Microscopic Mechanism of SEI Layer Formation in Highly Concentrated Electrolytes Based on the Nonflammable Trimethyl Phosphate Solvent

Amine Bouibes[1*], Norio Takenaka[2], Soumen Saha[1,3], Masataka Nagaoka[1,3]

[1]Graduate School of Informatics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan;
[2]Graduate School of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[3]ESICB, Kyoto University, Kyodai Katsura, Nishikyo-ku, Kyoto 615-8520, Japan;
* bouibes@ncube.human.nagoya-u.ac.jp

The microscopic understanding of the formation process of the solid electrolyte interphase (SEI) layer is an important challenge to design the safe lithium-ion battery (LIB). Recent experimental study has proposed the highly salt concentrated (HC) electrolyte to introduce the trimethyl-phosphate (TMP), popular as flame-retardant solvent, as unique solvent in the electrolyte [1]. This HC electrolyte showed an excellent self-extinguishing property in addition to an attractive charge-discharge performance. However, the microscopic mechanism of its solid electrolyte interface (SEI) layer formation still remains an open question.

To investigate such SEI layer formation, we employed the Red Moon (RM) method [2] which has shown great efficiency to reproduce atomic structure of SEI film [3]. The present atomistic reaction simulations were executed in 1.0, 2.3 and 5.3 mol.L^{-1} LiFSA salt concentrations. Based on quantum mechanical (QM) calculations, the primary chemical reactions of LiFSA/TMP electrolyte are shown in Scheme 1.

By executing the RM simulations, the experimental observations were successfully reproduced where the SEI layers were formed in the "bottom-up" manner resulting a thinner and denser SEI layer mainly based on salt reduction in HC electrolyte (Fig. 1) [4]. It was revealed that a large amount of salt anions is localized on the SEI surface in HC electrolyte, enhancing the network formation of a dense inorganic layer with SEI salt-derived species (Fig.2) [4]. It was, further, shown that the size of TMP molecule itself prevents its insertion in SEI layer, leading to the formation of a pure dense inorganic SEI layer (Fig.1), which should considerably improve the stability of SEI layer and would bring about a long lifetime of advanced safe LIB.

$TMP + e^-$	→	TMP^-	(R1)
TMP^-	→	$(OCH_3)_2P(O)O^{\bullet -} + \dot{C}H_3$	(R2)
$\dot{C}H_3 + \dot{C}H_3$	→	C_2H_6	(R3)
$TMP^- + e^-$	→	$DMP^- + CH_3O^-$	(R4)
$FSA^- + e^-$	→	$F(SO_2)_2N^- + F^-$	(R5)
$TMP^- + FSA^-$	→	$TMP + F(SO_2)_2N^- + F^-$	(R6)

Scheme 1: Primary chemical reactions

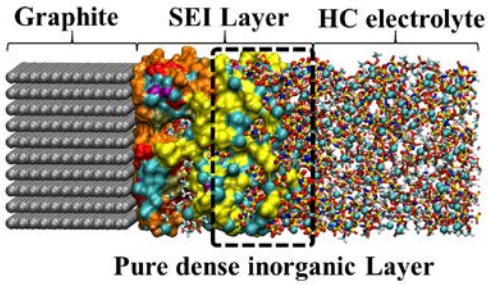

Fig.1: Typical SEI layer in HC electrolyte (Calculateted)

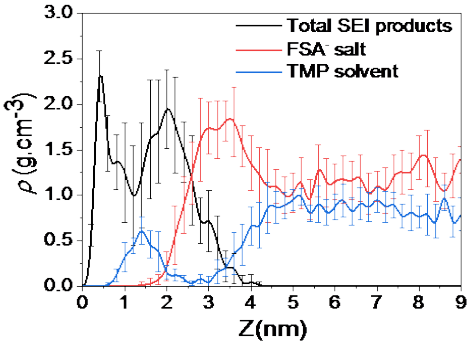

Fig.2: Mass density distribution of SEI layer and HC electrolyte.

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