

Microscopic Mechanisms of SEI Film Formation in Li-Ion Batteries with Highly Concentrated Electrolyte

Norio Takenaka^{a,b}, Takuya Fujie^b, Amine Bouibes^b, Yuki Yamada^{a,c}, Atsuo Yamada^{a,c}, Masataka Nagaoka^{a,b,d}

^a ESICB, Kyoto University, Kyoto 615-8245, Japan

^b Graduate School of Informatics, Nagoya University, Nagoya 464-8601, Japan

^c Department of Chemical System Engineering, University of Tokyo, Tokyo 113-8656, Japan

^d Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, Honmachi, Kawaguchi 332-0012, Japan

E-mail: takenaka@ncube.human.nagoya-u.ac.jp

Introduction The lifetime and stability of Li-ion batteries are found to be strongly dependent on the nature of passivation film called solid electrolyte interphase (SEI) film formed on the anode surface. According to recent experimental studies, the use of highly concentrated (HC) electrolyte can be quite useful to improve the battery performance, enhancing the SEI film formation [1,2]. However, its molecular mechanism remains still unknown. To investigate this mechanism, atomistic reaction simulations were performed using a Red Moon method [3-5].

Method The present atomistic reaction simulations were executed in LiFSA/acetonitrile (AN) electrolyte solutions on the carbon anode by using five different salt concentrations of 1.0, 2.0, 3.0, 4.0 and 5.0 molL⁻¹.

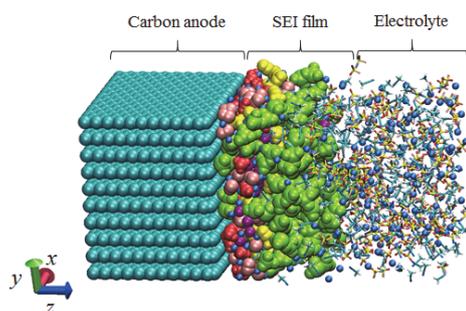


Figure 1. Typical snapshot of SEI film formed in LiFSA/AN electrolyte at 5.0 molL⁻¹ (stick model: AN and FSA⁻, ball model: Li⁺ and SEI film components).

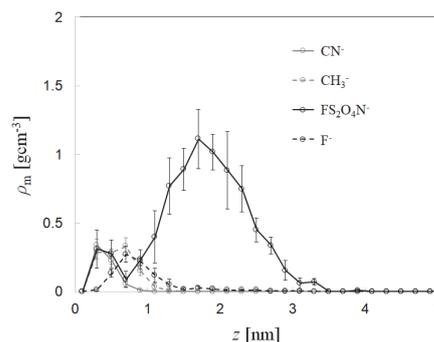


Figure 2. Mass density distributions ρ_m of the reaction products in LiFSA/AN electrolyte at 5.0 molL⁻¹.

Results and discussion By executing the Red Moon simulations, the stable SEI film was formed in the HC electrolyte at 5.0 molL⁻¹ (Fig. 1). Fig. 2 shows the mass density distributions of the reaction products inside the SEI film. It was found that the solvent-based reaction products (CH₃⁻, CN⁻) are present near the anode surface, while the Li salt-based reaction products (FS₂O₄N⁻) are mainly distributed in the outer region of the SEI film. This is clearly consistent with the experimental observations where the Li salt-based SEI film is formed in the HC electrolyte. In addition, it was found that the SEI film becomes denser as the salt concentration increases. It is considered therefore that the formation of dense passivation film in the HC electrolyte leads to the good cycle performance during the charge-discharge cycles.

References:

- [1] Yamada, Y. *et al.*, *J. Am. Chem. Soc.* 136 (2014) 5039-5046.
- [2] Yamada, Y. *et al.*, *ChemElectroChem* 2 (2015) 1687-1694.
- [3] Nagaoka, M. *et al.*, *Chem. Phys. Lett.* 583 (2013) 80-86.
- [4] Takenaka, N. *et al.*, *J. Phys. Chem. C* 118 (2014) 10874-10882.
- [5] Takenaka, N. *et al.*, *J. Phys. Chem. C* 119 (2015) 18046-18055.