

Mon. Jul. 28<sup>th</sup>

## **The 2<sup>nd</sup>, CREST Workshop**

# **The Collaboration with the “Elements Strategy” and its Molecular Technological Basis**

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# “Elements Strategy”

## “Crisis of Elements”

- Continuous stable supply of rare metals is of increasing concern in Japan, and such supply restriction makes it difficult to manufacture industrial products and materials.

To avoid this problem,

“reduction”, “substitution”, “recycle” of rare metals are essential.

“MEXT” = “Ministry of Education, Culture, Sports, Science & Technology”

For this purpose, **MEXT** in Japan drives forward elements strategy initiative (ESI) as a national strategy.

[Reference in Japanese] “Elements Strategy to create a path toward future (未来を拓く元素戦略)” (KAGAKU-DOJIN).

MEXT program

## Elements Strategy Initiative for Catalysts and Batteries: Interplay Between Experimental and Theoretical Studies

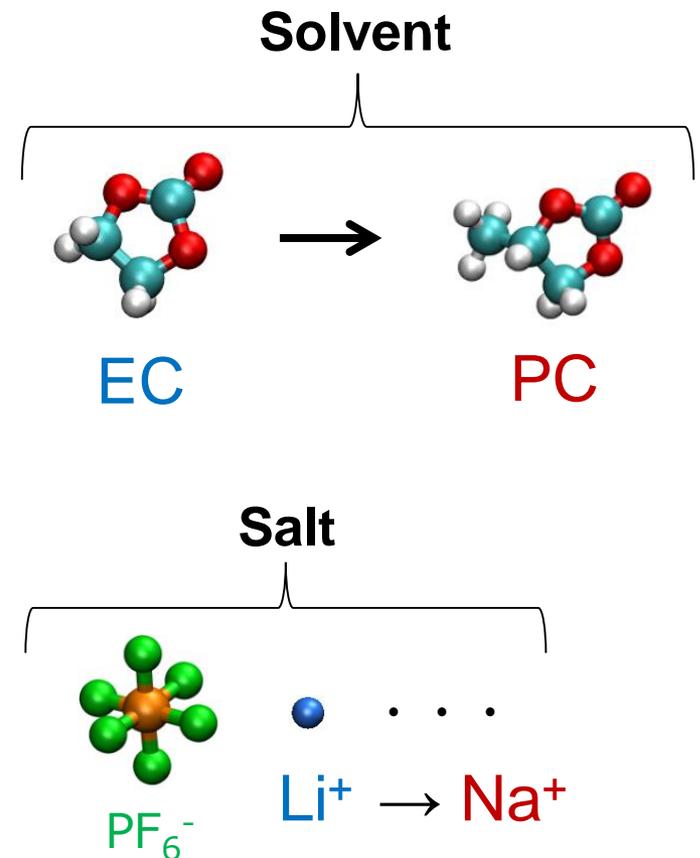
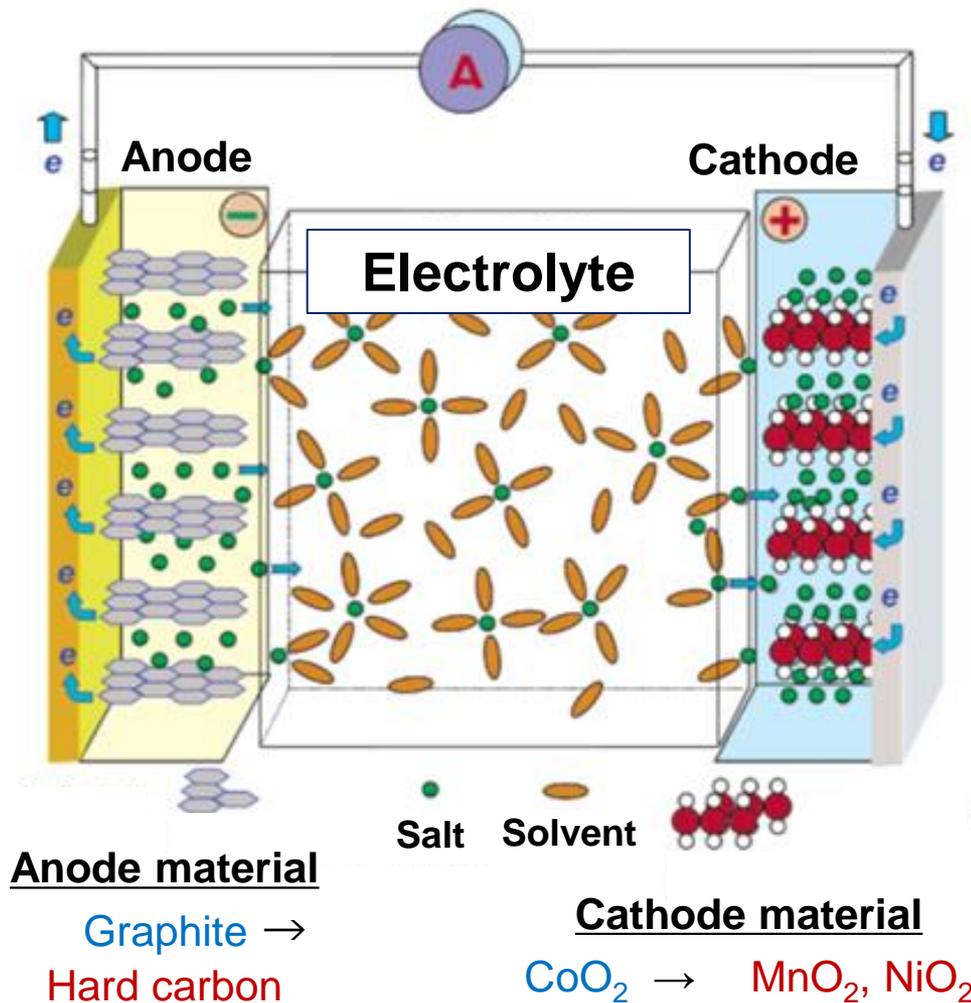
Primary objective is to develop **rare metals-free catalysts and batteries**.  
To accomplish this objective, we reveal the microscopic mechanism in the catalysts and batteries which are complex materials by the interplay between the experimental and theoretical studies.

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)

# From Li-Ion Battery to Na-Ion Battery

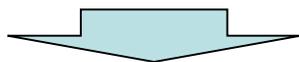
- To produce the practical **Na-ion battery**, the optimized design of materials is required because **Na<sup>+</sup>** is larger than **Li<sup>+</sup>**.



# Our Research Subject: Multi-Scale Simulation for Electrode and Electrolyte in Secondary Battery

## Solid Electrolyte Interphase (SEI) film

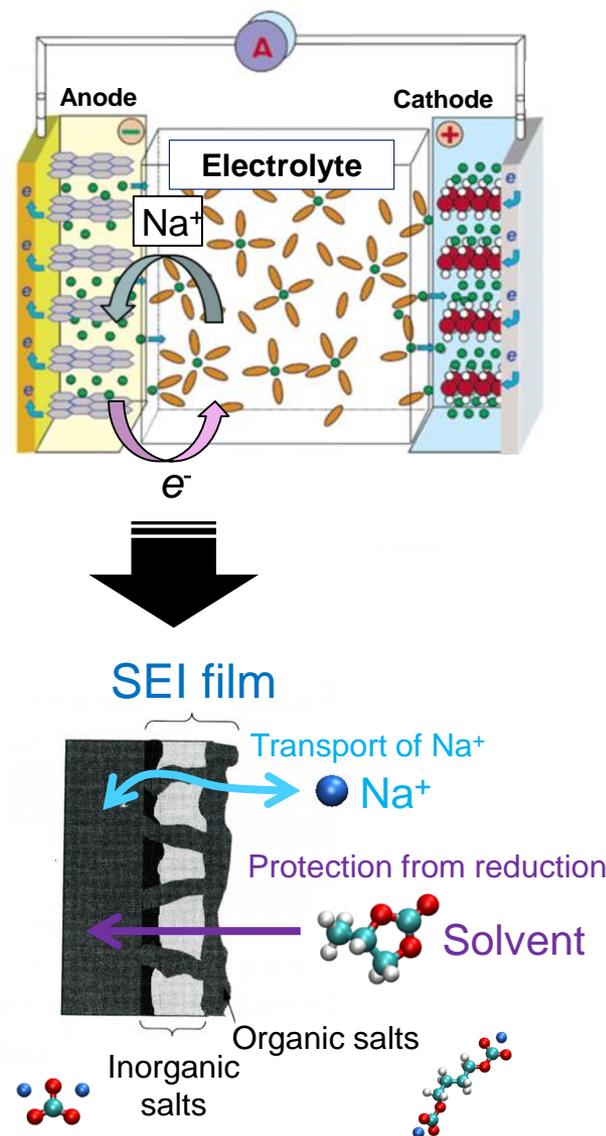
- At the charging process of battery, the solvents and salts in electrolyte are decomposed because the electric potential of anode becomes very low.
- A number of reduction products form a thin **SEI film**, which should protect the electrolyte from further reductive decomposition.



- **Estimation of elementary reactions** by the electronic state calculations, QM/MM method.
- **Hybrid MC/MD reaction simulations**

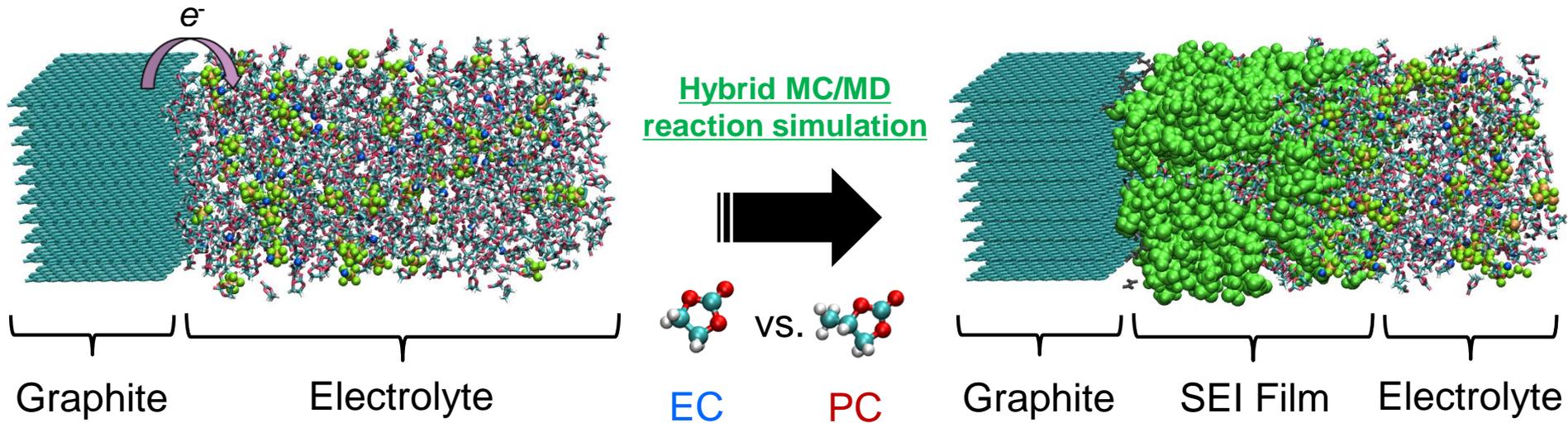


By elucidating microscopic mechanism in the **SEI film formation**, we aim to theoretically accomplish the optimized design of materials in the Na-ion battery.



# Research Plan for 2013

- The present research purpose is to elucidate the microscopic mechanism of the SEI film formation by the molecular simulation and design the high-performance secondary battery. Last year, I have established the method to simulate the SEI film formation process, and clarified the validity in the Li-ion battery (LIB) [1].
- In actual, we have investigated the electrolyte dependent characteristic (**EC** vs. **PC**) of the SEI film formation on the graphite anode with the hybrid Monte Carlo (MC)/molecular dynamics (MD) reaction method [2].

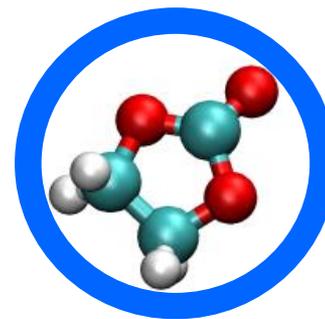
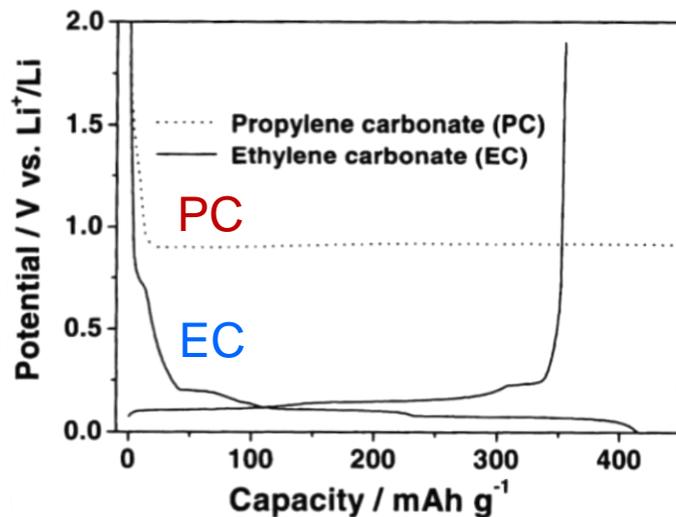


[1] NT, Y. Suzuki, H. Sakai, M. Nagaoka, *J. Phys. Chem. C*, **118**(20), 10874 (2014).

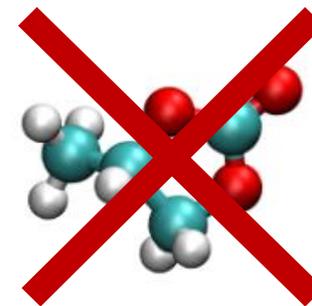
[2] M. Nagaoka, Y. Suzuki, T. Okamoto, NT, *Chem. Phys. Lett.*, **583**, 80 (2013).

# Background of Present Research

- No effective SEI film is formed on the graphite anode when the pure **PC** is used as the solvent of the electrolyte in the LIB.
- It is not clear why the SEI film formation becomes insufficient only in the **PC**-based electrolyte despite the close structural similarity between **EC** and **PC**.



EC

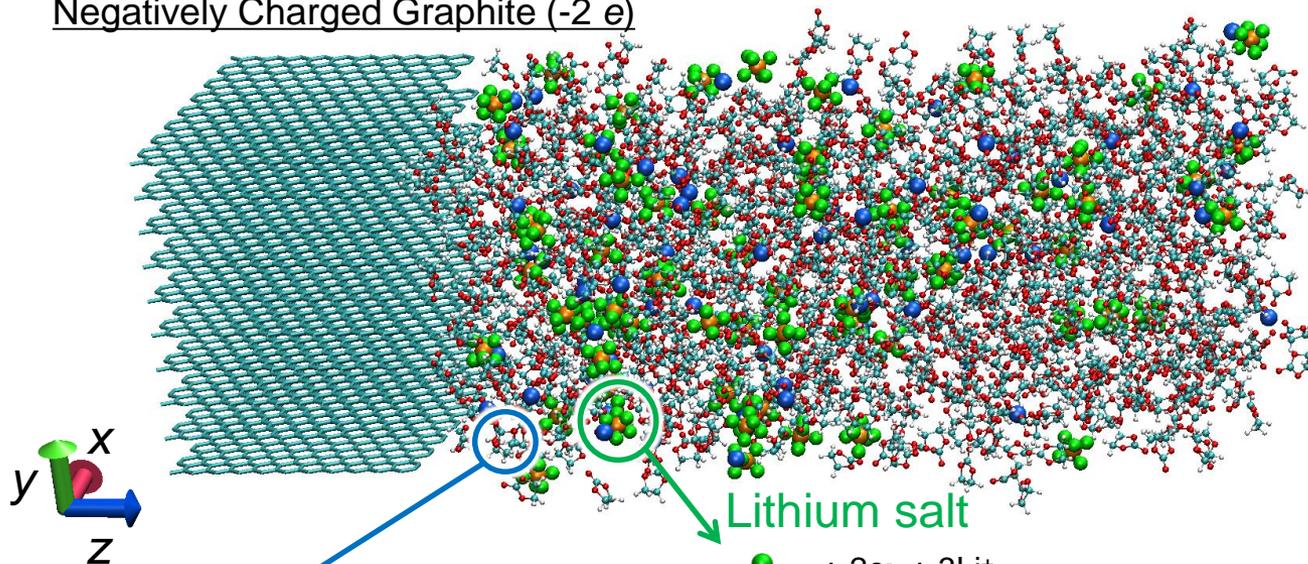


PC

First charge and discharge characteristics[3]

# Simulation Model and Reaction Scheme

Negatively Charged Graphite ( $-2 e$ )



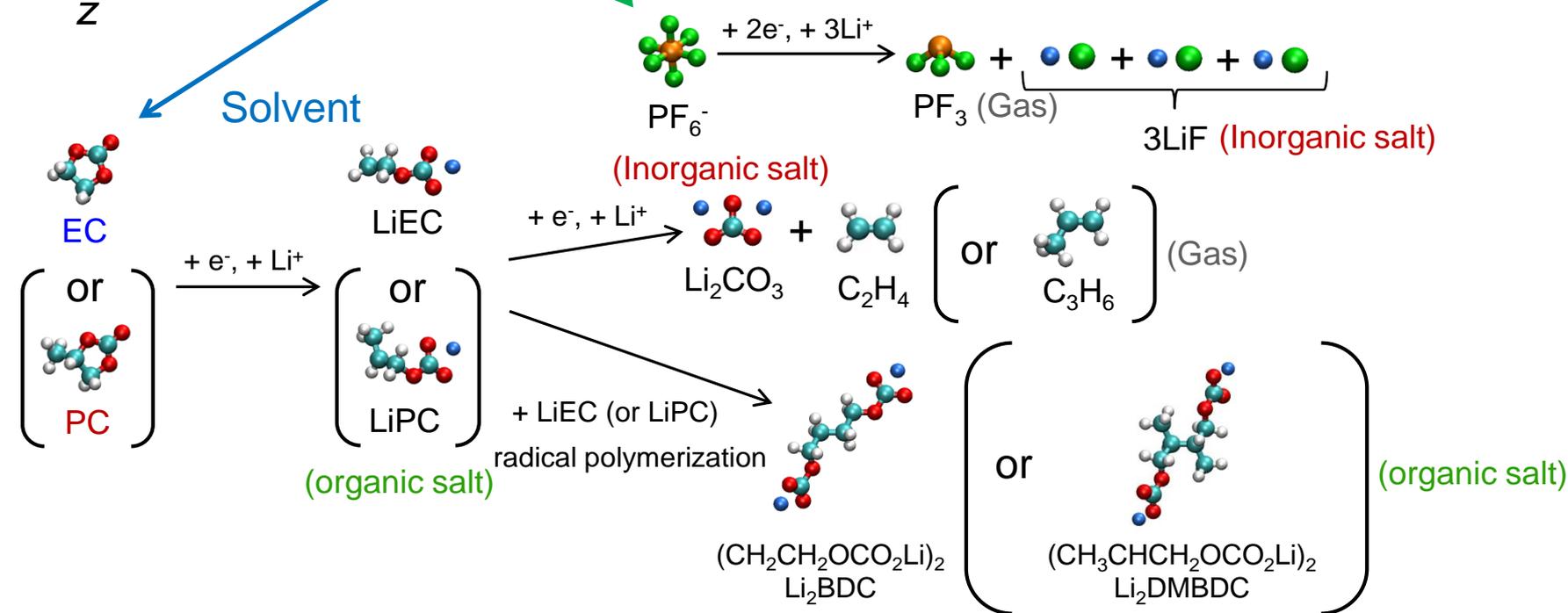
Temperature: 298 K

Force field: GAFF

Charge: RESP

1.1M  $\text{LiPF}_6$  EC (or PC) electrolyte

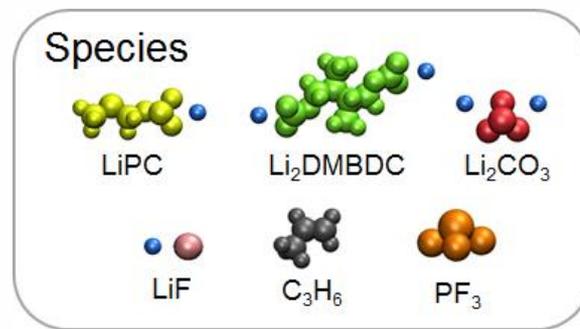
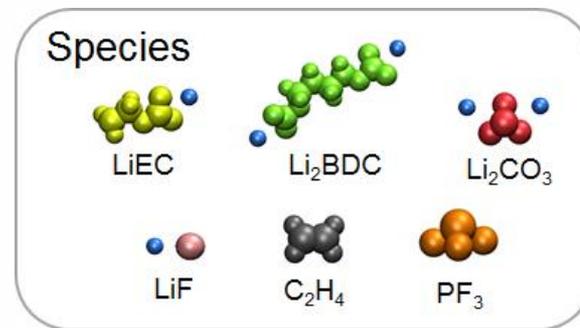
EC:	850	PC:	850
$\text{Li}^+$ :	69	or	$\text{Li}^+$ : 87
$\text{PF}_6^-$ :	67		$\text{PF}_6^-$ : 85





# SEI Film Formation Processes – EC vs. PC –

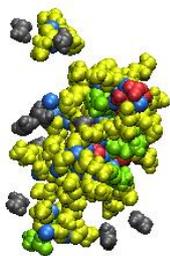
(Electrolyte : non-display)



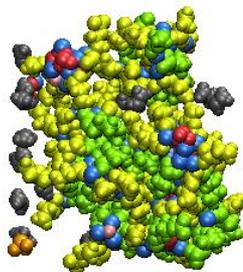
10 Å

0 cycle

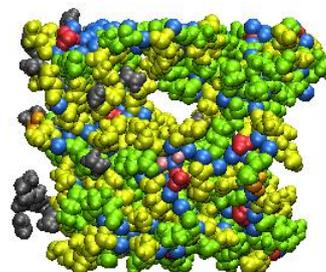
# SEI Film Formation Process – EC –



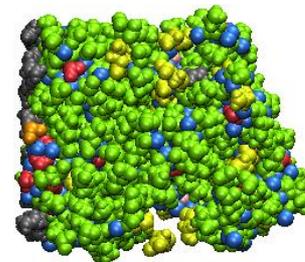
(a) 200 cycle



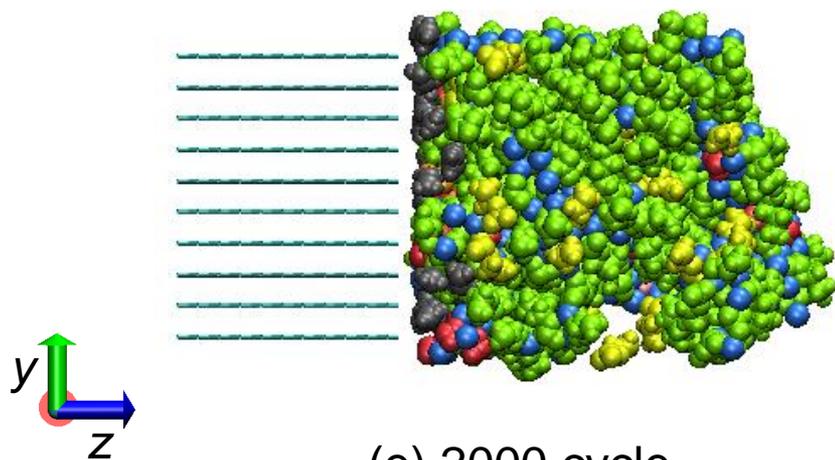
(b) 400 cycle



(c) 800 cycle



(d) 1600 cycle



(e) 2000 cycle

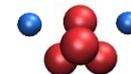
## Species



LiEC



Li<sub>2</sub>BDC



Li<sub>2</sub>CO<sub>3</sub>



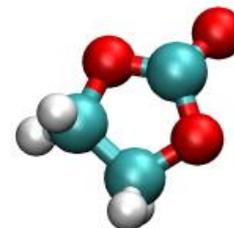
LiF



C<sub>2</sub>H<sub>4</sub>

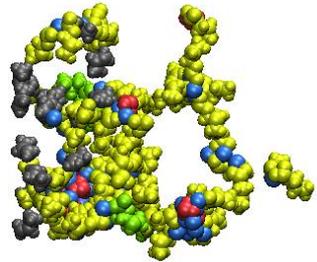


PF<sub>3</sub>

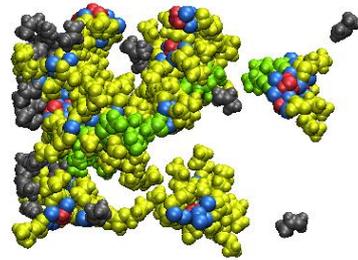


EC

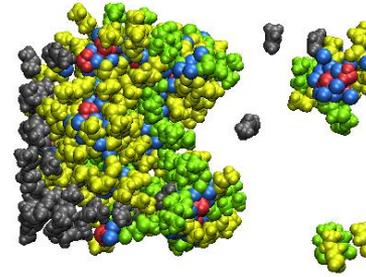
# SEI Film Formation Process – PC –



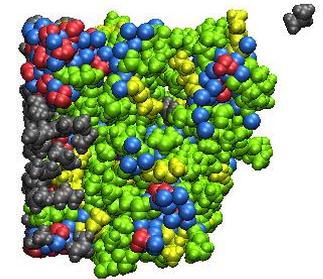
(a) 200 cycle



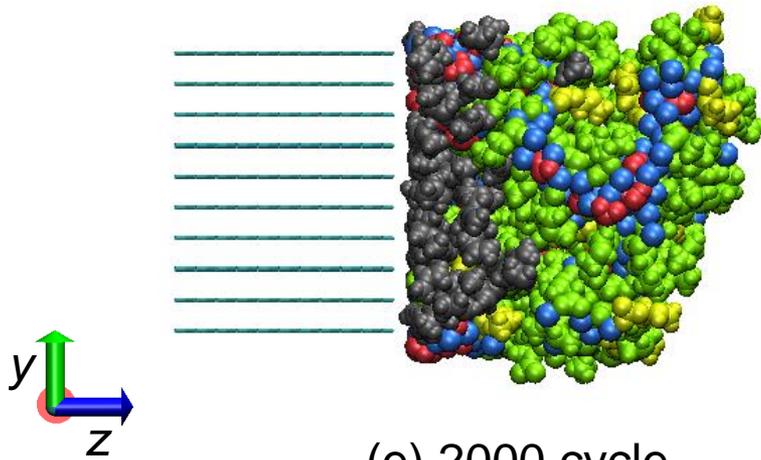
(b) 400 cycle



(c) 800 cycle

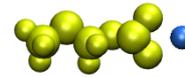


(d) 1600 cycle



(e) 2000 cycle

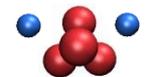
## Species



LiPC



Li<sub>2</sub>DMBDC



Li<sub>2</sub>CO<sub>3</sub>



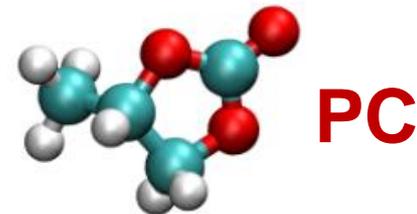
LiF



C<sub>3</sub>H<sub>6</sub>



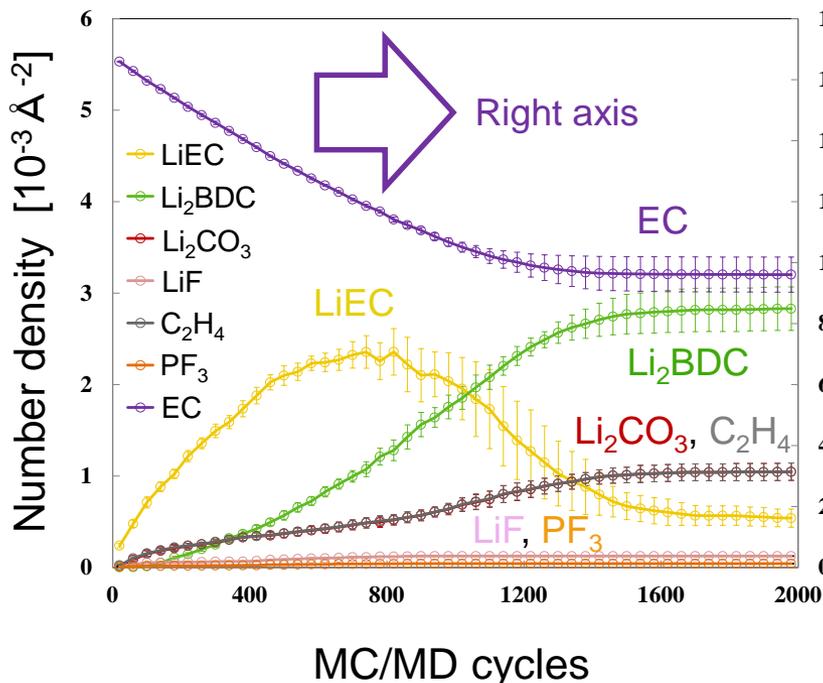
PF<sub>3</sub>



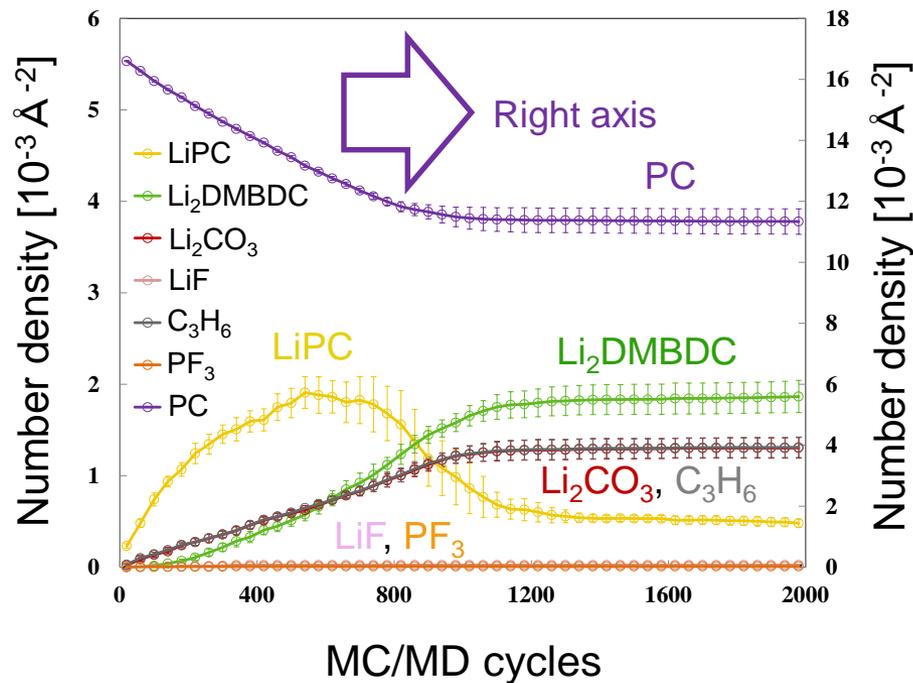
PC

# Change of Number Densities – EC vs. PC –

(They are obtained by different 10 initial configurations.)



(a) EC

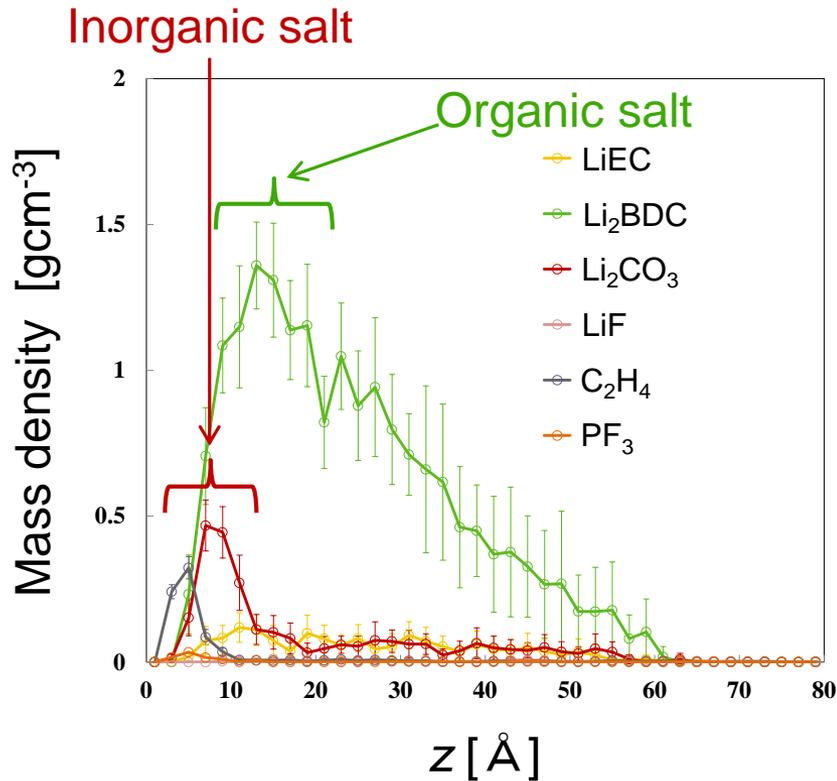


(b) PC

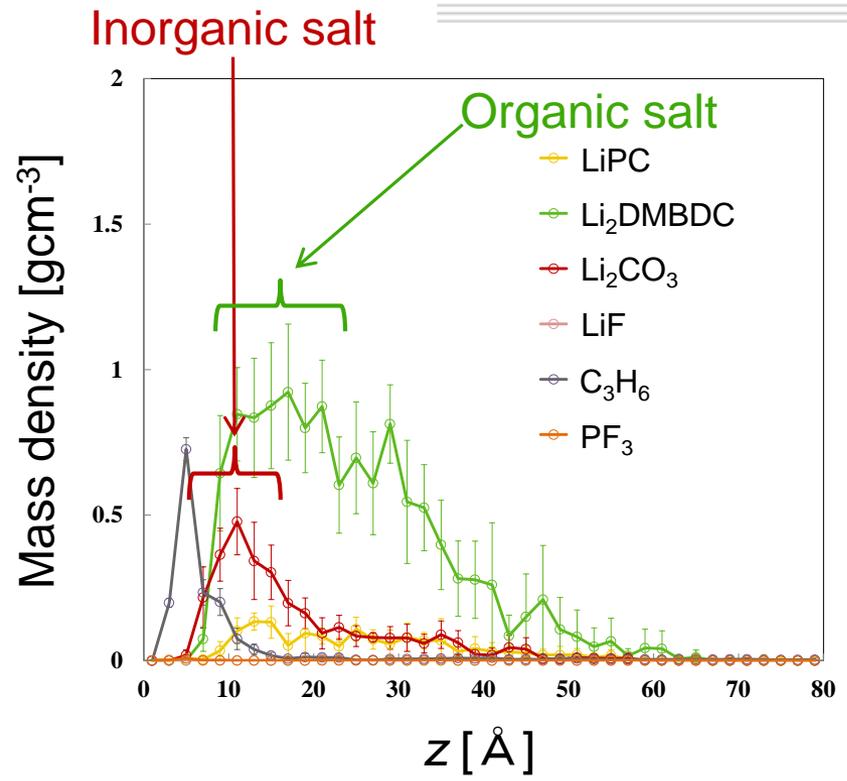
• In particular, the number of dimers (Li<sub>2</sub>BDC) was found to become considerably increased in the EC-based electrolyte.

# Mass Density Distributions in the SEI Film

## – EC vs. PC –



(a) EC

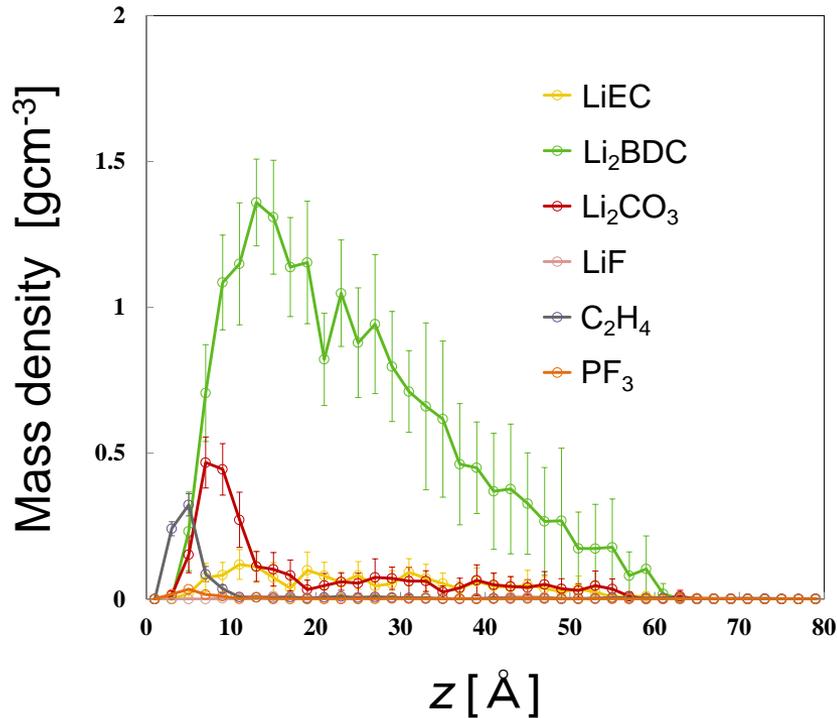


(b) PC

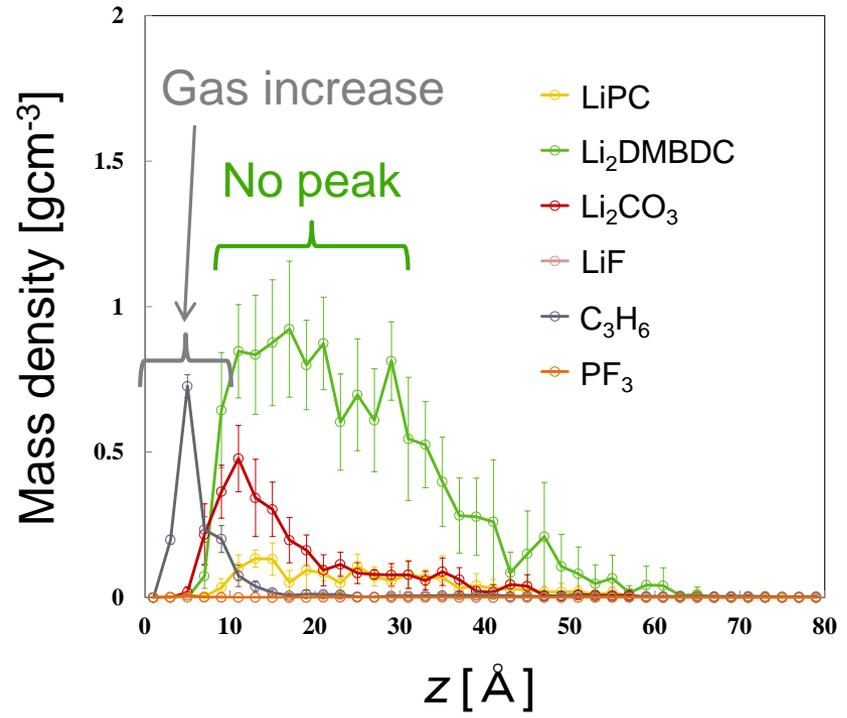
• In the resulting SEI films, it was found that the **inorganic salts** tend to be closer to the graphite, while the **organic ones** are mainly do in the outer layer as is the same in the experimental observations.

# Mass Density Distributions in the SEI Film

## – EC vs. PC –



(a) EC



(b) PC

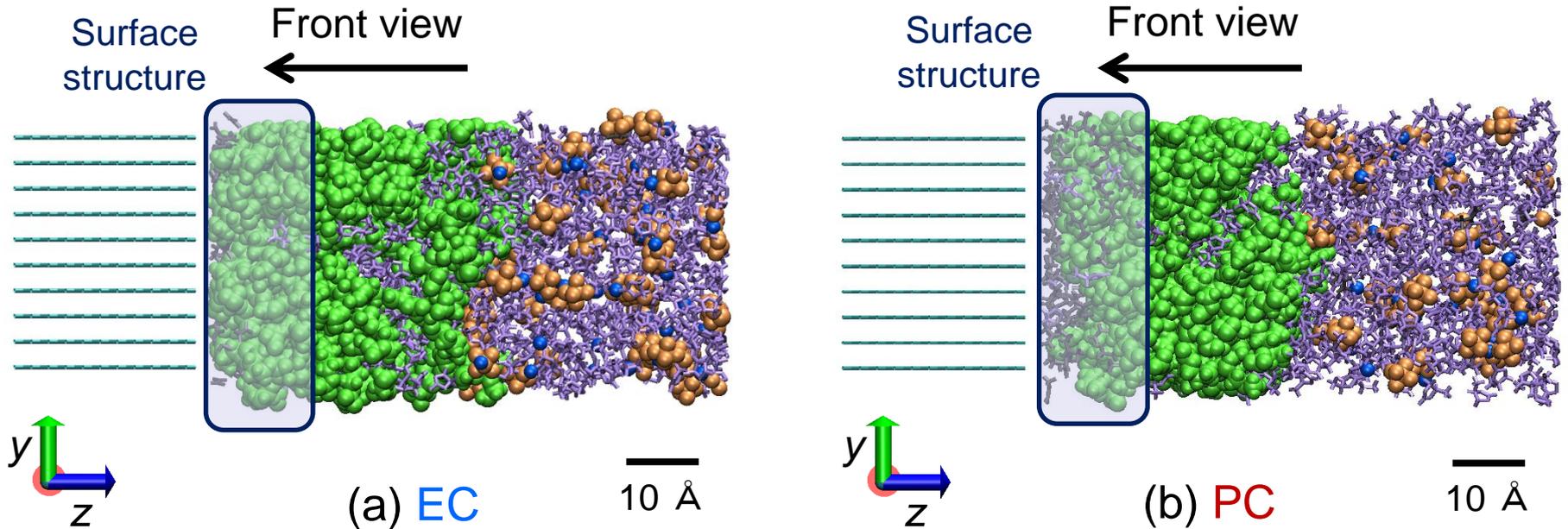
• The increase of the gases should bring about the destabilization of the SEI film formation in the PC-based electrolyte [4,5].

[4] R. Fong, U. von Sacken, J. R. Dahn, *J. Electrochem. Soc.*, **137**, 2009 (1990).

[5] Z. X. Shu, R. S. McMillan, J. J. Murray, *J. Electrochem. Soc.*, **140**, 922 (1993).

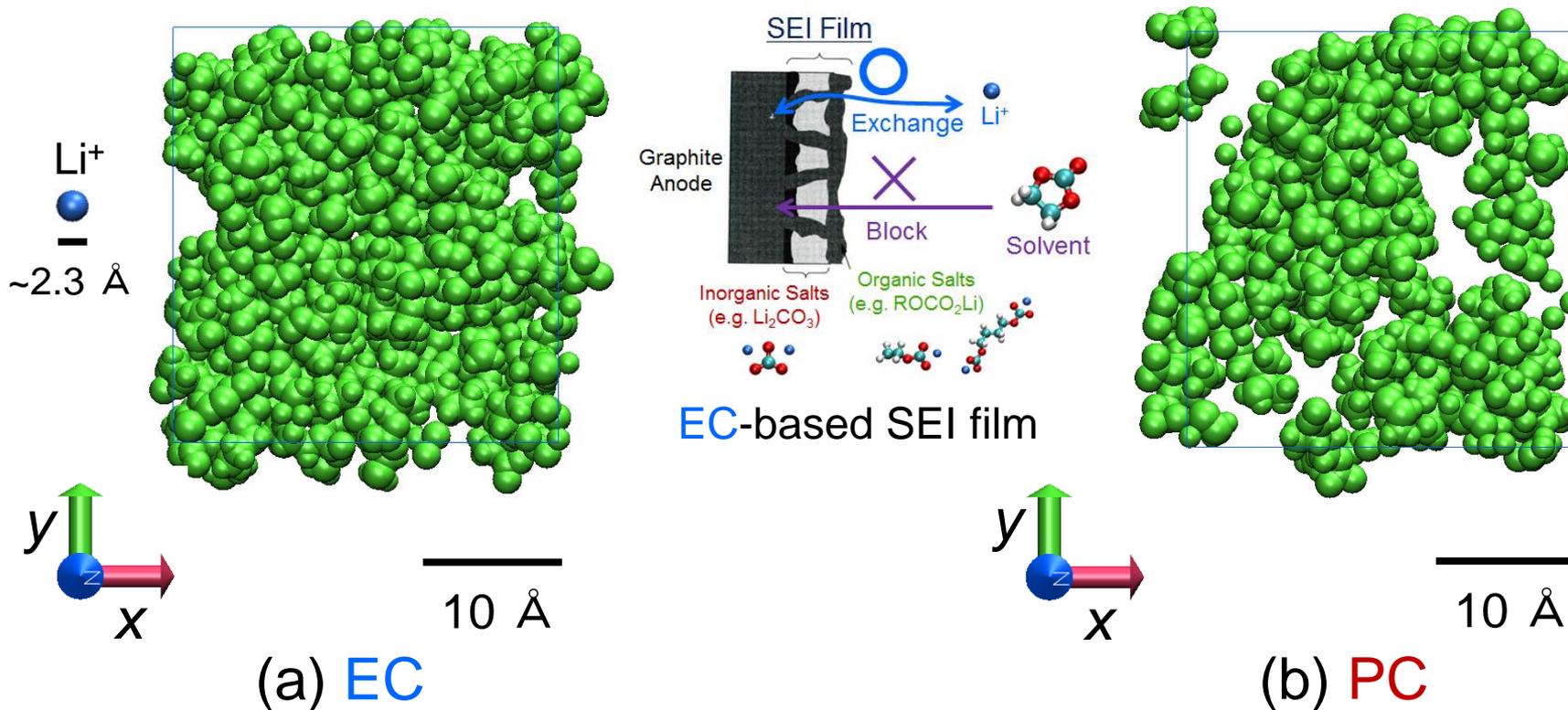
# Side Views of the SEI film and Electrolyte

Green: SEI film , Purple: Solvent, Gray: Gas, Blue:  $\text{Li}^+$ , Orange:  $\text{PF}_6^-$



- The EC-based SEI film could protect the electrolyte from the reduction on the graphite anode. In contrast, in the PC-based one, the protection of the electrolyte was insufficient.

# Front Views of the Surface Structures in the SEI Film



- The surface structures ( $0 \leq z \leq 20$  Å) in the EC-based SEI film was found to become denser, providing some cavities ( $>2.3$  Å) which have sufficient size for passing of Li<sup>+</sup>.



# Summary of Research for 2013

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- In the present study, we have investigated the electrolyte dependent characteristic (**EC** vs. **PC**) of the SEI film formation on the graphite anode with the hybrid MC/MD reaction method.
- In the resulting SEI films, the inorganic salts tend to be closer to the graphite, while the organic ones are mainly do in the outer layer.
- The dense **EC**-based SEI film could protect the electrolyte from the reduction, providing the cavities which have sufficient size for passing of Li<sup>+</sup>.
- In contrast, the SEI film formation in the **PC**-based electrolyte became insufficient due to the methyl groups of the **PC**.

# Research Plan for 2014

- For the development of Na-ion battery, it is essential to elucidate the microscopic mechanism of the additive effect for the SEI film formation. Additionally, although the hard-carbon is known to be more reasonable than the graphite as the electrode, its theoretical account is not understood.
- Therefore in this year, (1) I will study the additive effects ( $\text{Na}^+$  and FEC) for the SEI film formation with two research collaborator (Dr. Purushotham and Mr. Sakai). At the same time, (2) to investigate the effect of electrode, I will prepare the simulation model and implement some necessary calculation techniques (e.g., constant potential method) into the AMBER code.

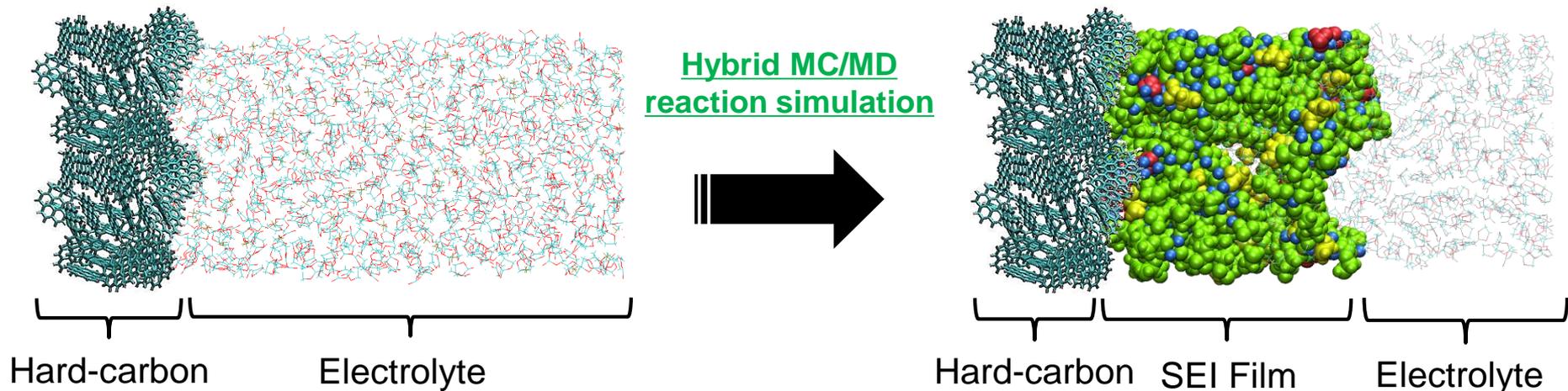


Figure. Schematic illustration of second research plan for 2014