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FY2016's 6th, CREST Workshop

Salt concentration effect on SEI film formation and ion transport in sodium-ion battery

Norio Takenaka[1,2]

[1]Graduate School of Information Science, Nagoya University

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

Background

- By increasing the salt concentration in Li-ion battery (LIB), its performance was found to be improved [1-3]. But, its microscopic mechanism is still not found.

- The use of such highly concentrated electrolyte is one of effective strategy to develop Na-ion batteries (NIB) for practical use with performance comparable with that of LIB.

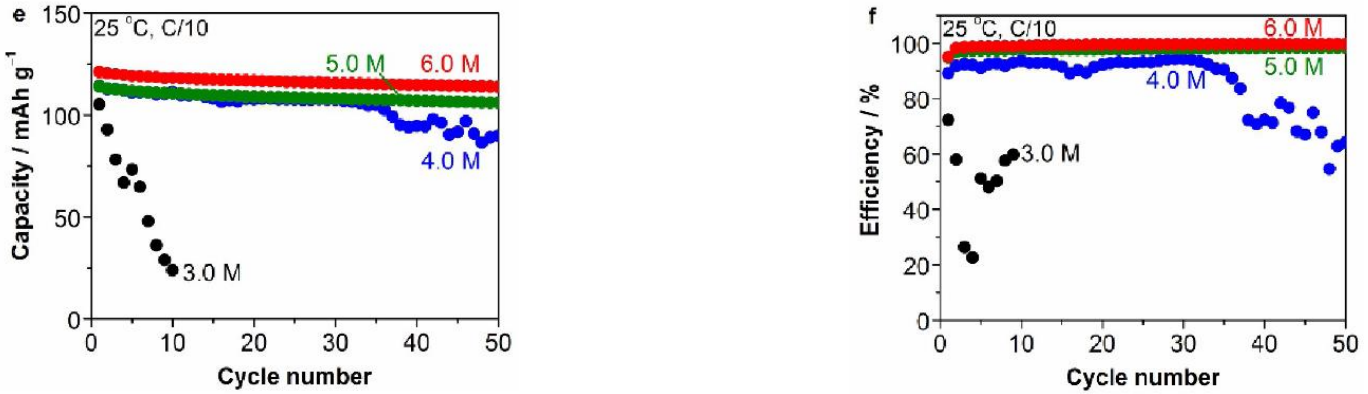
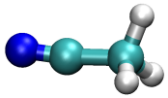


Fig. Capacity and Coulomb efficiency of $LiMn_2O_4$/Li cell at C/10 and 25 ℃ [1].

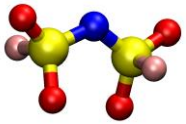
[1] Y. Yamada, M. Yaegashi, T. Abe, A. Yamada, *Chem. Commun.*, **49**, 11194 (2013).
[2] Y. Yamada, K. Furukawa, K. Sodeyama, K. Kikuchi, M. Yaegashi, Y. Tateyama, A. Yamada, *J. Am. Chem. Soc.*, **136**, 5039 (2014).
[3] Y. Yamada, C. H. Chiang, K. Sodeyama, J. Wang, Y. Tateyama, A. Yadama, *ChemElectroChem*, **2**, 1687 (2015).

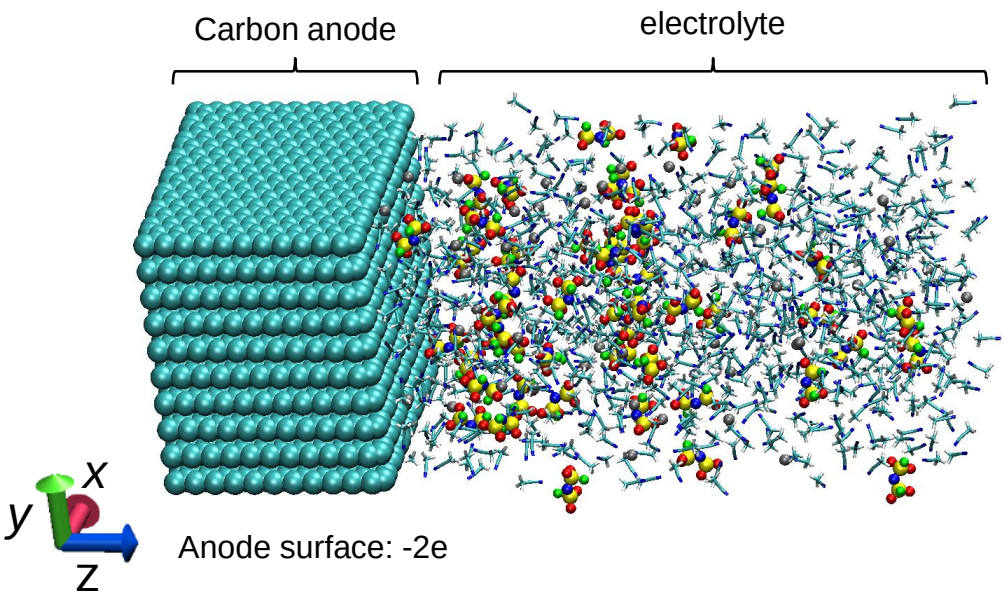
Hybrid MC/MD reaction simulation

To investigate the microscopic mechanism of salt concentration effect on SEI film formation, the hybrid MC/MD reaction simulation was executed in the AN-NaFSA electrolyte solution by changing the salt concentration.


: Acetonitrile (AN)


: Na^+


: FSA^-



Molecule number of electrolyte:

(a) 1.0 M : 800 AN, 52 Na^+, 50 FSA^-

(b) 2.0 M : 800 AN, 112 Na^+, 110 FSA^-

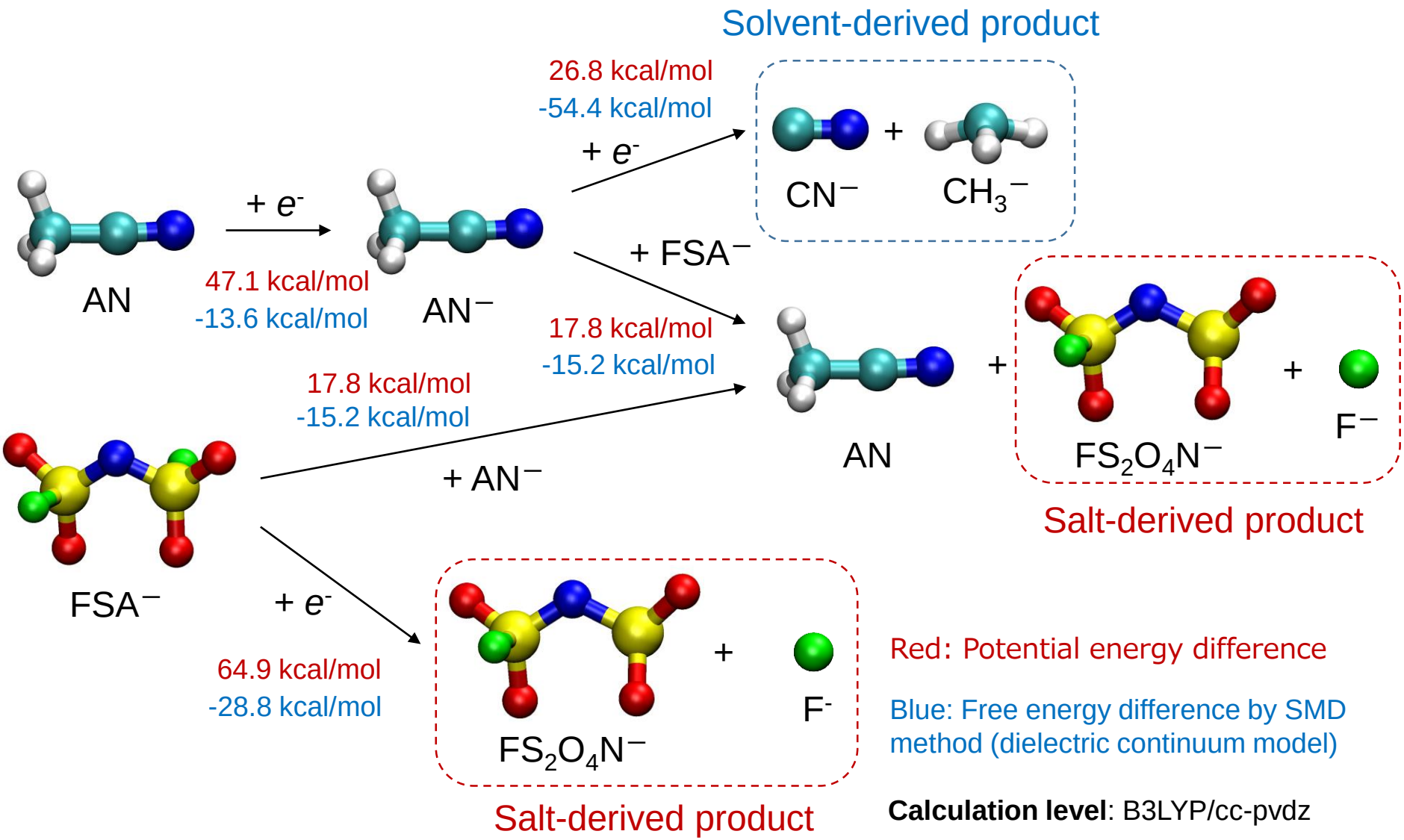
(c) 3.0 M : 800 AN, 177 Na^+, 175 FSA^-

(d) 4.0 M : 800 AN, 252 Na^+, 250 FSA^-

Calculation condition

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

Reaction scheme for simulations

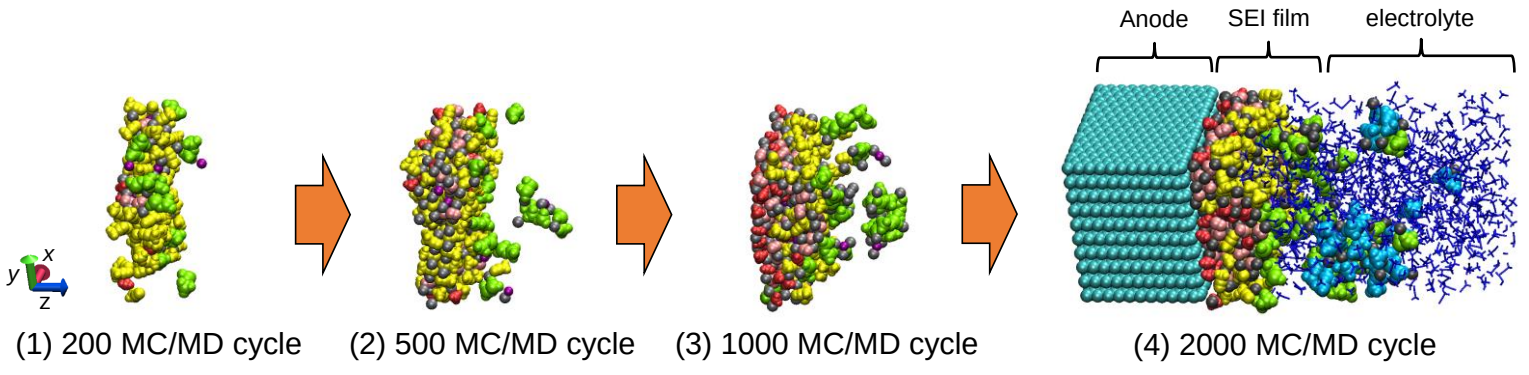


Red: Potential energy difference

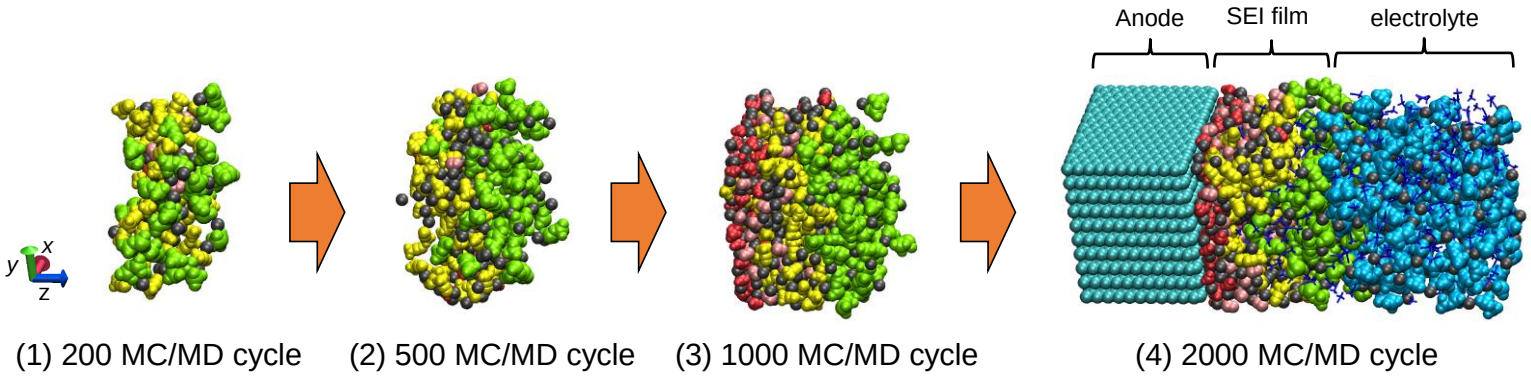
Blue: Free energy difference by SMD method (dielectric continuum model)

Calculation level: B3LYP/cc-pvdz

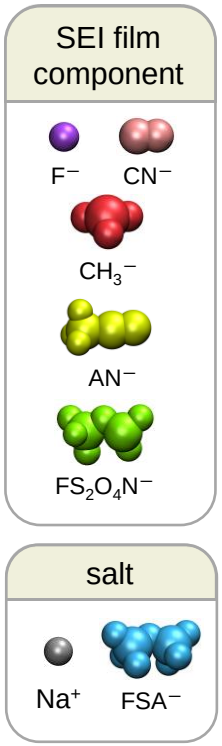
SEI film formation processes



(a) Low salt concentration (1.0 molL^{-1})



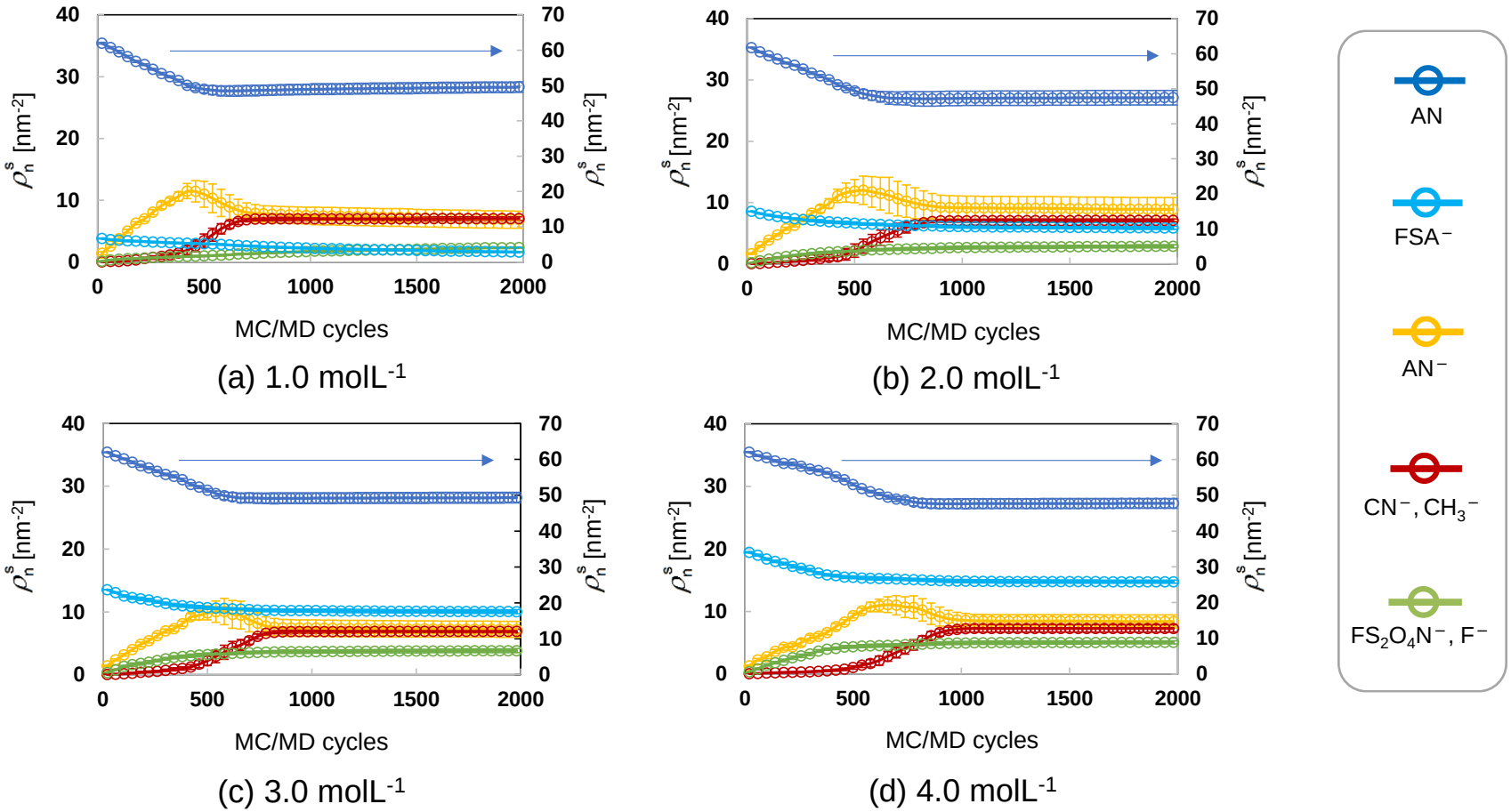
(b) High salt concentration (4.0 molL^{-1})



- At the **low salt concentration**, the reaction products were drift away from the anode surface because the desolvation easily occurs. On the other hand, such dissolution was suppressed **at the high salt concentration**.

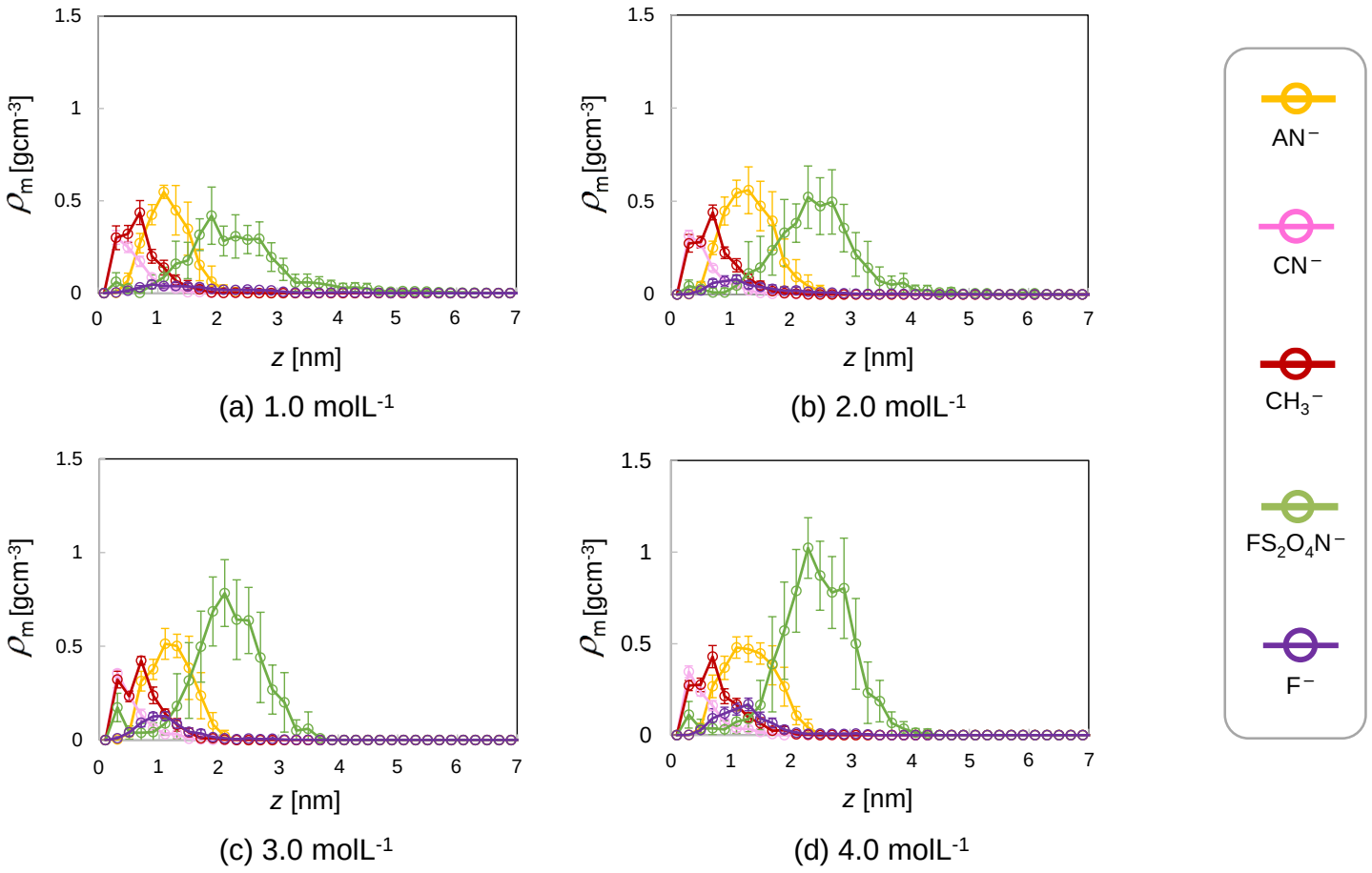
Change in surface number density of reaction products

(They are obtained by different 10 initial configurations.)



- By increasing the salt concentration, the production amount of salt-derived reaction products ($FS_2O_4N^-$, F^-) was found to drastically increase due to the increase in the collision of salt (FSA^-) in the higher salt concentration.

Mass density distributions of reaction products



- The salt-derived reaction products such as $FS_2O_4N^-$ was present in the outer region to protect the electrolyte from the reduction. Then, as the salt concentration increases, its peak height clearly increased.

Mass density of reaction products in SEI film

Table. Mass density of reaction products in SEI film

Species	Salt concentration [molL^{-1}]			
	1.0	2.0	3.0	4.0
AN^-	0.118 ± 0.023	0.152 ± 0.032	0.124 ± 0.021	0.144 ± 0.017
CN^-	0.044 ± 0.002	0.045 ± 0.002	0.043 ± 0.002	0.046 ± 0.004
CH_3^-	0.076 ± 0.004	0.077 ± 0.003	0.075 ± 0.004	0.079 ± 0.006
$FS_2O_4N^-$	0.151 ± 0.005	0.188 ± 0.014	0.258 ± 0.021	0.340 ± 0.017
F^-	0.018 ± 0.001	0.022 ± 0.002	0.030 ± 0.002	0.040 ± 0.002
Total	0.407 ± 0.028	0.484 ± 0.047	0.530 ± 0.044	0.649 ± 0.036

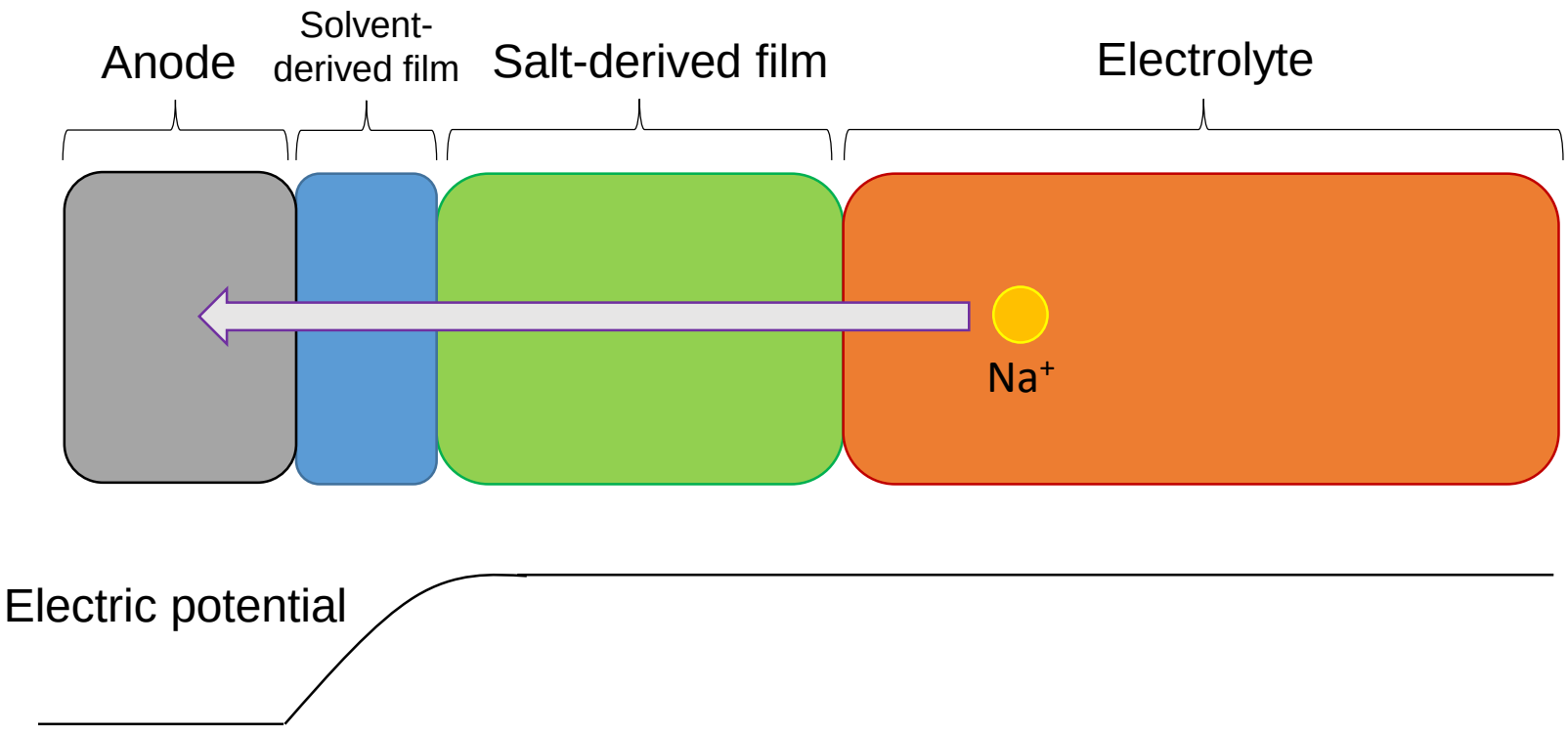
(They are estimated by assuming 4 nm of SEI film thickness.)

- The present calculation results clearly show that the SEI film becomes dense by increasing the salt concentration.

- It can be understood that the salt-derived reaction products such as $FS_2O_4N^-$ are main components to protect the electrolyte from the reduction.

Ion transport mechanism of Na^+

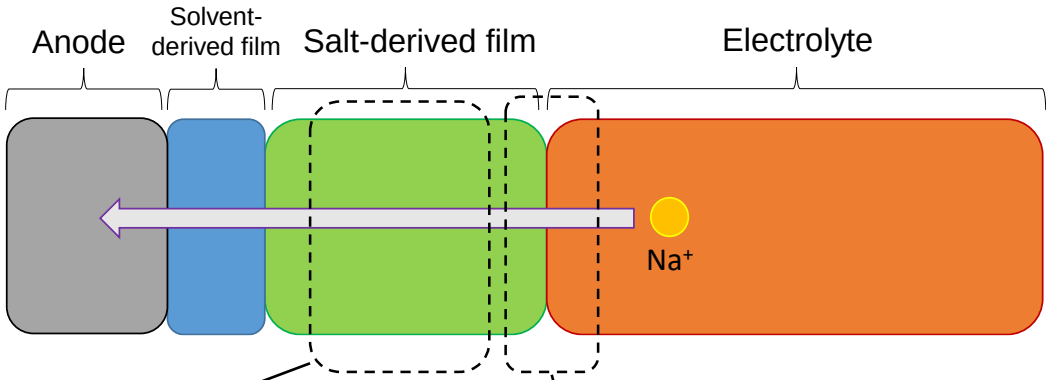
- According to the present simulation results, we can assume the simple ion transport mechanism.



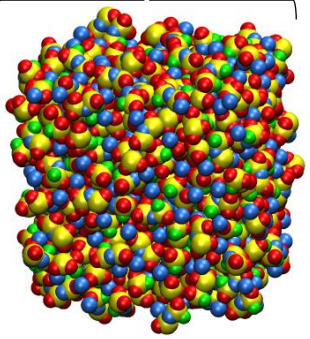
➢ There are two important processes, which are (1) ion transfer inside salt-derived film and (2) ion transfer at the electrolyte-salt-derived film interface.

Simulation model

- To investigate the ion transport mechanism, the activation barriers based on ion conductivity were estimated by using two simulation models.

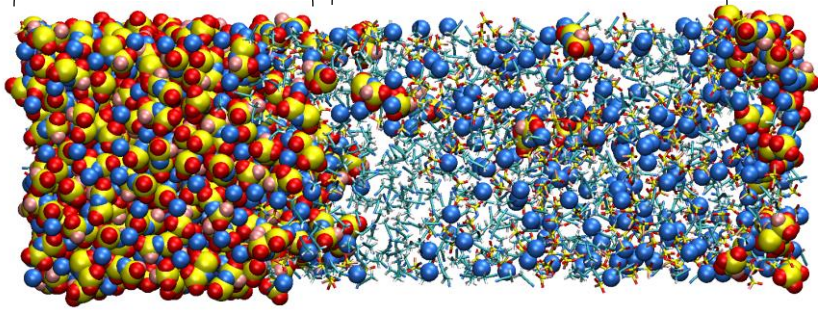


Bulk salt-derived film



400 $FS_2O_4N^-$, 400 Na^+

Salt-derived film Electrolyte (1.0, 2.0, 3.0, 4.0 $molL^{-1}$)

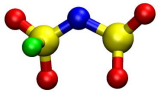


(a) 1.0 M : 800 AN, 50 Na^+, 50 FSA^-

(b) 2.0 M : 800 AN, 110 Na^+, 110 FSA^-

(c) 3.0 M : 800 AN, 175 Na^+, 175 FSA^-

(d) 4.0 M : 800 AN, 250 Na^+, 250 FSA^-



: $FS_2O_4N^-$

: Na^+

How to estimate ion conductivity

- Based on the Green-Kubo formula, the ion conductivity is expressed as

$$\sigma = \frac{1}{R_{\mathrm{ct}}} = \frac{1}{3k_{\mathrm{B}}TV}\int_0^\infty dt \left\langle \mathbf{J}(t)\cdot\mathbf{J}(0)\right\rangle \qquad (1)$$

$$\mathbf{J}(t) = \sum_i q_i \,\mathrm{v}_i(t) \qquad (2)$$

q_i: charge of ith ion, $\mathbf{v}_i$: velocity of ith ion, T: temperature, V: system volume

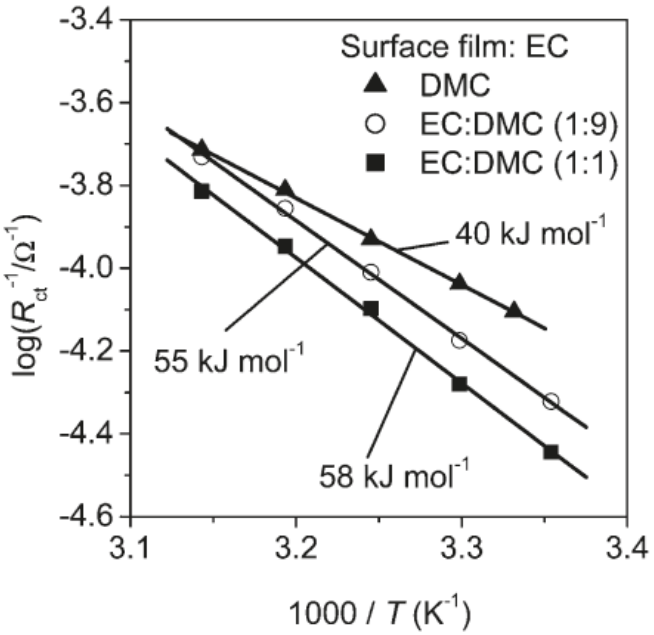
- By neglecting cross-correlation effect, the Nernst-Einstein equation is obtained as

$$\sigma_{\mathrm{NE}} = \frac{1}{k_{\mathrm{B}}T}\sum_I q_I^2 \rho_I D_I \qquad (3)$$

q_I: charge of Ith ionic species, ρ_I: density of Ith ionic species

D_I: diffusion constant of Ith ionic species

Activation barrier based on ion conductivity



Ogumi el al., Langumir, **25(21)**, 12766 (2009).

Fig. 2 Temperature dependency of ion conductivity in LIB

Arrhenius plot

$$\sigma = A\exp\left(-\beta E_a\right)$$

$$\ln\sigma = -AE_a\left(\frac{1}{T}\right) + \ln B$$

(A, B: proportional constant)

- The experimental activation barrier is estimated by using “ion conductivity σ”.
- According to the experimental observations, it was found that the ion desolvation process is the rate-limiting step.

Calculated activation barrier inside film

- By using the Nernst-Einstein equation, the ion conductivities were estimated by changing the temperature to estimate the activation barrier.

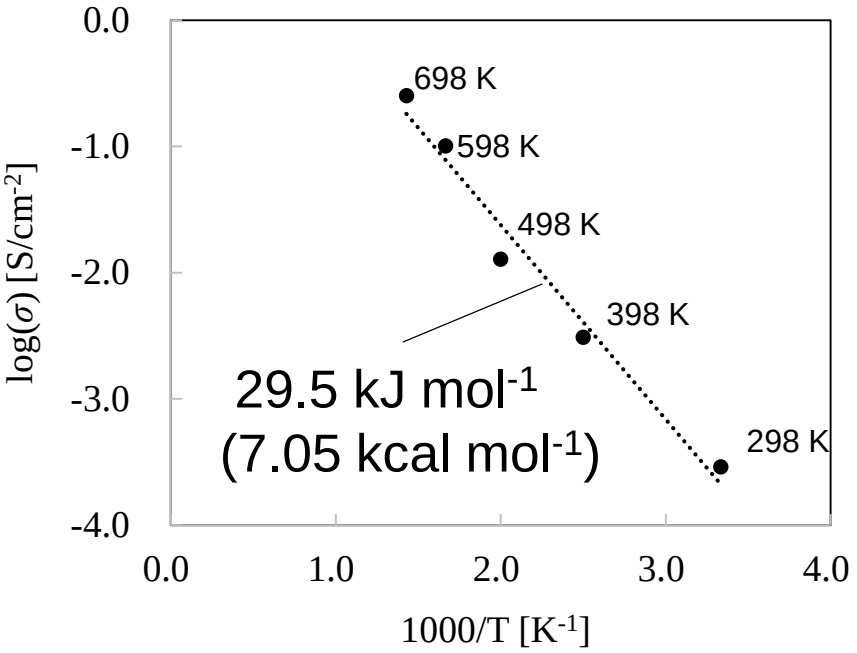
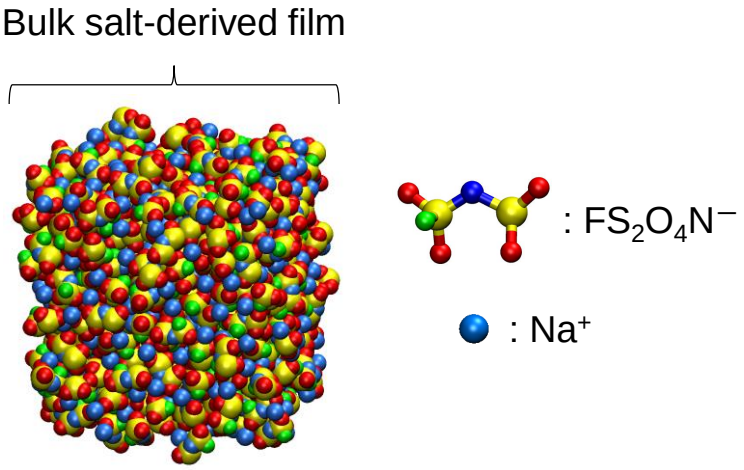


Fig. Calculated Arrhenius plot

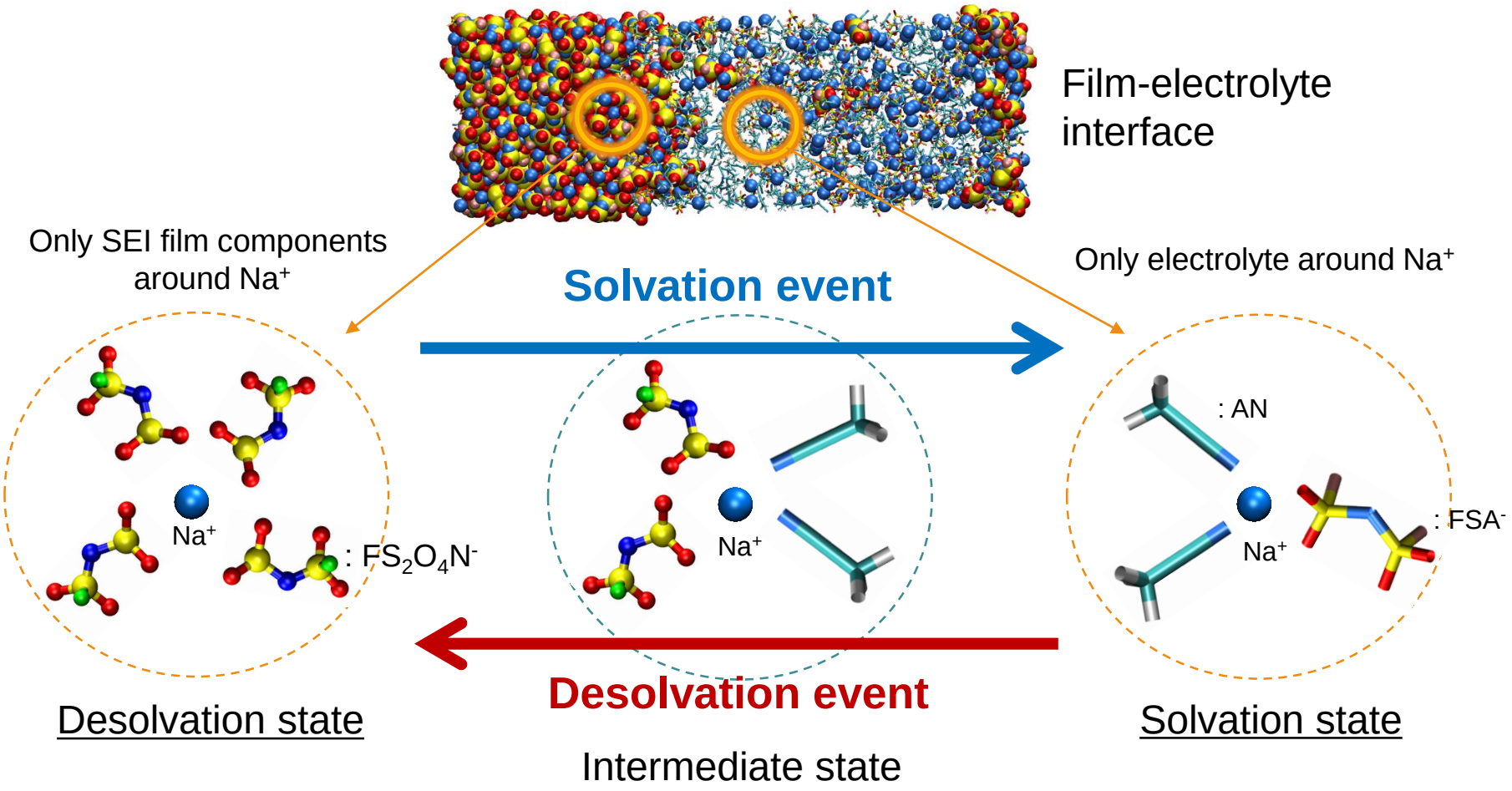


Calculation condition

- Temperature: 298, 398, 498, 598, 698 K
- 10 ns (10000 ps) MD simulations

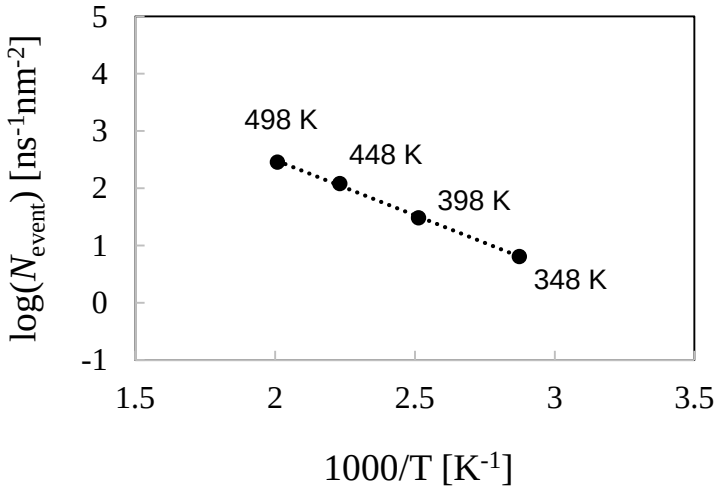
How to treat solvation-desolvation events

- The numbers of solvation-desolvation event (N_{event}) for all Na^+ in the system was counted during the MD simulations as with the previous study [*].

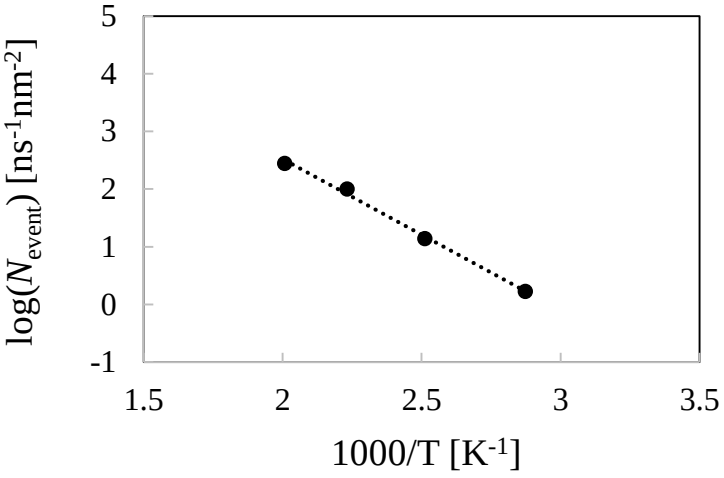


[*] O. Borodin, D. Bedrov, *J. Phys. Chem. C*, **118**, 18362-18371 (2014).

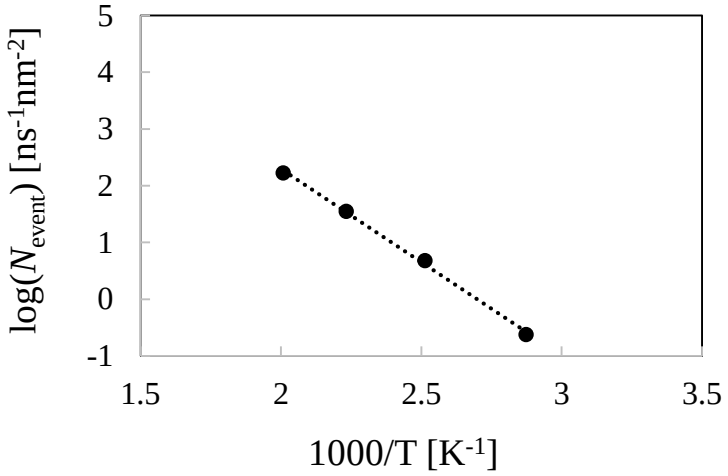
Arrhenius plots for solvation-desolvation events



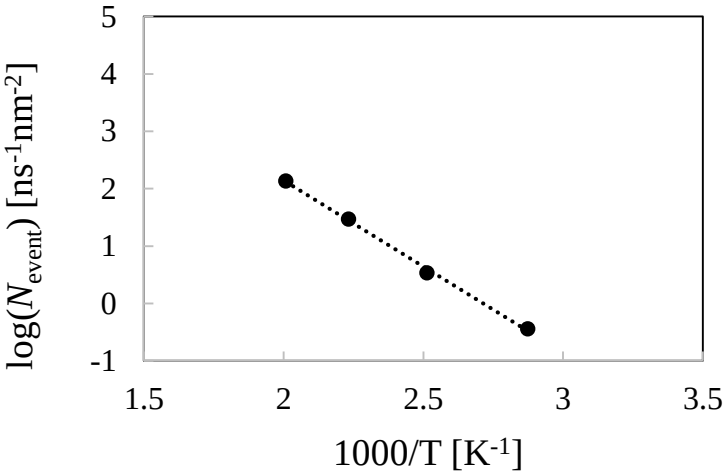
(a) 1.0 molL^{-1}



(b) 2.0 molL^{-1}



(c) 3.0 molL^{-1}



(d) 4.0 molL^{-1}

Activation barriers for desolvation and solvation

Table. Effective activation barriers and frequency factors

Salt concentration	Activation barrier (kcal/mol)	Frequency factor (ns^{-1})
1.0 M	9.03 ± 0.96	6.35
2.0 M	12.42 ± 1.18	7.76
3.0 M	15.40 ± 0.88	8.86
4.0 M	14.15 ± 1.29	8.15

(They are obtained by different 10 initial configurations.)

- The present simulation results clearly show that **the desolvation-solvation process is rate-determining step** for ion transport in this system because their activation barterers are higher than that in bulk film (7.05 kcal/mol).

- The activation barriers were found to be strongly dependent on the salt concentration. In next CREST workshop, I will focus on this topic.