

09/18/2018

*Theoretical Study of Concentration Effect
of Fluoroethylene Carbonate on SEI Film
Formation in Sodium-Ion Batteries Using
Red Moon Method*

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2nd CREST Workshop

Why sodium (Na)-ion batteries (NIB)?



Secondary battery

Li-ion battery
(LIB)



Na-ion battery
(NIB)

Applications



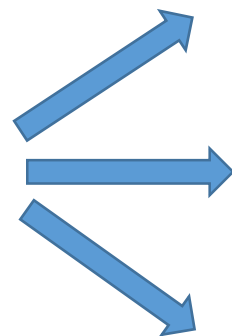
Notebook PC



Electric storage
device



Electric car

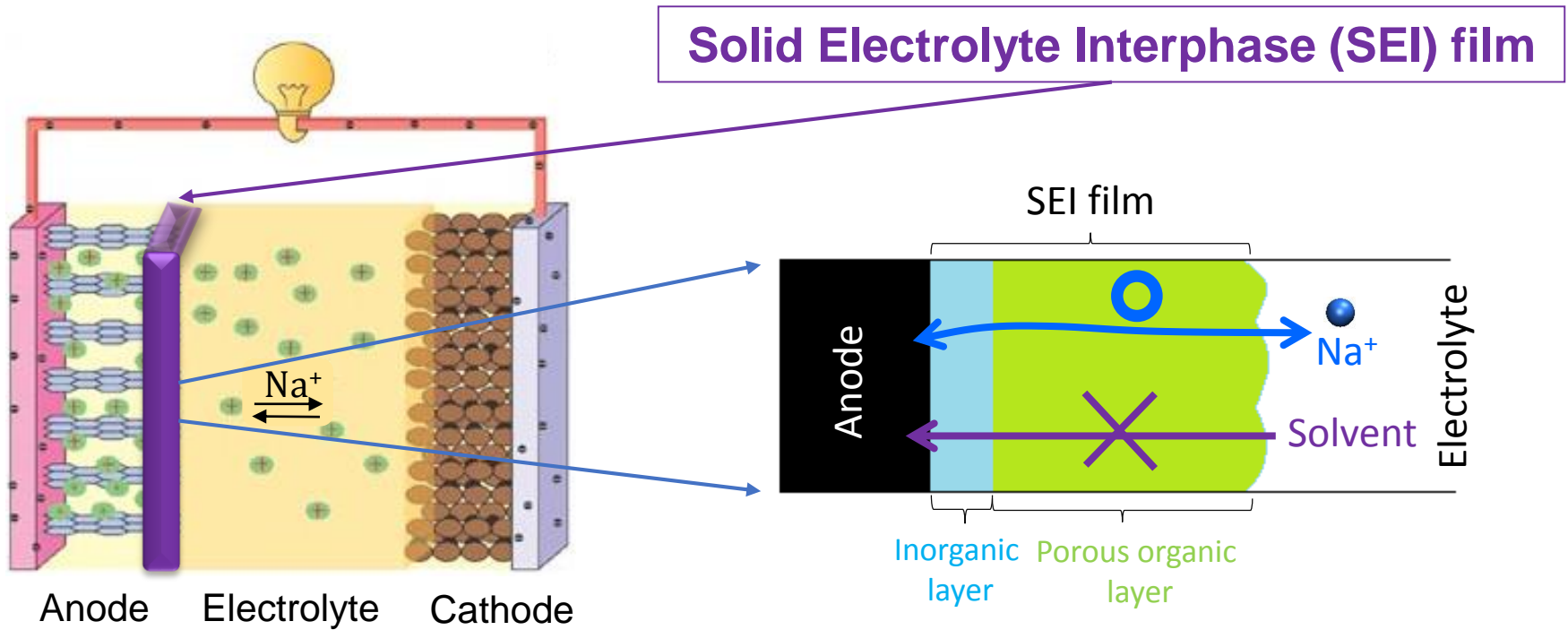


High availability of Sodium metal

Low-cost

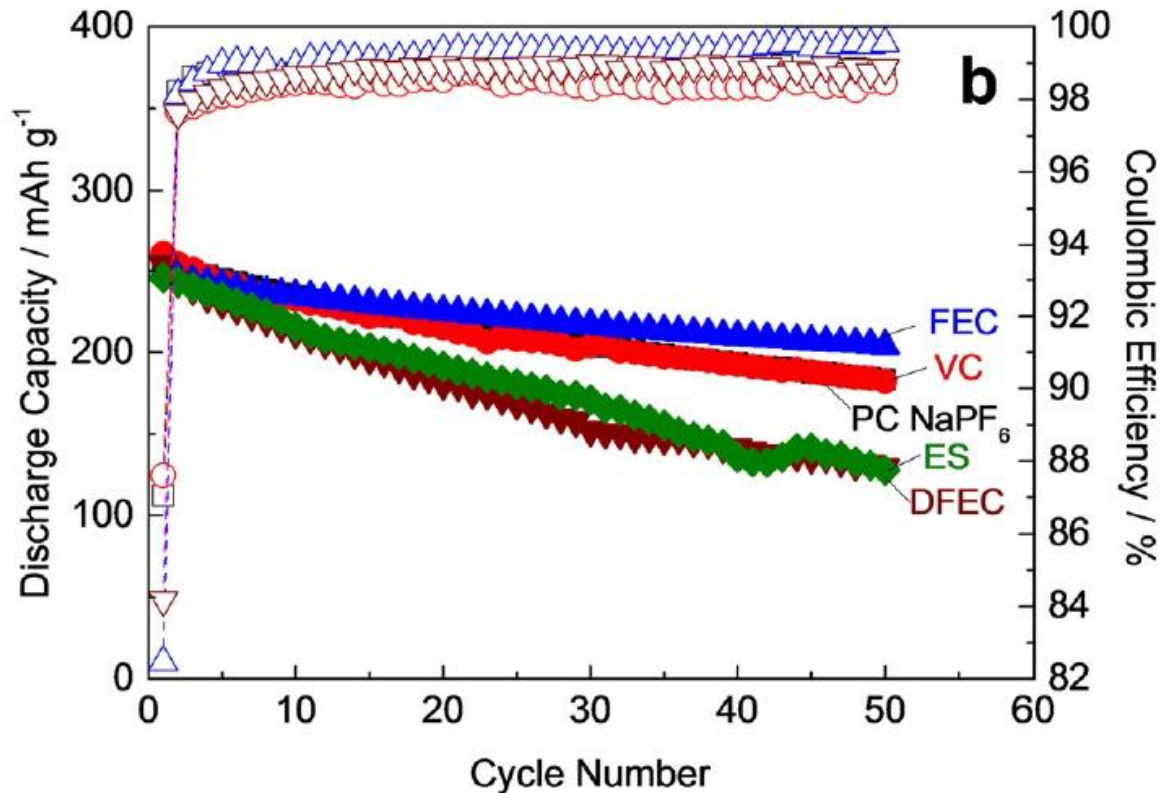
Safety

Solid electrolyte interphase (SEI) film



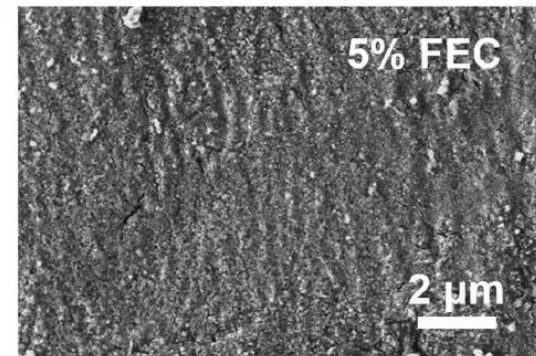
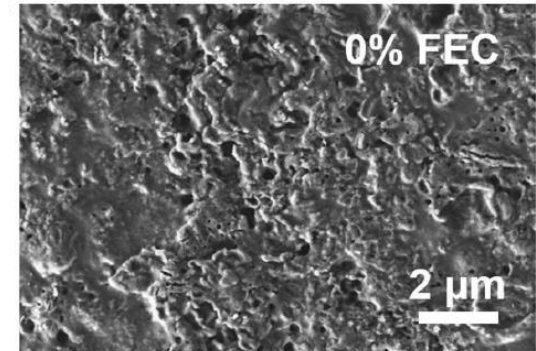
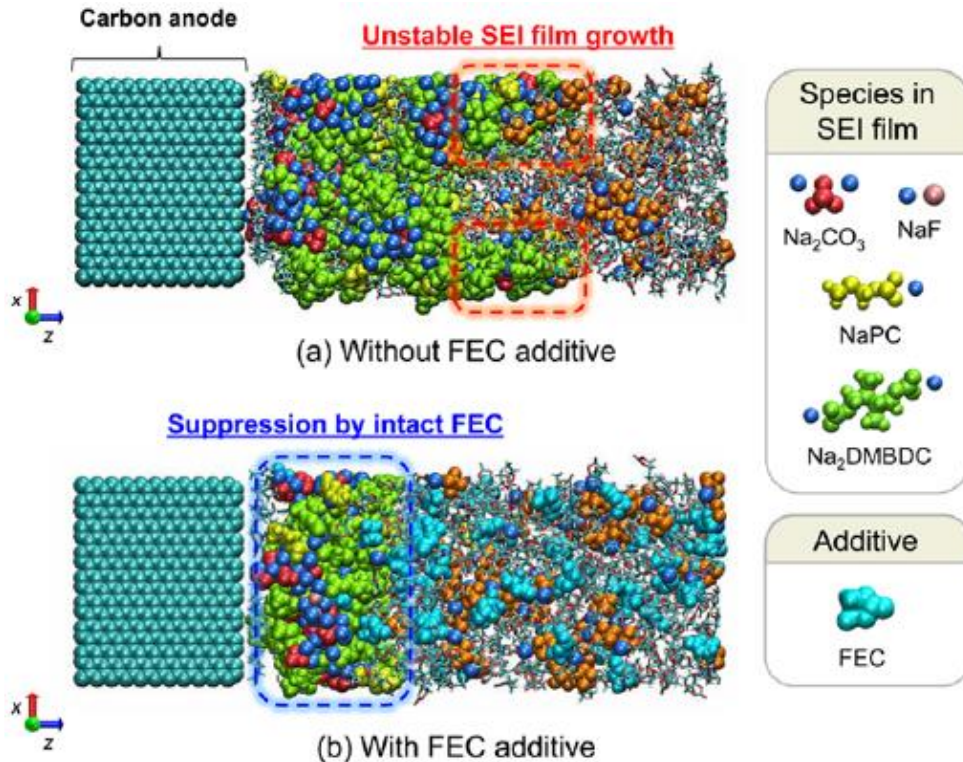
- The performance of secondary batteries depends strongly on the stability of the SEI film.
- However, it is difficult to observe the SEI film formation processes in experiment.

Fluoroethylene carbonate (FEC) additive



Fluoroethylene carbonate (FEC) was the most appropriate additive among other additives for NIB. [1]

FEC additive effect

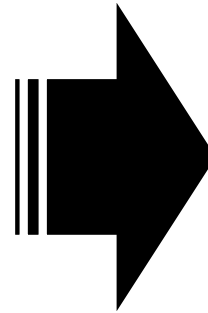
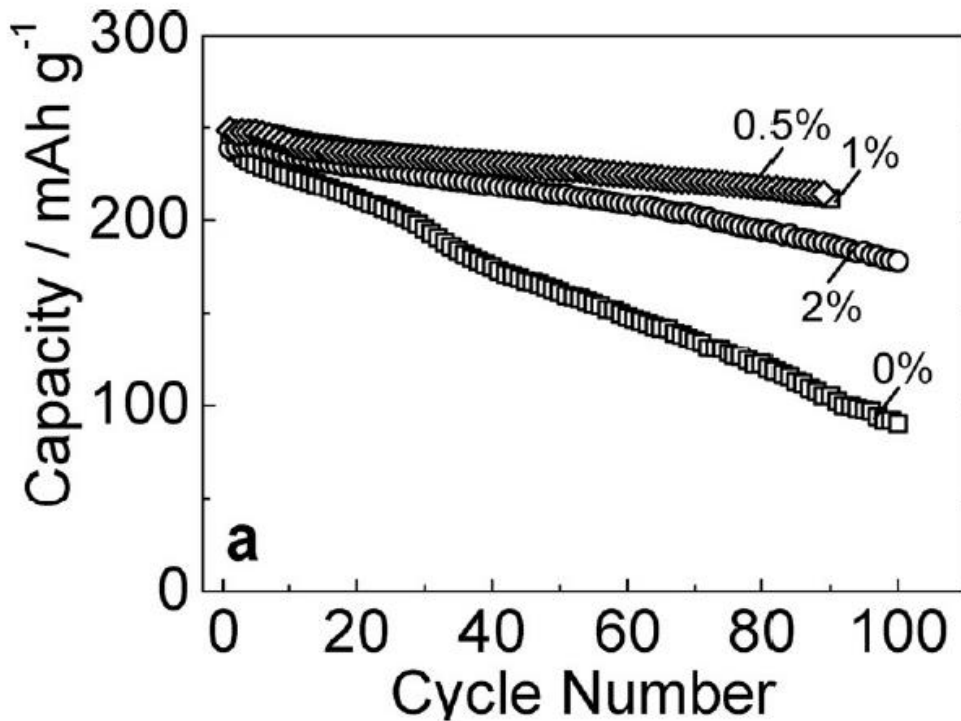


The surface structure of the SEI film which is in contact with the electrolyte became smoother in FEC-added electrolyte. [2-3]

[2] Takenaka et al. *J. Phys. Chem. C* **119**.32 : 18046-18055 (2015).

[3] Zhang, et al. *Adv. Funct. Mat.* **27**.10 (2017).

FEC additive concentration



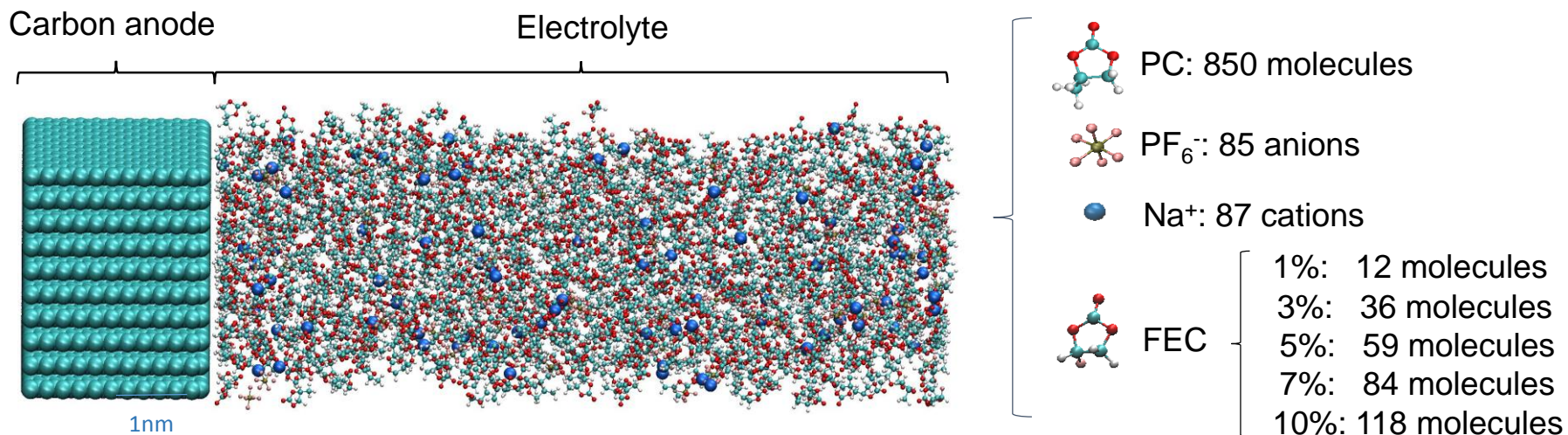
Problematic:

SEI film formation dependency on FEC additive concentration.

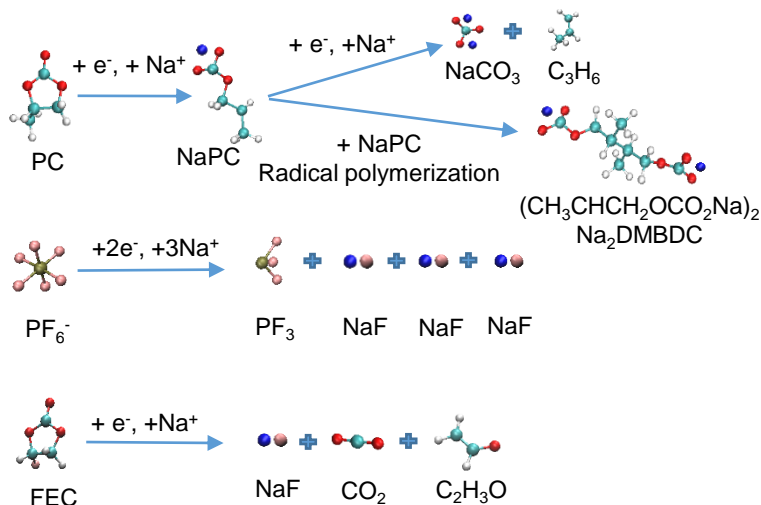
The **0.5%** of FEC added in total volume of NaPF₆/PC electrolyte was optimal. [1]

Model systems and computational details

1. Model system



2. Reaction scheme

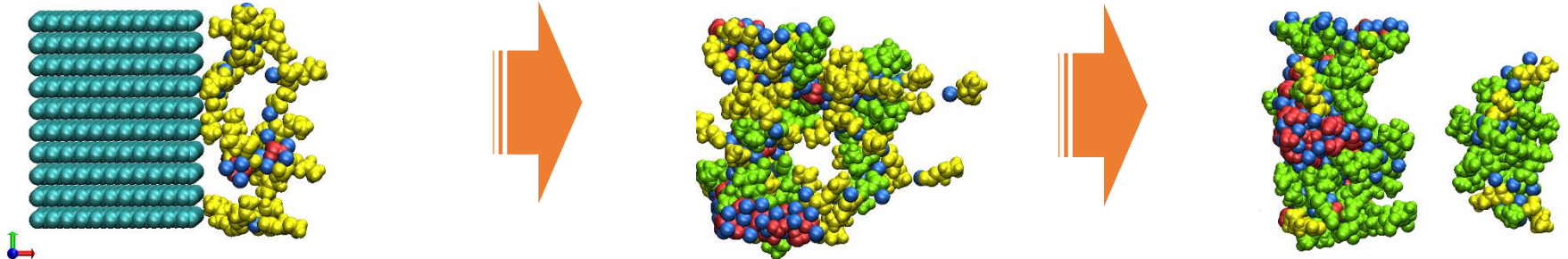


3. Computational details:

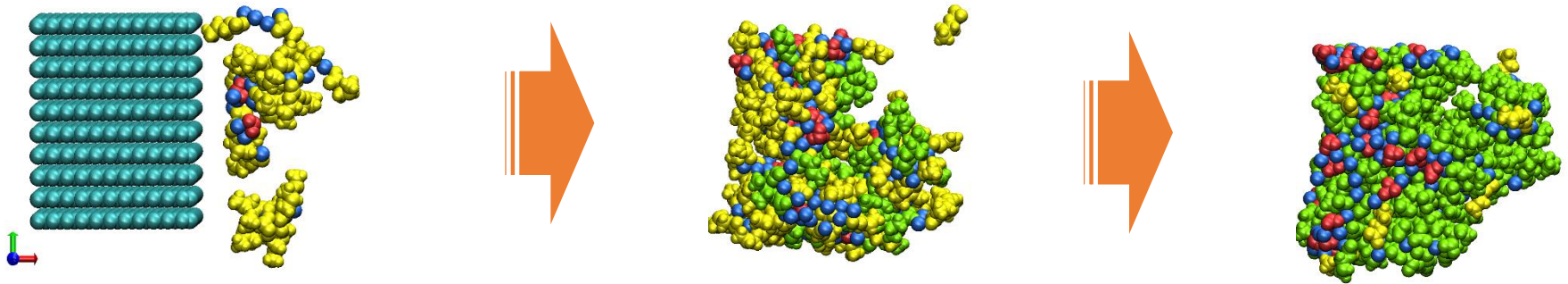
- Red Moon Method (Hybrid MC/MD reaction)
- Anode surface : 3.41nm × 3.7nm
- Negative charge of anode surface: -2e
- 2000 MC/MD Cycles.
- GAFF Force field
- Temperature: 298 K

SEI film formation process

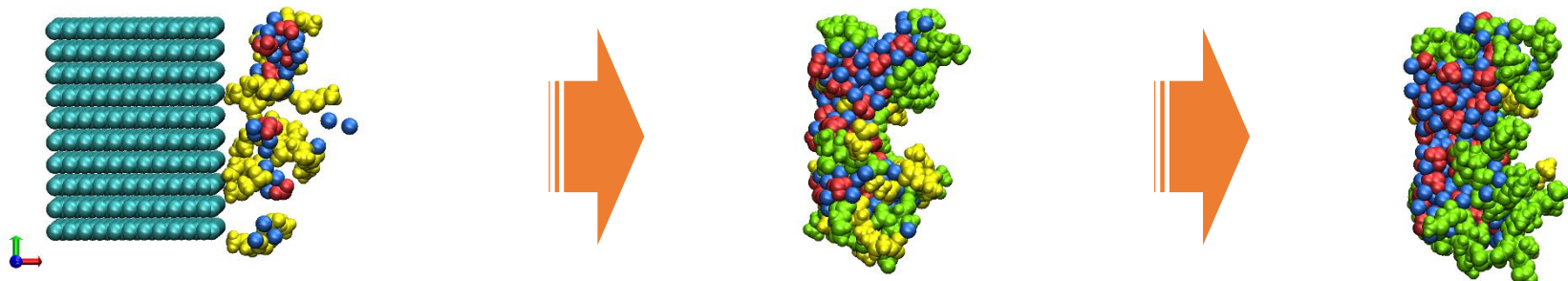
- Without FEC additive



- Small FEC concentration (1 vol%)



- High FEC concentration (10 vol%)

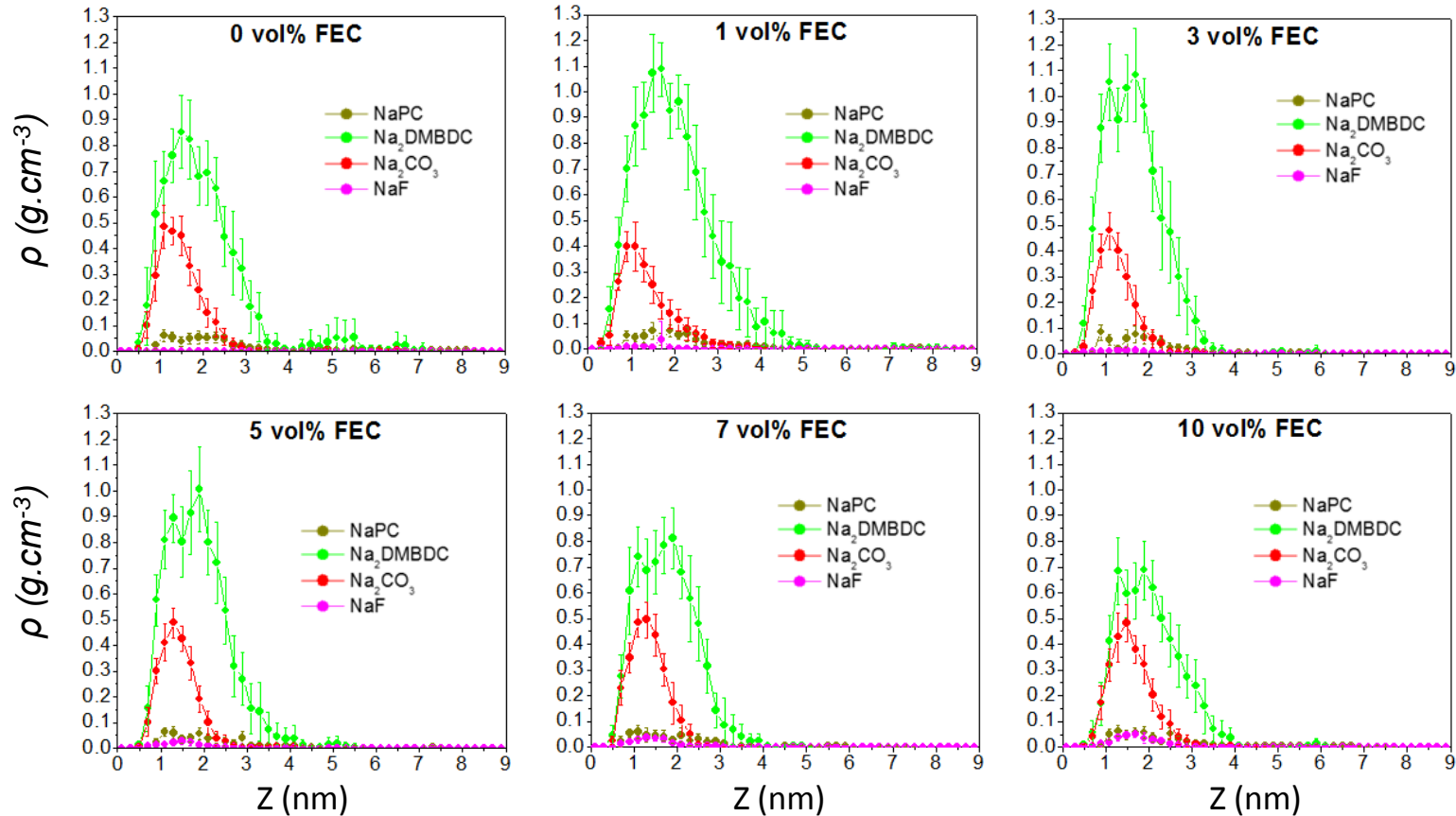


100 MCMD cycle

500 MCMD cycle

2000 MCMD cycle

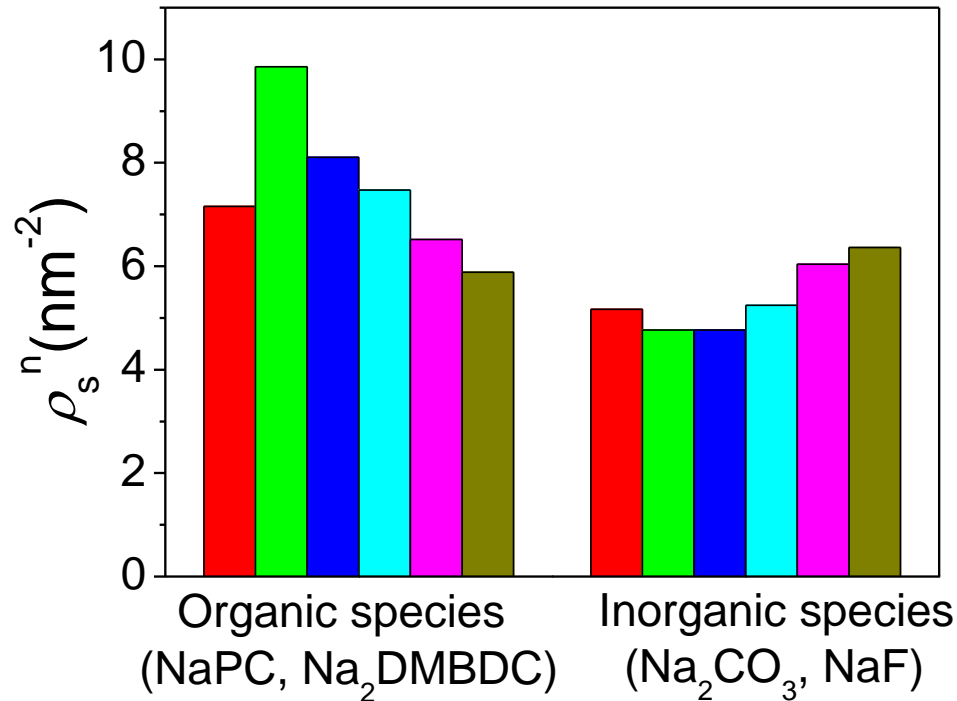
Structural properties of SEI film



- Inorganic products (Na_2CO_3 and NaF) were produced on anode surface, while the organic ones (NaPC , Na_2DMBDC) were extended to the outer region of SEI film. This result was in excellent agreement with experimental observations.

Structural properties of SEI film

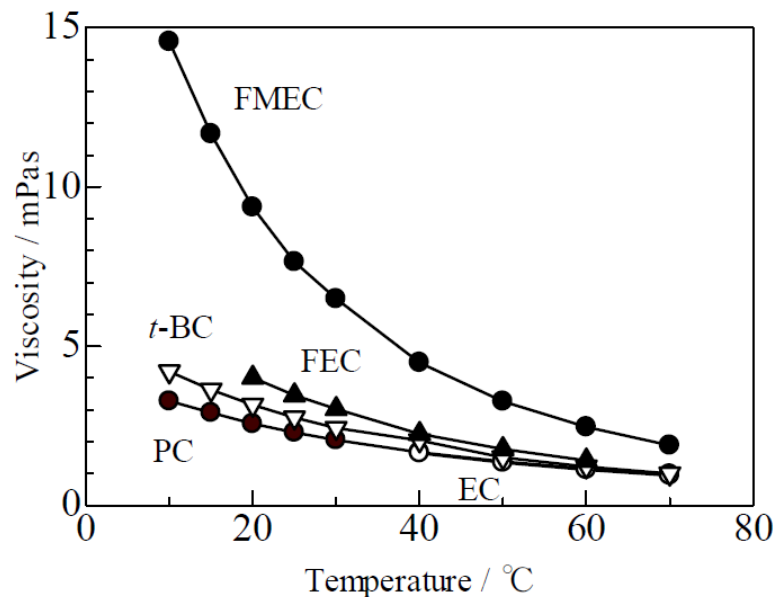
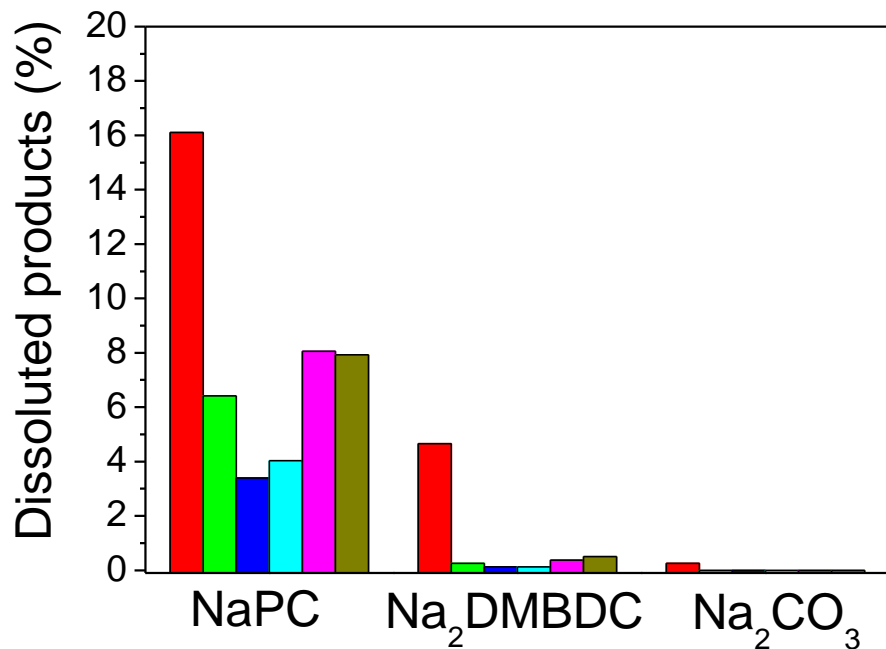
FEC concentration: ■ 0 vol%, ■ 1 vol%, ■ 3 vol%, ■ 5 vol%, ■ 7 vol%, ■ 10 vol%



- Organic products were higher at 1% FEC concentration, and decreased by increasing FEC amounts additive on electrolyte solution.
- Inorganic products and intact FEC inside SEI film increased by increasing FEC additive concentration on electrolyte solution.

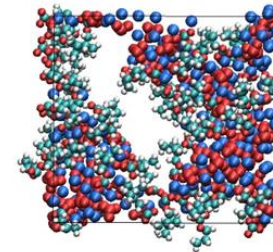
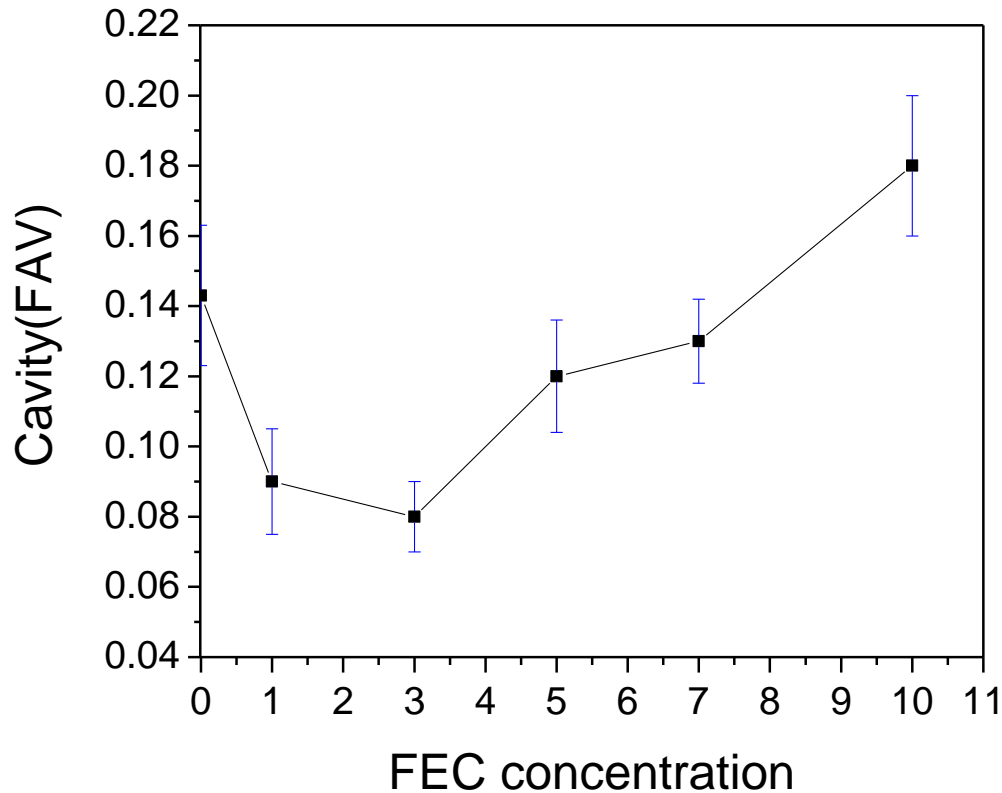
Dissociation ratio of SEI film products

FEC concentration: ■ 0 vol%, ■ 1 vol%, ■ 3 vol%, ■ 5 vol%, ■ 7 vol%, ■ 10 vol%

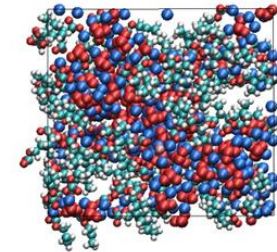


FEC additive suppressed remarkably dissociation of SEI film compounds because of its high viscosity. [4]

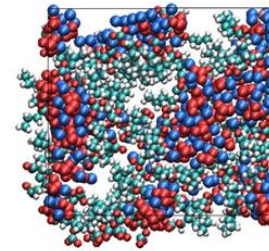
Cavity size inside SEI film



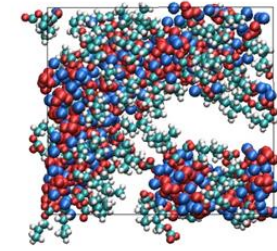
0 vol% FEC



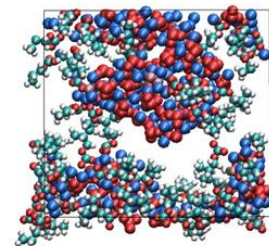
1 vol% FEC



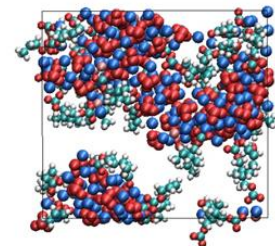
3 vol% FEC



5 vol% FEC



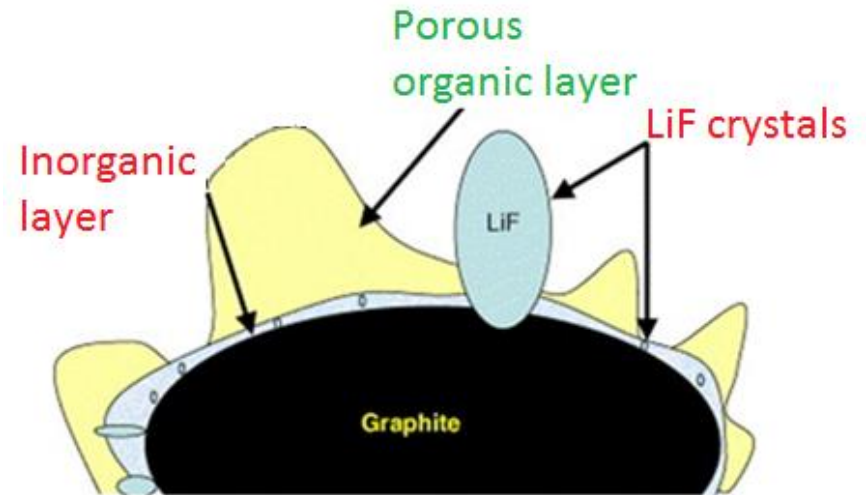
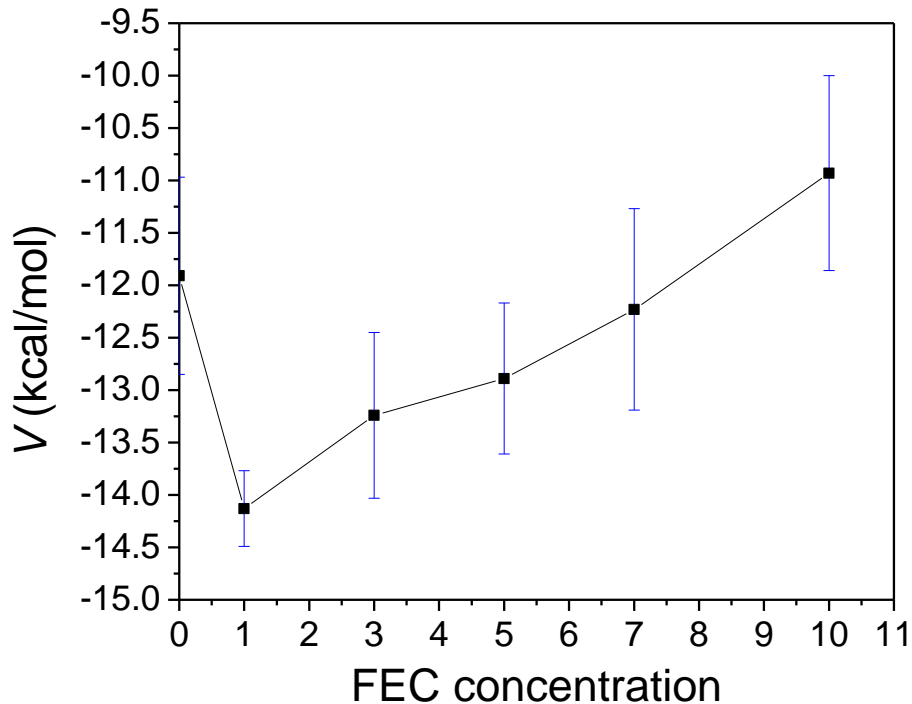
7 vol% FEC



10 vol% FEC

- The SEI film became denser at small FEC concentration.
- By increasing FEC amounts, the cavity size of SEI film increased.

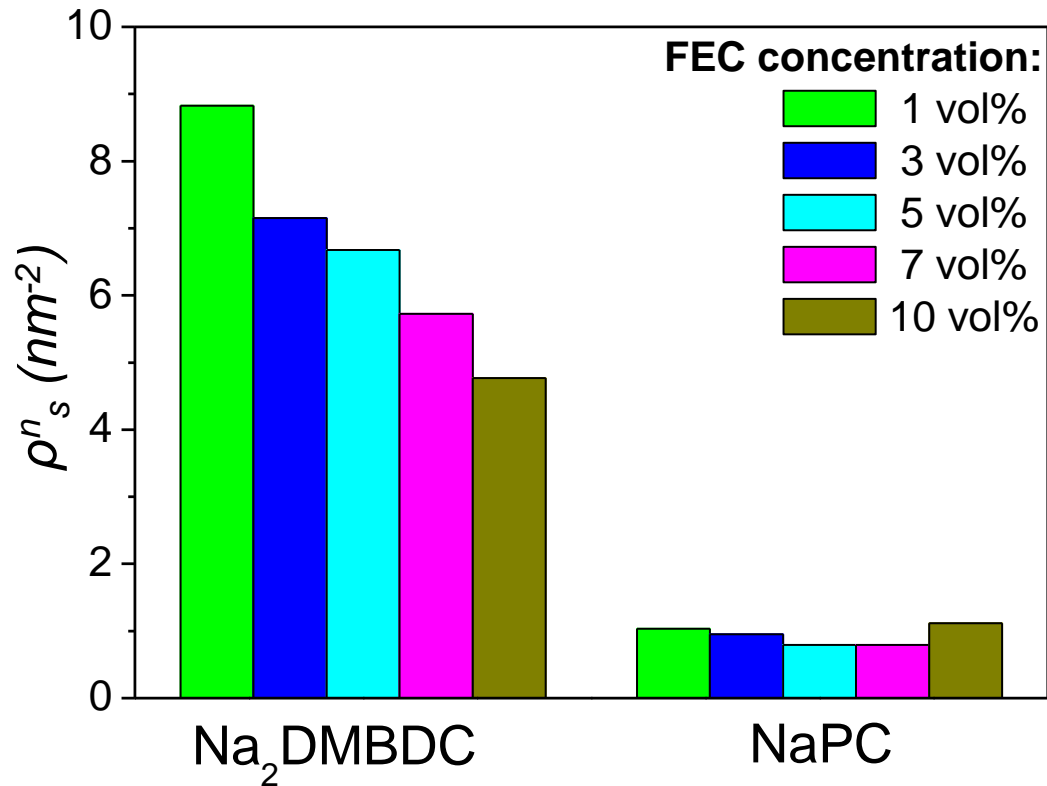
Structural stability of SEI film



- Thickness of SEI film: ~ 35 nm.
- Thickness of *inorganic layer*: 4.5 ± 0.5 nm.

- The potential energies per atom (V) of the organic species in the SEI films was more stable at **1%** of FEC concentration.
- According to experimental studies, the organic species were observed in outer region of SEI film and constitute around 85 % of SEI film. [5]
- **SEI film was more stable at 1% of FEC concentration.**

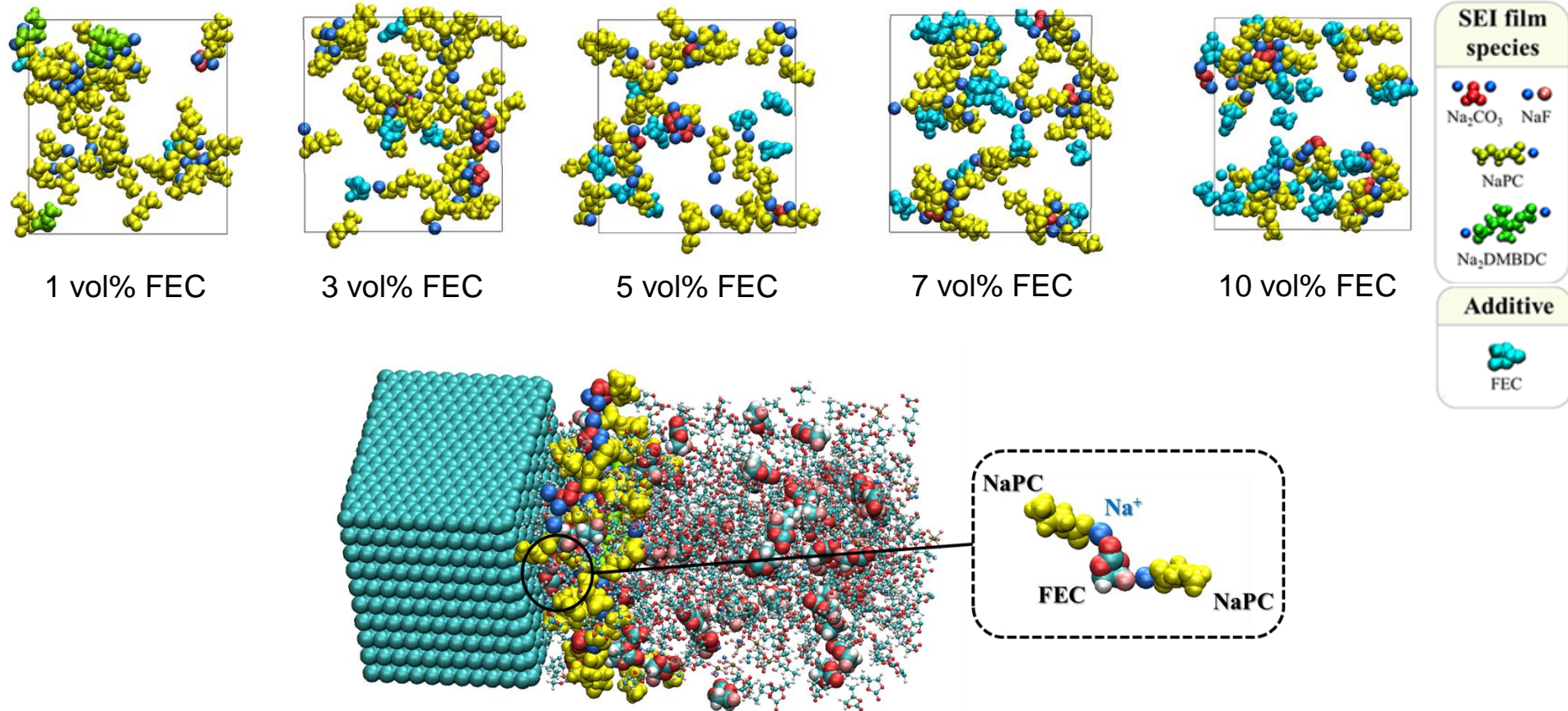
Mechanism of FEC concentration effect



- The production of organic dimers (Na₂DMBDC) depended on the FEC concentrations.

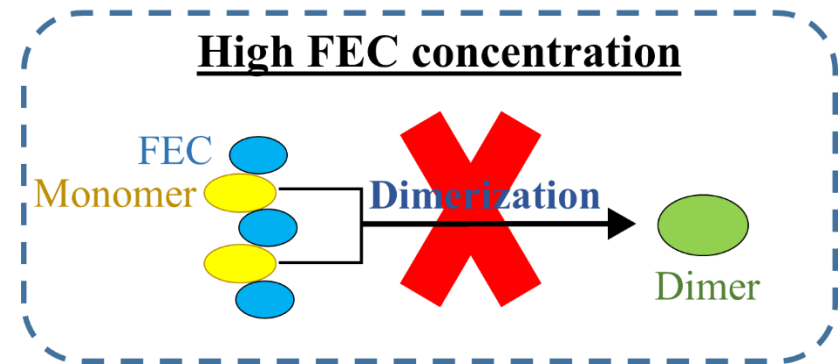
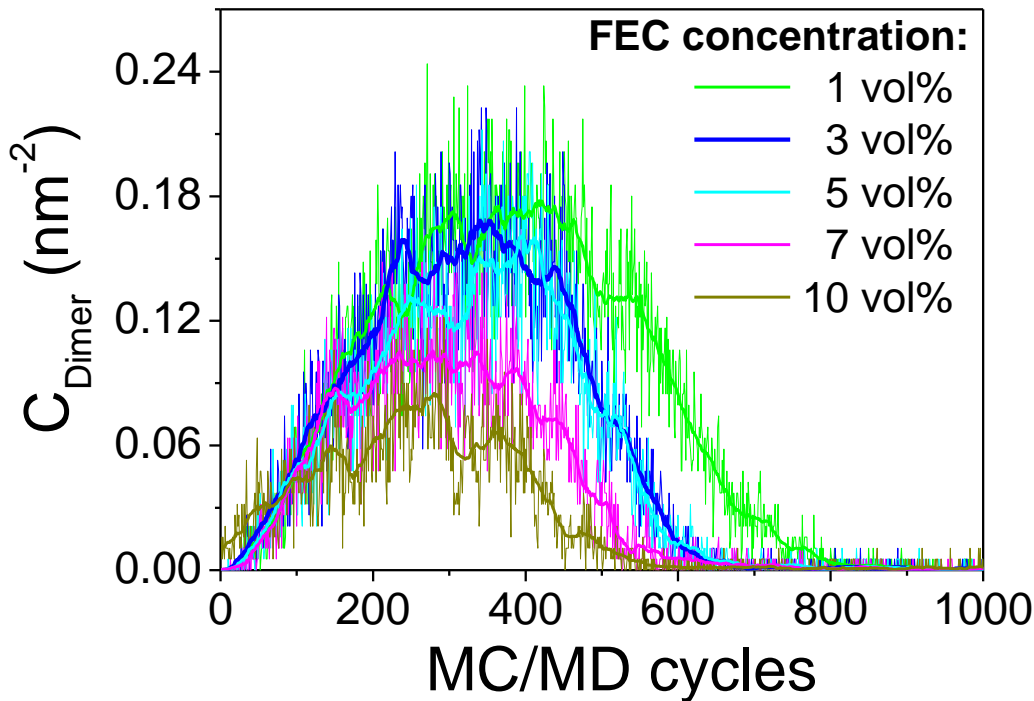
Mechanism of FEC concentration effect

Initial stage of SEI films formation (100 MC/MD cycle)



FEC molecules formed a bridge between two different NaPCs because of its two negative parts (-F and $-\text{CO}_3$ groups)

Mechanism of FEC concentration effect



- The formation of FEC bridges between NaPCs prevented the formation of Na_2DMBDC dimers.

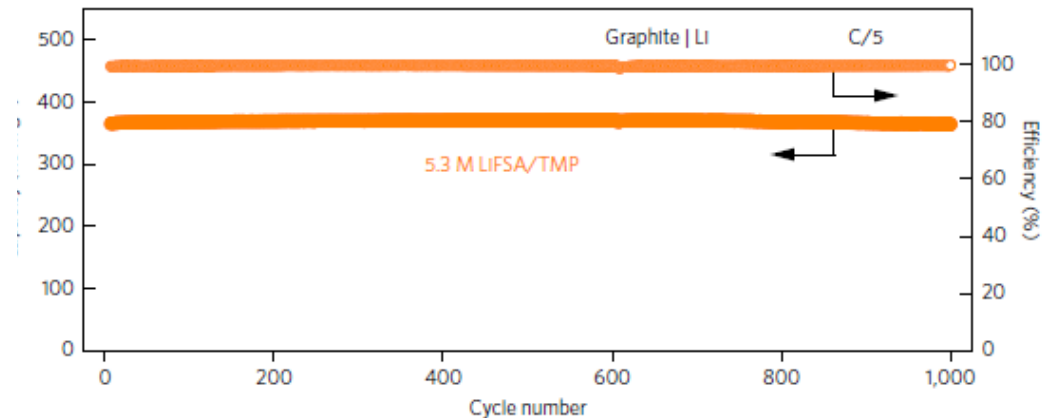
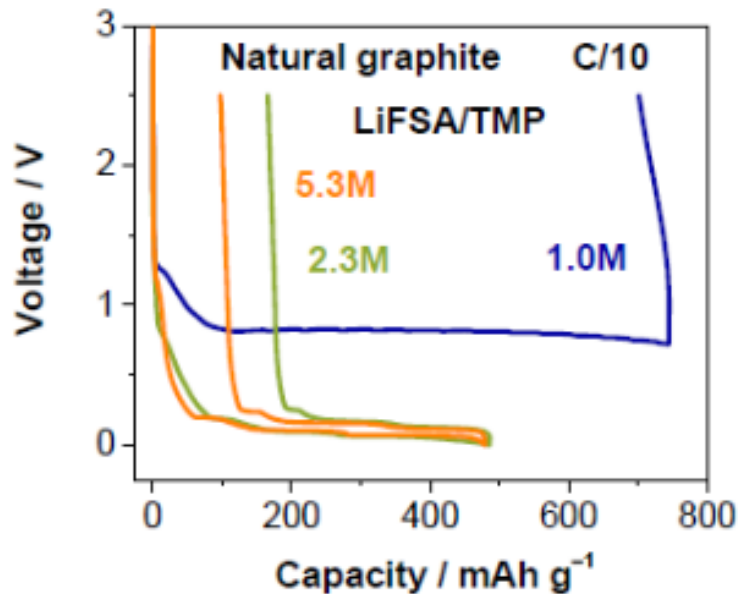
Conclusion

- Red moon simulation results showed that SEI film is more stable at small FEC concentration leading to long lifetime of NIB during charge-discharge cycles. This results is in good agreement with experimental data.
- The present study showed that the stability of SEI film was mainly related to the production of dimer organic products.

- FEC bridge effects:
 - At small FEC concentration: suppress the dissociation of SEI film products.
(POSITIVE effect)
 - At high FEC concentration: suppress the production organic dimers.
(NEGATIVE effect)

Current study

Investigation of Fire-extinguishing organic electrolytes for safe batteries.



- By increasing the concentration of LiFSA salt, the SEI film formation as well as lifetime of Li-ion batteries were significantly improved.

➤ **However:**

The microscopic mechanism of SEI film formation is still not found.