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Towards understanding FEC additive effects on solid electrolyte interface film formation in Na-ion batteries using RedMoon method

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3th CREST Workshop

Introduction: Why Na-ion Batteries ?

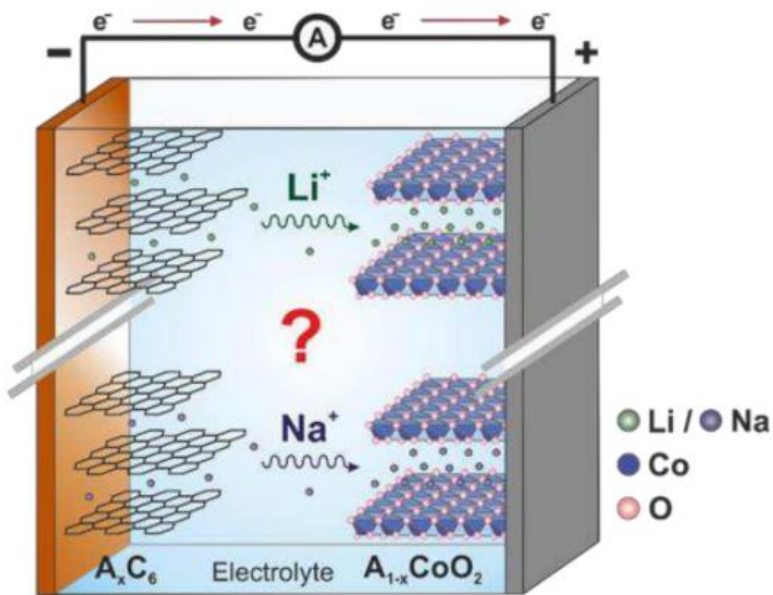
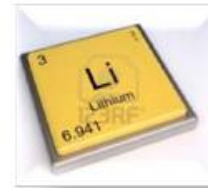
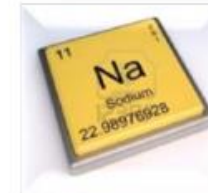


Fig.1: Principle of rechargeable batteries.



LITHIUM

4.11-4.49 euro kg⁻¹



SODIUM

0.07-0.37 euro kg⁻¹

Fig.2: Lithium and Sodium price [1].

- ✓ High availability [2]:
 - Na in the earth: **10³ ppm**
 - Na in the sea: **10⁵ ppm**

➤ **Ideal Sodium battery :**

- High cell voltage and specific capacity
- High energy density
- Safety
- Low-cost
- Long cycle life.



➤ **Constituent optimisation:**

- Electrodes
- *Electrolyte: Additive.*

[1] <http://www.theenergyreport.com>.

[2] Palomares et al., Energy Environ. Sci., 5, 5884 (2012)

Introduction: Additive vs Performance

- The impact of additives on Na-ion batteries performance: fluoroethylene carbonate (FEC), vinylene carbonate (VC), ethylene sulfite (ES), and difluoroethylene carbonate (DFEC) additives, which are well known for use in Li-ion cells.
- The impact of FEC additive on different electrolyte solutions for Na-ion batteries .

- The performance is higher for hard carbon negative electrode in NaPF₆/PC based electrolyte solution with FEC additive. [3-4]

[3] Dahbi, et al. *Chem Electro Chem* **3** : 1856-1867 (2016).

[4] Komaba, et al. *ACS Appl. Mater. Interfaces*, **3**: 4165 (2011).

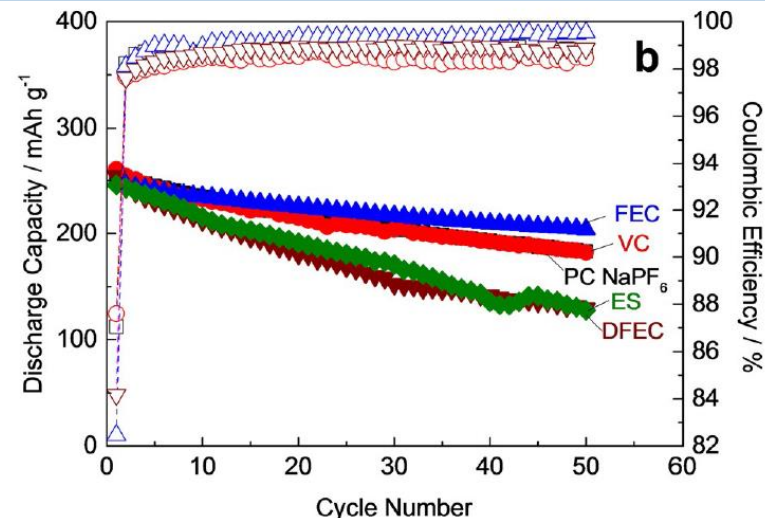


Fig.2: Capacity and Coulombic efficiency of hard-carbon electrodes in NaPF₆/PC electrolyte solution with different additives.

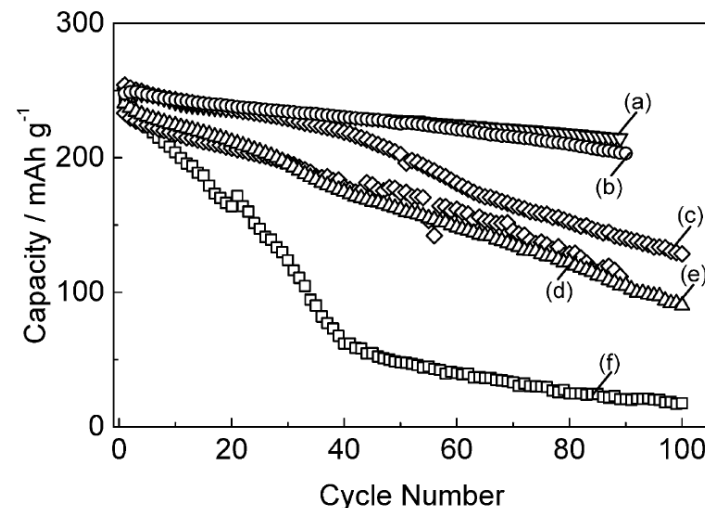


Fig.3: Capacity retention for hard-carbon electrodes in : a) NaPF₆ in PC/0.5% FEC, b) NaPF₆ in PC/EC/0.5% FEC, c) NaPF₆ in PC/EC, d) NaClO₄ in PC/2% FEC e) NaPF₆ in PC and f) NaClO₄ in PC.

Introduction: FEC additive effect on SEI Film formation

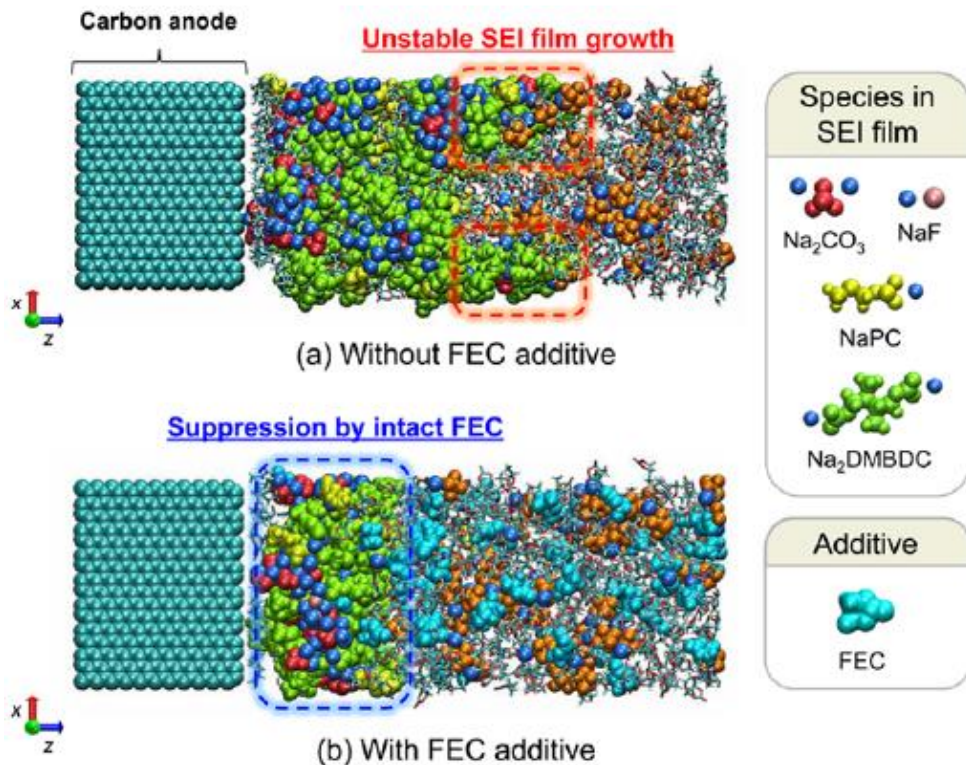


Fig.4: Typical snapshot of SEI films on a carbon based anode in NaPF_6/PC electrolyte solution with and without FEC additive. [4]

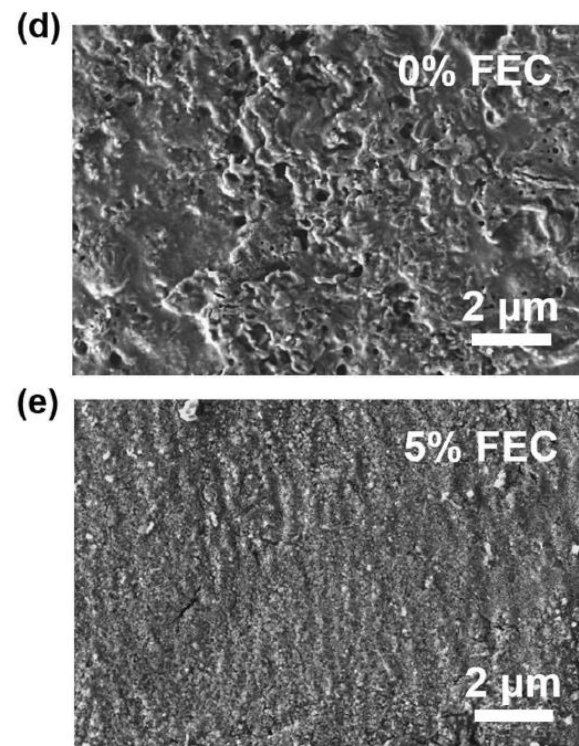


Fig.5: SEM images of the LiB anode surfaces from the Li | NMC cells at 1 C after cycling for 50 cycles with d) 0% and e) 5% FEC.[5]

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

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

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

Problematic: FEC concentration effect on SEI film formation.

- An additional voltage plateau located at approximately 0.7V versus Na/Na⁺ appears during the first reduction, which is associated with the addition of FEC.
- The percentage of added FEC strongly affects the reversible capacity retention of Na-ion batteries during the charge-discharge cycle.
- The **0.5%** of FEC added in total volume was optimal.

Problematic: *Why this small difference of FEC concentration in total volume of electrolyte has this big effect on SIB performance ?*

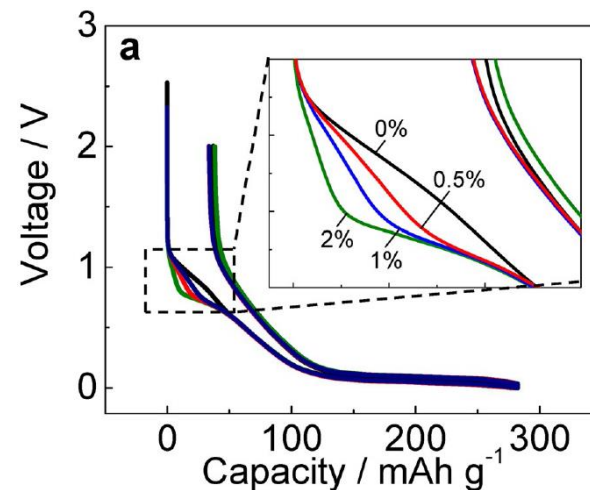


Fig.6: Initial charge/discharge curves of NaPF₆/PC electrolyte containing 0, 0.5, 1 and 2% of FEC. [3]

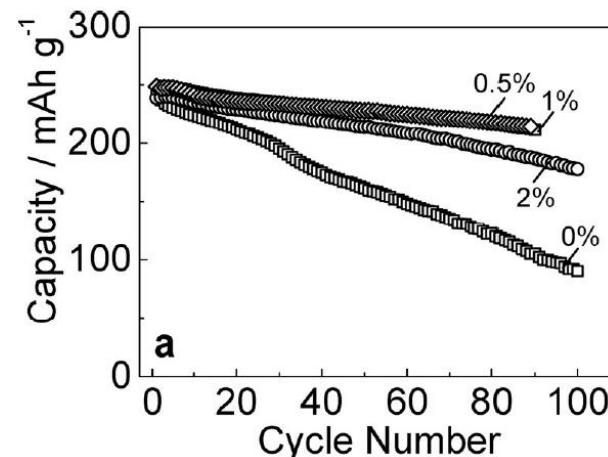


Fig.7: Capacity retention of NaPF₆/PC electrolyte containing 0, 0.5, 1 and 2% of FEC. [3]

1. Model system

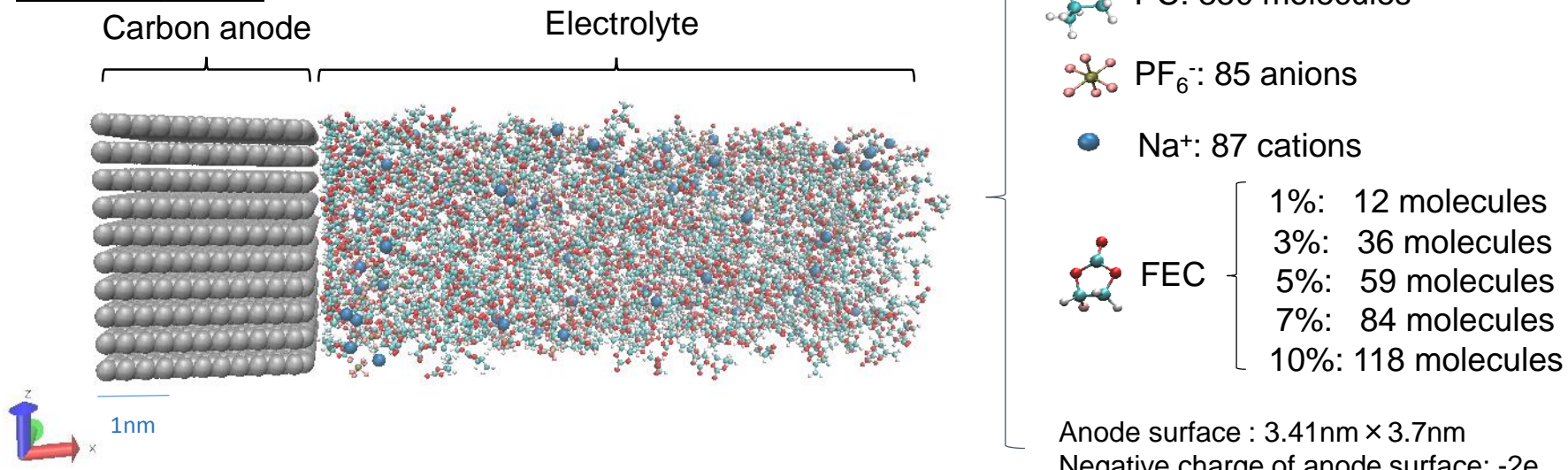
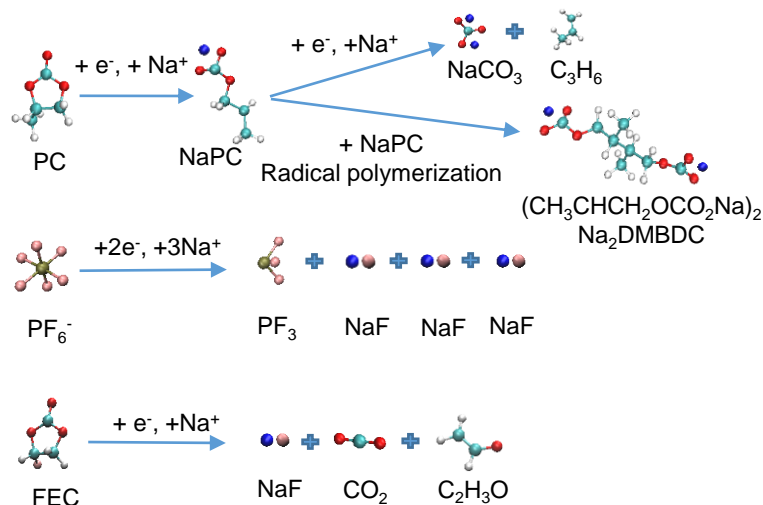


Fig.8: Model system, carbon based anode, NaPF₆/PC based electrolyte solution.

2. Reaction scheme



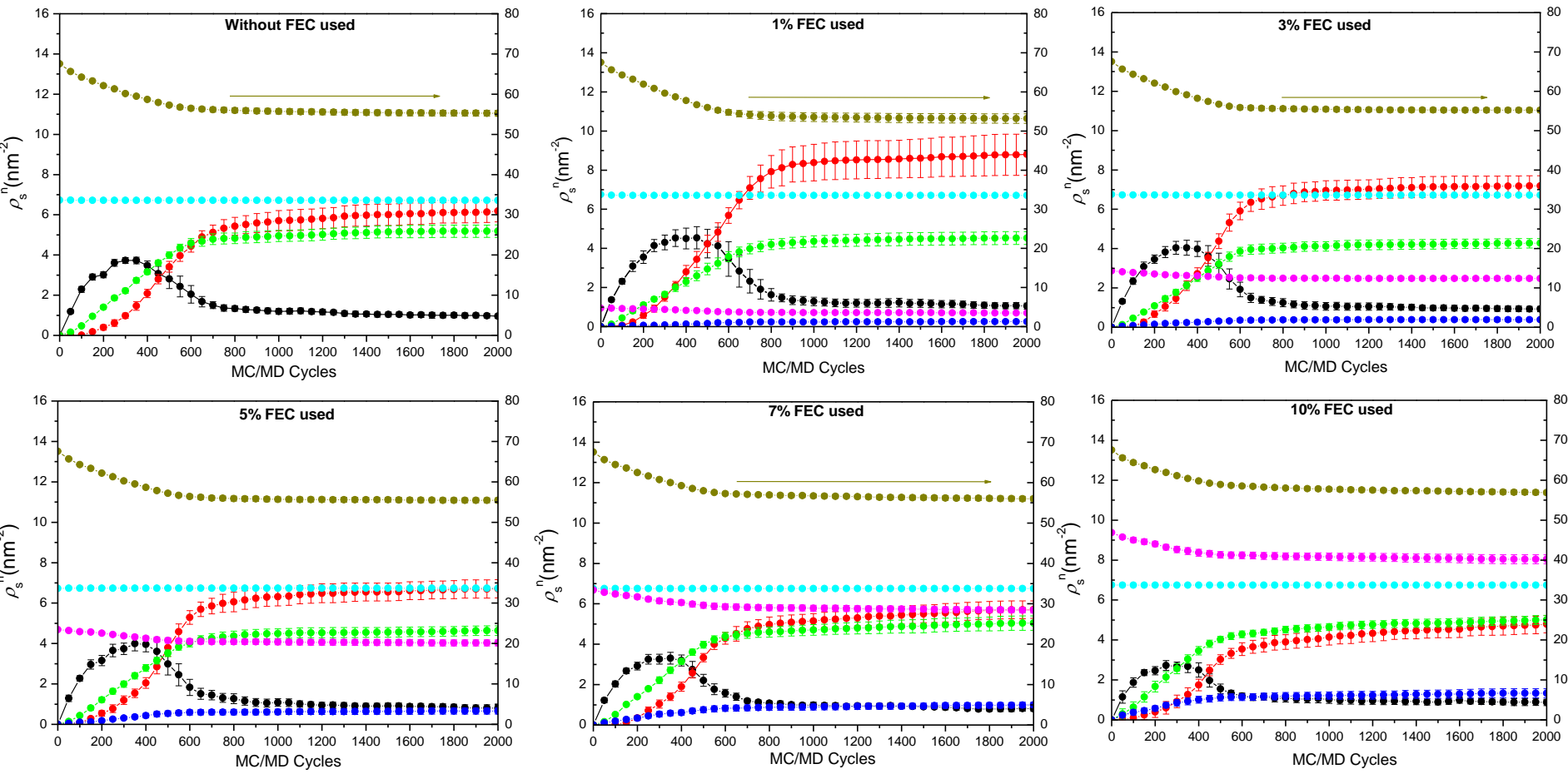
3. Computational method:

- Red Moon Method (Hybrid MC/MD reaction)
- 2000 MC/MD Cycles.
- GAFF Force field
- Temperature: 298 K
- Cutoff distance for LJ interactions: 8 Å

Results and discussions : Number density of SEI Film compounds

From 15 initial structures

—●— NaPC; —●— Na₂DMBDC; —●— Na₂CO₃; —●— NaF; —●— PF₆⁻; —●— FEC; —●— PC

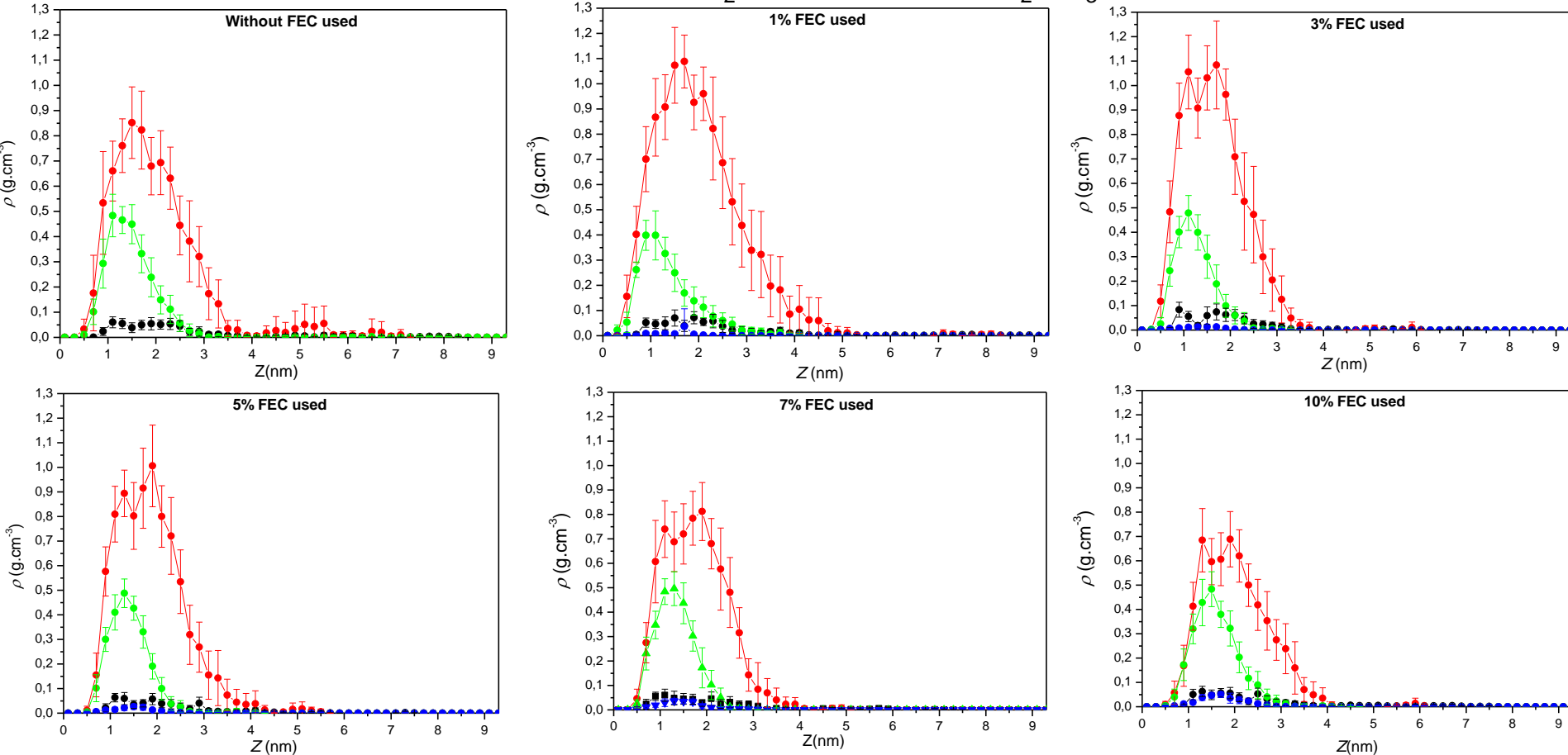


- The production of organic products NaPC and Na₂DMBDC is higher at 1% of FEC used to total electrolyte volume and decreases by increasing FEC additive concentration.

Results and discussions : Mass density of SEI Film compounds

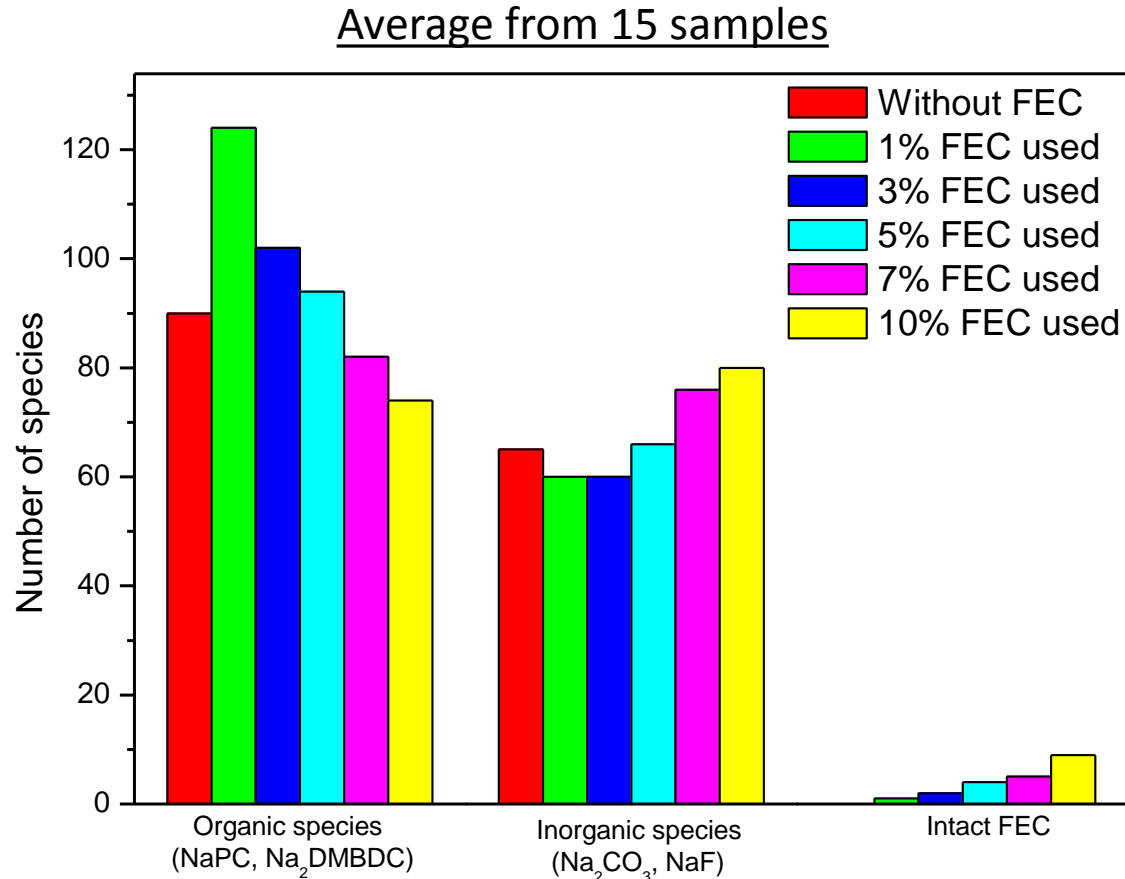
From 15 initial structures

—●— NaPC; —●— Na₂DMBDC; —●— Na₂CO₃; —●— NaF



- Inorganic products (Na₂CO₃ and NaF) are produced on anode surface which is in excellent agreement with experimental observations.

Results and discussions : Number of SEI compound species



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

Results and discussions : Normalized number of dissolved species

Average from 15 samples

	Na_2DMBDC	NaPC	Na_2CO_3	NaF
FFC Concentration:				
0%	0.0037	0.0128	0.0002	0.0000
1%	0.0002	0.0051	0.0000	0.0000
3%	0.0001	0.0027	0.0000	0.0000
5%	0.0001	0.0032	0.0000	0.0000
7%	0.0003	0.0078	0.0000	0.0000
10%	0.0004	0.0063	0.0000	0.0000

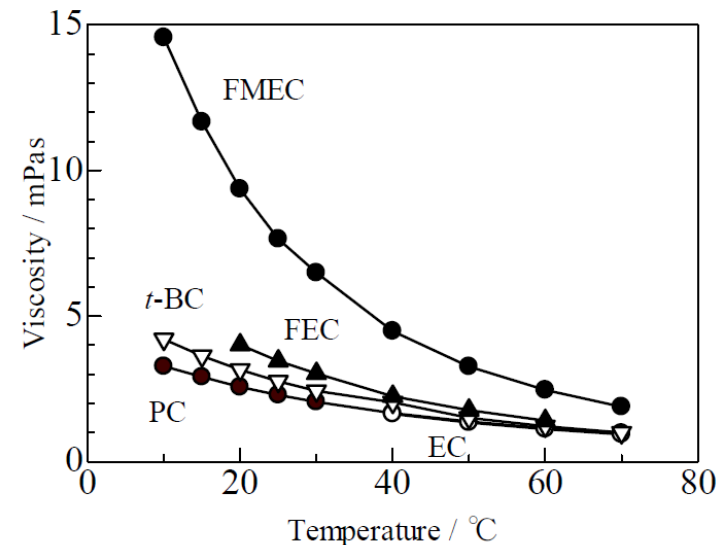
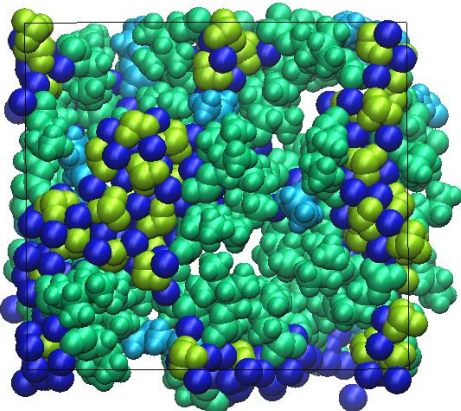
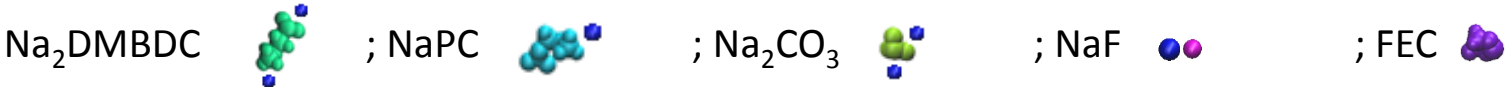


Fig.9: Temperature dependence of viscosity [6]

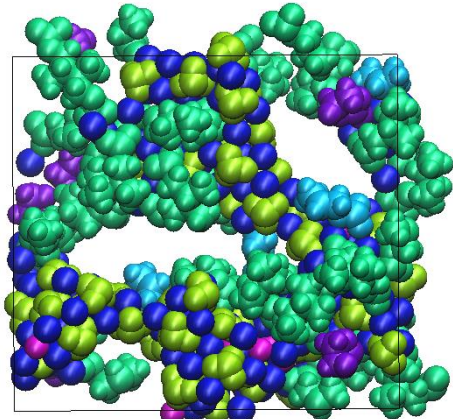
- FEC additive suppress remarkably dissociation of SEI film compounds.
- The dissociation of SEI film products is minimum at 3% of FEC concentration.

[6] Ohtake et al, *Electro. chem. Soc.*, **802** : 175 (2008).

Results and discussions : Cavity analysis



3% FEC used



10% FEC used

Average from 15 samples

<i>FEC Concentration:</i>	0%	1%	3%	5%	7%	10%
Cavity (FAV)	0.143	0.099	0.077	0.120	0.130	0.180
Error bar	±0.020	±0.015	±0.015	±0.016	±0.012	±0.020

- The SEI film became denser at 3% of FEC concentration.
- By increasing FEC amounts, the cavity size of SEI film increased.

Results and discussions : Stability of SEI film

Average from 15 samples

FEC Concentration:	0%	1%	3%	5%	7%	10%
V(Kcal/mol)	-11.91	-14.13	-13.24	-12.89	-12.23	-10.93
Error bar	±0.94	±0.36	±0.79	±0.72	±0.96	±0.93

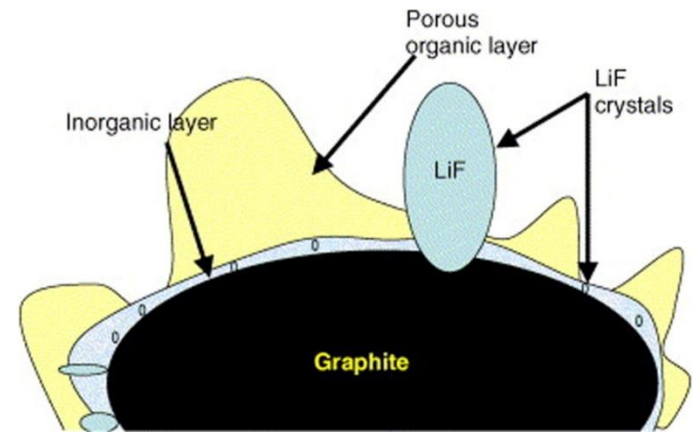
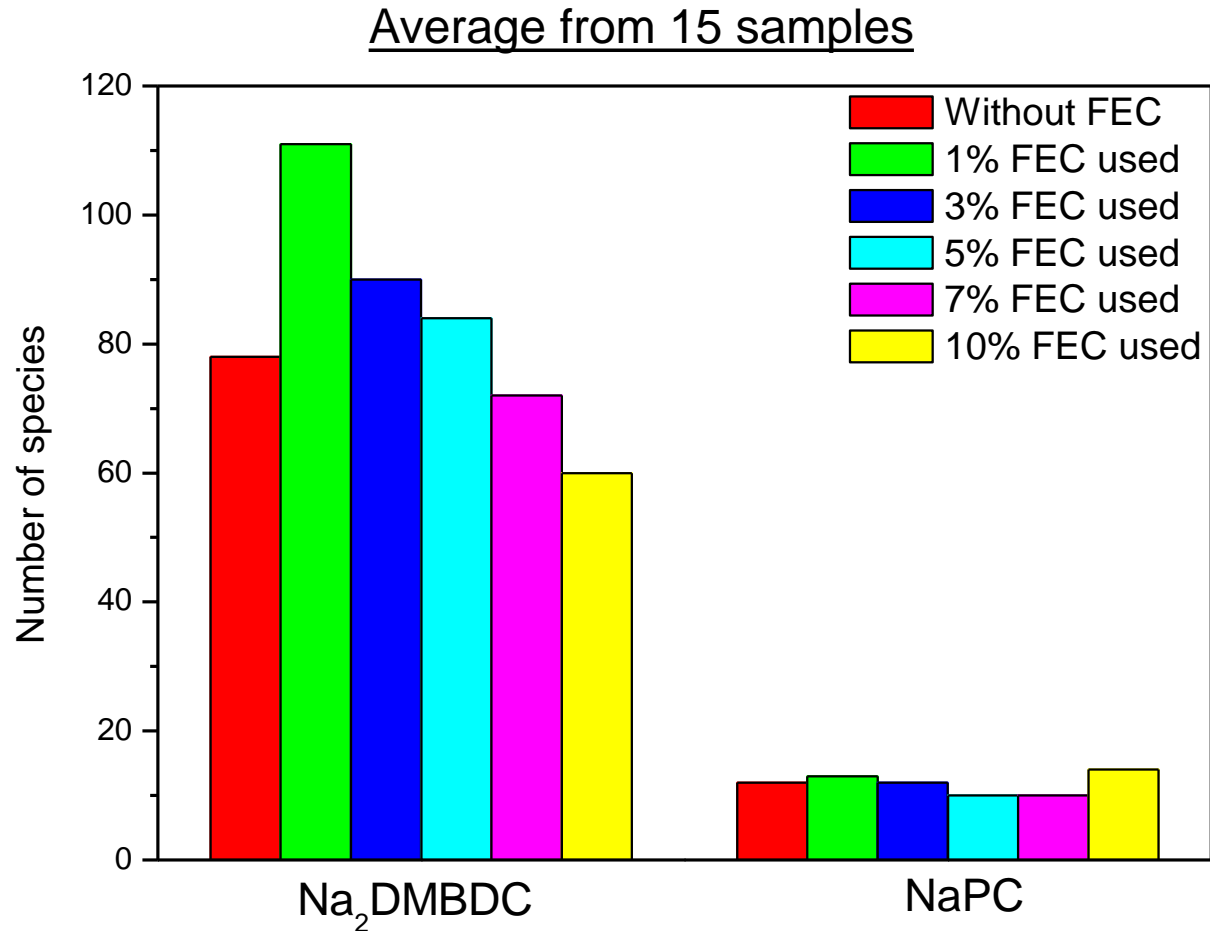


Fig10: A schematic picture of the SEI on graphite particle [7]

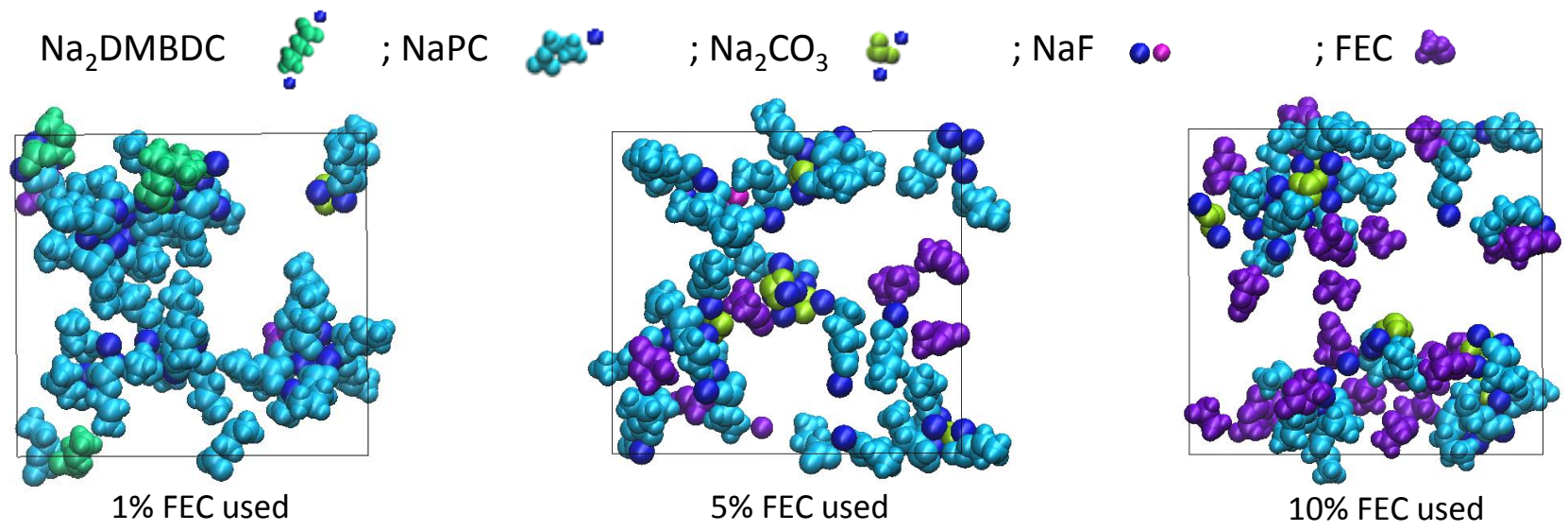
- Thickness of SEI film: ~ 35 nm [7].
- Thickness of inorganic layer : $45 \pm 5 \text{ \AA}$ [7].

- The potential energies per atom (V) of the organic species in the SEI films is 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 [7].
- SEI film is more stable at 1% of FEC concentration.



- Na₂DMDC production depends on the FEC concentration.
- Final NaPC products is related to electrode surface.

Discussions : SEI Film formation at 100 MC/MD cycle.



- $\text{NaPC} + \text{NaPC} \longrightarrow \text{Na}_2\text{DMBDC}$ (1)
- By increasing FEC concentration, the number of NaPC organic products decreases.
- NaPC is attracted by Intact FEC additive.

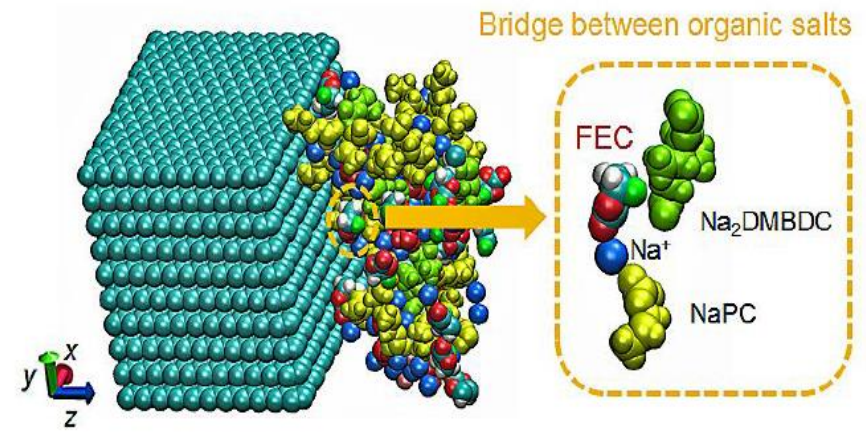
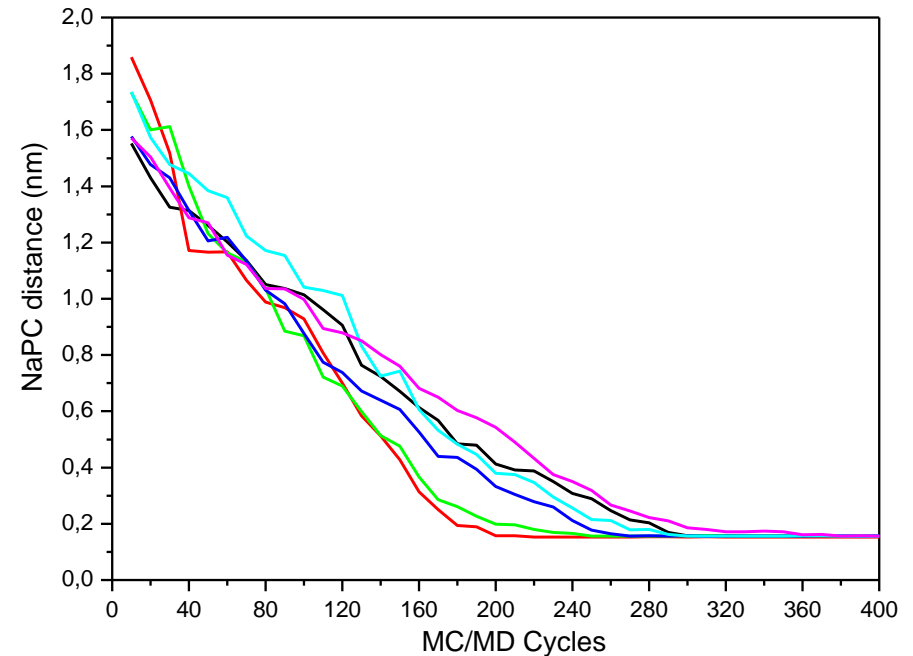
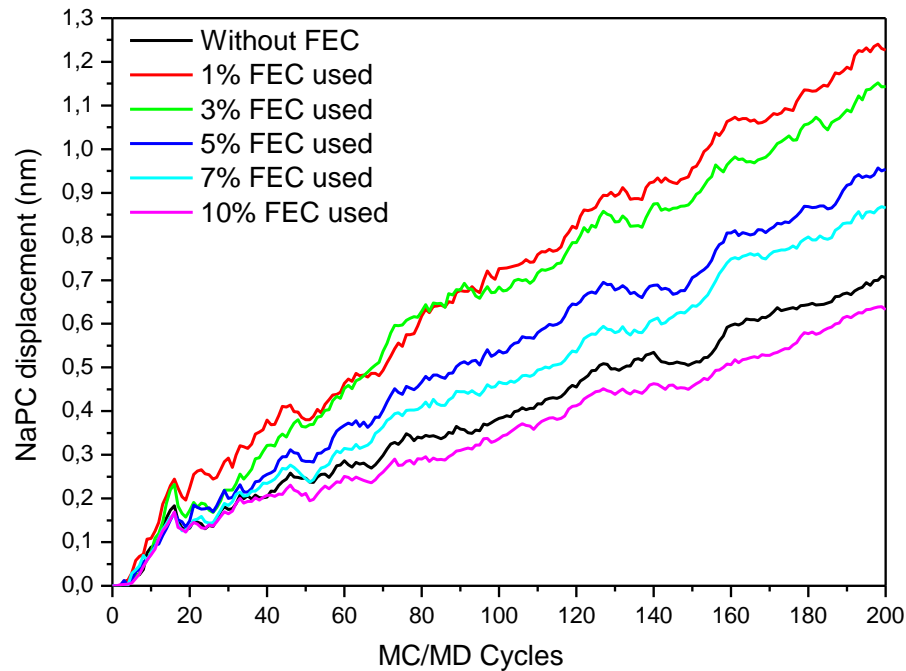


Fig.11: Typical snapshot of SEI film formation process at 500 MC/MD cycle in FEC-added electrolyte solution (yellow, NaPC; green, Na_2DMBDC ; red, Na_2CO_3 ; pink, NaF) [4].

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

Average from 15 samples



- NaPC displacement is higher at 1% FEC concentration.
- By increasing FEC concentration, the number of intact FEC increases on the anode surface which decreases NaPC displacement.
- NaPC displacement is proportional to NaPC distance convergence towards dimerization distance.

Conclusion :

- Red moon simulation results shows that SEI film is more stable at 1% of FEC concentration leading to long lifetime of NIB during charge-discharge cycles. This results is in good agreement with experimental data.
- Stability of SEI film is mainly related to the production of Organic Products.
- FEC additive effects :

Positive	Negative
<ul style="list-style-type: none">✓ Suppress the dissociation of SEI film.✓ Very small amounts of FEC enhance NaPC products diffusion.	<ul style="list-style-type: none">○ Reduce the NaPC diffusion.○ Suppress organic species production.

The optimum concentration of FEC additive is the balance value between enhancing dynamic properties and reducing dissociation of SEI film compounds.