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Salt concentration effect on SEI film formation in lithium-ion battery: Comparison with experimental observation

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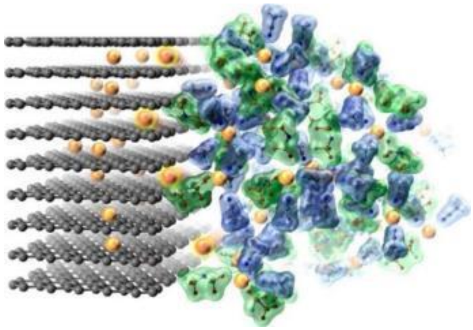
Background



Highly concentrated electrolyte[1]

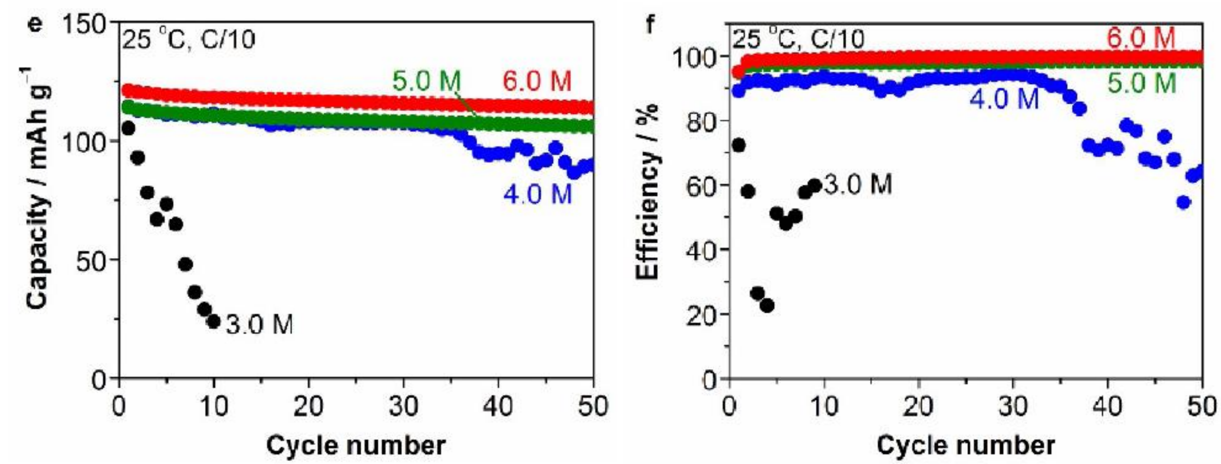


Fig. Electric capacity and Coulomb efficiency in LiFSA/acetonitrile (AN) electrolyte in lithium-ion battery [3]

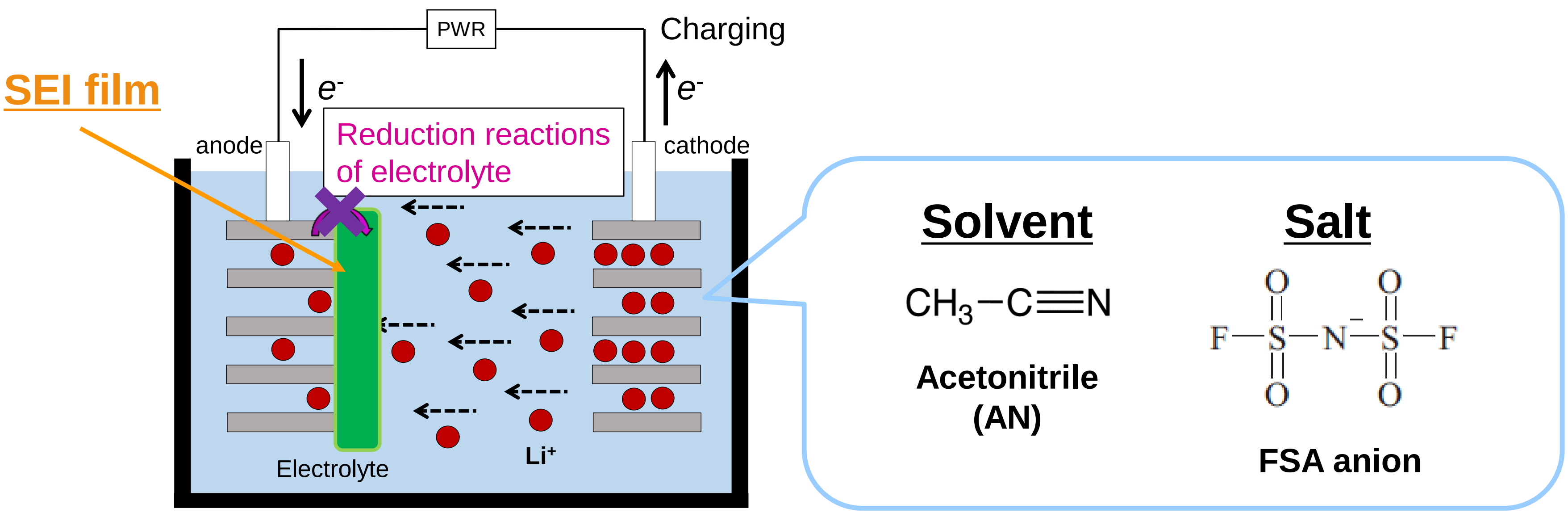
- ✓ It is well known that the lifetime and stability of lithium-ion batteries (LIB) are significantly improved by increasing the salt concentration [1-3].

- ✓ However, the microscopic mechanism of salt concentration on the SEI film formation is still not found.

[1] Y. Yamada et al., *J. Am. Chem. Soc.*, **136**, 5039 (2014).
[2] Y. Yamada et al., *J. Electrochem. Soc.*, **162**, A2406 (2015).
[3] Y. Yamada et al., *ChemElectroChem*, **2**, 1687 (2015).

Purpose of study

✓ To compare the simulation results with the experimental observations, the SEI film formation mechanism was investigated in LIB with AN solvents and LiFSA salts.



Schematic illustration of lithium-ion battery

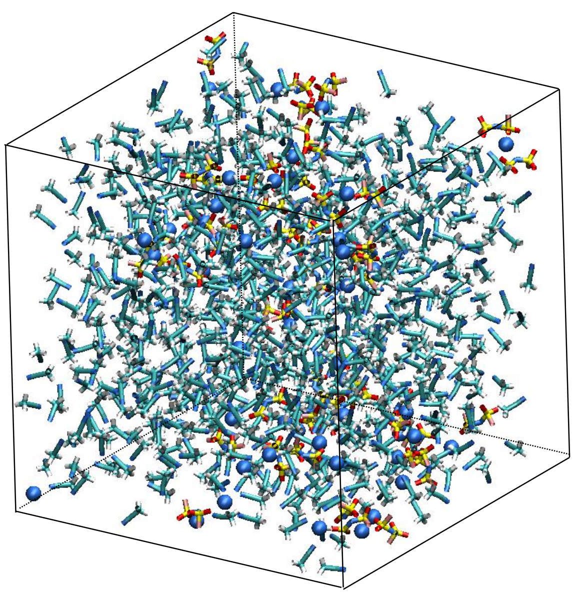
Adjustment of number of molecules

Table.　Mass density and molecular ratio

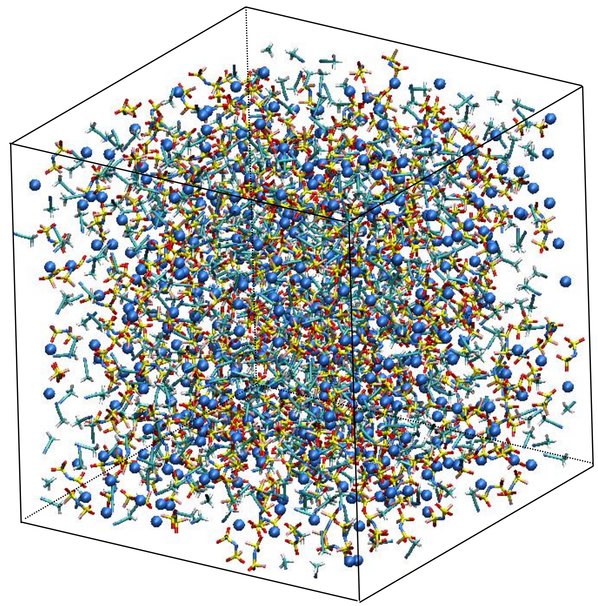
		Salt concentration [molL^{-1}]					
		1.0	2.0	3.0	4.0	5.0	6.0
Number of molecules	AN	800	800	800	800	800	800
	FSA^-	50	105	167	240	340	470
	Li^+	50	105	167	240	340	470
Molecular ratio (AN/LiFSA)		16 (17)	7.3	4.8 (4.7)	3.3 (3.1)	2.3 (2.1)	1.7 (1.5)
Mass densty [gcm^{-3}]		0.86 (0.89)	1.01	1.15 (1.14)	1.28 (1.26)	1.41 (1.37)	1.53 (1.48)

Experimental values in parenthesis

Y. Yamada et al., *ChemElectroChem*, **2**, 1687 (2015).



(a) 1.0 M LiFSA/AN electrolyte

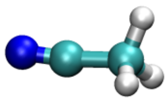


(b) 6.0 M LiFSA/AN electrolyte

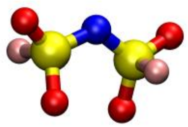
Calculation condition:

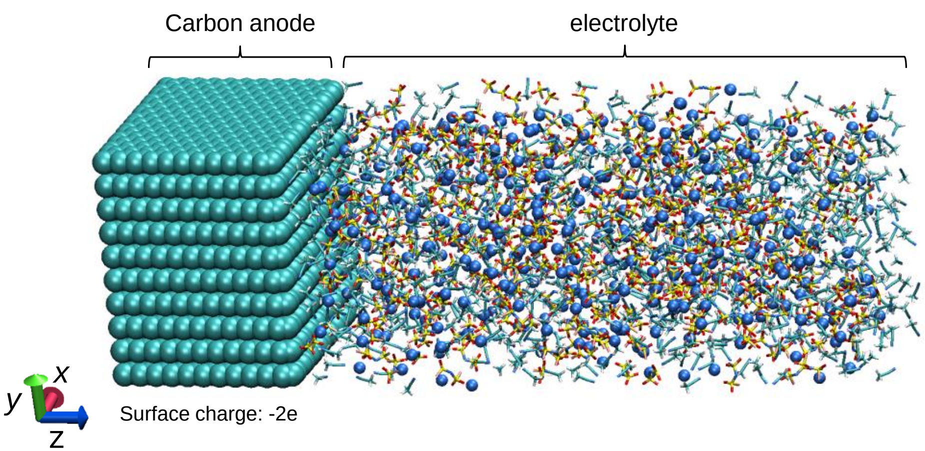
Force fiekd: GAFF
Charge: RESP
Temperature: 298 K
Pressure: 1 atm

Model system and reaction scheme

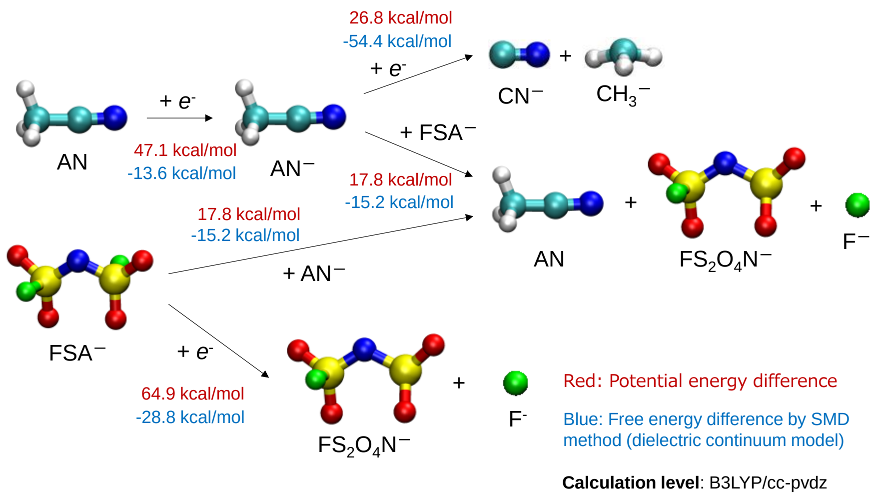

: Acetonitrile (AN)


: Li^+


: FSA^-



(a) Model system

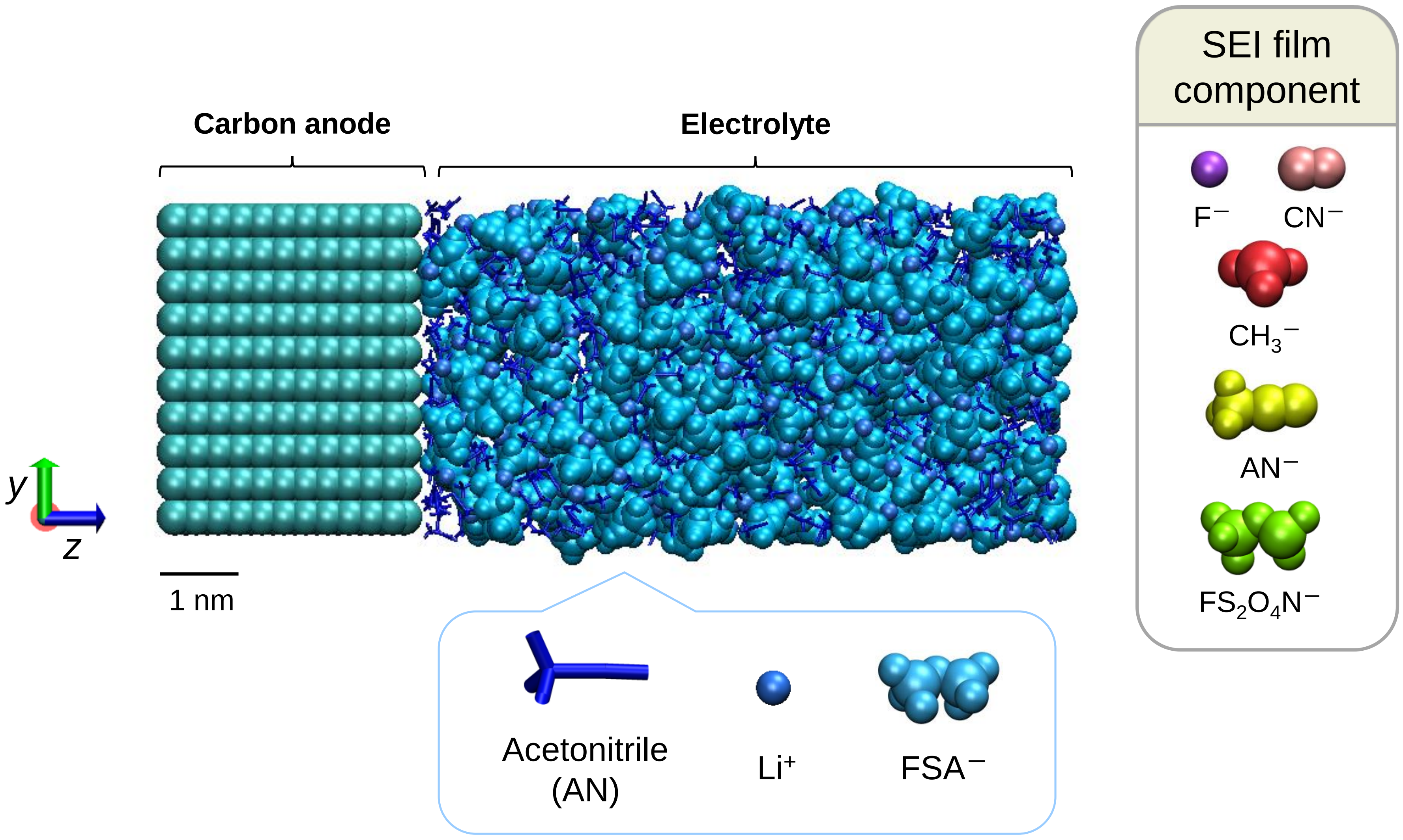


(b) Reaction scheme

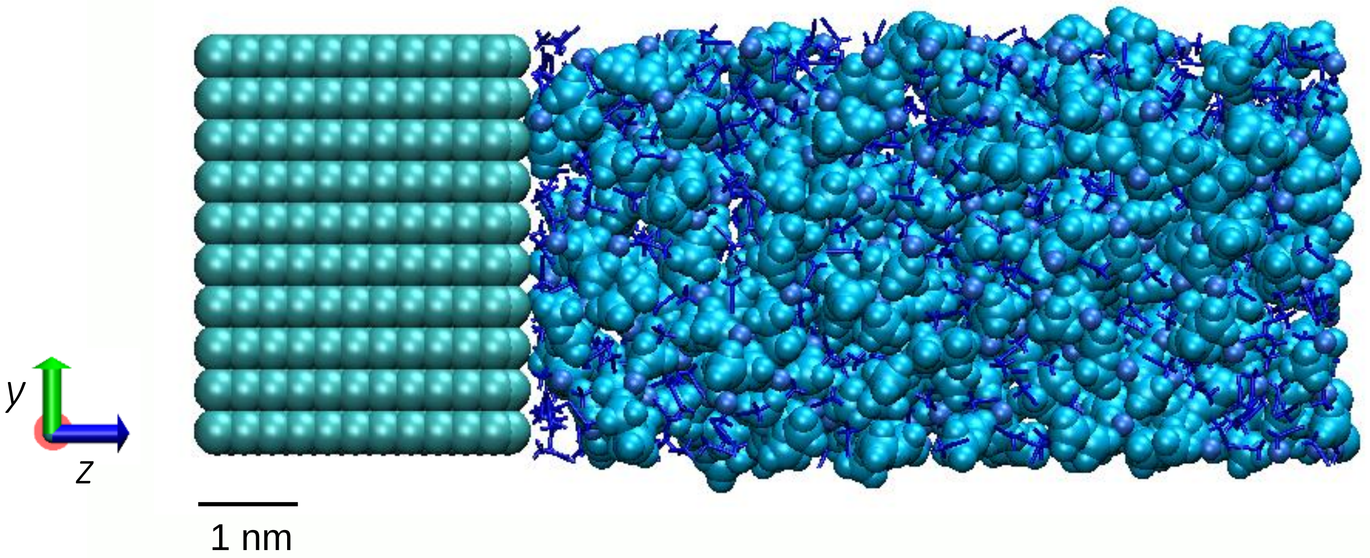
Calculation condition in hybrid MC/MD reaction method

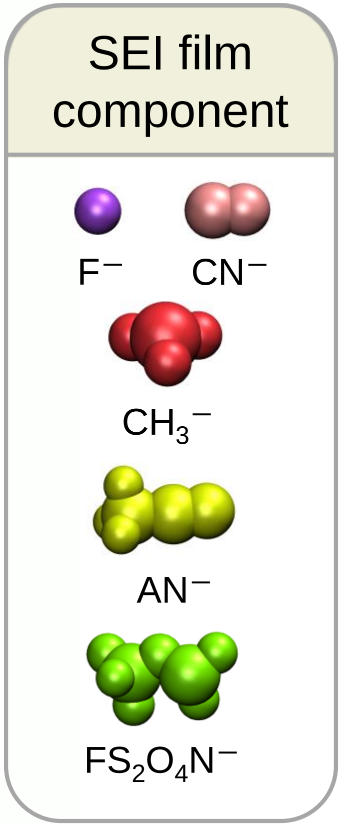
・Temperature: 298 K　　・10 ps per 1 MC/MD cycle

SEI film formation simulation at 5.0 M

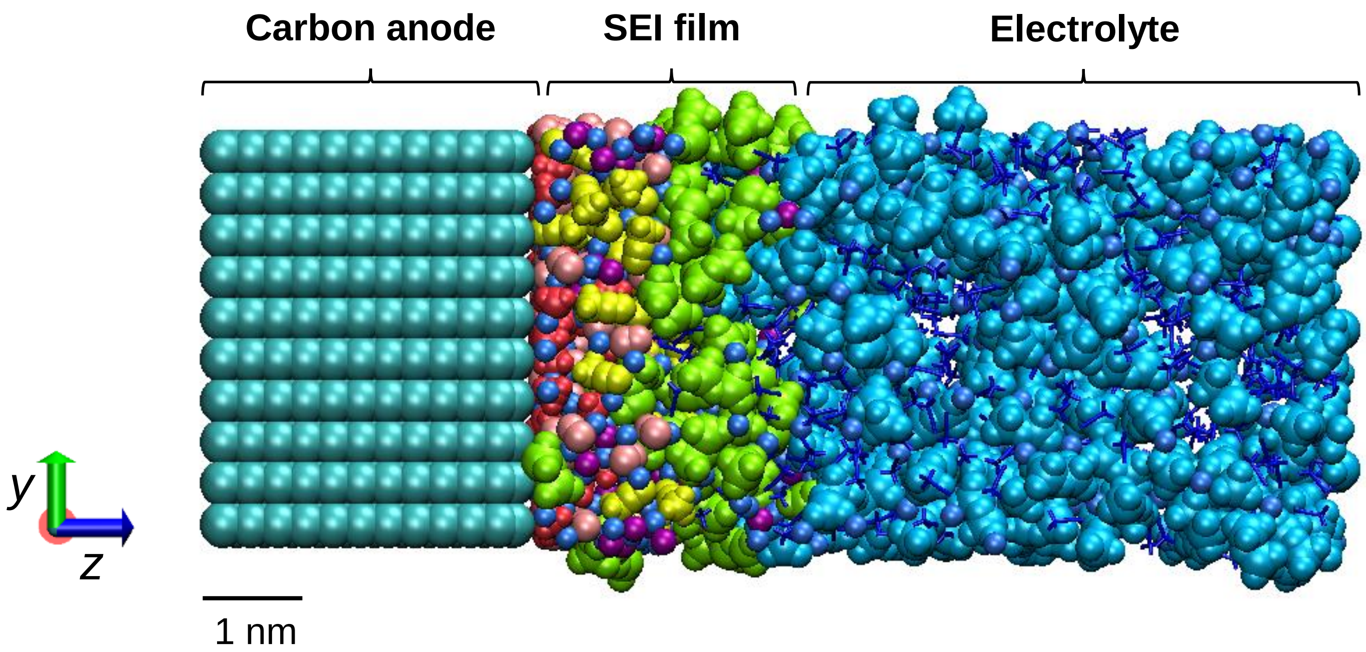


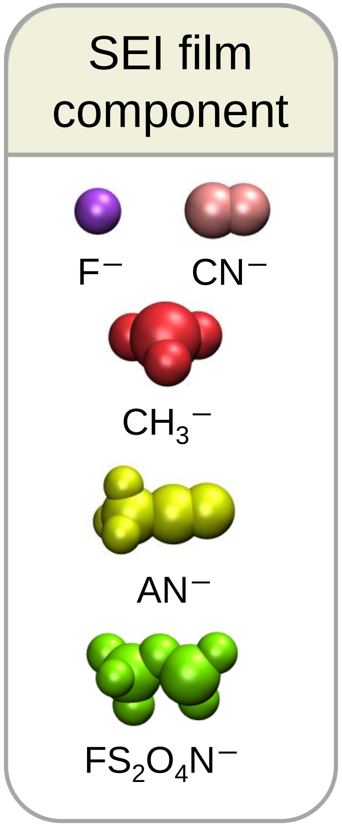
SEI film formation simulation at 5.0 M





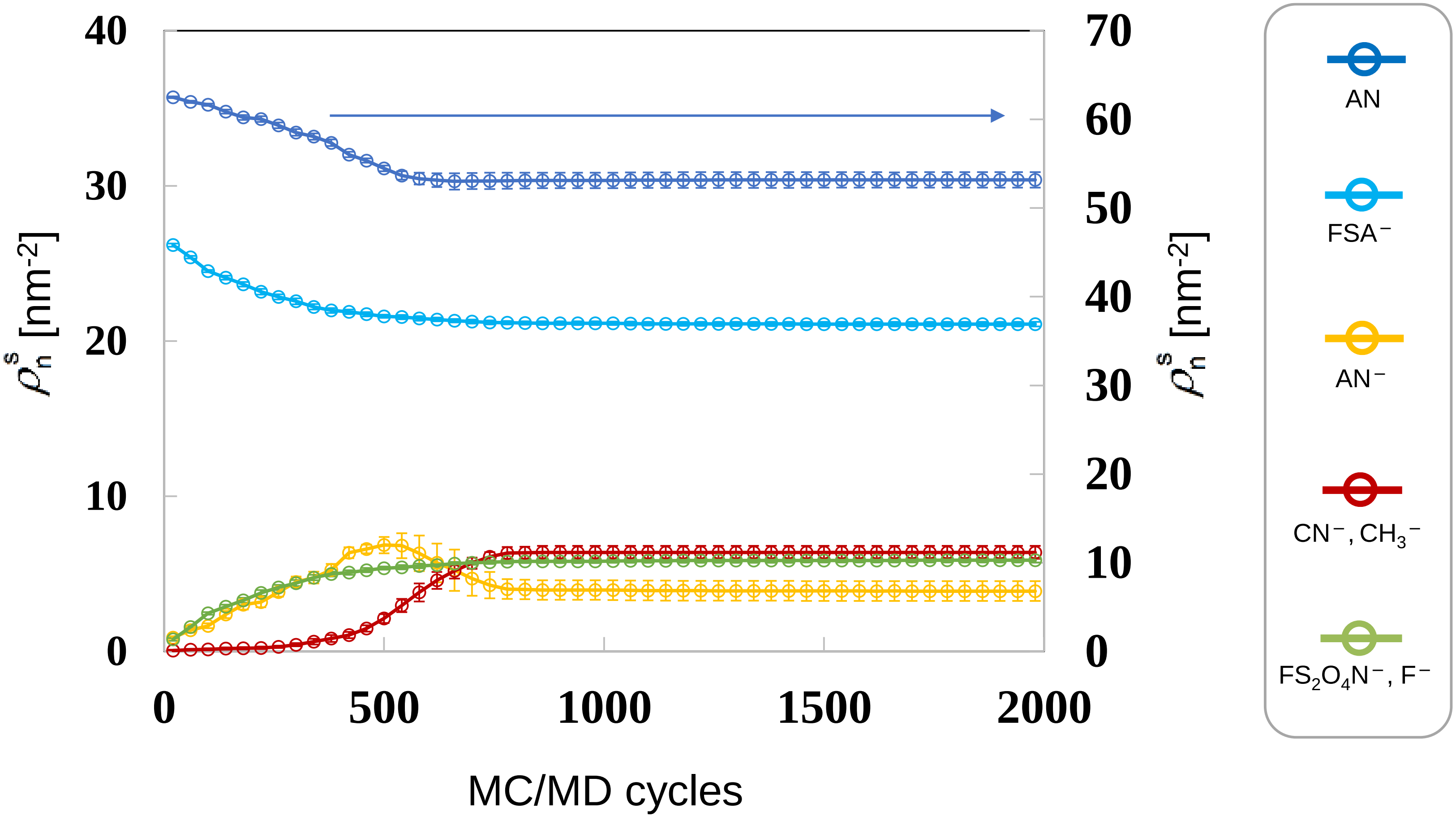
SEI film formation simulation at 5.0 M





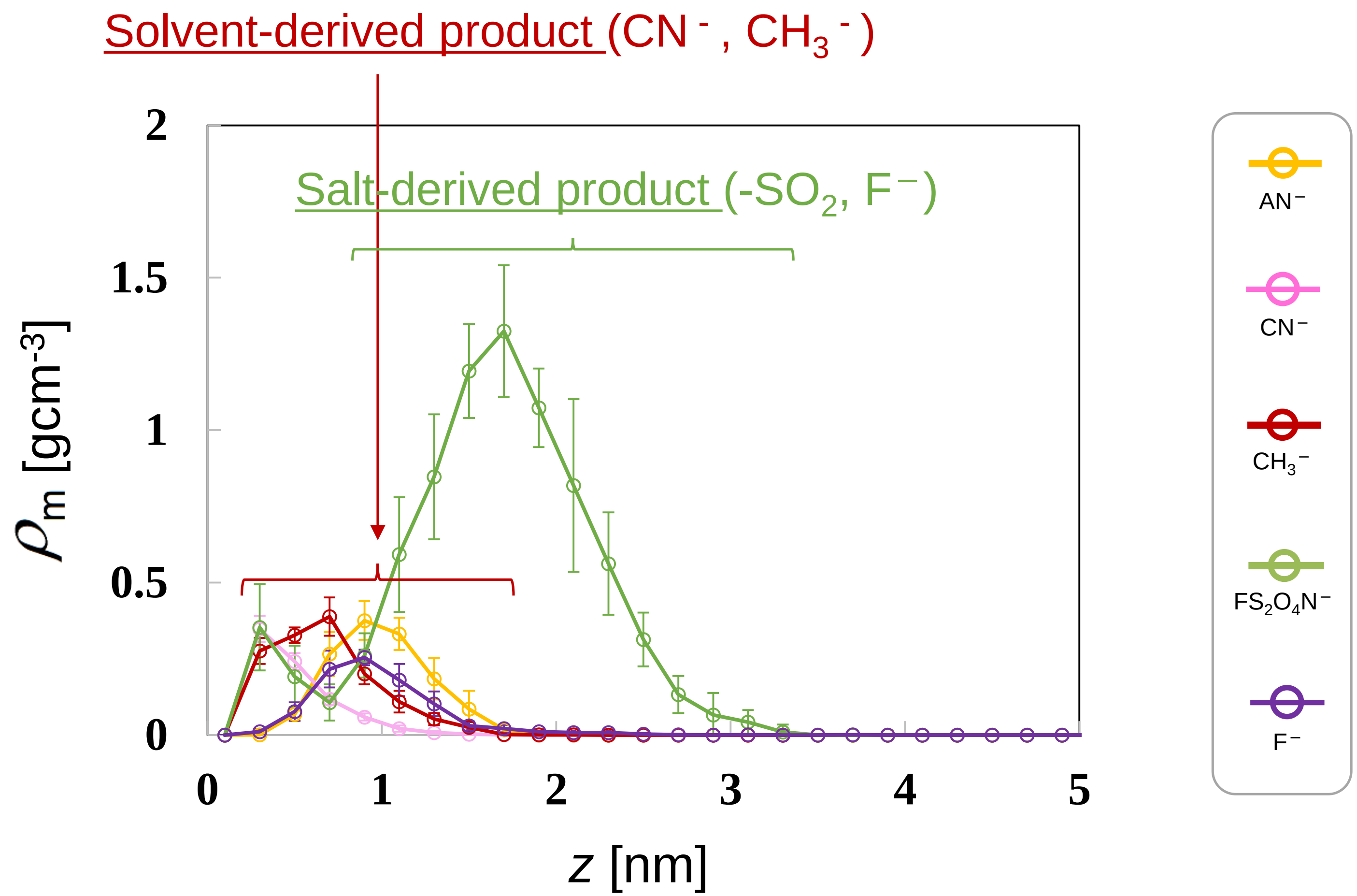
Change in surface number density (5.0 M)

(They are obtained by different 10 initial configurations.)



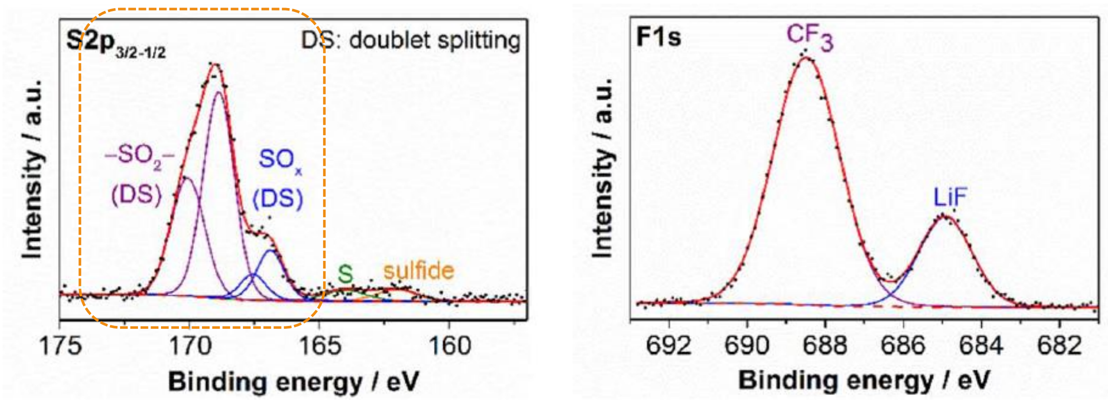
- In highly concentrated electrolyte, the FSA anions were preferentially reduced, and then, the AN solvents were reduced until the system reaches the steady state.

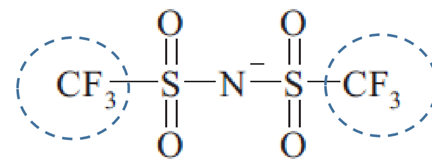
Mass density distributions (5.0 M)



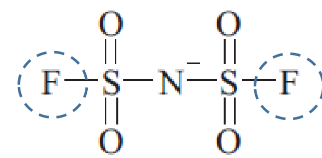
➢ In highly concentrated electrolyte, the salt-derived products such as $LiFS_2O_4N$ formed the passivate film in the side of electrolyte.

Comparison with experimental observation





TFSA⁻



FSA⁻

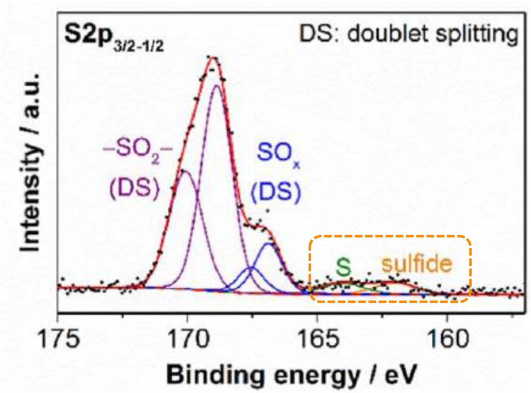
XPS analyses for SEI film components in LiTFSA/AN electrolyte [1]

→ It was found that the **sulfur-based passivation film (SEI film)** is formed in LiTFSA/AN electrolyte.

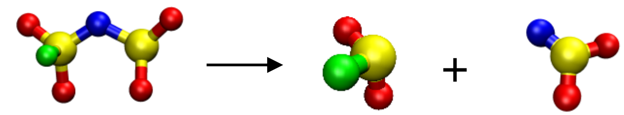
➢ The present simulation results are expected to reproduce the experimental observation.

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

Comparison with experimental observation



Proposed reaction mechanism



$FS_2O_4N^-$ → SO_2F^- + NSO_2^-

XPS analyses for SEI film components
in LiTFSA/AN electrolyte [1]

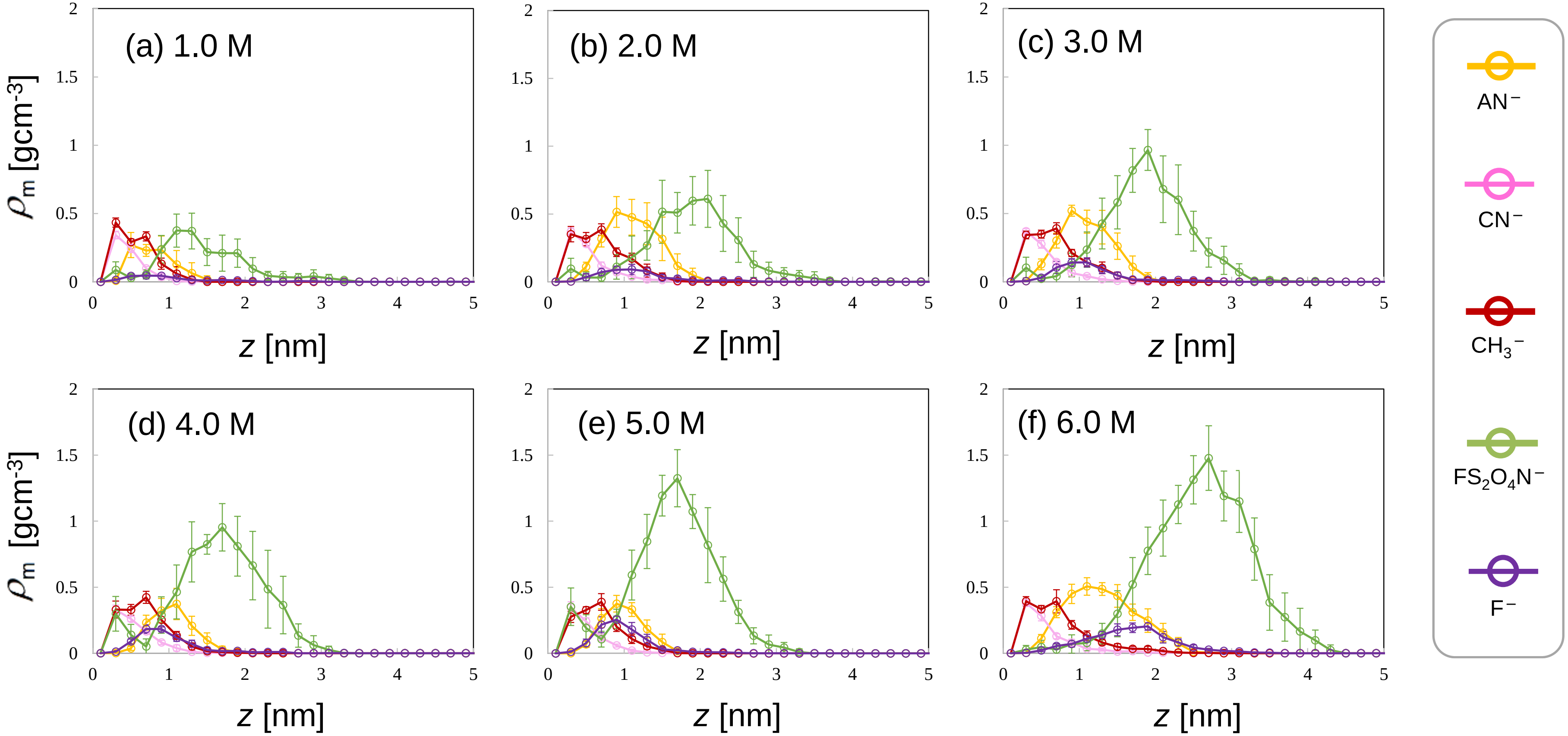
LiFSA ionic liquid electrolyte [2]

- ✓ According to previous study [2], the authors suggested that the FS_2O_4N- anions are further reduced in the LiFSA ionic liquid electrolyte.

- ➢ According to the DFT calculation (B3LYP/6-31+G(d) with SMD model), <u>the calculated activation energy was found to be quite large (44 kcal/mol)</u>. It is considered that this chemical reaction can occur if there is a strong electric field.

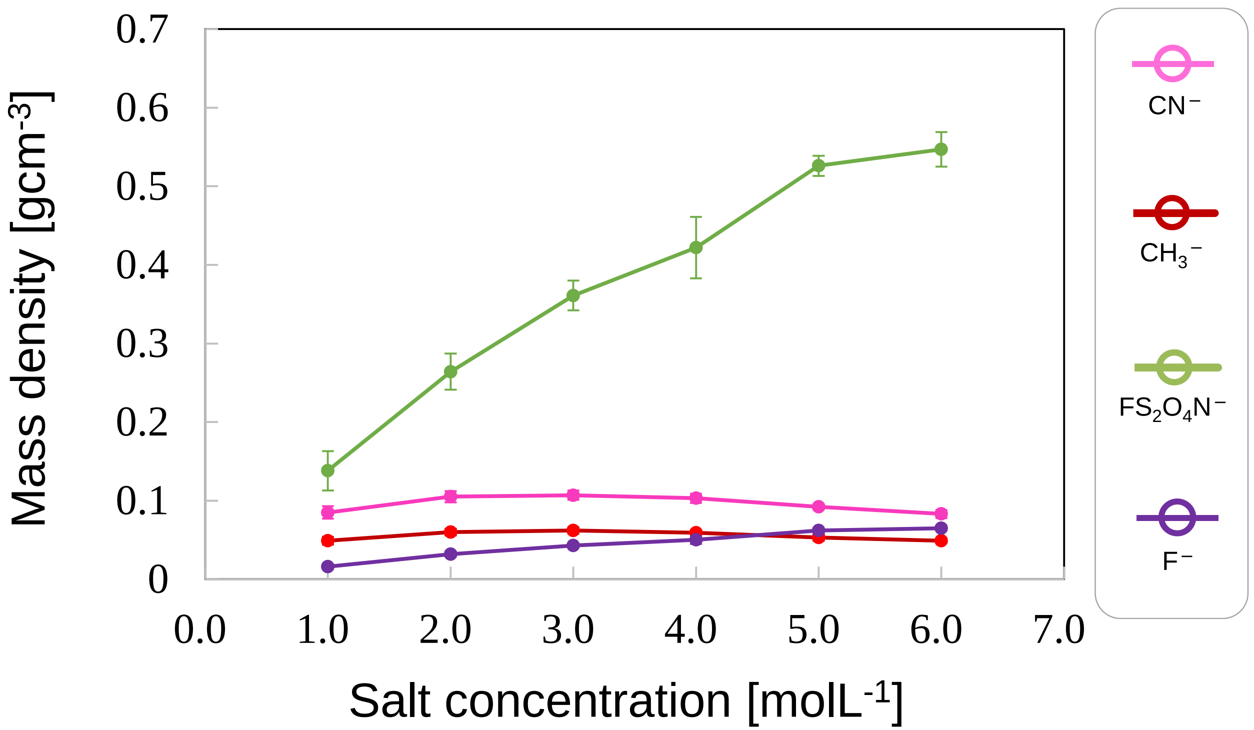
[1] Y. Yamada et al., *J. Am. Chem. Soc.*, **136**, 5039 (2014).
[2] I. A. Shkrob et al., *J. Phys. Chem. C*, **118**, 19661 (2014).

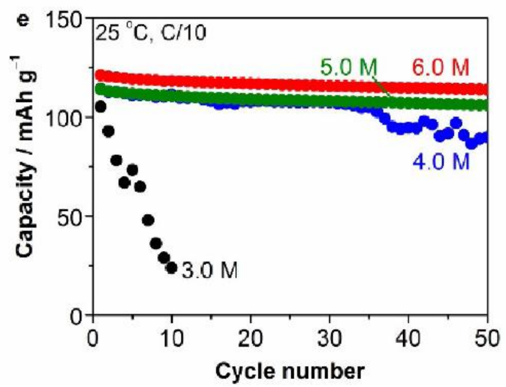
Dependency on the salt concentration



- By increasing the salt concentration, the sulfur-based SEI film becomes dense and has roles to protect the electrolyte from the reduction.

Dependency on the salt concentration



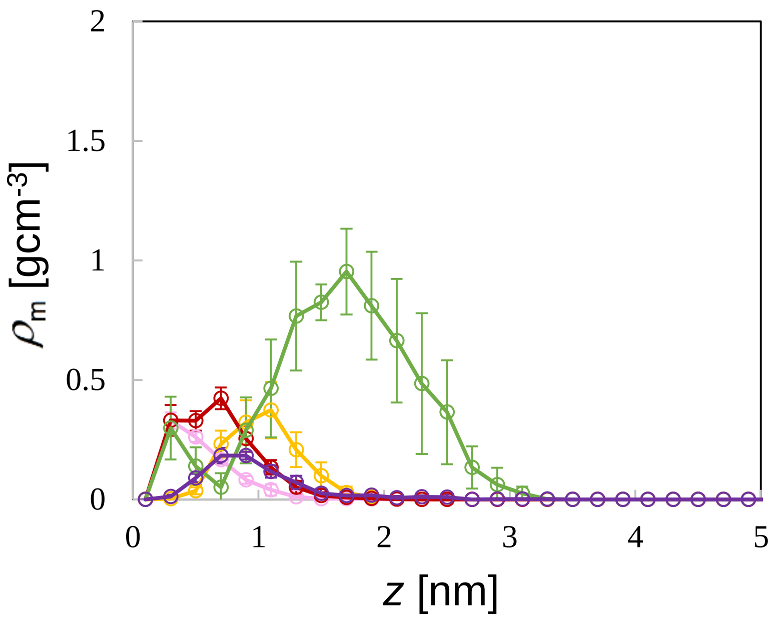


Experimental results of Electric capacity [1]

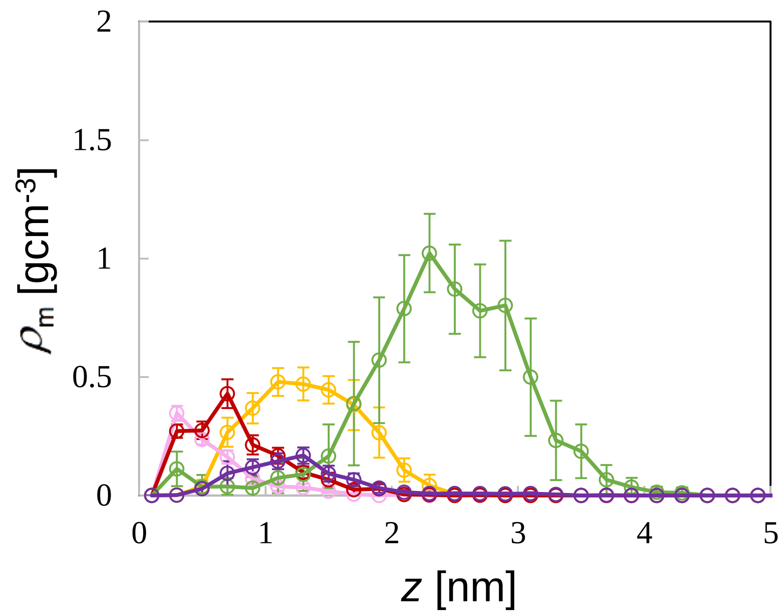
[1] Y. Yamada et al., *J. Am. Chem. Soc.*, **136**, 5039 (2014).

- The stable SEI film can be formed at the higher salt concentration so as to increases the lifetime of LIB.

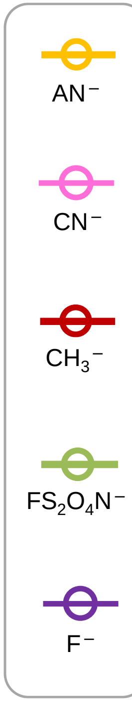
Comparison between LIB and NIB (4.0 M)



(a) Li-ion battery
(LIB)



(b) Na-ion battery
(NIB)



- In the NIB, the SEI film thickness was found to increases because the aggregation of reaction products becomes unstable in comparison to LIB.

Summary

- In this study, to compare the simulation results with the experimental observations, the SEI film formation mechanism was investigated in LIB.

- According to the SEI film formation simulations, it was found that the sulfur-based SEI film is formed as with the experimental observation.

- The stable SEI film can be formed at the higher salt concentration so as to increases the lifetime of LIB.

- Now, to develop the high performance secondary battery, I try to investigate the SEI film formation in the novel electrolyte system by collaborating with Yamada group in Tokyo University.