Mon. Jun. 19th

FY2017's 1st, CREST Workshop

Theoretical analyses of SEI film formation in Na-ion batteries with highly concentrated electrolyte

Norio Takenaka[1,2]

Graduate School of Information Science, Nagoya University[1],

Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University[2]

Background

MEXT program

Elements Strategy Initiative for Catalysts and Batteries: Interplay Between Experimental and Theoretical Studies (ESICB)

Primary object is

- To develop rare metals-free high performance catalysts and batteries
- To understand the principle of material science

As one of specific targets,

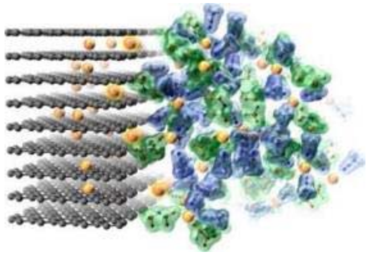
we develop the rare metals-free secondary battery.

Li-ion battery ⟶ **Na-ion battery**

(Li = rare metal) (Na = common metal)

Background

Yamada group in Tokyo University



Highly concentrated electrolyte

After one day After one week

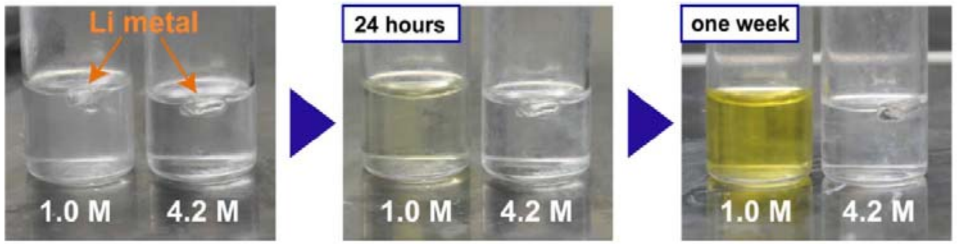


Fig. Reactivity of Li metal in LiTFSA/acetonitrile (AN) electrolyte

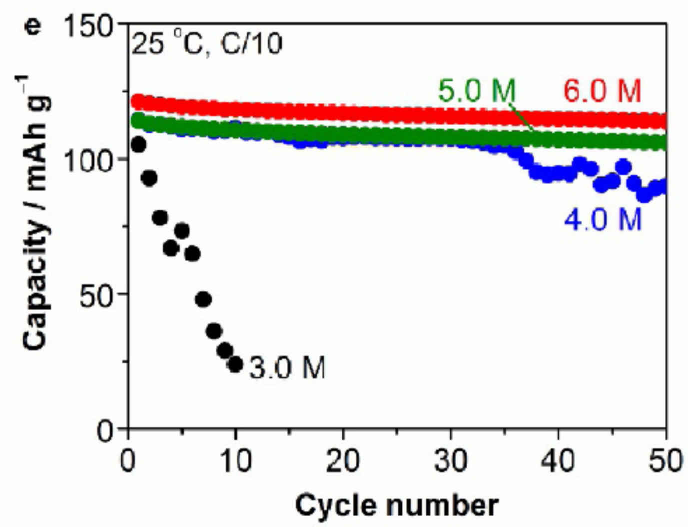


Fig. Capacity changes with LiFSA/AN electrolyte in Li-ion battery [3]

✓ It was reported that the lifetime and stability of Li-ion batteries are significantly improved by increasing the salt [1-3].

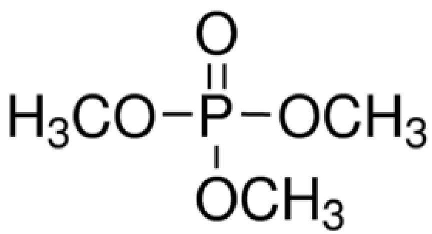
➡ <u>Such strategy should be useful for the development of Na-ion batteries.</u>

[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).

Favorable solvent in Na-ion battery

- ✓ Trimethyl phosphate (TMP) is a best solvent in Na-ion battery according to the preceding study of Yamada group in Tokyo University.

- ✓ Although TMP cannot form the SEI film at the usual salt concentration, it can form the stable film in the highly concentrated electrolyte.



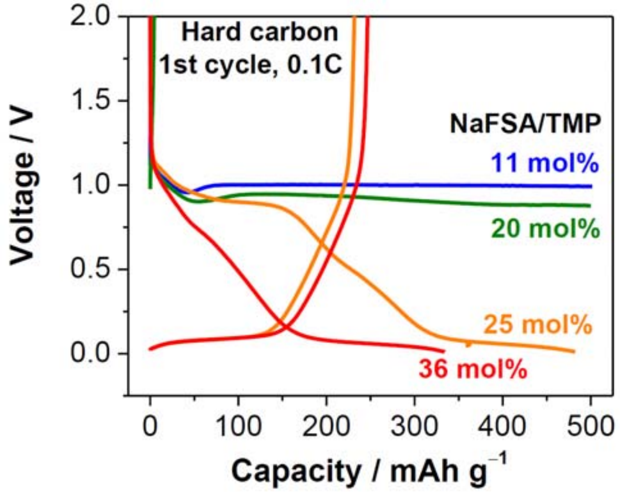
TMP

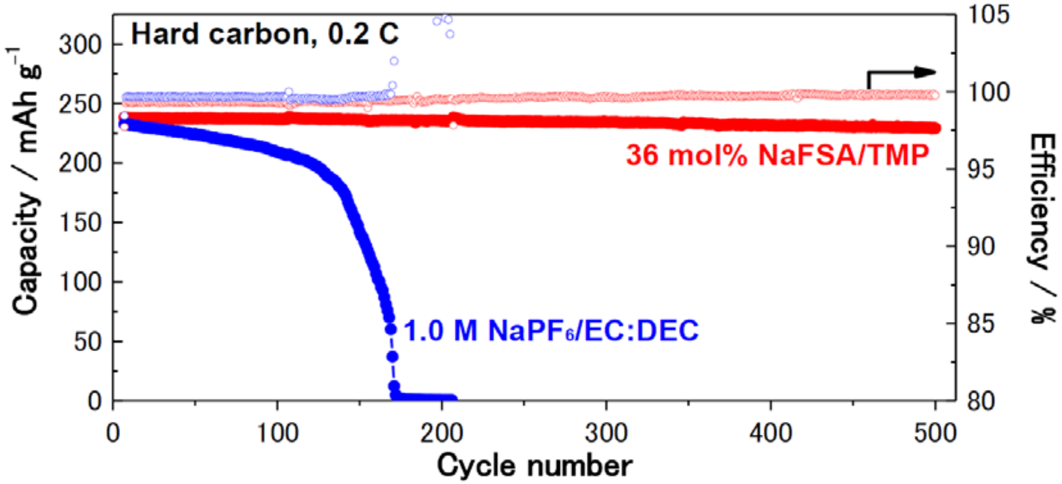
○ Flame resistance

× SEI film is not formed.

Increase in salt concentration → Problem is solved!!

Battery stability with NaFSA/TMP electrolyte





- ✓ By increasing the concentration of NaFSA salt, the lifetime of Na-ion batteries was significantly improved.

- ➢ However, its microscopic mechanism is still not found. Therefore, the theoretical studies are required to understand such mechanism.

Reaction mechanism of TMP in experiment

✓ The reactions of trimethyl phosphate (TMP), triethyl phosphate (TEP), and tributhyl phosphate (TBP) with sodium in liquid ammonia was investigated in the previous experimental study [1].

[1] D. C. Isbell and R. R. Dewald, J. Phys. Chem, 91, 6695 (1987).

➢ One mole of the trialkyl phosphate was found to react with two moles of sodium to yield the alkoxide and dialkyl phosphite.

$$(RO)_3PO + 2e_{am}^- \rightarrow (RO)_2PO^- + RO^-$$

➢ The reaction of trialkyl phosphates with sodium in liquid ammonia is consistent with the following sequence of reactions.

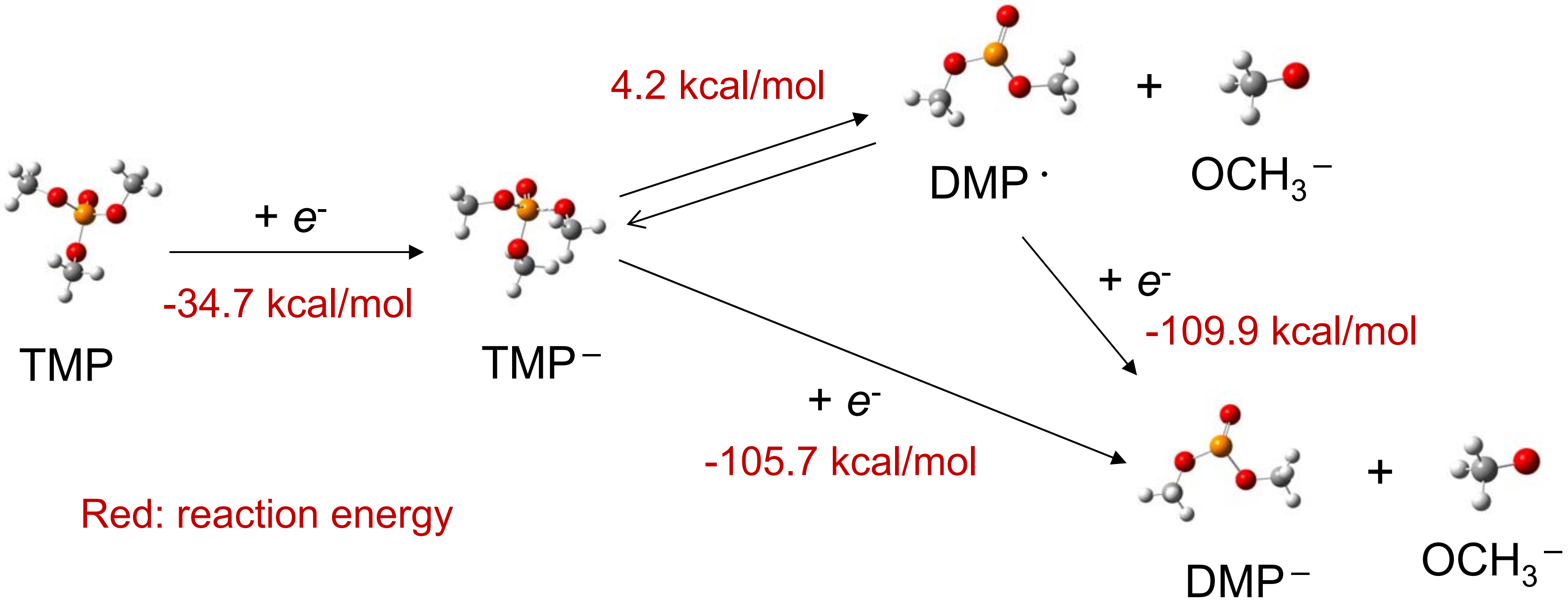
$$e_{am}^- + (RO)_3PO \rightarrow (RO)_2PO^\bullet + RO^- \qquad \text{(slow)}$$

$$(RO)_2PO^\bullet + e_{am}^- \rightarrow (RO)_2PO^- \qquad \text{(fast)}$$

Quantum chemical calculations for TMP

Calculation level: B3LYP/6-31+G(d) with SMD (μ = 20.6) and VFA

VFA: vibration frequency analysis

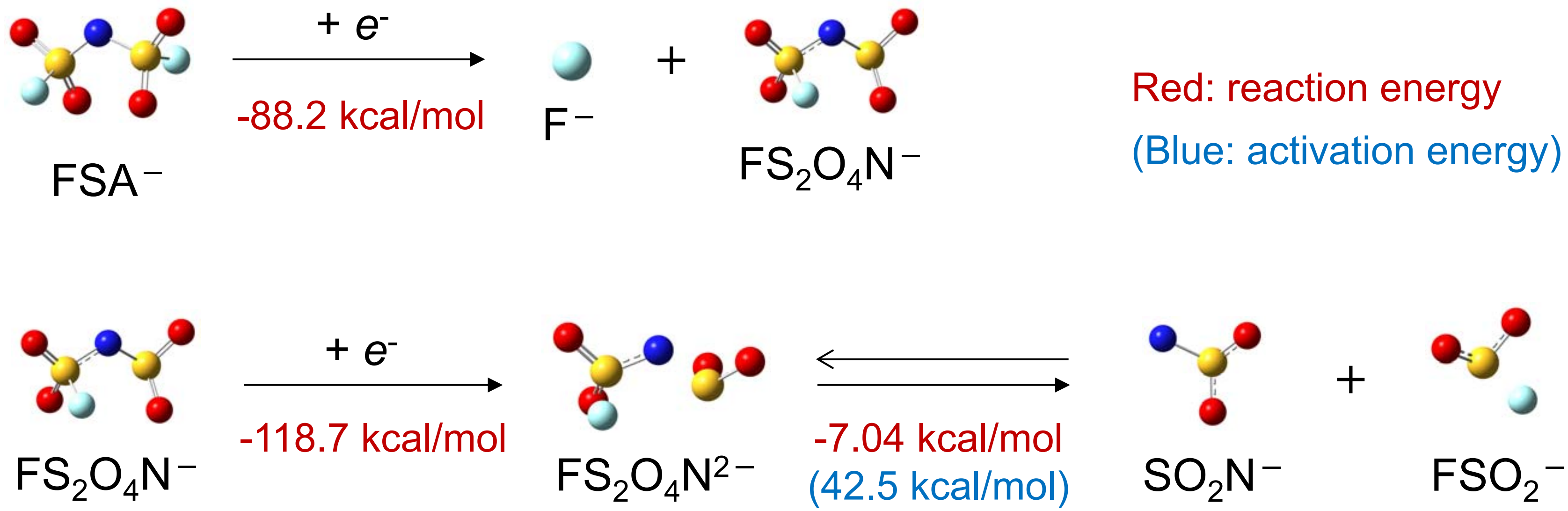


- Since the concentration of DMP· must be small in comparison to TMP$^-$, the pathway from DMP· can be neglected in the SEI film formation simulation.

[1] D. C. Isbell and R. R. Dewald, J. Phys. Chem, 91, 6695 (1987).

Quantum chemical calculations for FSA

Calculation level: B3LYP/6-31+G(d) with SMD (μ = 20.6) and VFA



- Although the decomposition of $FS_2O_4N^-$ was proposed in LIB with ionic electrolyte [2], such reaction should not kinetically occur at the normal condition.

[2] I. A. Shkrob et al., *J. Phys. Chem. C*, **118**, 19661 (2014).

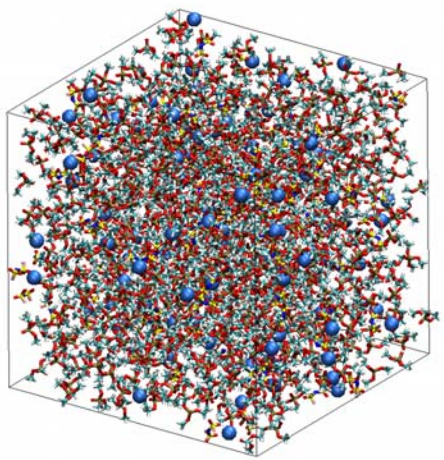
Electrolyte properties of NaFSA/TMP solution

Table 1. Calculated electrolyte properties of NaFSA/TMP solution

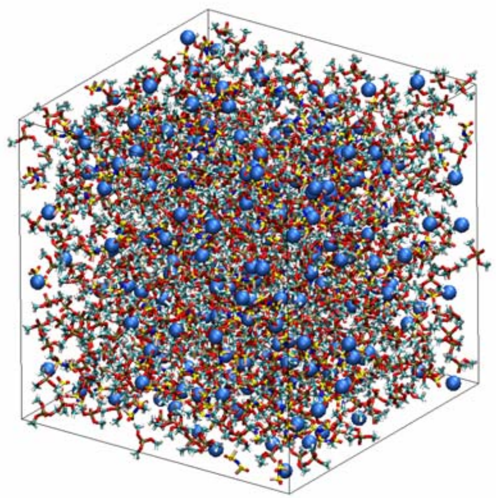
		Salt concentration [$molL^{-1}$]		
		1.0	2.2	3.3
Number of species	TMP	800	800	800
	FSA^-	105	267	444
	Na^+	105	267	444
Molecular ratio (TMP/NaFSA)		7.6	3.3	1.8
Mass density [gcm^{-3}]		1.27	1.37	1.50
Ionic conductivity [$mScm^{-1}$]		4.08	0.80	0.37

Calculation condition:

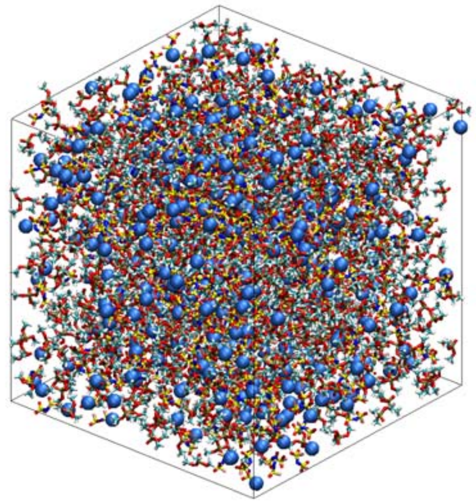
Force field: GAFF
Charge: RESP
Temperature: 298 K



(a) 1.0 M NaFSA/TMP

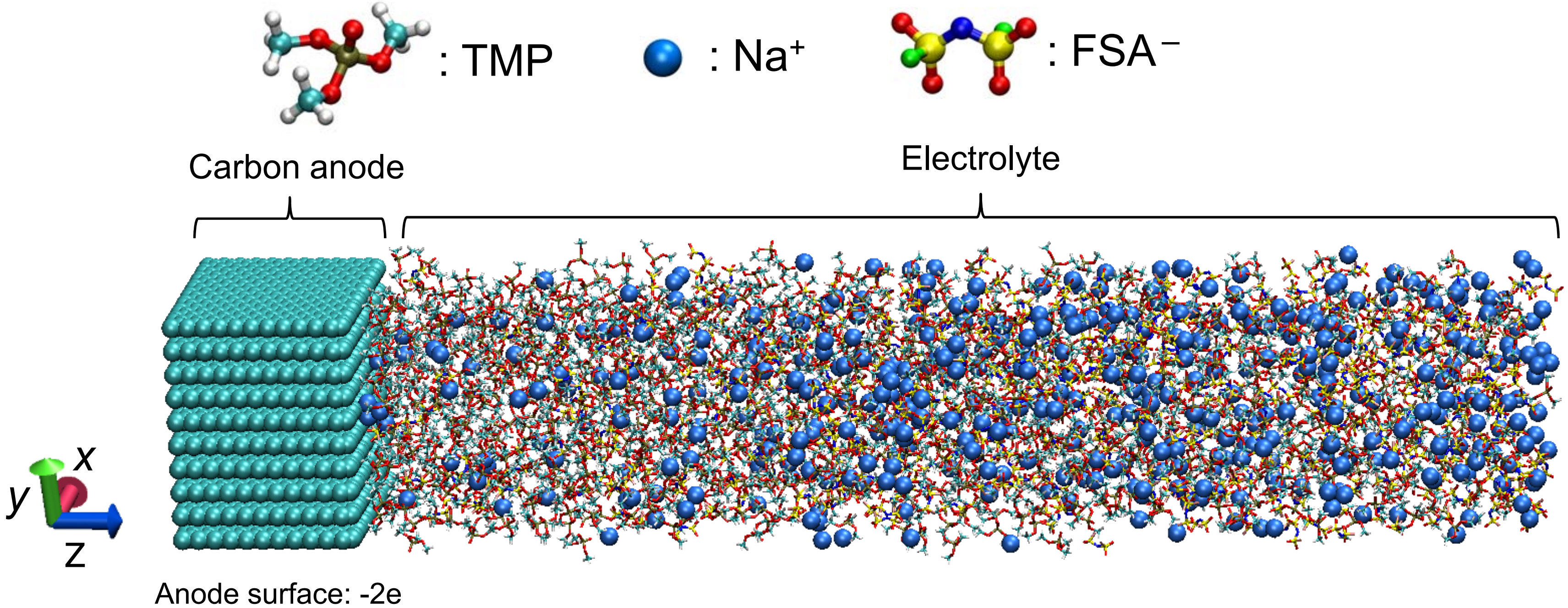


(b) 2.2 M NaFSA/TMP



(C) 3.3 M NaFSA/TMP

Model system and reaction scheme



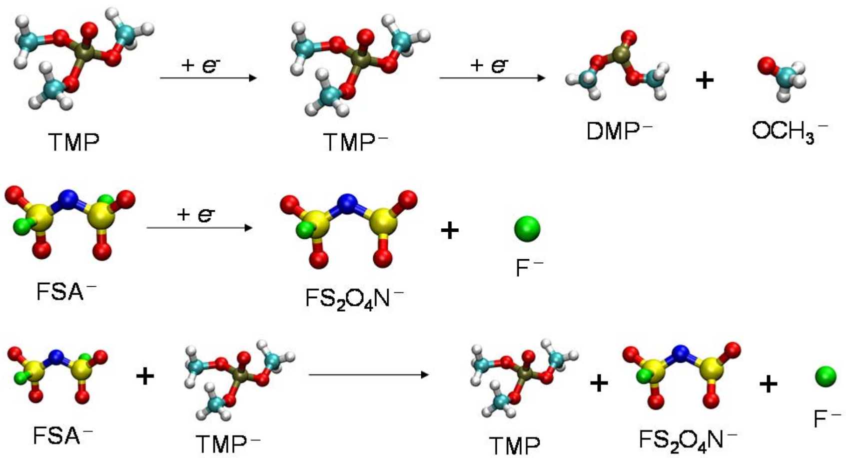


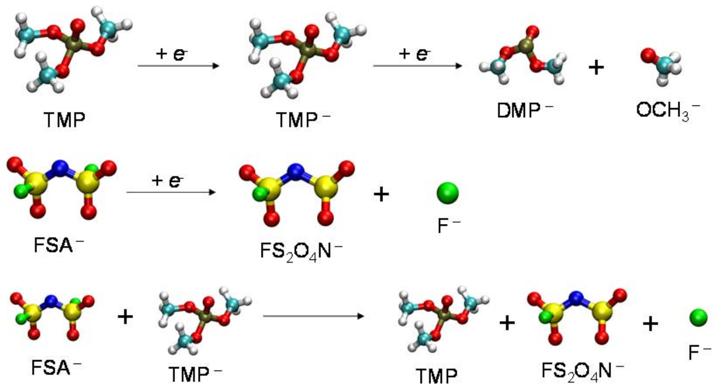
Table. Number of molecules

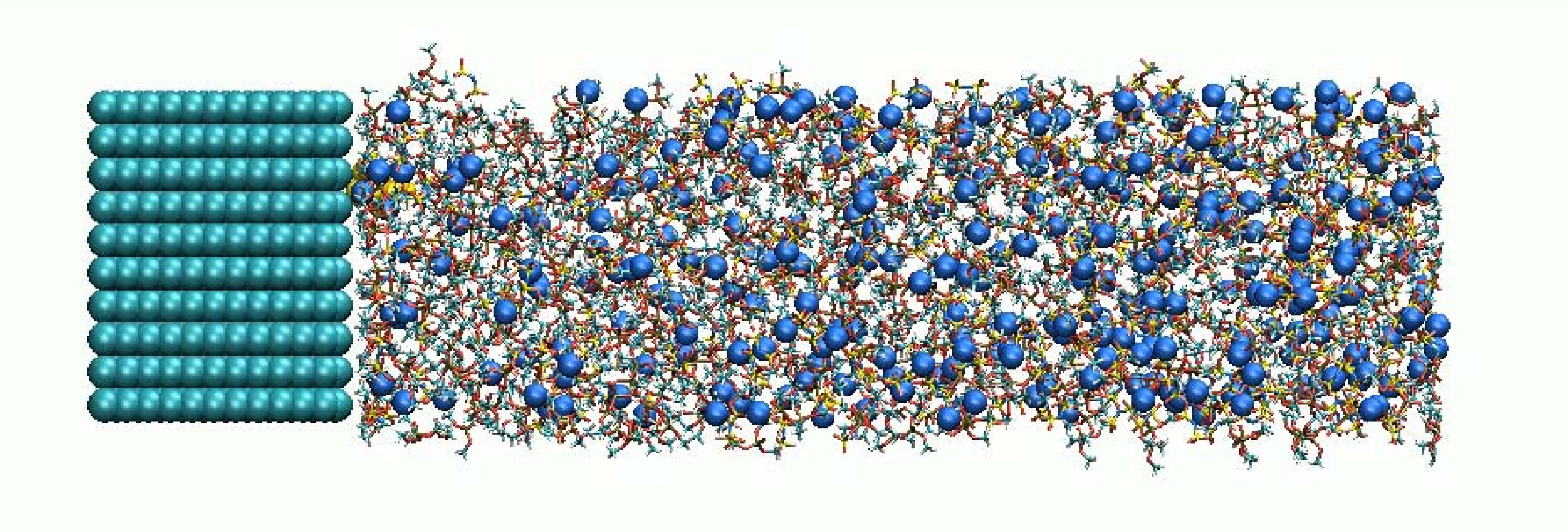
		Salt concentration [molL^{-1}]		
		1.0	2.2	3.3
Number of species	TMP	800	800	800
	FSA$^-$	105	267	444
	Na$^+$	107	269	446

Red Moon simulation (3.3 mol L^{-1})

Color

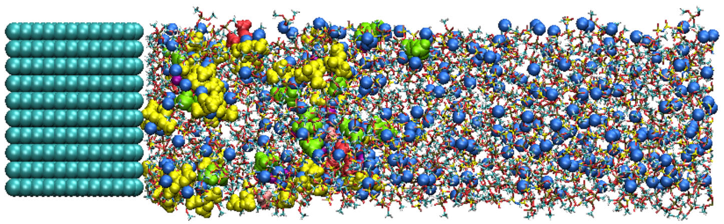
Yellow: TMP^-, Green: $FS_2O_4N^-$,
Red: DMP^-, Pink: OCH_3^-,
Purple: F^-, Blue: Na^+

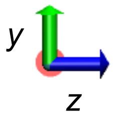




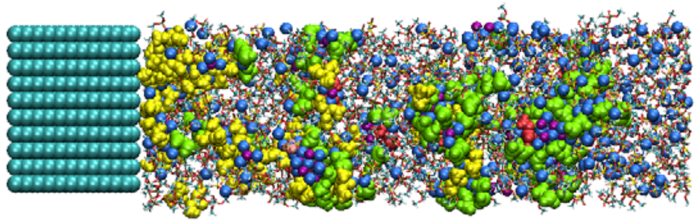
Snapshots of SEI film formation at 3.3 mol L^{-1}

Yellow: TMP^-, Green: $FS_2O_4N^-$, Red: DMP^-, Pink: OCH_3^-, Purple: F^-, Blue: Na^+

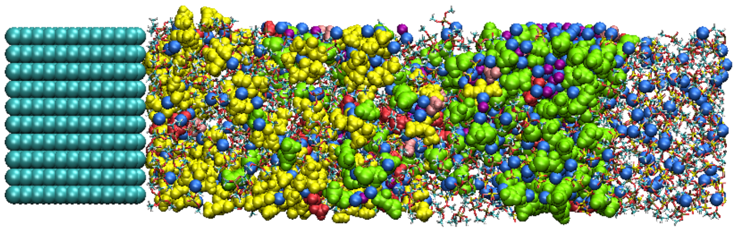




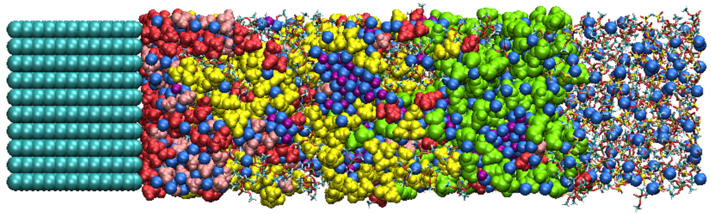
(a) 100 MC/MD cycle



(b) 500 MC/MD cycle



(c) 1000 MC/MD cycle

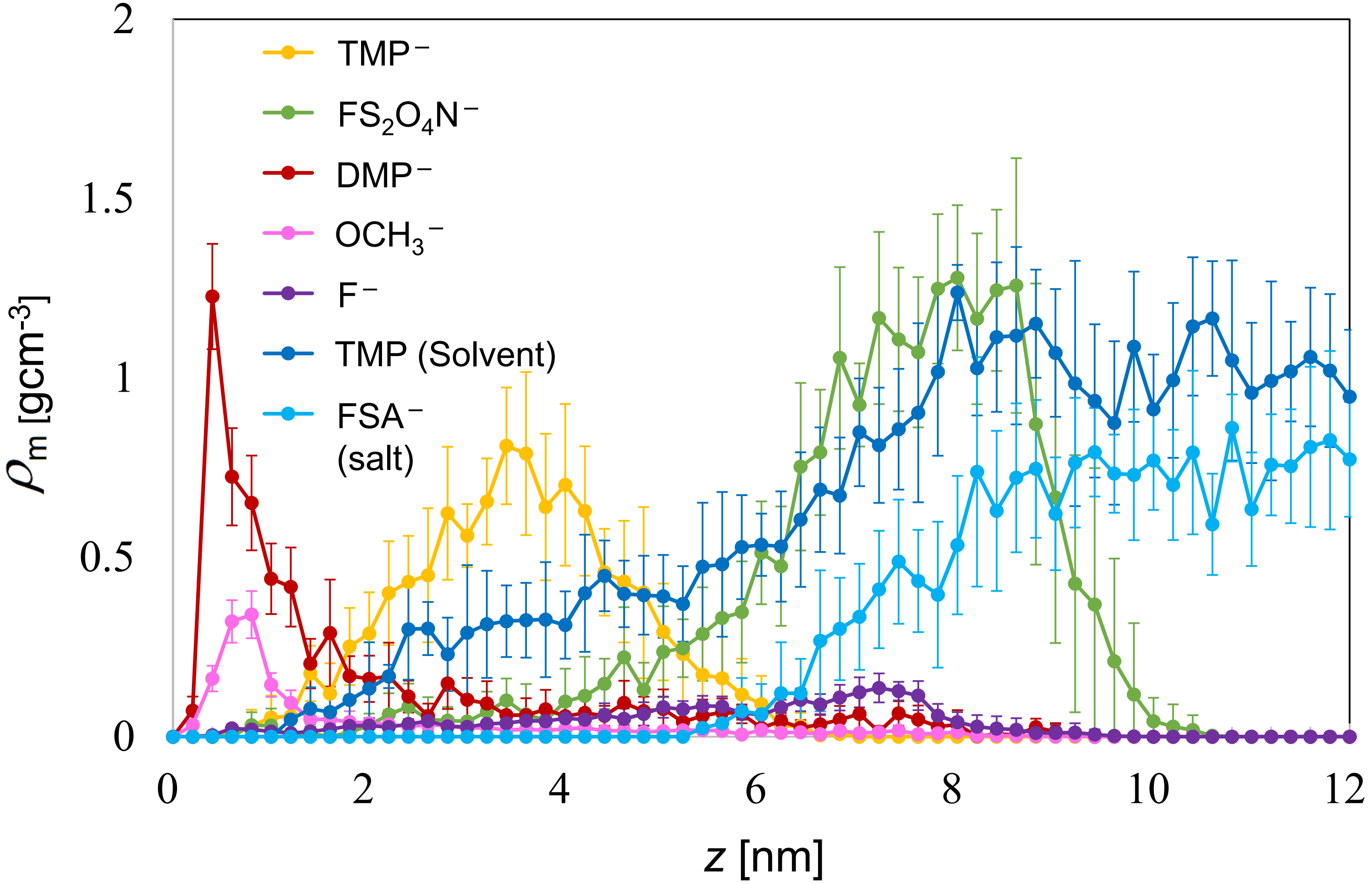


(c) 2000 MC/MD cycle

- ➢ It was found that the salt-derived reaction product ($FS_2O_4N^-$) mainly form the passivation film.

Mass density distributions at 3.3 M

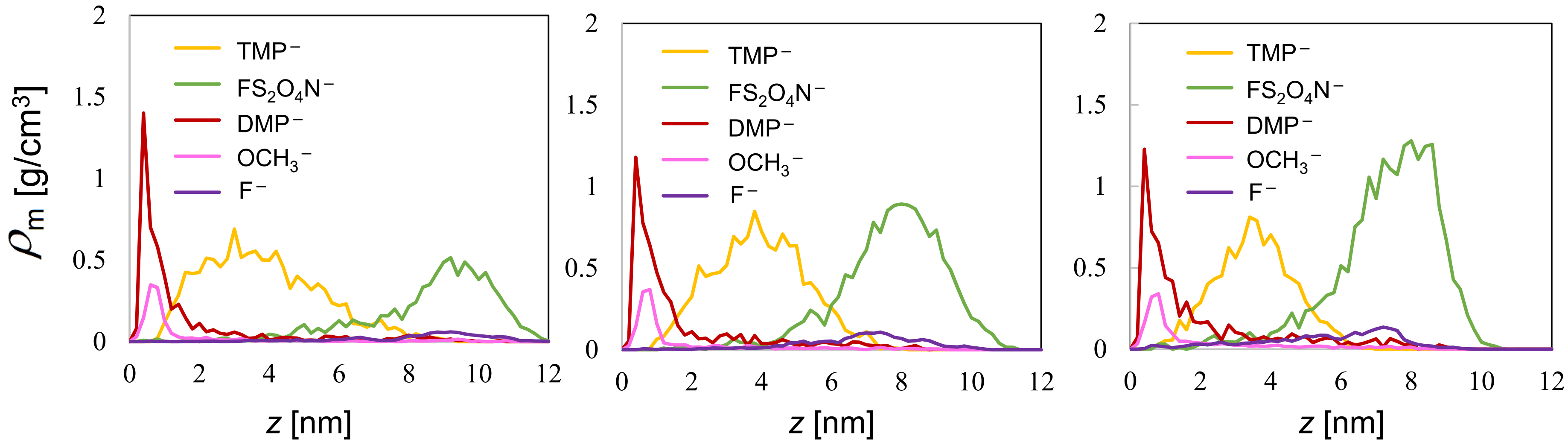
(They are obtained by different 10 initial configurations.)



✓ The salt-derive reaction products such as $FS_2O_4N^-$ were distributed in the outer region inside the SEI film.

Dependency of mass density distributions

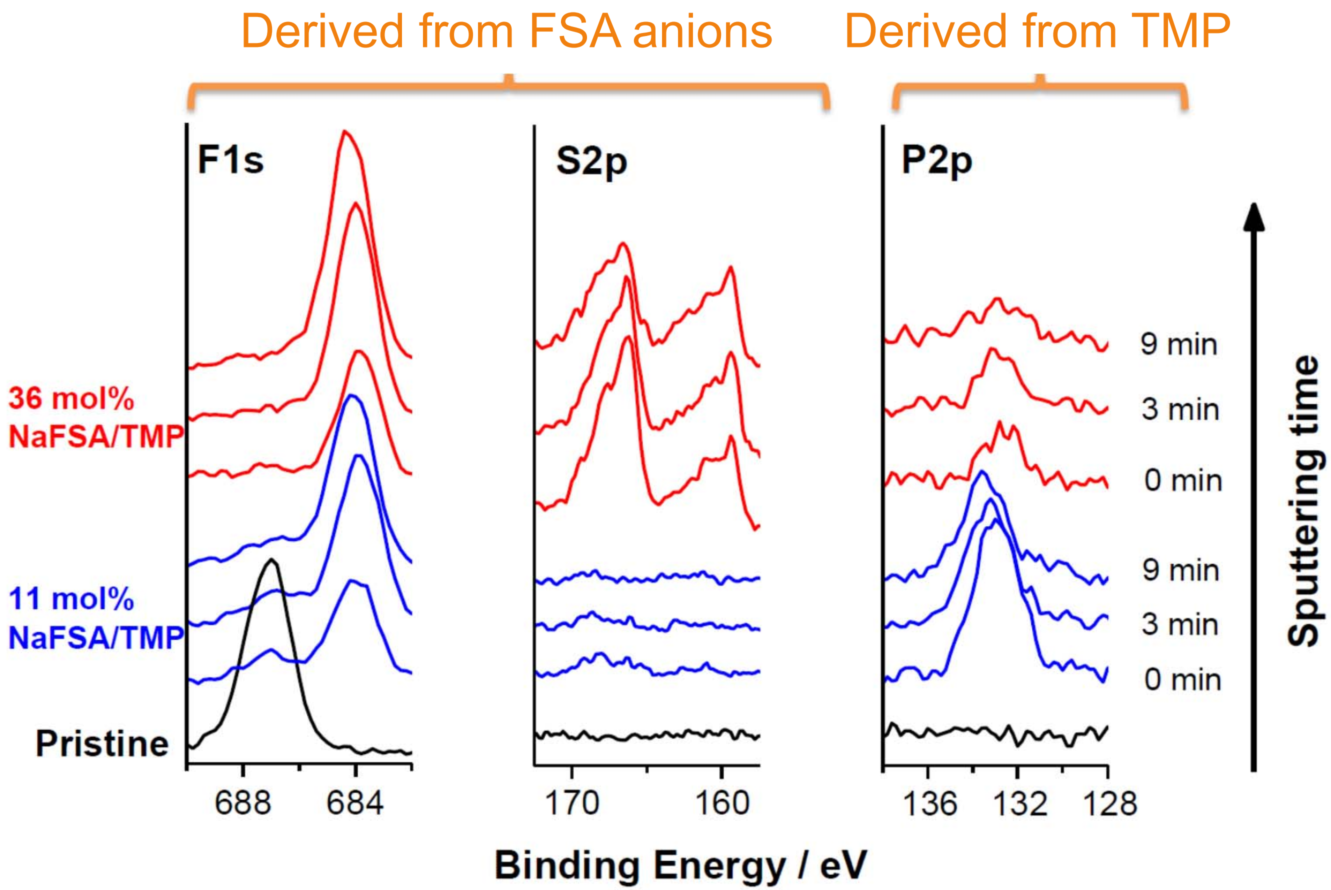
(They are obtained by different 10 initial configurations.)



(a) 1.0 mol L^{-1} (b) 2.2 mol L^{-1} (c) 3.3 mol L^{-1}

- By increasing the salt concentration, the sulfur-based passivation film by $NaFS_2O_4N$ became denser.

Experimental observation



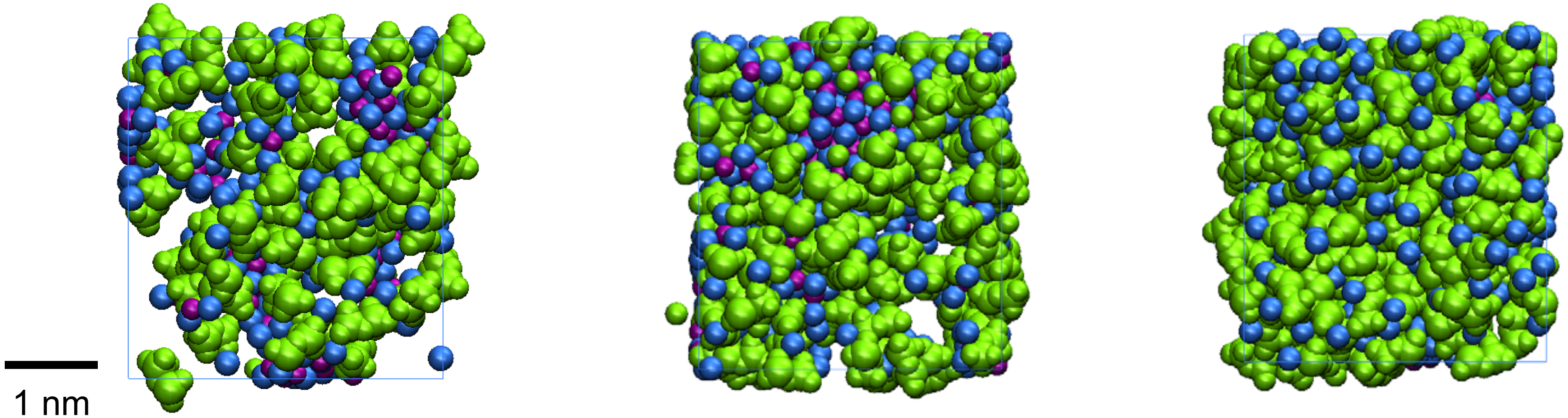
✓ By increasing salt concentration, the amount of salt-derived products increased.

➢ <u>The present simulation results were consistent with this tendency</u>.

Salt-derived passivation films (Front view)

Green: $FS_2O_4N^-$, Purple: F^-, Blue: Na^+

Fractional accessible volume (FAV) is used to estimate the **cavity size** in the salt-derived passivation film.



(a) 1.0 mol L^{-1} (b) 2.2 mol L^{-1} (c) 3.3 mol L^{-1}

FAV:	0.43 ± 0.09	0.20 ± 0.06	0.07 ± 0.03

✓ By increasing the salt concentration, the **cavity size** clearly decreased.

➢ Such dense film formed in the highly concentrated electrolyte should prevent the TMP solvent molecules in the bulk electrolyte.

Summary

- In this study, to investigate the salt concentration effect on the SEI film formation in Na-ion batteries, the Red Moon simulations were executed in NaFSA/TMP electrolyte solution with the carbon anode.

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

- By increasing the salt concentration, the sulfur-based passivation film by $NaFS_2O_4N$ became denser, decreasing the cavity sizes.

- Such stable SEI film should lead to the long lifetime of Na-ion batteries with NaFSA/TMP electrolyte.