Microscopic Effect of FEC Additive Concentration on SEI Film Formation in Na-ion Batteries

Amine Bouibes [a,b*] , Norio Takenaka [a,c] , Takuya Fujie [a] , Masataka Nagaoka [a,b,c]

[a]*Graduate School of Informatics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan*
[b]*Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, Honmachi, Kawaguchi 332-0012, Japan*
[c]*ESICB, Kyoto University, Kyodai Katsura, Nishikyo-ku, Kyoto 615-8520, Japan*
E-mail: bouibes@ncube.human.nagoya-u.ac.jp

Fruoethylene carbonate (FEC) is an effective additive to improve the performance of Na-ion batteries (NIB), enhancing solid electrolyte interphase (SEI) film formation on the anode surface [1-3]. Recently, an experimental study was shown that small amount of FEC enhanced NIB performance, while it decreased by increasing the FEC amount [3]. Toward understanding the microscopic mechanism of this observation, the dependency of the SEI film formation on the FEC concentration has been investigated in $NaPF_6$/PC electrolyte solution by using the Red Moon method [2]. This method has shown great efficiency to reproduce atomic structures of SEI film [2]. In the present study, six different FEC concentrations were used, that is 0, 1, 3, 5, 7 and 10 vol%, in 1.1 mol/L $NaPF_6$ PC-based electrolyte on the carbon anode.

$$PC + e^- + Na^+ \rightarrow NaPC \quad (R1)$$
$$NaPC + NaPC \rightarrow Na_2DMBDC \quad (R2)$$

Scheme: Chemical reactions producing organic dimer.

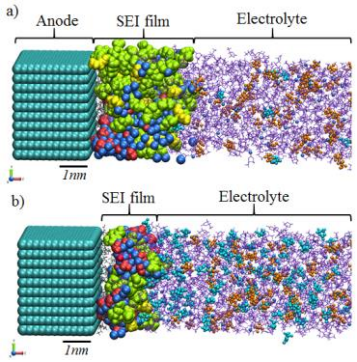

Fig.1: Typical snapshot of SEI film formed in $NaPF_6$/PC electrolyte solution at (a) 1 vol% and (b) 10 vol% of FEC concentration.

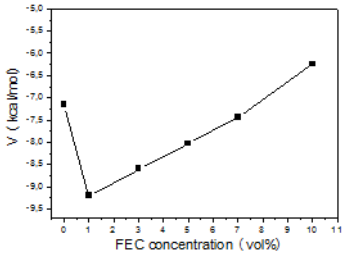

Fig.2: Potential energies per atom of obtained SEI films at the different FEC concentrations.

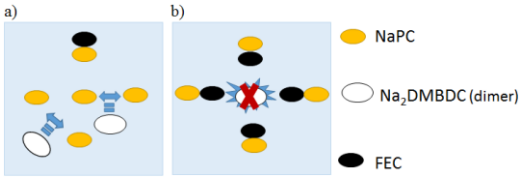

Fig.3: Small (a) and high (b) FEC concentration effect on NaPC dimerization.

Fig.1 shows the obtained structures of SEI films. This study reveals that the production of organic dimer (R2) is enhanced at small additive concentration, while it is suppressed at higher FEC concentration. Accordingly, the stability of SEI film deacreased with the increase in the FEC amount (Fig.2). This is clearly consistent with the experimental tendency [3]. It is considered that at high FEC concentration, the production of organic dimer (Na_2DMBDC) is supressed since a lot of FEC molecules inhibit the dimerization reactions necessary to contact between NaPCs (Fig.3). It is concluded therefore that the appropriate adjustment of FEC additive amount is essential to improve the NIB performance.

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References:

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