

Charge Compensation Mechanism in Li-Excess Oxides with Different Ionic or Covalent Characters

Kentaro Yamamoto^a, Naoaki Yabuuchi^b, Koji Nakanishi^c, Tomoki Uchiyama^a,
Yuki Kobayashi^b, Rina Yamamoto^a, Yuki Orikasa^d,
Toshiaki Ohta^c & Yoshiharu Uchimoto^a

^a Graduate School of Human and Environmental Studies, Kyoto University, Yoshidahonmachi, Sakyo, Kyoto 606-8501, Japan

^b Department of Applied Chemistry, Tokyo Denki University, 5 Senju Asahi-cho, Adachi, Tokyo 120-8551, Japan

^c SR Center, Ritsumeikan University, 1-1-1 Noji-higashi, Kusatsu, Shiga 525-8577, Japan

^d Department of Applied Chemistry, Ritsumeikan University, 1-1-1 Noji-higashi, Kusatsu, Shiga 525-8577, Japan

E-mail: yamamoto.kentaro.4e@kyoto-u.ac.jp

Li-excess metal oxide, in which anion redox occurs for the charge compensation during charge/discharge processes, has been expected to realize higher energy density in lithium-ion batteries. Several lithium-excess positive electrode materials have been studied extensively in order to use effectively the charge compensation of oxide ions.[1-5] In 4*d* and 5*d* metal oxides Li₂RuO₃-based systems[1] and Li₂IrO₃,[2] high covalent bond between 4*d* orbital of transition-metal and 2*p* orbital of oxygen enables charge compensation by the oxidation of oxide ions to peroxo-like dimer. On the other hand, in a 3*d* transition-metal oxide, Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O₂ exhibits formation of isolated holes on oxide ions because highly ionized 3*d* transition-metal ions stabilize the isolated holes on the oxide ions surrounded by lithium ions. [3, 4] Other 3*d* transition-metal oxides such as Li_{1.2}Ti_{0.4}Mn_{0.4}O₂, also exhibit stable oxide ions redox.[5]

According to the previous studies, covalent character or ionic character between transition-metal ions and oxide ions in Li-excess metal oxides is a key factor to stabilize oxide ions redox. However, behavior of oxide ions redox in Li-excess positive electrode materials with different covalent character or ionic character has not been systematically examined. Moreover, for understanding essentially the mechanism of oxide ions redox, it is important to observe electronic states of oxide ions in these materials under battery operating condition. In this study, we focus on four different Li-excess positive electrode materials, Li₂MeO₃ (Me = Mn and Ru) and Li_{1.2}Ti_{0.4}Me_{0.4}O₂ (Me = Mn and Fe), as models with different covalent character or ionic character. Developing a new *operando* soft X-ray absorption spectroscopy, we observed directly the electronic state of the oxide ions in these materials during charge process via the technique.[6]

References:

- [1] Sathiyaraj, M. *et al.*, and Tarascon, J.-M. *Nat. Mater.* **2013**, 12, 827.
- [2] McCalla, E. *et al.*, and Tarascon, J.-M. *Science* **2015**, 350, 1516.
- [3] Luo, K. *et al.*, and Bruce, P. G. *Nat. Chem.* **2016**, 8, 684.
- [4] Seo, D.-H. *et al.*, and Ceder, G. *Nat. Chem.* **2016**, 8, 692.
- [5] Yabuuchi, N. *et al.*, and Ohta, T. *Nat. Commun.* **2016**, 7, 13814.
- [6] Yamamoto, K. *et al.*, and Uchimoto, Y. *submitted*.

Acknowledgement:

This research was financially supported by the Japan Science and Technology Agency (JST), Advanced Low Carbon Technology Research and Development Program (ALCA), Specially Promoted Research for Innovative Next Generation Batteries (SPRING) Project.