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Study on Reversibility of Anionic Redox for Mn-based Li-rich Oxides by Soft X-ray Absorption Spectroscopy

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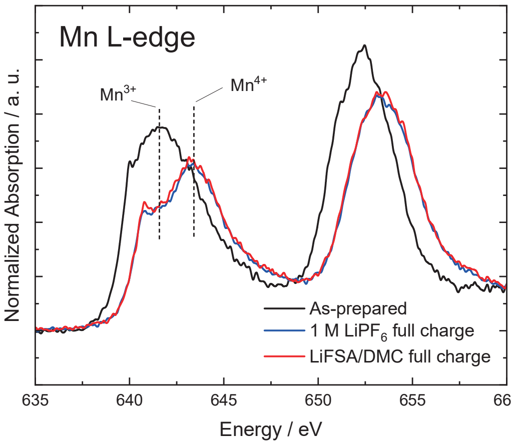
High-capacity electrode materials made by abundant elements are necessary to develop cost-effective energy storage applications. Emerging new chemistry is found in a series of electrode materials with a cation-disordered rocksalt structure, and Li-excess and Mn-based oxides with the disordered structure are attractive candidates for this purpose. Large reversible capacities for these electrode materials are obtained through both cationic/anionic redox.[1] Nevertheless, cyclability associated with insufficient reversibility of anionic redox in carbonate-based electrolyte solutions is not acceptable for practical applications.

Recently, highly concentrated electrolyte consisting of $LiN(SO_2F)_2$ (LiFSA) and dimethyl carbonate (DMC) is proposed as efficient electrolyte, which improve the cyclability of high-voltage electrode materials.[2] In this study, concentrated electrolyte was applied for Li-excess electrode materials with anionic redox, and the significant improvement of electrode reversibility is achieved. The origin of improvement is studied by X-ray absorption spectroscopy (XAS). To study changes in electronic structures of nanosized $Li_{1.14-y}Ti_{0.29}Mn_{0.57}O_2$ in conventional electrolyte and concentrated electrolyte, soft XAS spectra were collected at BL-11 (O K-edge and Mn $L_{II,\ III}$-edges) in Synchrotron Radiation Center. Samples for XAS measurements were handled in the Ar-filled glove box after disassembling electrochemical cells, and the electrode samples were transferred to the spectrometer using a laboratory-made transfer vessel without air exposure. Soft XAS study at Mn L-edge XAS spectra reveals that the oxidation state of Mn ions in nanosized $Li_{1.14-y}Ti_{0.29}Mn_{0.57}O_2$ is originally trivalent state, and a clear peak shift, which originates from oxidation of Mn ions into tetravalent state, is observed for both electrolyte solutions. No clear difference is observed for Mn ions after charge regardless of the difference in electrolyte (**Fig. 1**). In contrast, some differences are noted for O K-edge XAS spectra, and larger intensity is observed at 530 eV for the sample charged with concentrated electrolyte with LiFSA/DMC. This peak at 530 eV is a specific feature for the activation of anionic redox.[1] The difference of O K-edge XAS spectra after charge for both electrolyte solutions is indicative of better stability of anionic redox for concentrated electrolyte.



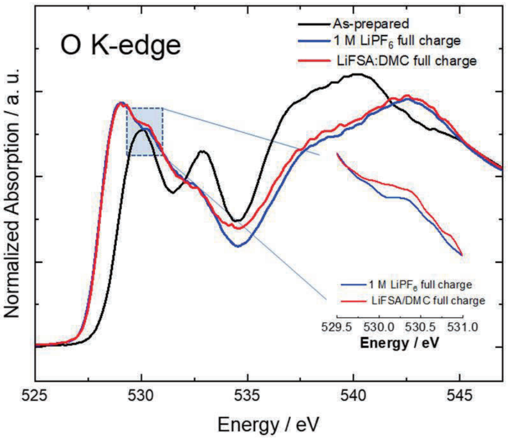


Fig. 1 (top) Mn L-edge XAS and (bottom) O K-edge spectra of $Li_{1.14}Ti_{0.29}Mn_{0.57}O_2$ charged with different electrolyte solutions. The data of as-prepared sample is also shown for comparison.

References

[1] Y. Kobayashi *et al.*, and N. Yabuuchi, *Mater. Today*, **2020**, *37*, 43.

[2] J. Wang *et al.*, and A. Yamada, *Nature Commun.*, **2016**, *7*, 12032.

[3] N. Shimada, Y. Ugata, S. Nishikawa, D. Shibata, T. Ohta, and N. Yabuuchi, *Energy Advances*, in-press, DOI: 10.1039/D3YA00066D.