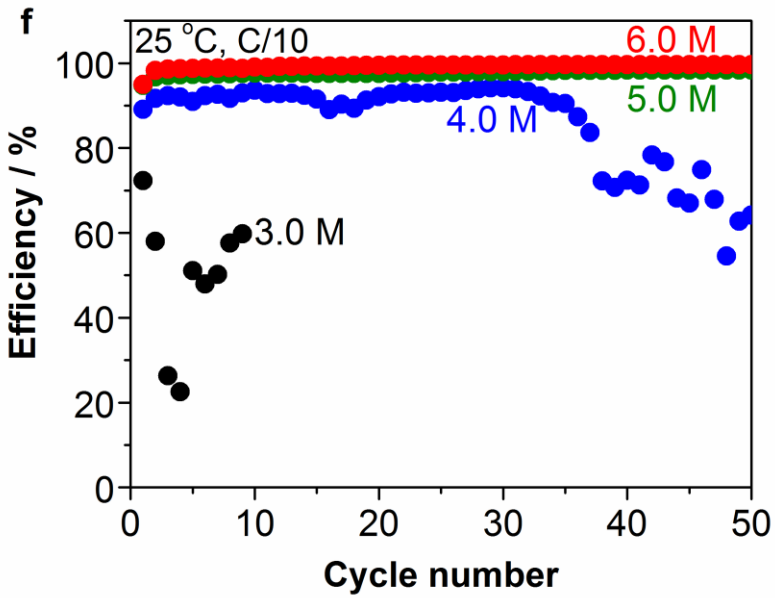
$LiMn_2O_4$/Li cell reversibility

With free solvents

Without free solvents





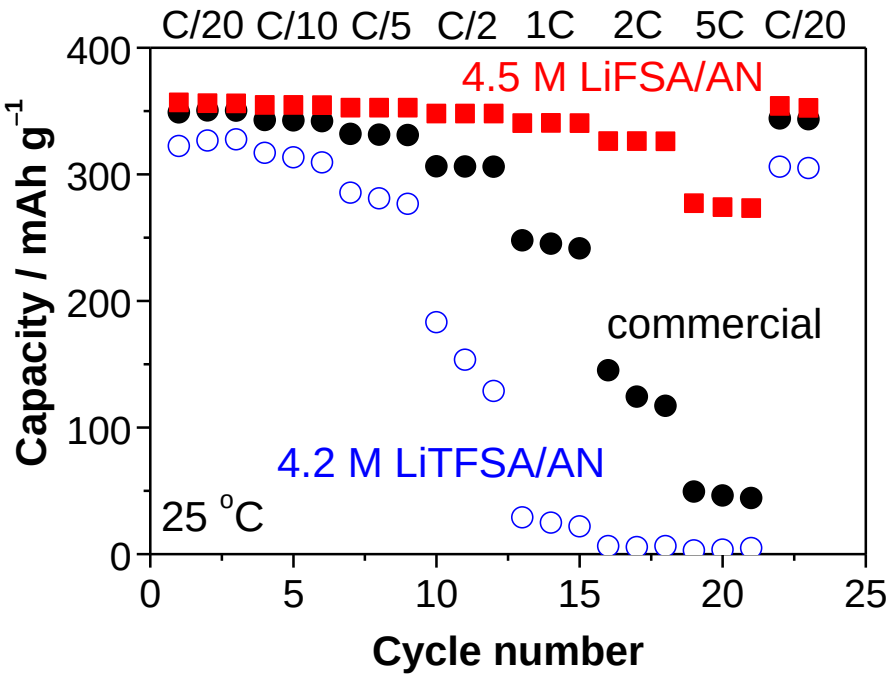


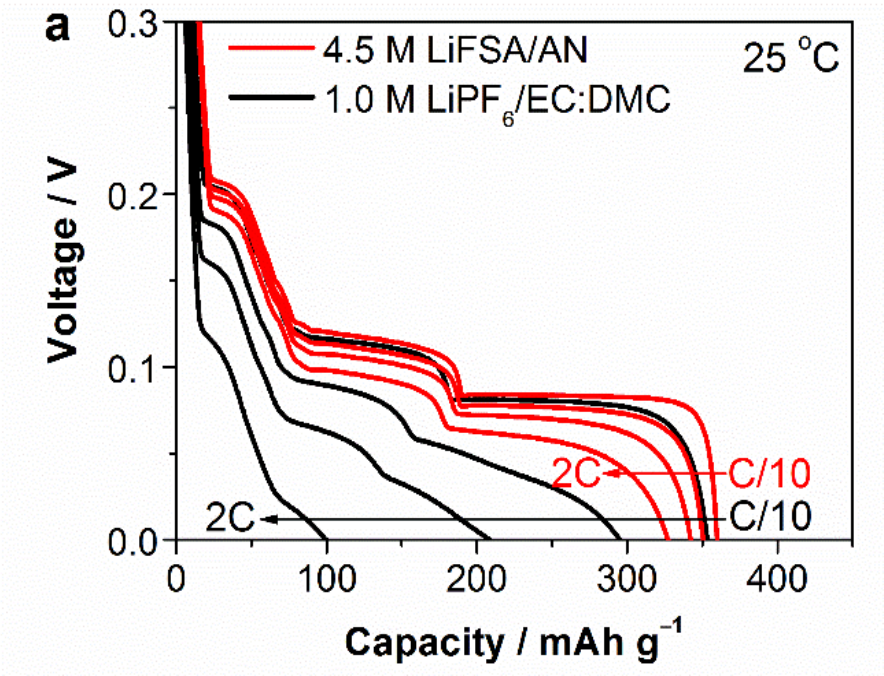
Topic

- Enhanced reduction stability
- Suppression of Al corrosion
- Fast reaction

Super-high rate beyond EC

Graphite half cell





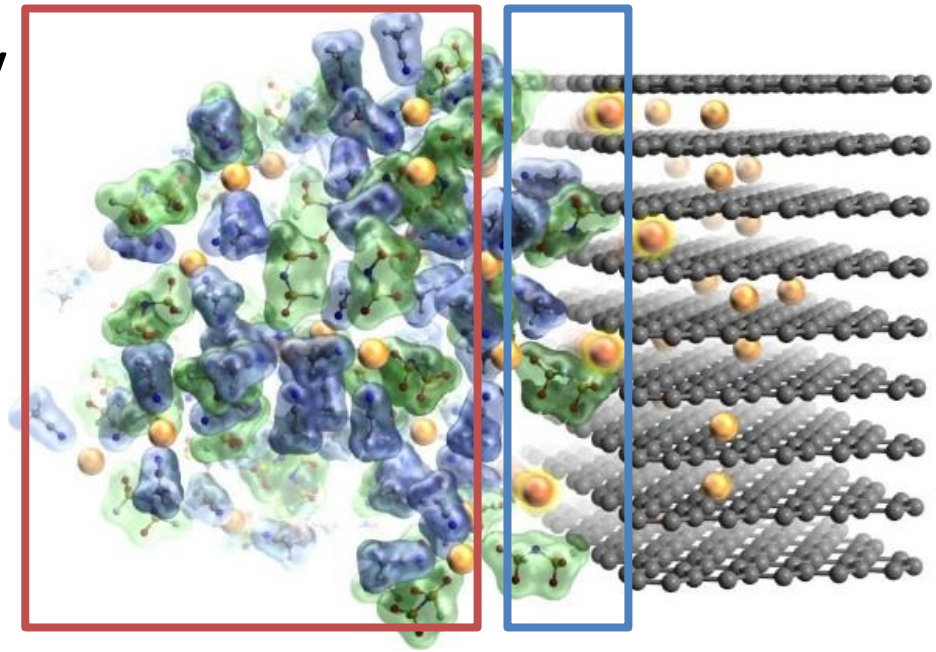
Li intercalation kinetics is much faster than in commercial EC-based electrolyte.

Y. Yamada et al., ***Chem Commun.***, 49, 11194 (2013).
Y. Yamada et al., ***J. Am. Chem. Soc.***, 136, 5039 (2014).

Mechanism of fast reaction in LiFSA concentrated electrolyte

1) Ion transport in electrolyte

Ionic conductivity

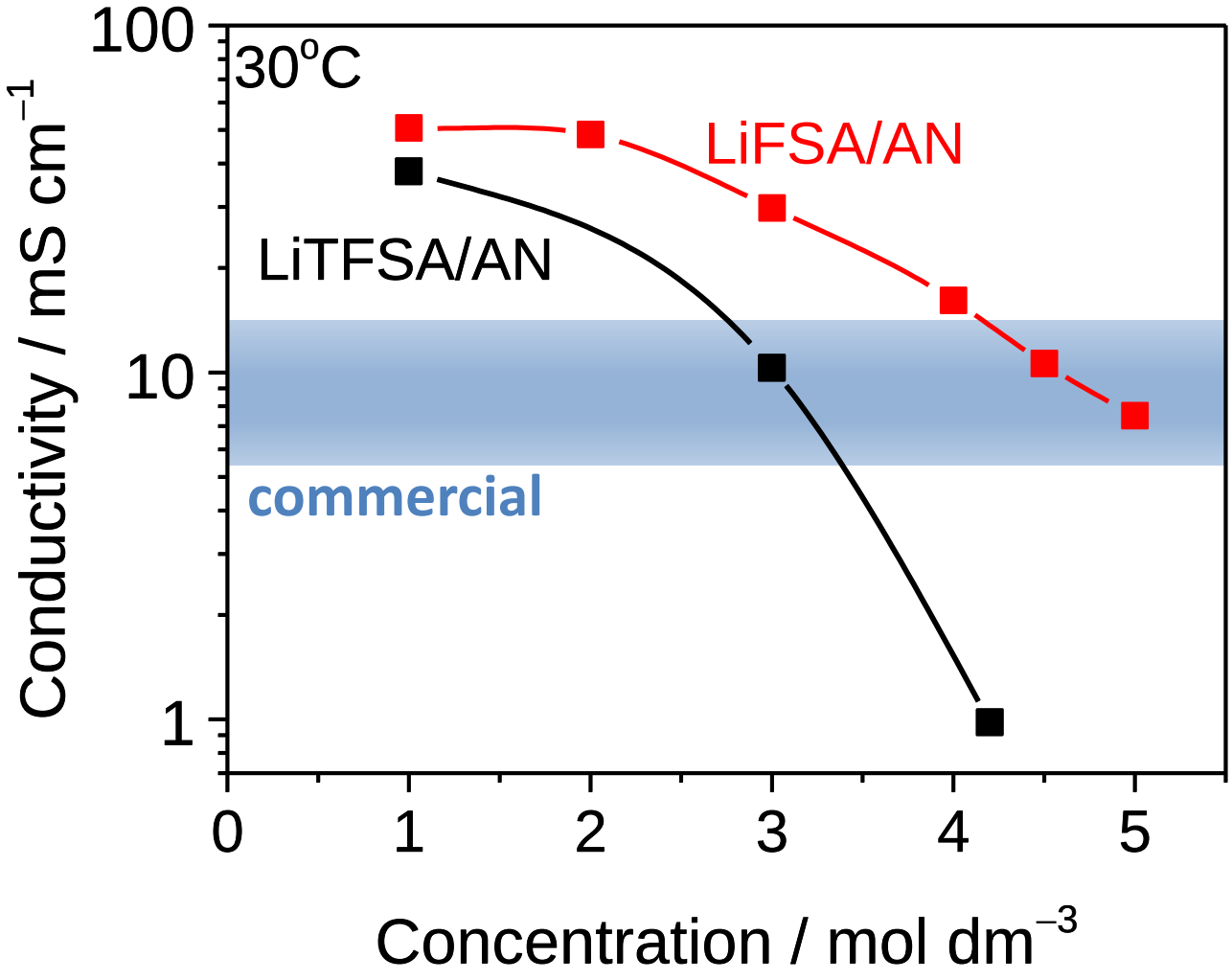


2) Charge transfer at interface

- Activation energy
- Frequency factor

Ionic conductivity

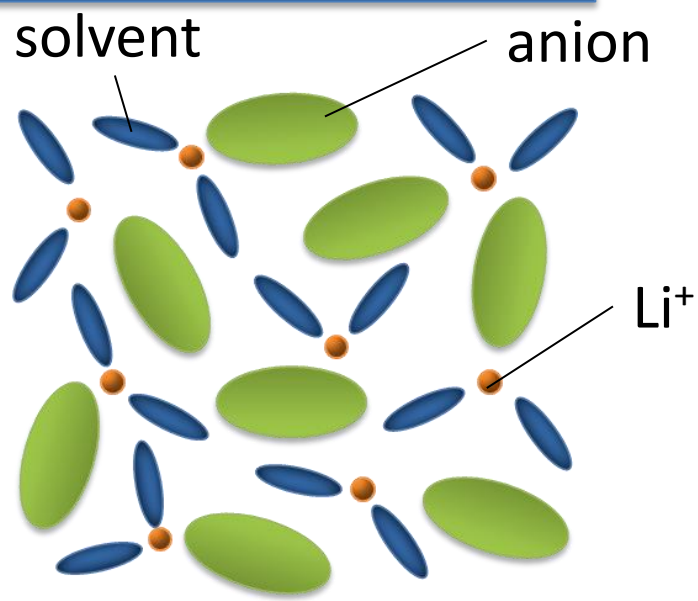
Anion is important



Ionic conductivity

Li^+-anion interaction is a decisive factor

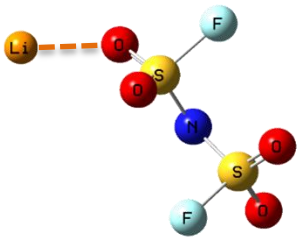
Concentrated solution



Extensive association of Li^+ and anion

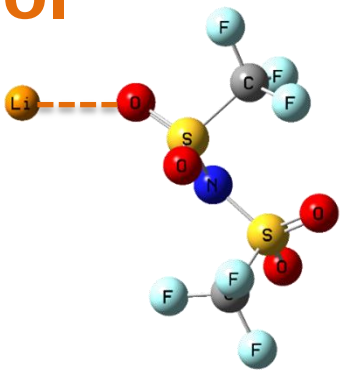
Binding energy*

594 kJ mol^{-1}



LiFSA

606 kJ mol^{-1}



LiTFSA

*P. Johansson, ***Phys. Chem. Chem. Phys.***, 9, 1493 (2007).

Interfacial activation energy

Li^+-anion interaction makes a large impact

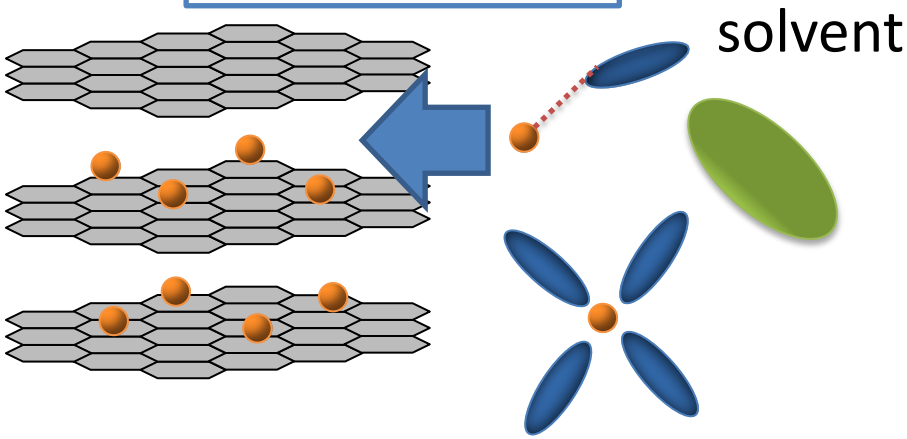
Low concentration

Electrolyte	E_a / kJ mol^{-1}
Commercial EC	50-58

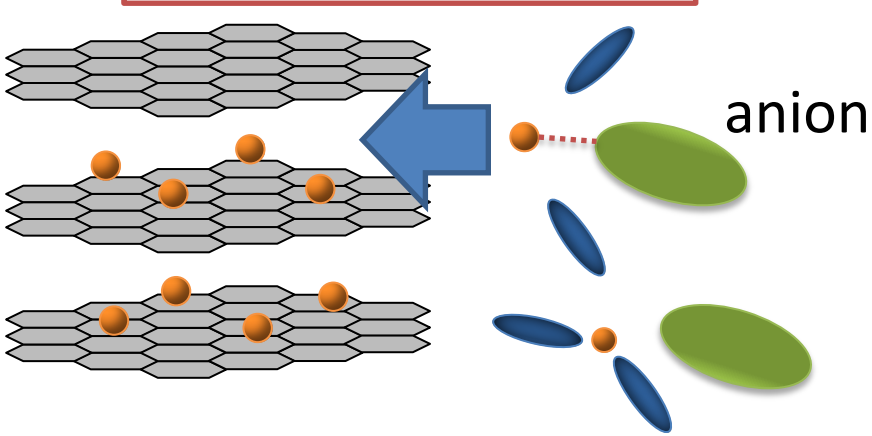
High concentration

Electrolyte	E_a / kJ mol^{-1}
LiFSA/AN	58-63

De-solvation



De-complexation

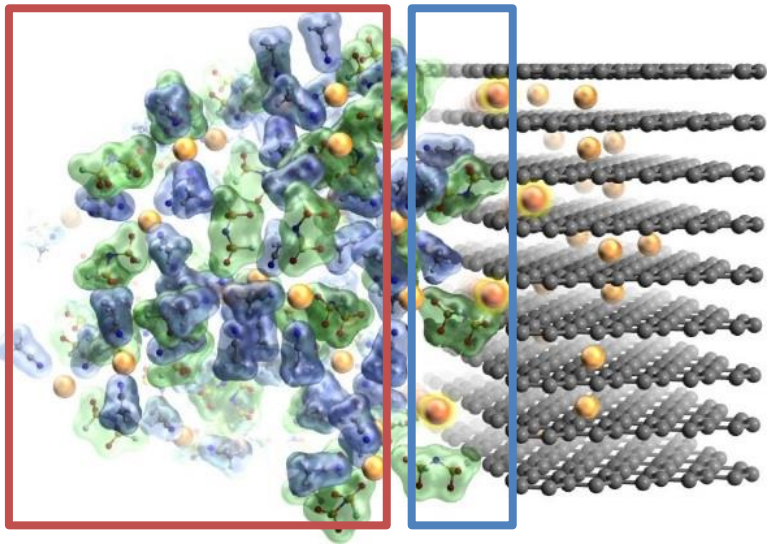


T. Abe et al., ***J. Electrochem. Soc.***, 151, A1120 (2004).
Y. Yamada et al., ***Langmuir***, 25, 12766 (2009).

Mechanism of fast reaction in LiFSA concentrated electrolyte

1) Ionic conductivity

comparable to commercial electrolyte



2) Charge transfer

- Activation energy
  comparable to or slightly larger than commercial electrolyte

- Frequency factor → **Important for fast reaction**
  - **Interfacial Li^+ concentration**
  - **LiFSA-based SEI**

Conclusions

- ✓ **Enhanced reduction stability**
  *Peculiar LUMO characters
  *Li salt-based SEI

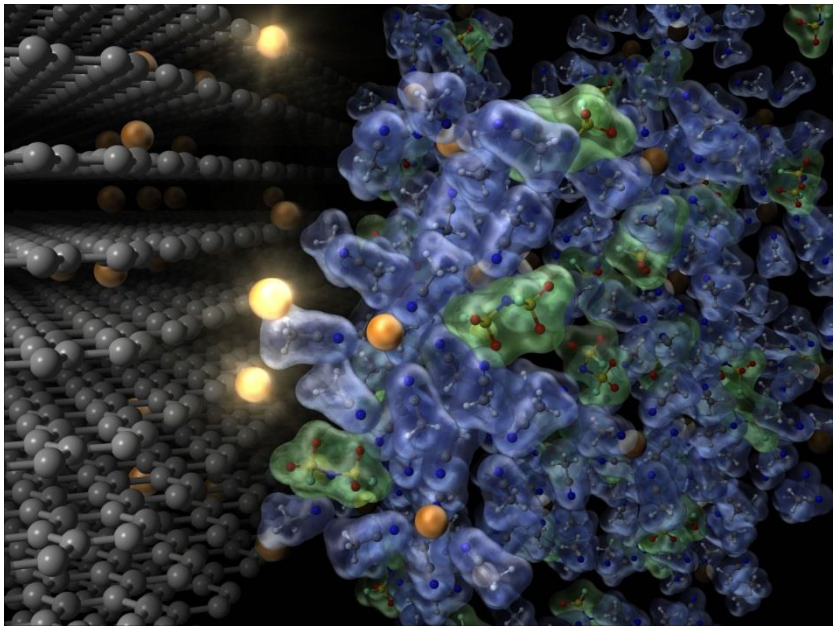
- ✓ **Suppression of Al corrosion**
  *No free solvents

- ✓ **Fast reaction**
  *Importance of anion
  *High frequency factor

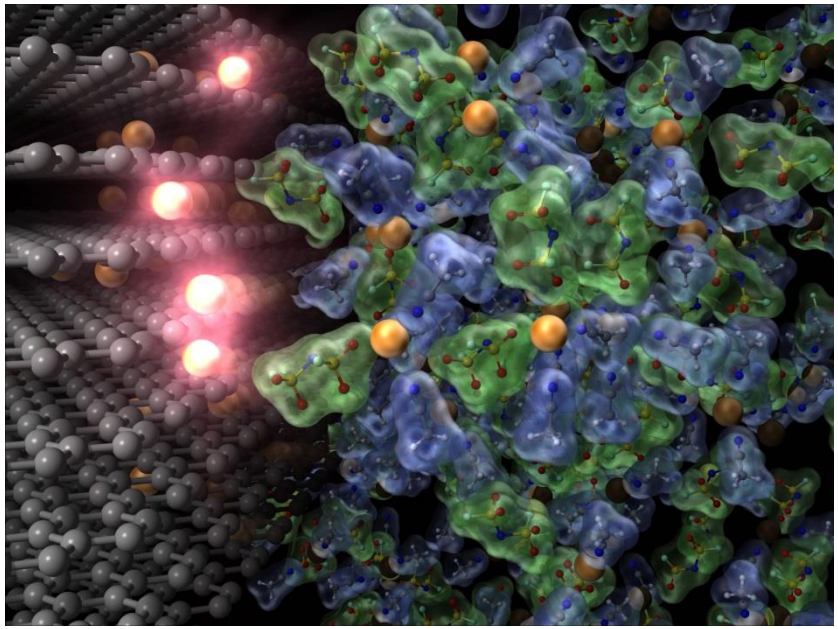
Distinguished New Material

NOT a simple extension

Dilute (ca. 1 mol/L)



Super-Concentrated (> 3 mol/L)



Acknowledgements

ESICB project of Japan
(Elemental Strategy Initiative for Catalysts and Batteries)
Lab. members