

Soft X-Ray Absorption Spectroscopic Studies of Spinel-Type Lithium Nickel Manganese Oxides for Li Rechargeable Batteries

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Spinel structured $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ has been attracting great attention as a high power cathode material due to its high operating potential (~ 4.7 V vs. Li^+/Li^0) compared with parent LiMn_2O_4 and LiCoO_2 (around 4 V in both cases) [1]. This gain in voltage is attributed to the redox activity of the formal $\text{Ni}^{2+}/\text{Ni}^{4+}$ couple while Mn is an inactive spectator as +4 state [2,3]. The higher voltage of operation makes it a material of interest for the next-generation of high energy and high performance batteries. There are earlier studies describing the electronic and local structure of this compound by x-ray absorption spectroscopy (XAS) [2,4,5]. Most of them focused on the K-edge of the transition metals (Ni and Mn) to observe the oxidation state of metals, their local symmetries, covalent bond strength, etc., thus leading to the elucidation of the charge compensation mechanism. However, by using soft x-ray absorption spectroscopy, more direct information about the electronic structural changes from the metals and oxygen sites can be achievable [6]. Moreover, difference in the electronic structures between bulk and surface can be distinguishable using multiple detectors (TEY vs. FY). In this study, the L-edges of metals and K-edge of O were investigated to establish the charge compensation mechanism during electrochemical cycling.

Spinel structured lithium nickel manganese oxides were synthesized by a coprecipitation method using lithium hydroxide, nickel sulfate, and manganese sulfate [7]. The samples were cycled in Li half cells using 14.7 mA/g ($=C/10$) between 3.5 and 5 V, and then harvested at different charged states in the glove box. Soft XAS measurements were carried out at BL10-1 and BL8-2 at Stanford Synchrotron Radiation Lightsource (SSRL) and 8.0.1 at Lawrence Berkeley National Lab (LBNL). The beam area was less than 1 mm² with the resolution of ~ 0.1 eV. Data were obtained both in total electron yield (TEY) and fluorescence yield (FY) modes at different sample-detector angles to get depth resolved information from the materials.

According to the XAS results (Fig. 1), the charge compensation when cycling between 3.5 and 5 V, is achieved mainly by the oxidation of Ni^{2+} ions, but there is a significant contribution from oxygen ions. Furthermore, subtle differences were observed between TEY and FY data, which indicates that there are substantial differences between the surface and bulk of the electrode materials. A more detailed discussion will be presented.

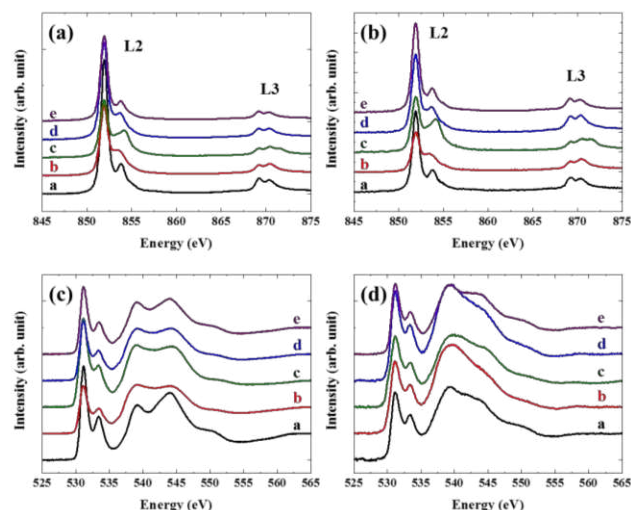


Fig. 1. (a) and (b) TEY and FY of Ni L-edges and (c) and (d) TEY and FY of O K-edge. Labels of a, b, c, d, and e represent pristine, 50% SOC, 100% SOC, 50% DOD, and 100% DOD during the 1 cycle, respectively.

Acknowledgements

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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