

# First-Principles Study on Adsorption and Decomposition of Carbonate Electrolyte Molecules at $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode Interface

Yukihiro Okuno<sup>a</sup>, Keisuke Ushirogata<sup>a</sup>, Keitaro Sodeyama<sup>b,c</sup>, Yoshitaka Tateyama<sup>b,c,d</sup>

<sup>a</sup>Research and Development Management Headquarters, FUJIFILM Corporation, 210 Nakanuma, Minamiashigara, Kanagawa 250-0193, Japan

<sup>b</sup>Center for Materials Research Information Integration (cMI<sup>2</sup>), Research and Services Division of Materials Data and Integrated System (MaDIS), National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

<sup>c</sup>Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, 1-30 Goryo-Ohara, Nishikyo-ku, Kyoto 615-8245, Japan

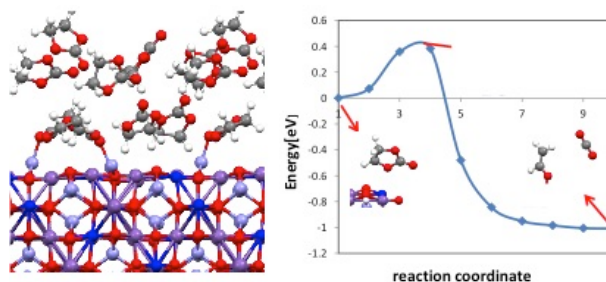
<sup>d</sup>Center for Green Research on Energy and Environmental Materials (GREEN), NIMS, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

E-mail: TATEYAMA.Yoshitaka@nims.go.jp

Electrolyte decomposition on the cathode surfaces of lithium-ion batteries has attracted considerable attention because it leads to battery degradation and formation of cathode solid-electrolyte interphase (CEI). [1] In this study, we used density functional theory (DFT) calculations to investigate the adsorption distribution of ethylene carbonate (EC) electrolyte molecules as well as EC decomposition reactions on the (100) surfaces of lithiated (pristine) and de-lithiated forms of spinel-type  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO) as model cathode surfaces. [2]

DFT molecular dynamics (MD) simulations indicated that EC molecules have two characteristic adsorption modes, which can well explain the experimental observations and suggest a new feature of electrolyte -cathode interface in terms of the control of interfacial dipole. Based on the DFT-MD results, we examined several possible pathways of EC decomposition on the LNMO (100) surfaces and estimated their activation barriers. We then found that the pristine LNMO (100) surface is inert for the EC decomposition, whereas, on de-lithiated surfaces, two-fold-coordinated surface oxygen atoms generated by the de-lithiation process serve as active sites for nucleophilic attack on the carbonyl carbon and the methylene group of adsorbed EC molecules. The former attack induces ring-opening of the EC molecule leading to the CEI formation, while the latter causes hydrogen abstraction from the methylene group and subsequent  $\text{CO}_2$  generation, which was actually observed in experiments.

Fig. (left) A snapshot of the equilibrium trajectory of EC electrolyte – LNMO (100) interface. (right) An energy profile of EC decomposition on LNMO(100) surface toward  $\text{CO}_2$  evolution.



## References:

- [1] K. Leung, J. Phys. Chem. C 116 (2012) 9852-9861.
- [2] Y. Okuno, K. Ushirogata, K. Sodeyama, Y. Tateyama, submitted.