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**Theoretical discussion on ion
transport in Na-ion batteries with
acetonitrile solutions**

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Background (Salt concentration effect)

- Yamada group experimentally reported the battery performance of Li-ion batteries (LIB) is drastically improved by increasing the salt concentration in the electrolyte [1-3].

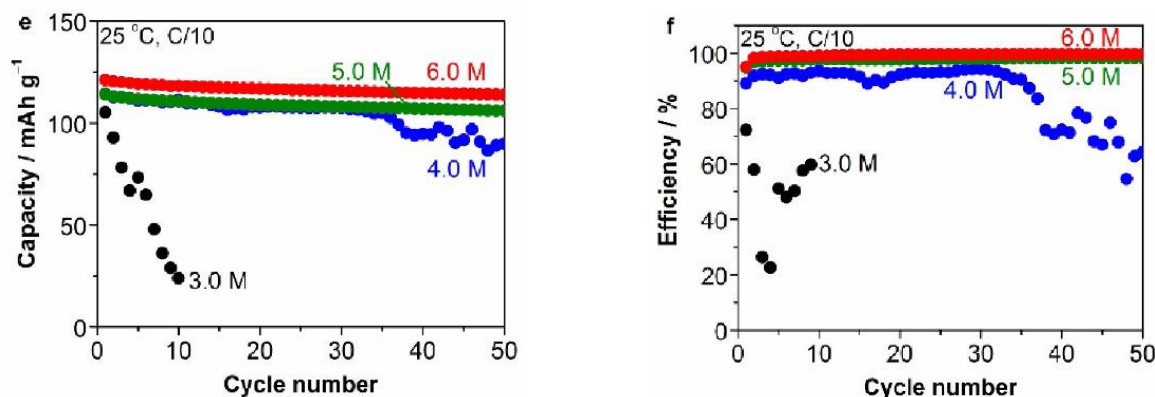


Fig. Capacity and Coulomb efficiency of LiMn₂O₄/Li cell at C/10 and 25 °C [1].

[1] Y. Yamada, M. Yaegashi, T. Abe, A. Yamada, *Chem. Commun.*, **49**, 11194 (2013).

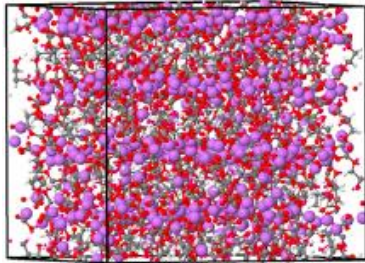
[2] Y. Yamada, K. Furukawa, K. Sodeyama, K. Kikuchi, M. Yaegashi, Y. Tateyama, A. Yamada, *J. Am. Chem. Soc.*, **136**, 5039 (2014).

[3] Y. Yamada, C. H. Chiang, K. Sodeyama, J. Wang, Y. Tateyama, A. Yamada, *ChemElectroChem*, **2**, 1687 (2015).

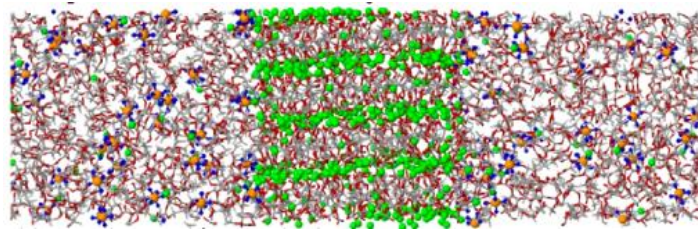
- The application of such highly concentrated electrolyte is the effective strategy to improve the performance of Na-ion batteries (NIB).

Background (Ion transport)

- Borodin group theoretically investigated the ion transport mechanism in LIB by using two simple calculation models [4,5].



Bulk Li₂EDC model [4]



Li₂EDC (SEI)-electrolyte interface [5]

[4] O. Borodin, G. V. Zhuang, P. N. Ross, K. Xu, *J. Phys. Chem. C*, **117**, 7433-7444 (2013)

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

- The activation barrier for the Li⁺ diffusion in bulk Li₂EDC model was estimated to be 15 kcal/mol, which is similar to the experimental value (12 ~ 24 kcal/mol). On the other hand, the activation barrier of solvation-desolvation (9.6 kcal/mol) was smaller than that in bulk Li₂EDC.
- The Li⁺ transfer inside the SEI film should be a rate-determining step.

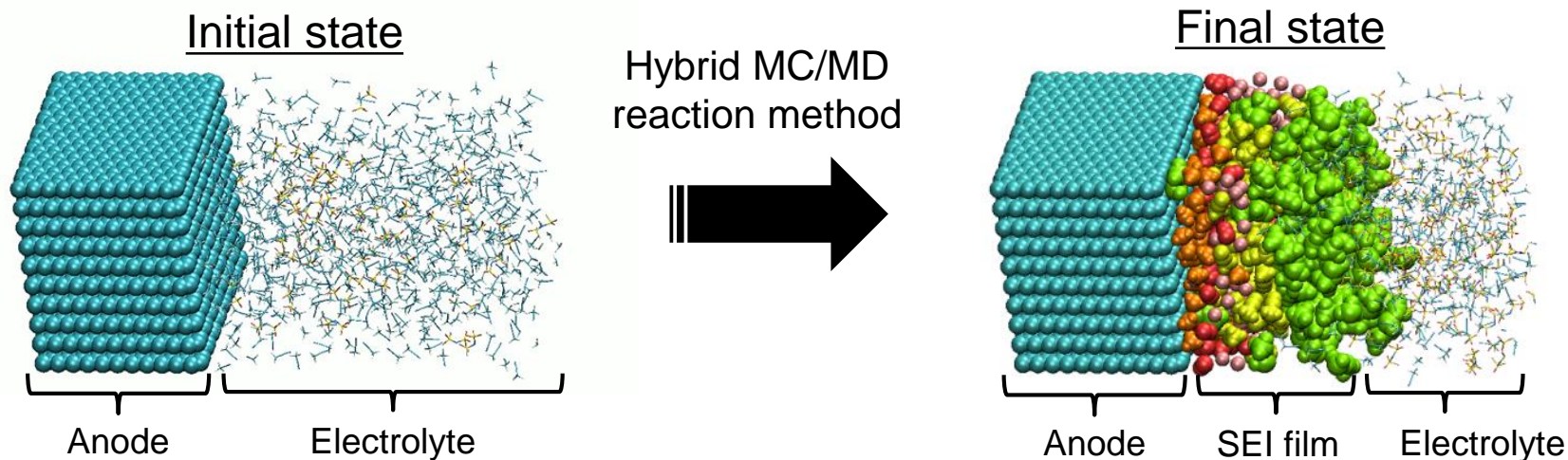
Purpose of this study

- In the previous 2nd CREST workshop (May 30th), the dependency on the salt concentration of SEI film formation with acetonitrile solutions has been investigated by using a **hybrid MC/MD reaction method** [6-8].

[6] M. Nagaoka, Y. Suzuki, T. Okamoto, N. Takenaka, *Chem. Phys. Lett.*, **583**, 80 (2013).

[7] N. Takenaka, Y. Suzuki, H. Sakai, M. Nagaoka, *J. Phys. Chem. C*, **118**, 10874 (2014).

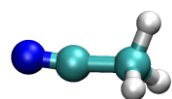
[8] N. Takenaka, H. Sakai, Y. Suzuki, P. Uppala, M. Nagaoka, *J. Phys. Chem. C*, **119**, 18046 (2015).



- In this study, I investigated the ion transfer mechanism inside the SEI film by using the same methodology as Borodin group [5]. First, I prepared the simple bulk SEI model. Next, I estimated the activation barriers by using Arrhenius plots for the ion diffusion in the bulk SEI model.

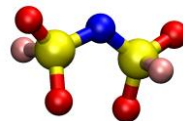
Calculation models and conditions

For this purpose, I employed the AN-NaFSA electrolyte solution at (a) 1.0 M, (b) 2.0 M, (c) 3.0 M and (d) 4.0 M concentration conditions.

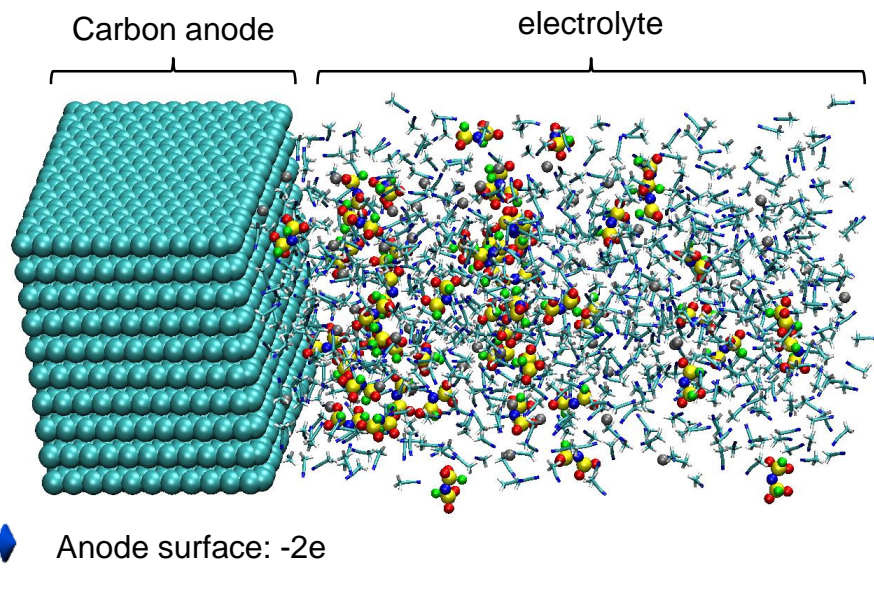


: Acetonitrile (AN)

● : 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⁻

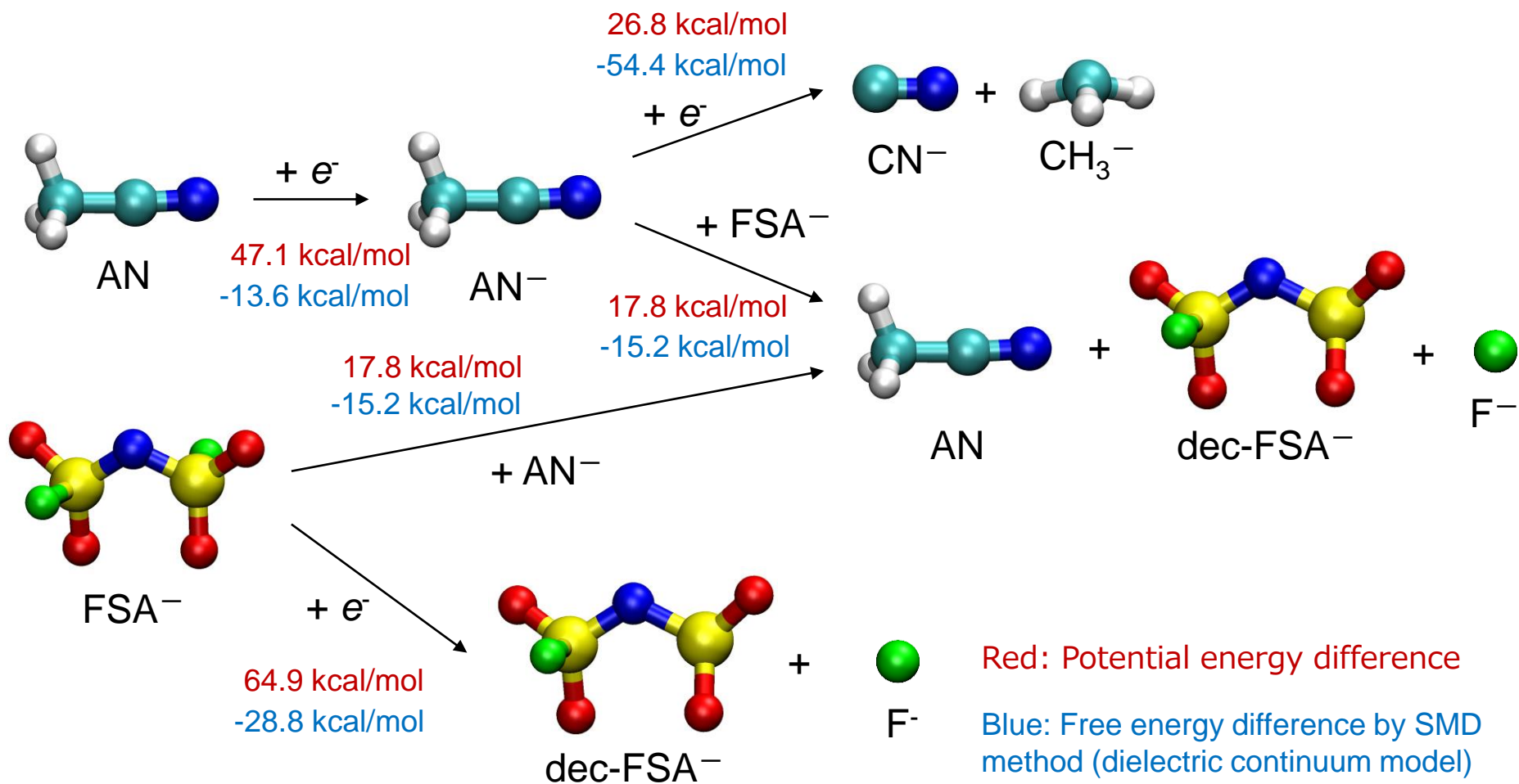
(c) 3.0 M : 800 AN, 177 Na⁺, 175 FSA⁻

(d) 4.0 M : 800 AN, 252 Na⁺, 250 FSA⁻

Calculation condition

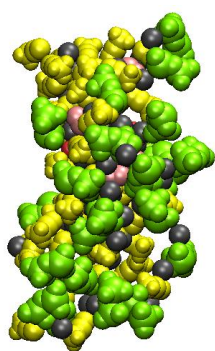
- Temperature: 298 K
- GAFF
- 10 ps per 1 MC/MD cycle

Reaction scheme for simulations

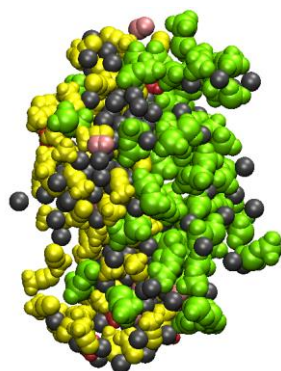


Calculation level: B3LYP/cc-pvdz

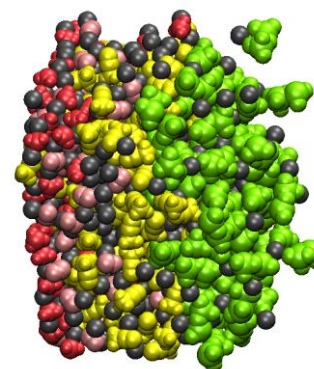
SEI film formation at high concentration (4.0 M)



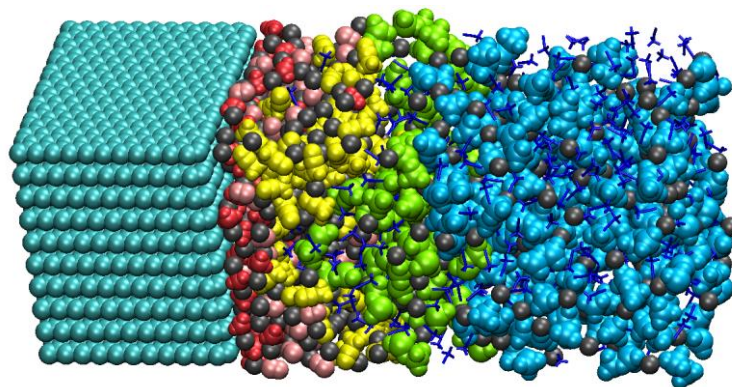
(a) 200 MC/MD cycle



(b) 500 cycle

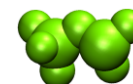
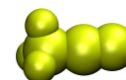
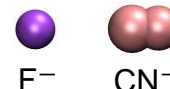


(c) 1000 cycle

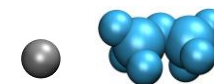


(e) 2000 cycle

Species in SEI film



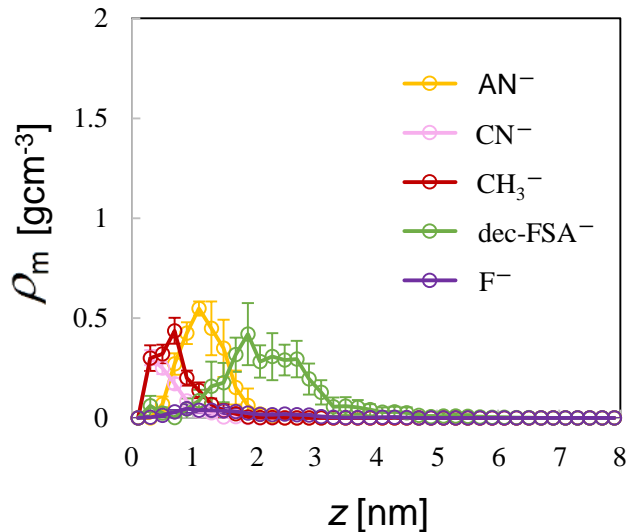
Salt



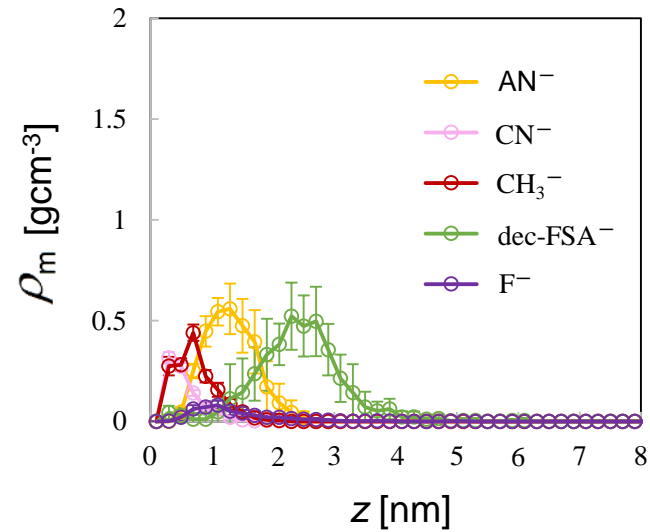
- At high concentration condition, the dec-FSA anions formed the stable film so as to prevent the electrolyte molecules from their approaching.

Mass density distributions of reaction products

(They are obtained by different 10 initial configurations.)



(a) 1.0 M

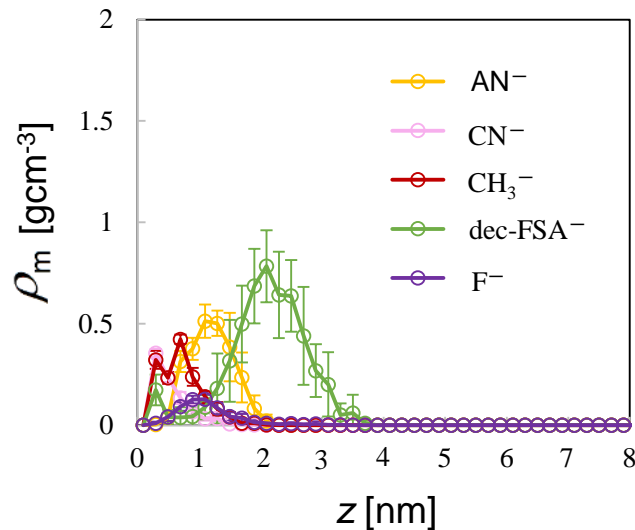


(b) 2.0 M

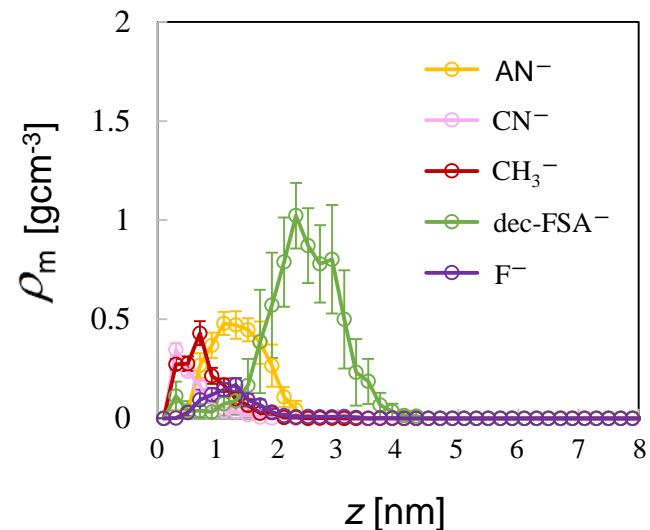
- The CH₃ and CN anions were mainly distributed near the anode surface, and the peak heights of their distributions were almost same in all conditions. Thus, the salt concentration should not affect the production of these layers.

Mass density distributions of reaction products

(They are obtained by different 10 initial configurations.)



(c) 3.0 M

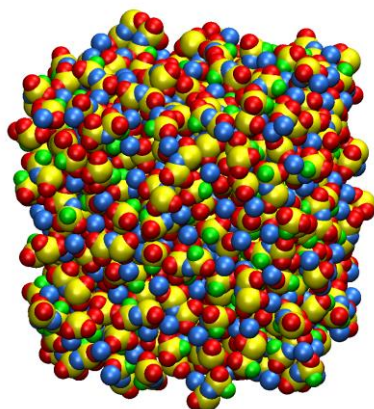


(d) 4.0 M

- As the salt concentration increases, the peak height of **dec-FSA** anions clearly increased, meaning that the SEI film becomes denser and stable. Therefore, to understand the ion transport mechanism at the high salt concentration, the Na⁺ diffusion in the **dec-FSA**⁻ layer can be essentially important.

Preparation of Bulk SEI model

To estimate the activation barrier for the ion diffusion inside SEI film by using Arrhenius plot, I prepared the bulk SEI (dec-FSA⁻) model, and calculated the mean-squared displacement at 5 different temperatures.



Bulk SEI (dec-FSA⁻) model



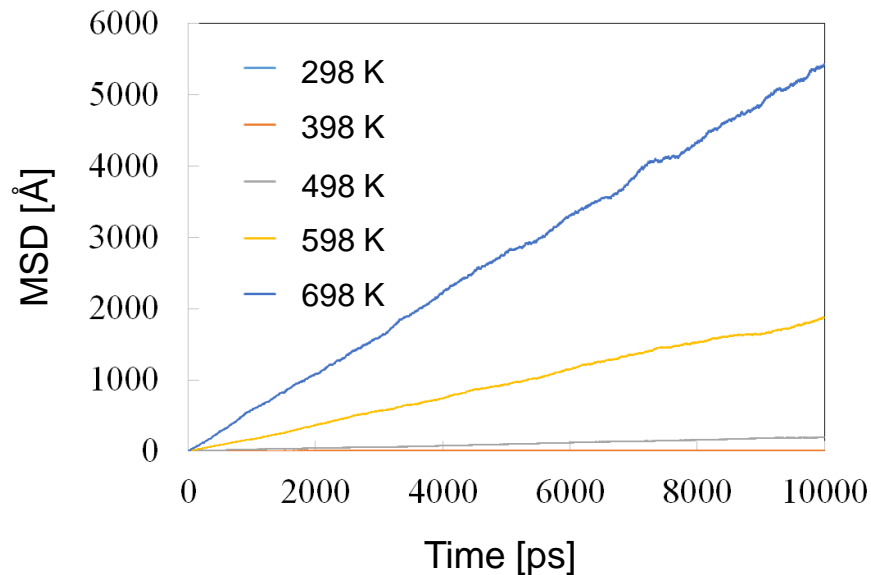
Molecule number of electrolyte:

400 dec-FSA⁻, 400 Na⁺

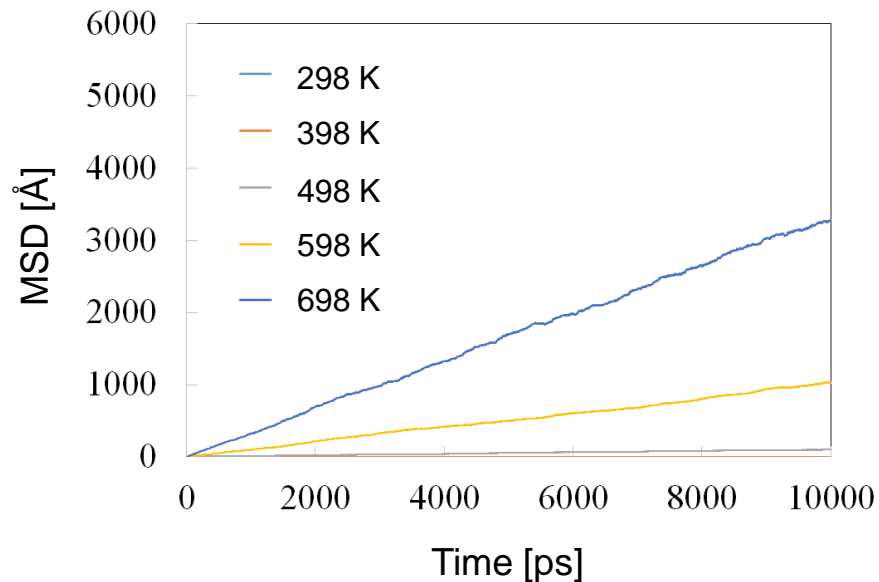
Calculation condition

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

Mean-squared displacement (MSD)



(a) Na⁺



(b) dec-FSA⁻

- The calculated MSDs drastically increased as the temperature increases.
- It was found that the Na⁺ diffusion is faster than that of dec-FSA anion due to its smaller size.

Estimation of ion conductivities

- The uncorrelated ion conductivity λ is estimated by equation (1).

$$\lambda = \lim_{t \rightarrow \infty} \frac{e^2}{6tVk_B T} \int_i^n z_i^2 \left\langle \left[R_i(t) - R_i(0) \right]^2 \right\rangle$$

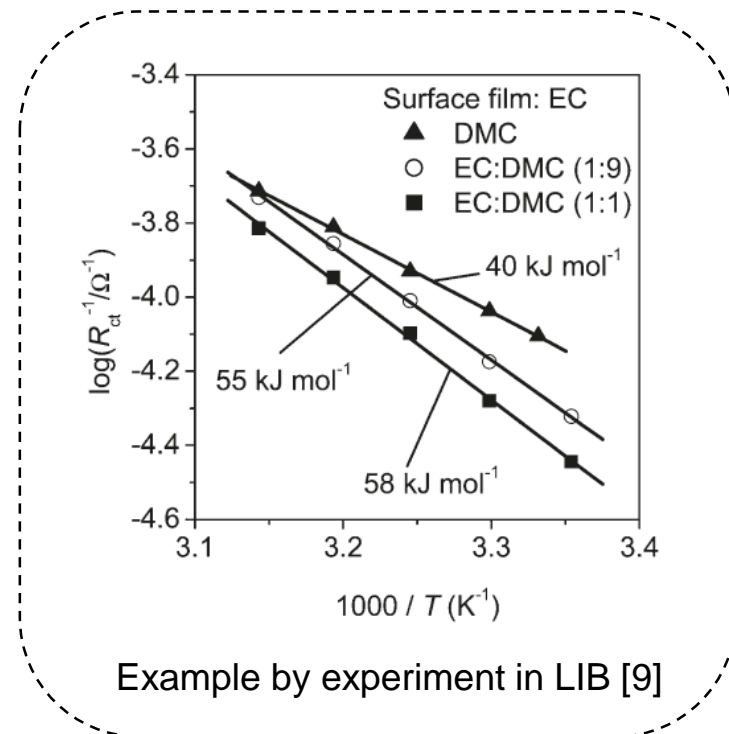
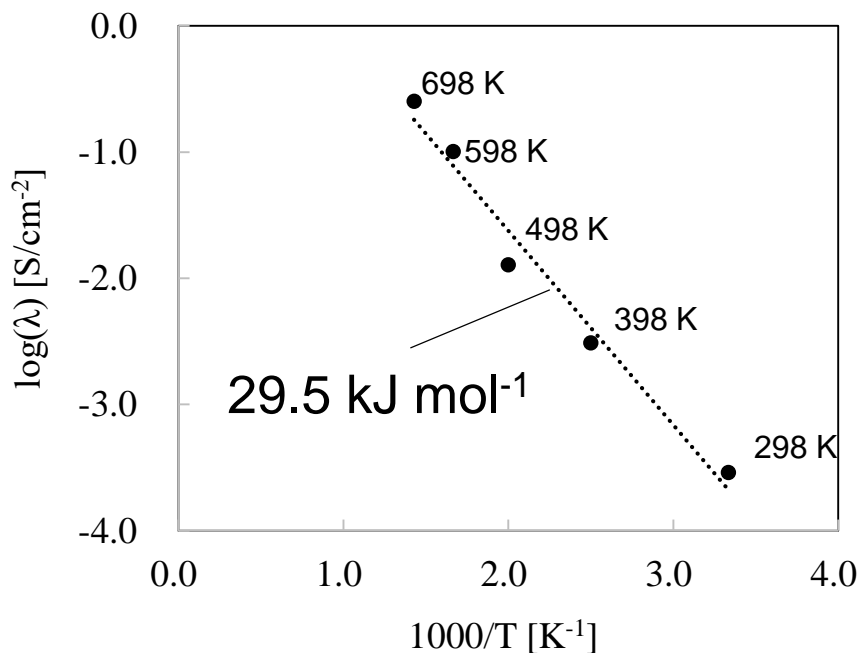
$$= \frac{e^2}{Vk_B T} \left(n_{\text{Na}^+} D_{\text{Na}^+} + n_{\text{dec-FSA}^-} D_{\text{dec-FSA}^-} \right) \quad (1)$$

t : time, V : volume, T : temperature, e : quantum of electricity, z : charge, R : displacement of ion
 n : number of ion, D : diffusion constant

Table 1. Diffusion constants and ion conductivities

Temperature [K]	D_{Na^+} [$10^{-6}\text{cm}^2/\text{s}$]	$D_{\text{dec-FSA}^-}$ [$10^{-6}\text{cm}^2/\text{s}$]	λ [S/cm]	S: siemens (SI unit)
298	0.0042	0.0023	0.00029	
398	0.0087	0.0052	0.0031	
498	0.33	0.17	0.013	
598	3.15	1.68	0.10	
698	9.04	5.53	0.25	

Calculated activation barrier



[9] Ogumi et al., Langmuir, **25(21)**, 12766 (2009).

- By using Arrhenius plot, the calculated activation barrier for the ion diffusion became 29.5 kJ mol^{-1} ($7.05 \text{ kcal mol}^{-1}$). It should be noted that this value changes depending on the calculation accuracy of force field.

Summary

- ❑ In this study, I investigated the ion transport mechanism by estimating the activation barrier of ion diffusion inside the SEI film.
- ❑ According to the SEI film formation simulations, it was found that the dec-FSA anions form the stable SEI film at the higher salt concentration.
- ❑ Based on Arrhenius plot, the calculated activation barrier of ion diffusion inside dec-FSA⁻ layer became 7.05 kcal/mol although this value may be different from the experiment one due to the accuracy of force field.
- ❑ In the next CREST work shop, I will show the activation barrier of solvation-desolvation by using the SEI-electrolyte interface model, and compare qualitatively it with that of ion diffusion inside SEI film.