# Theoretical analysis of Li ion transport in solid-electrolyte interphase film

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# Lithium ion battery and SEI film

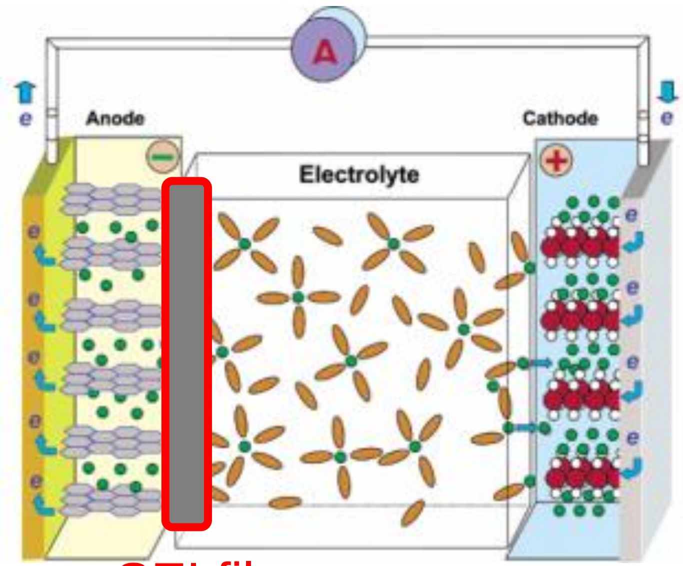
Li ion batteries are promising candidates for the energy conversion technology

high energy density, compact size, light-weight body, and long cycle life


## Solid-electrolyte interphase (SEI) film

passivation film formed on the anode surface to prevent solvent degradation

Correct understanding of electrochem. processes related to SEI film is needed to achieve innovative high-performance rechargeable batteries




SEI film

# Li ion transport

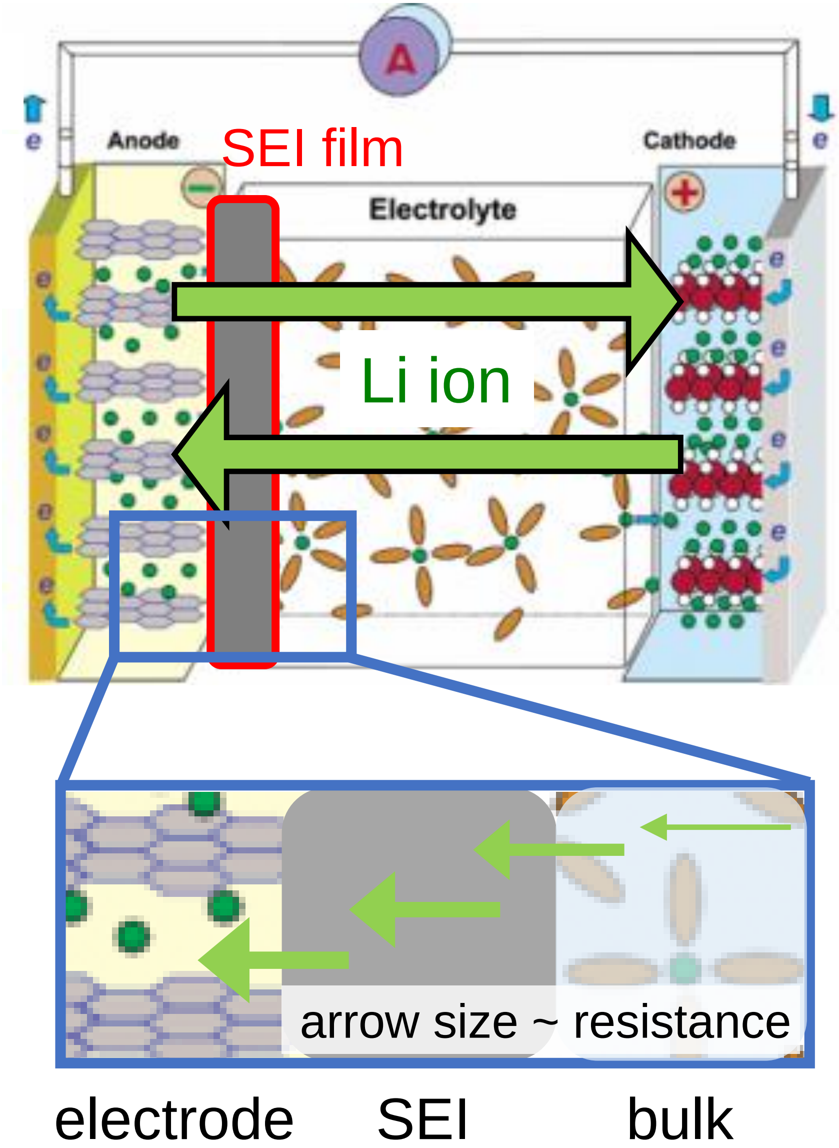
One of the most critical processes

… charging/discharging process
~ Li ion transport btwn electrodes

- Bulk electrolyte
- electrolyte/SEI film
- SEI film
- SEI film/electrode

Resistance:
R(SEI film/electrode) ≥ R(SEI film)
>> R(other regions)

Here, we try to computationally estimate the Li ion transport resistance in SEI film.



# How to estimate resistance?

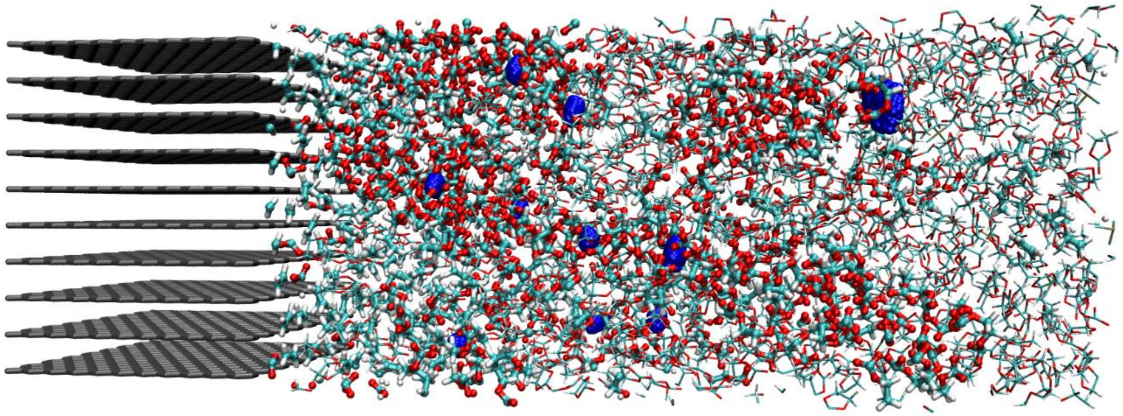
## Conventional approach 1

diffusion coefficient → ionic conductivity → (specific) resistance

MD simulation $\sigma = q^2 cD/k_{\mathrm{B}}T$

Dynamics calc. (ion diffusion) is used for the estimate.

However, Li ions in SEI film are unlikely to diffuse at 300 K.



**Blue spheres**: trajectories of Li ions.

Standard deviation: 0.26 ± 0.11 Å

(300 K, 10ns MD, and randomly selected 10 Li ions)

**The approach does not work well.**

# How to estimate resistance?

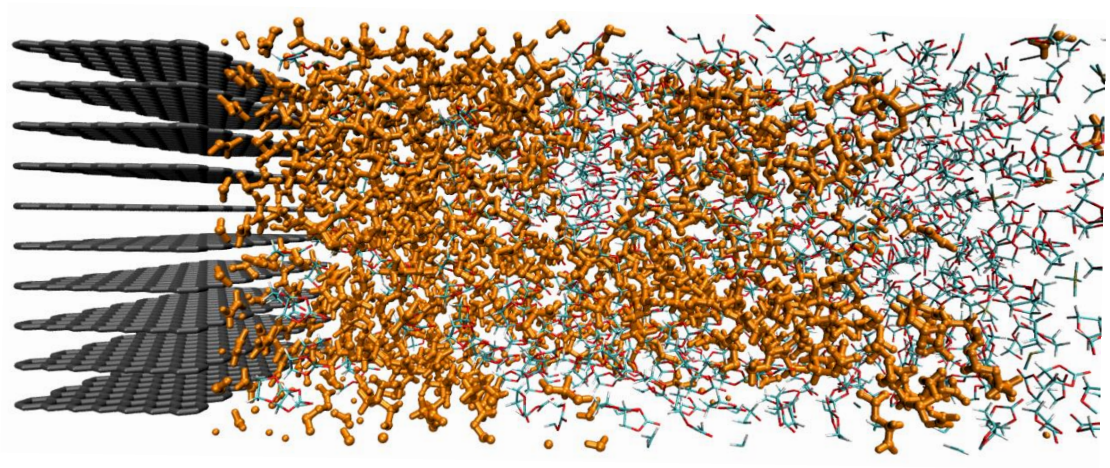
Conventional approach 2

minimum energy path → rate constant → diffusion coefficient →

DFT calc. TST $D = d^2 k$

Static calc. are used for the estimate.

However, Li ion transport path in SEI film is unobvious.



**Orange colors**: SEI film components

Width of SEI film: ~70 Å

**The approach also does not work well.**

# Our strategy to estimate resistance

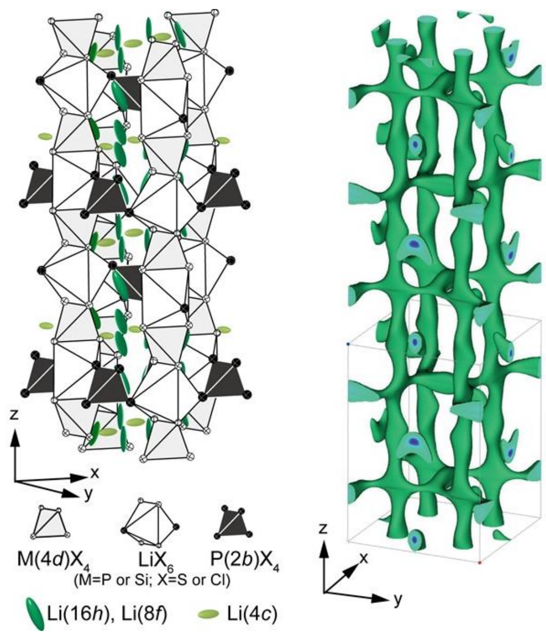
Using a statistical method, Li ion transport path is determined based on the free energy landscape.

**1.** Obtain Li ion distribution in SEI film

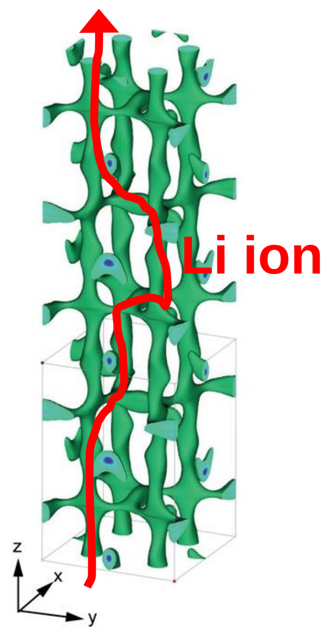
**2.** Determine Li ion transport path

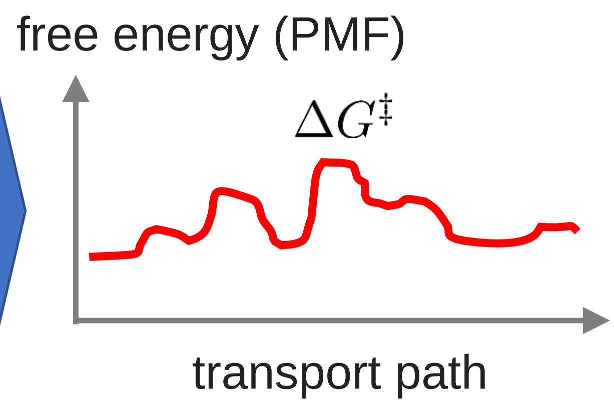
**3.** Estimate barrier (rate constant)

conceptual drawing




*Nat. Energy*, 1, 16030 (2016)




rate constant

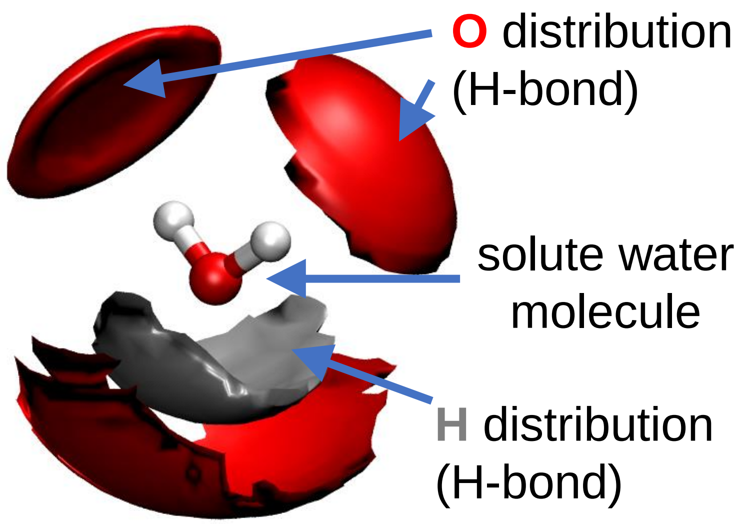
$$k = \nu \exp(-\beta \Delta G^{\ddagger})$$

# Method for Li ion distribution

3D-RISM method is the most suitable for the calculation

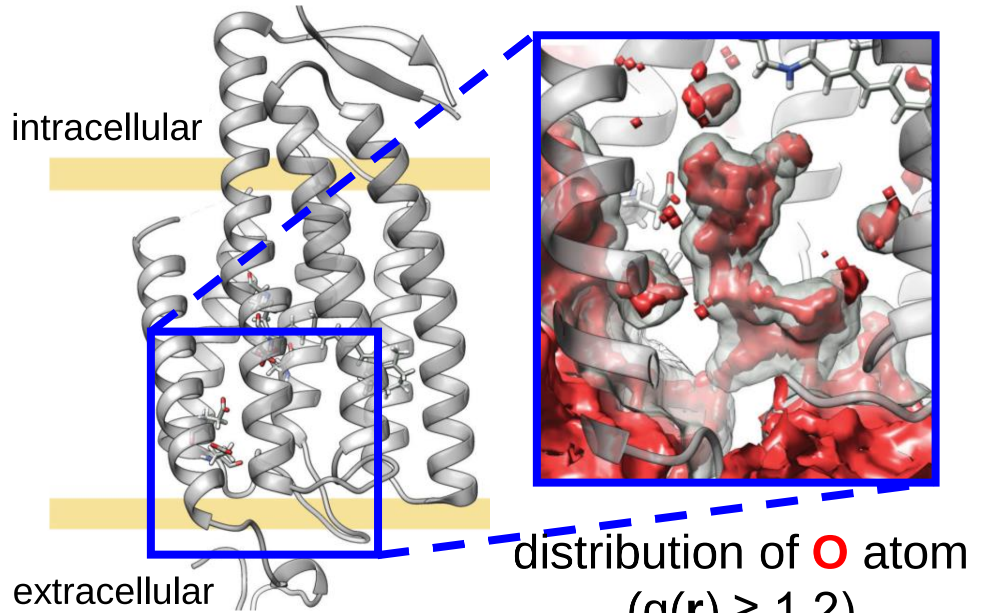
On the basis of the statistical mechanical theory of liquids,
it calculates solvent probability distribution around a solute.

water in water




distribution of H and O atoms of water (isosurface plot at g(**r**) = 2.5 )

water around channelrhodopsin

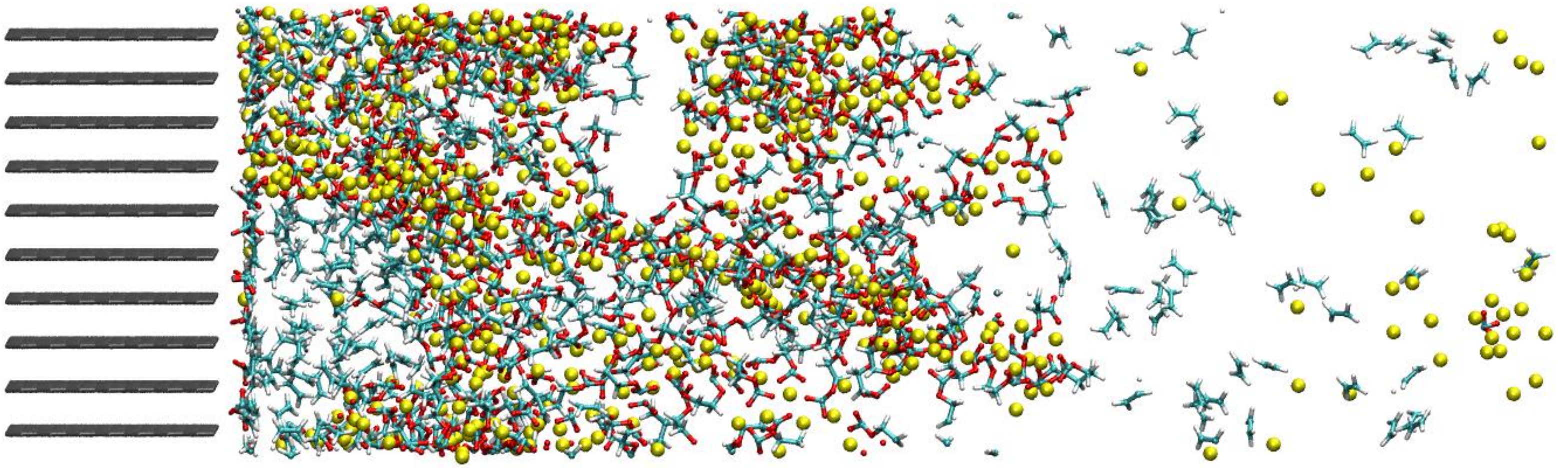



distribution of O atom
(g(**r**) ≥ 1.2)

*Chem. Phys. Lett.*, 699, 22 (2017)

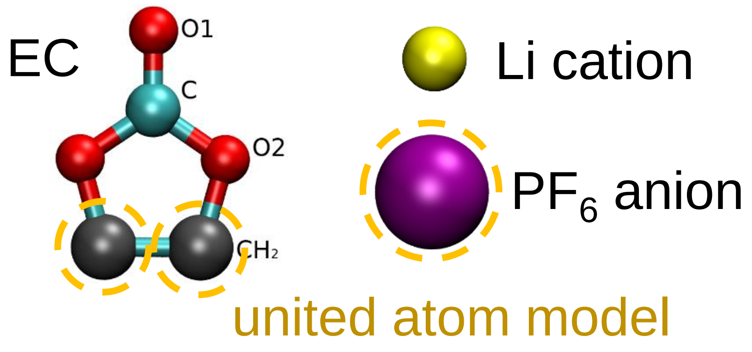
# 3D-RISM calc. conditions

- solute: electrode & SEI film (including **Li ions**)



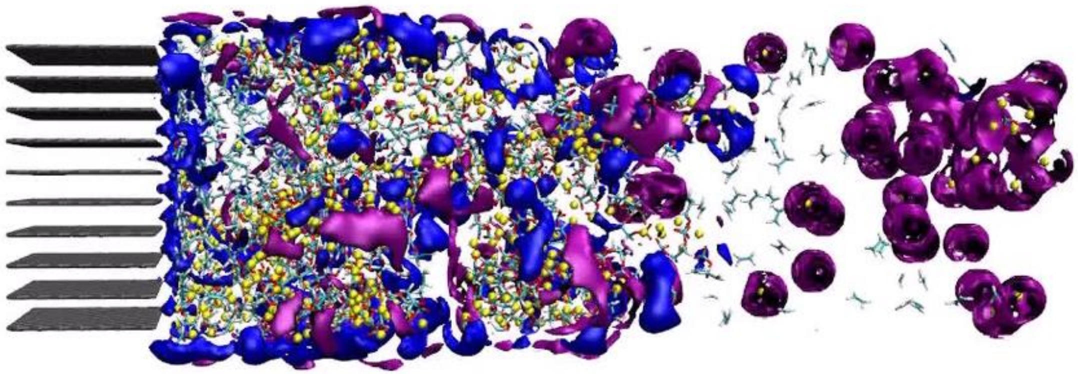
- solvent: electrolyte solution

  15 M ethylene carbonate & 1.1 M $LiPF_6$




- 3D-RISM box: 64 × 64 × 256 Å$^3$ (buffer size ~ 30 × 30 × 128 [Å] )
- solute total charge: 17.0 $e$
- electrode charge: zero
- temperature: 300 K
- closure: Kovalenko-Hirata closure

# 3D distribution of salt ions



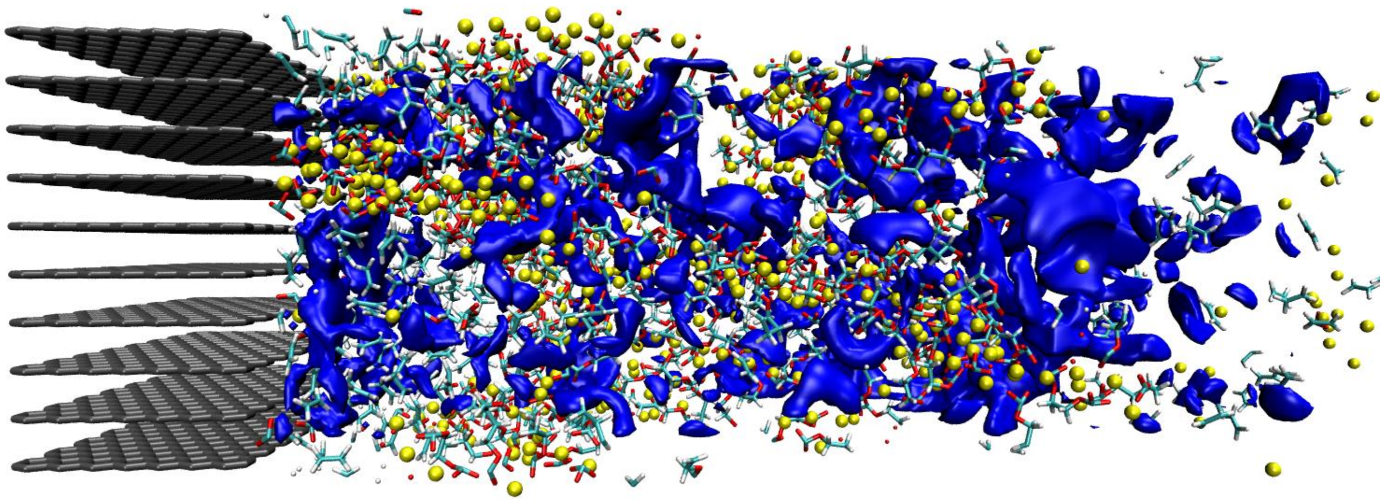
**blue**: $Li^+$ distribution, **purple**: $PF_6^-$ distribution (g(**r**) = 15)

- Solute charge was compensated by RISM solvent

  ( solute = 17 $e$, $N_{Li}$ = 662.29, $N_{PF_6}$ = 681.30 ⇒ total charge: 0.01 $e$ )

- Solvent $Li^+$ ($PF_6^-$) distributes around oxygens (solute $Li^+$).

# 3D distribution of salt ions



$g_{Li}(\mathbf{r}) = 3$

**r** in SEI film

**blue**: $Li^+$ distribution, **purple**: $PF_6^-$ distribution ($g(\mathbf{r}) = 15$)

- Solute charge was compensated by RISM solvent

  ( solute = 17 $e$, $N_{Li}$ = 662.29, $N_{PF_6}$ = 681.30 ⇒ total charge: 0.01 $e$ )

- Solvent $Li^+$ ($PF_6^-$) distributes around oxygens (solute $Li^+$).

- Solvent $Li^+$ distributes also in the SEI film.

  ⇒ Transport path is expected to exist in the SEI film.

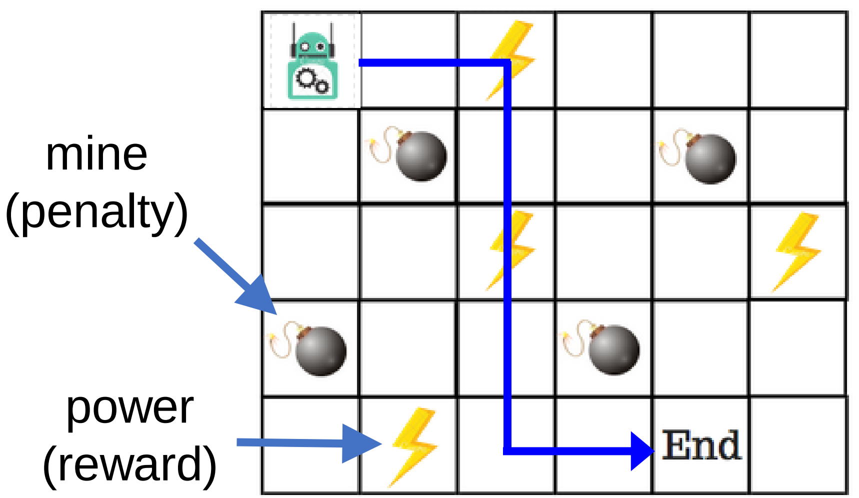
# Path search method

Li ion distribution is too complicated,
so it is difficult to determine the path by chemical intuition.

➡ Machine learning technique was applied.

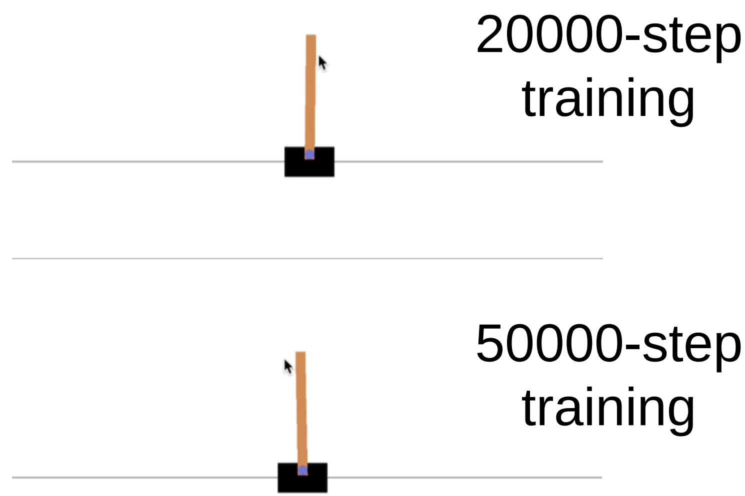
Q-learning (one of reinforcement learning) was tried.

simple maze (path search)



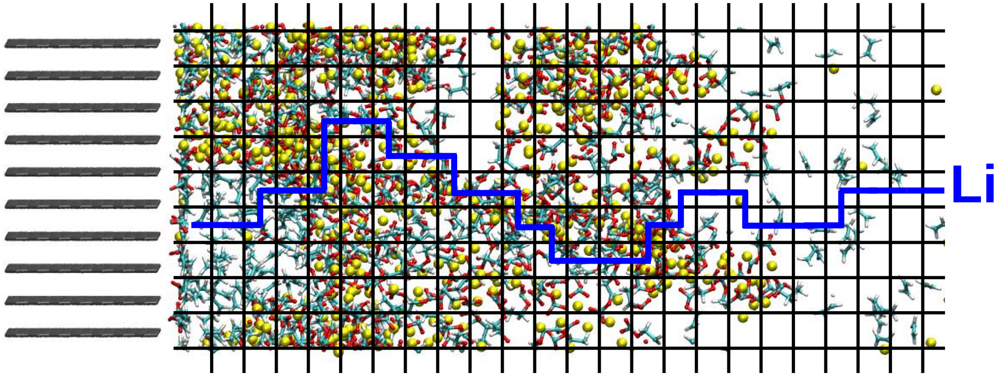

FreeCodeCamp webpage (@ADL, 2018/09/03)

cartpole game




Qiita webpage (@kznx, 2018/02/10)

# Q-learning for Li ion transport




conceptual drawing

3D space in SEI film was divided into grids (Δ = 0.5 Å).

Each grid has PMF value, which guides Li ion migration.

Each grid also has **Q value** which assesses a candidate path.

Basically, Li ion moves to a next grid with the smallest Q value.

However, initial Q value is not optimized for a desired path.

⇒ Q value is updated (i.e., trained) by actually creating actions.

Update formula is as follows:

$$Q(s_t, a_t) \leftarrow Q(s_t, a_t) + \alpha \left[ r_{t+1} + \gamma \min_a \{ Q(s_{t+1}, a) \} - Q(s_t, a_t) \right]$$

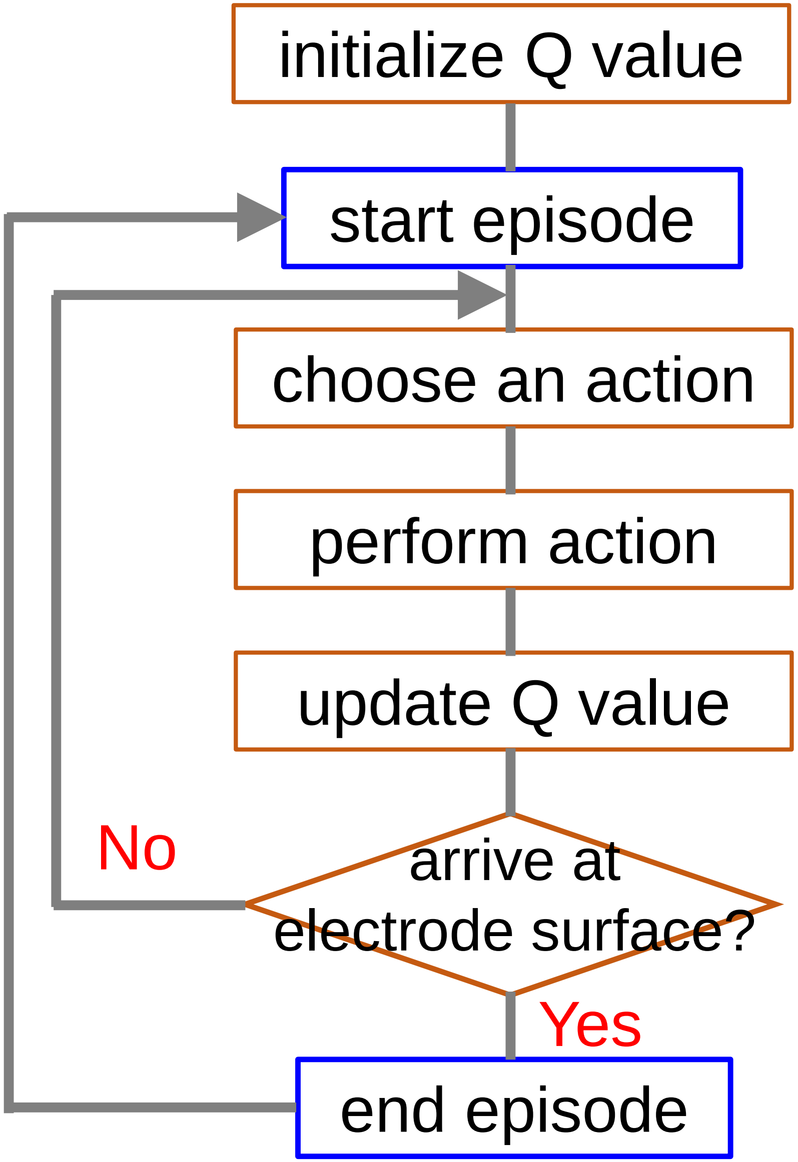
$s_t$ : state (position) at step $t$

$a_t$ : possible action at step $t$ (migration to next grid)

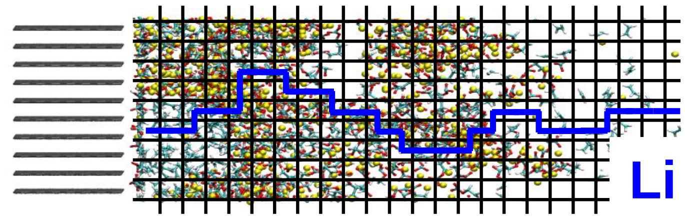
$r$ : reward or penalty

$\alpha, \gamma$ : parameters

# Q-learning procedure & conditions




・・・ set Q-table by random number (0,1)




one episode of transport

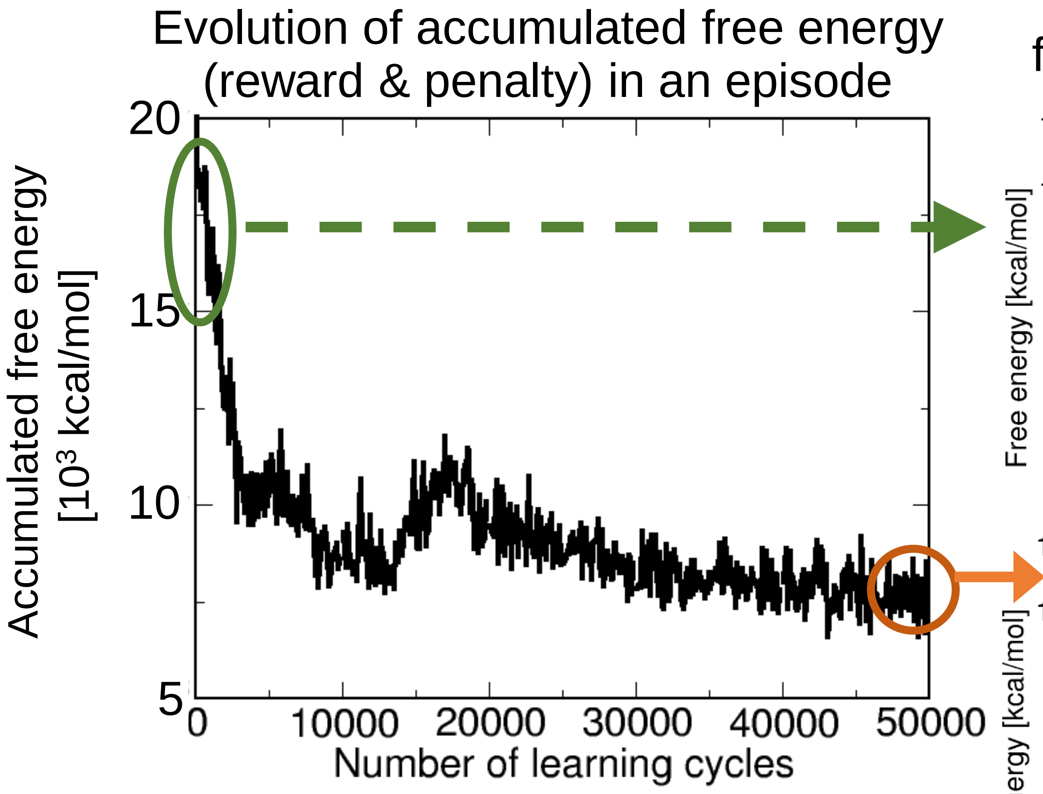
・・・ $\varepsilon$-greedy algorithm

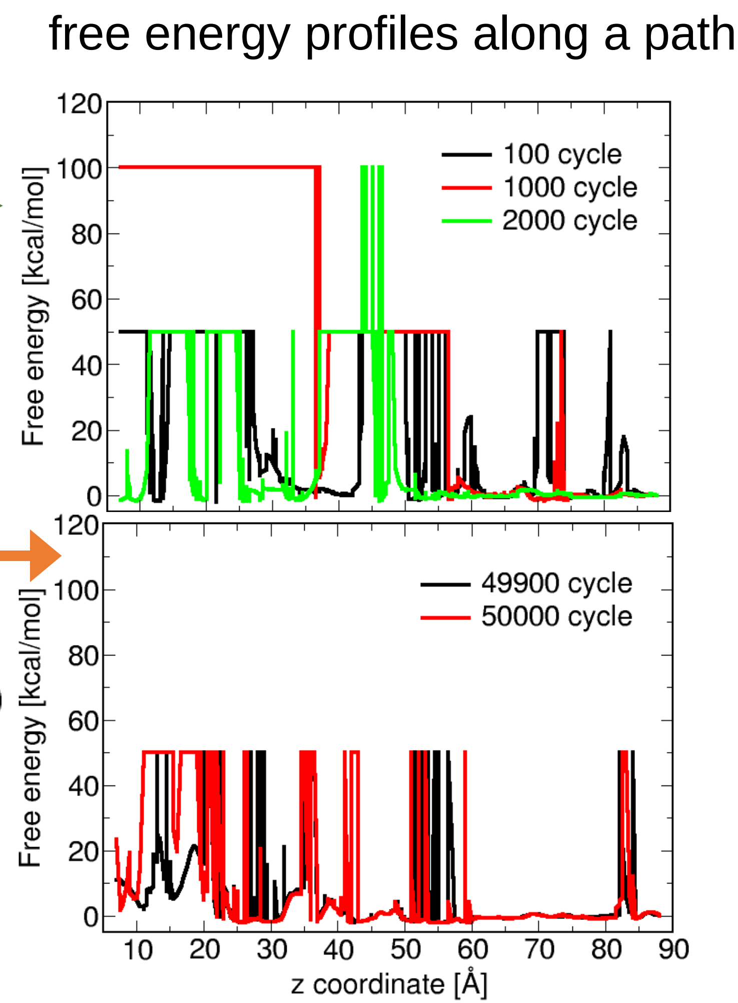
Randomly choose an action with $\varepsilon$ = 30% probability

## Conditions ( energy in kcal/mol )

- reward: free energy value (on grid)
  −100 (electrode surface)
- penalty: 100 (out of film in $xy$ direction)
  50 (contact with atom)
- ( $\alpha$, $\gamma$ ) = ( 0.1 , 0.9 )

# Training process



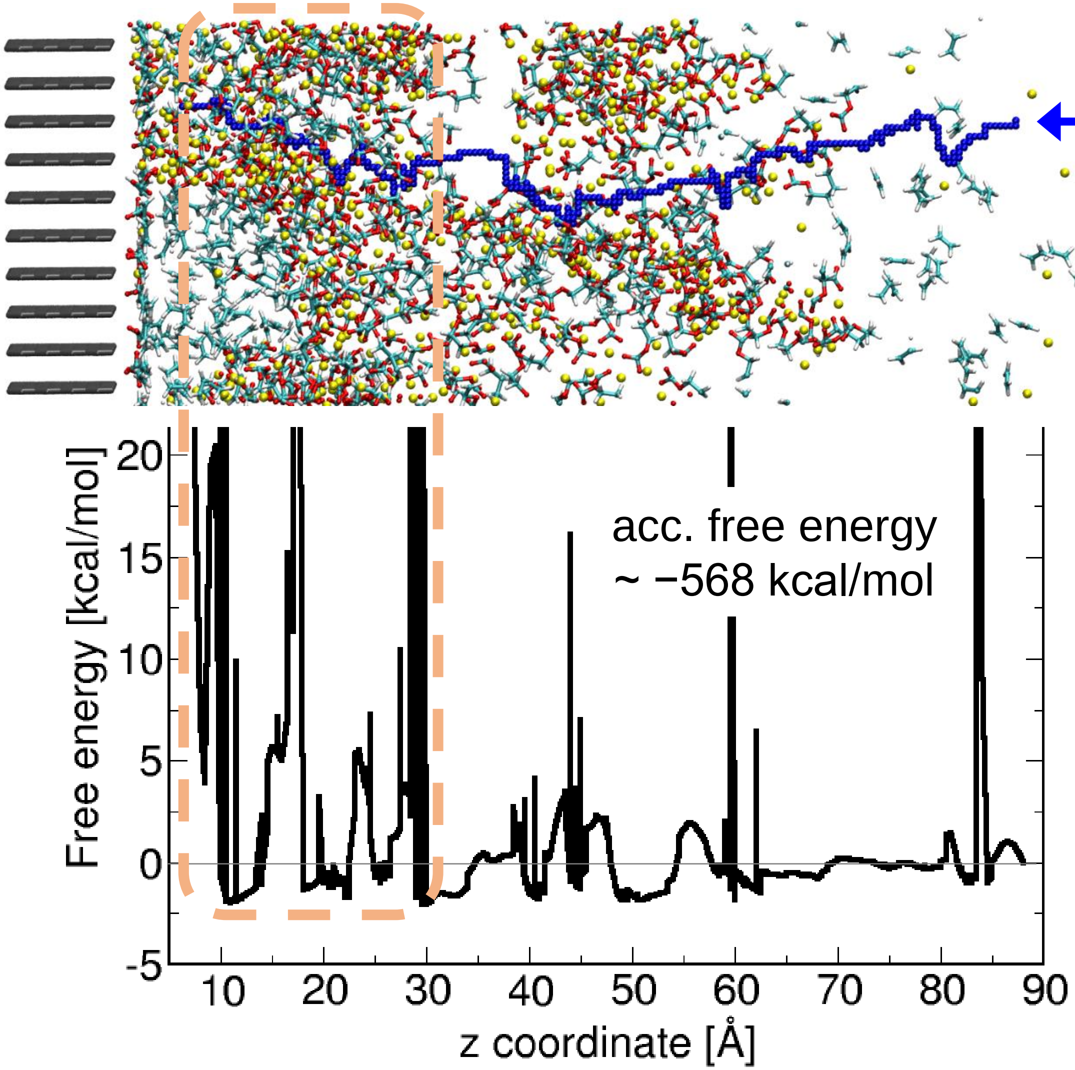

Initial stage … Li ion contacts with atoms and comes out of SEI film, frequently.

final stage … Li ion stays in SEI film and avoids a contact as much as possible.

⇒ Reasonable Q-table seems to be obtained.

# Q-learning production run

Path search was performed with $\varepsilon$ = 0.5% in $\varepsilon$-greedy.




Li ion transport path
(the best among 1000 paths)

The sparse and low PMF region seems to be selected.

PMF profile along the path
(projected on z coordinate)

Li ion contacts with atoms (PMF > 20 kcal/mol) in dens SEI film region (z~10-30 Å).

⇒ Reaction barrier for Li ion transport is difficult to be estimated from this path.

# Can we improve the path ?

## Computational point of view

- ➢ Are parameters employed reasonable ?
  - ∗ Reward at electrode surface
  - ∗ Penalty at out of SEI film & at contact with atoms
  - ∗ $\alpha$ & $\gamma$ parameters in the update formula of Q-value

Q-learning result is known to be sensitive to them.

## Physical & chemical point of view

- ➢ Are all the Li ion in SEI film unrelated to the transport ?

If they join that, they should be treated as RISM solvent.

- ➢ Does SEI film fluctuation assist the transport ?

If so, more sophisticated method will be needed.

e.g., 3D-RISM/MD and Deep Q Network combination

# Summary

- Theoretical investigation on the Li ion transport in the SEI film in Li ion batteries was started.
- A new approach combining the 3D-RISM method with the Q-learning technique was employed.
- 3D-RISM calculations gave a Li ion distribution in the SEI film configuration reasonably.
- Q-learning proposed some Li ion transport paths, but inevitable contacts with atoms were observed.
- One of the possible causes is to treat all the Li ions in the SEI film as components of solute molecules. Further investigation is needed.