

Study on Reaction Mechanisms of Manganese-based Li-excess Electrode Materials

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1 Introduction

Lithium-ion batteries, which have the highest gravimetric/volumetric energy density among practical battery technology, are the most important technology for energy storage applications, even though many alternative approaches were proposed. Emerging new chemistry is non-layered materials, *i.e.*, disordered rocksalt system.[1] Herein, cation-/anion-disordered Li-excess manganese oxides with different fluorine contents are tested as the high-capacity electrode materials with abundant manganese ions.

2 Experiment

Li-excess manganese oxides with different fluorine contents were synthesized by high-energy mechanical milling.[2] Although Li_2MnOF_2 only with divalent manganese ions cannot be synthesized, $\text{Li}_2\text{MnO}_2\text{F}$ and $\text{Li}_2\text{MnO}_{1.5}\text{F}_{1.5}$ are successfully synthesized.

Electrochemical properties of the oxides were studied by galvanostatic charge/discharge measurement in two-electrode cells. XAS measurement were conducted, and K-edge spectra of manganese were collected at each charge condition.

3 Results and Discussion

Electrode performance of $\text{Li}_2\text{MnO}_2\text{F}$ and $\text{Li}_2\text{MnO}_{1.5}\text{F}_{1.5}$ is compared in Fig. 1. Better capacity retention and higher energy density (730 mW h g^{-1}) are obtained for $\text{Li}_2\text{MnO}_{1.5}\text{F}_{1.5}$ with 4.4 V cut-off because of the enrichment of fluoride ions and activation of $\text{Mn}^{2+}/\text{Mn}^{4+}$ cationic redox. Moreover, electrode durability is significantly improved for $\text{Li}_2\text{MnO}_{1.5}\text{F}_{1.5}$, and good capacity retention without voltage decay is achieved for >180 cycles.

Electrode reaction mechanisms and reversibility of $\text{Li}_2\text{MnO}_2\text{F}$ and $\text{Li}_2\text{MnO}_{1.5}\text{F}_{1.5}$ were studied by hard XAS study. As shown in Fig. 2, on charge, the energy of XAS spectra shifts to the higher energy region, and the peak top energy at 6557 eV for the as-prepared $\text{Li}_2\text{MnO}_2\text{F}$ shifts to 6560 eV after charge. However, after discharge, an irreversible change is observed, which is indicative of oxygen loss on charge. In contrast, reversible changes on charge/discharge are observed for $\text{Li}_2\text{MnO}_{1.5}\text{F}_{1.5}$ as expected from electrochemical data.

References

[1] N. Yabuuchi, *Current Opinion in Electrochemistry*, **34**, 100978 (2022).

[2] A. Kanno *et al.*, and N. Yabuuchi, *ACS Energy Letters*, **8**, 2753 (2023).

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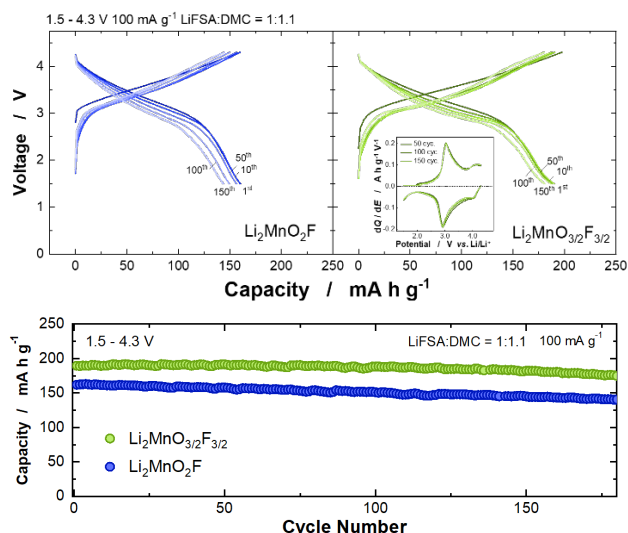


Fig. 1: Electrode reversibility of $\text{Li}_2\text{MnO}_2\text{F}$ and $\text{Li}_2\text{MnO}_{1.5}\text{F}_{1.5}$ with concentrated electrolyte at a rate of 100 mA h g^{-1} with 4.3 V cut-off; charge/discharge curves, and capacity retention.

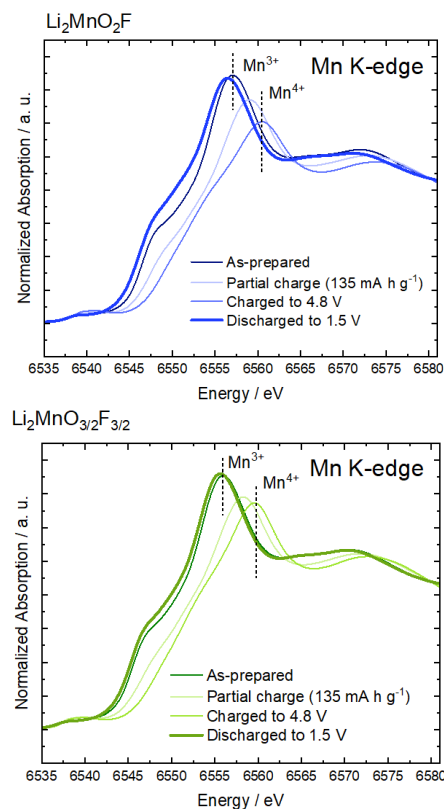


Fig. 2: Changes in Mn K-edge XAS spectra for $\text{Li}_{2-y}\text{MnO}_2\text{F}$ and $\text{Li}_{2-y}\text{MnO}_{1.5}\text{F}_{1.5}$ on electrochemical cycles.