Reaction mechanism of a new cathode material for potassium-ion battery

Titus Masese[1], Kazuki Yoshii[1], Toyoki Okumura[1], Junya Furutani[2], Yuki Orikasa[2], Hiroshi Senoh[1], and Masahiro Shikano[1]

1) *National institute of Advanced Science and technology, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan*
2) *Department of Applied Chemistry, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan*

Development of large-scale lithium ion batteries is required to meet the uptick in demand for electrical and automotive applications. Scarcity of lithium raw materials and market instability are hurdles to be resolved in order to effect the mass production of lithium-ion batteries. To effectively use the limited terrestrial resources and construct a sustainable society, it is necessary to consider the use of highly abundant elements. Potassium ion batteries are emerging as next-generation large-scale batteries due to not only the superiority in terms of resources but also as high voltage battery systems at par with lithium ion batteries. Recently, the research and development of their electrode materials is rapidly accelerating[1, 2]. Among monovalent alkali ions, K^+ has weaker Lewis acidity than Li^+ and Na^+ which induces smaller solvated cations in liquid electrolytes, thus enabling a fast ionic conductivity and high power. Furthermore, since the standard electrode potential (-2.925 V vs SHE) of K^+ is comparable to Li^+ (-3.045 V vs SHE), it is possible to utilize a low potential negative electrode material when K^+ is used as a carrier ion. It is also advantageous in terms of construction of a battery having a high voltage which is comparable to the current lithium ion battery and consequently as a high energy density of the battery. Therefore, it has potential as a low-cost next-generation large-scale energy storage device and can be said to be one of the ultimate forms of post-lithium ion batteries. However, since the ion radius of K^+ is large, the development of electrode materials (in particular, a positive electrode) which can be reversibly (de)inserted has not progressed. We have found that $K_{2/3}Ni_{2/3}Te_{1/3}O_2$ having the P2-type layered structure showed superior performance as a potassium ion battery positive electrode[3]. In this research, attempts were made to elucidate the mechanism by which high-capacity charge / discharge reaction is analysed by soft X-ray absorption spectroscopy.

$K_{2/3}Ni_{2/3}Te_{1/3}O_2$ active material was synthesized by solid solution method. Phase identification of the obtained sample was carried out by powder X-ray diffraction measurement. Using the synthesized active material, a positive electrode was prepared with active material: conductive auxiliary agent: binder = 85.0: 7.5: 7.5 wt.%. A positive electrode and a metal K negative electrode were used to prepare a battery, and the electrochemical characteristics were evaluated. For the sample before and after charging and discharging, the cell was disassembled in a glove box, washed and mounted on a transfer vessel. The samples were placed in a vacuum chamber without air exposure for XAS measurements. O K-edge XAS measurements in a fluorescence mode were performed at BL-2 in SR center (Ritsumeikan University).

$K_{2/3}Ni_{2/3}Te_{1/3}O_2$ positive electrode exhibits a reversible capacity of about 60 mAh g^{-1} at 25°C at a rate of C/20. This corresponds to approximately one third of potassium reversible insertion and extraction. A clear change of the O *K*-edge XAS of the $K_{2/3}Ni_{2/3}Te_{1/3}O_2$ positive electrode before and after charging and discharging was observed. The peak around 532 eV arises from the hybridization of O-2*p* and Ni-3*d* orbitals, and the peak on the high energy side emanates from the hybridization of O-2*p* orbital and Ni-4*s,p* orbitals[4]. Upon charging, a new peak is discernible at 528 eV (on the low energy side). This is thought to originate from the formation of ligand hole of oxygen, which is in good agreement with the behavior observed when $LiNiO_2$ is charged[5]. It was shown that the reversible charge / discharge cycling is due to the stable electron transfer by Ni and O hybrid orbital. The contribution of oxygen in the charging / discharging process of $K_{2/3}Ni_{2/3}Te_{1/3}O_2$ positive electrode was also confirmed by first principle calculations.

References

(1) S. Komaba et al., Electrochem. Commun., **2015**, 60, 172.
(2) K. Chihara et al., Chem. Commun., **2017**, 53, 5208.
(3) T. Masese et al., The 85th ECSJ Spring Meeting, **2018**, 3D01.
(4) H. Kanda et al., Phys. Rev., **1998**, 58, 9693.
(5) Y. Uchimoto et al., J. Power Sources, **2001**, 97-98, 326.