Charge Compensation Mechanisms of $Li_{1.2-x}Ti_{0.4}Me_{0.4}O_2$ (Me = Mn^{3+} and Fe^{3+}) on Electrochemical Lithium Extraction

There is growing research interest in the solid-state redox reaction of oxide ions (oxygen) for rechargeable lithium battery applications. Charge compensation mechanisms of $Li_{1.2}Ti_{0.4}Me_{0.4}O_2$ (Me = Mn^{3+} and Fe^{3+}) on lithium extraction are being examined by X-ray absorption spectroscopy at the Photon Factory. A reversible redox process for oxide ions is observed for $Li_{1.2-x}Ti_{0.4}Mn_{0.4}O_2$. In contrast, there is clear evidence of irreversible oxygen loss on charge for $Li_{1.2-x}Ti_{0.4}Fe_{0.4}O_2$, which originates from the high covalent nature of Fe and O ions. These findings may contribute to the development of high-energy rechargeable lithium batteries with the oxide ion redox reaction in the future.

During the past two decades, the technology of rechargeable lithium-ion batteries (LIBs) has become highly sophisticated and contributed to the development of today's convenient modern society with versatile portable electronic devices. However, due to the ever-increasing demand for energy density, there is a need to develop positive electrode materials with higher energy density. The energy density of commercial LIBs is currently limited by positive electrode materials. Lithium-excess positive electrode materials such as Li_2MnO_3 and their derivatives have been studied extensively in the past decade. In this system, the oxidation state of manganese ions is tetravalent, and therefore further oxidation of manganese ions is difficult on charge. Instead, oxide ions play a role in the charge compensation. However, oxidation of oxide ions for Li_2MnO_3-based electrode materials causes oxygen loss as an irreversible process [1].

To use effectively the charge compensation of oxide ions, several lithium-excess positive electrode materials have been reported. Recently, our group successfully synthesized new niobium- and titanium-based high-capacity positive electrode materials based on the solid-state redox reaction of oxide ions [2, 3]. **Figure 1** compares galvanostatic charge/discharge curves of Mn^{3+}- and Fe^{3+}-substituted Li_2TiO_3 samples, i.e., $Li_{1.2}Ti_{0.4}Mn_{0.4}O_2$ and $Li_{1.2}Ti_{0.4}Fe_{0.4}O_2$. Both samples deliver ca. 350 mA h g^{-1} of initial charge capacities with a voltage plateau at 4.1–4.3 V. However, a clear difference is noted for the discharge process. Polarization on discharge is much larger for the Fe-substituted sample, and the second charge curve is completely different from that of the initial charge curve. The long voltage plateau is observed only for the initial charge. In contrast, profiles of the initial and second charge curves

are similar for the Mn-substituted sample with the slope region for 3–4 V followed by the voltage plateau at 4.3 V. Reversible capacities of 300 mA h g^{-1} are observed for the Mn-substituted sample with relatively high voltage on discharge. Observed discharge capacities are much larger than the theoretical capacities calculated based on the Mn^{3+}/Mn^{4+} redox reaction. A study by soft X-ray absorption spectroscopy demonstrated clearly that charge compensation is realized by the reversible redox reaction of oxide ions for $Li_{1.2}Ti_{0.4}Mn_{0.4}O_2$ [3].

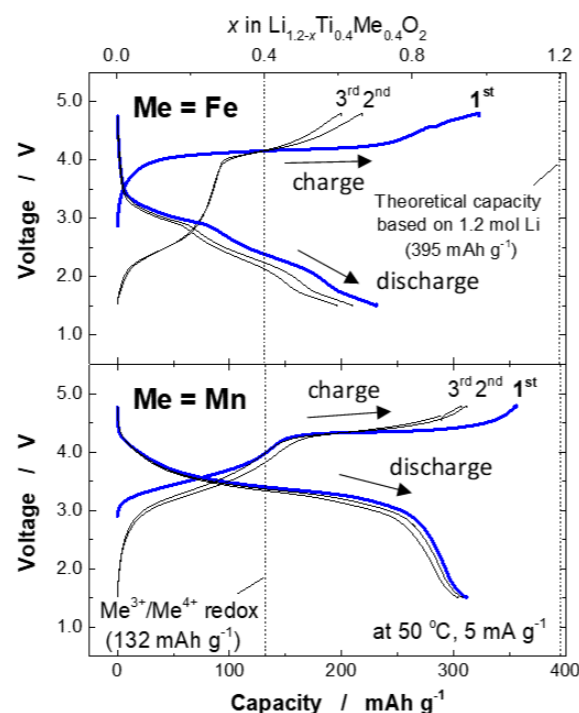**Figure 1:** Comparison of charge/discharge curves of $Li_{1.2}Ti_{0.4}Me_{0.4}O_2$ (Me = Mn^{3+} and Fe^{3+}) in Li cells at 50°C.

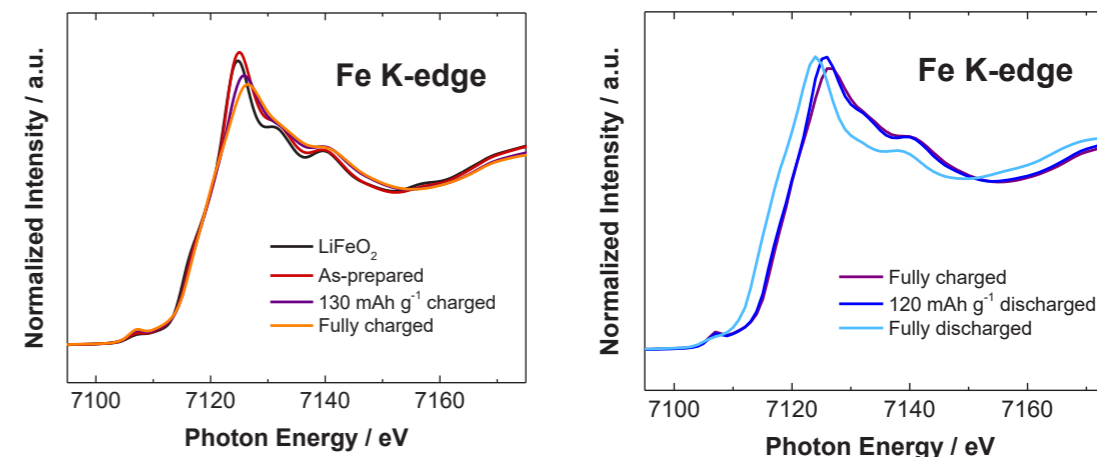**Figure 2:** Changes in Fe K-edge XAS spectra of $Li_{1.2-x}Ti_{0.4}Fe_{0.4}O_2$ on charge (left) and discharge (right).

Since large polarization is observed for $Li_{1.2}Ti_{0.4}Fe_{0.4}O_2$, charge compensation mechanisms were examined by hard X-ray absorption spectroscopy (XAS). As shown in **Fig. 2**, only a small change is observed for the Fe K-edge on charge, indicating that Fe is not responsible for the charge compensation process. In contrast, a clear change in the spectra is noted on discharge. The energy of the Fe K-edge XAS spectra is clearly shifted to a lower energy region, indicating the reduction of iron to a lower oxidation state. This result also suggests that oxygen loss occurs on charge, and then iron is electrochemically reduced from the trivalent to divalent state on initial discharge. Note that the formation of superoxide species is evidenced from O K-edge XAS spectra on charge, and it is proposed that the high covalent nature of iron and oxygen results in reductive coupling and the formation of superoxide species [3]. Since superoxide species are not electrochemically stable, oxygen loss is inevitable in further charge processes.

Use of the oxide ion redox is an effective strategy for further increasing the reversible capacities of positive electrode materials for LIBs because lithium contents

are potentially further enriched with fewer transition metal ions in the framework structure. Reversible capacities of electrode materials are not limited by the absence of oxidizable transition metal ions for redox centers. Instead, negatively charged oxide ions can donate electrons. XAS studies clearly revealed stabilization and destabilization mechanisms for the oxide ion redox, which may contribute to the development of high-capacity positive electrode materials in the future.

REFERENCES
[1] N. Yabuuchi, *Chem. Lett.* **46**, 412 (2017).
[2] N. Yabuuchi, M. Takeuchi, M. Nakayama, H. Shiiba, M. Ogawa, K. Nakayama, T. Ohta, D. Endo, T. Ozaki, T. Inamasu, K. Sato and S. Komaba, *PNAS* **112**, 7650 (2015).
[3] N. Yabuuchi, M. Nakayama, M. Takeuchi, S. Komaba, Y. Hashimoto, T. Mukai, H. Shiiba, K. Sato, Y. Kobayashi, A. Nakao, M. Yonemura, K. Yamanaka, K. Mitsuhara and T. Ohta, *Nature Commun.* **7**, 13814 (2016).

BEAMLINE
BL-12C

N. Yabuuchi (Tokyo Denki Univ.)