Evaluation of the oxidation state of transition metal in function of depth for cathode material with anionic substitution

Eugenio Otal

Shinshu University

キーワード：**EXAFS，Li-batteries.**

1. 背景と研究目的

Materials for Lithium batteries are an active field of research. The anionic substitution to improve the battery performance is a path to improving battery performance. In this proposal, we measured the O and F K edges and the Co, Ni and Mn $L_{2,3}$ edges in $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM) using different detectors (TEY, TFY and AEY) to understand the influence of XeF_2 in function of the depth.

2. 実験内容

The measurements of F-modified NCM were prepared in glove box and transferred without contact to air to the measuring chamber. The O K-edge was measured separated from the rest of the elements. The scan step and time were optimized by a preliminary scan of these two groups of elements.

3. 結果および考察

The spectra of Co and Mn showed no difference among the samples with and without XeF_2 treatment. In the case of Ni, the shape of $L_{2,3}$ was strongly affected by the fluoride treatment. Van Elp et al. reported that that the Ni $L_{2,3}$ edge is very sensitive to both the oxidation state (divalent Ni versus trivalent Ni) and the spin state (low-spin Ni^{2+} versus high-spin Ni^{2+}). Also, the Ni $L_{2,3}$ edge is sensitive to different structural Ni site symmetries. Differences in the main spectral features can be explained with a change in the electronic structure based on the crystal field structure, due to the $L_{2,3}$ edge have as the final state the d-symmetry state. Complementary experiments will disclose the changes in the Ni environment and correlate with electrochemical performance.

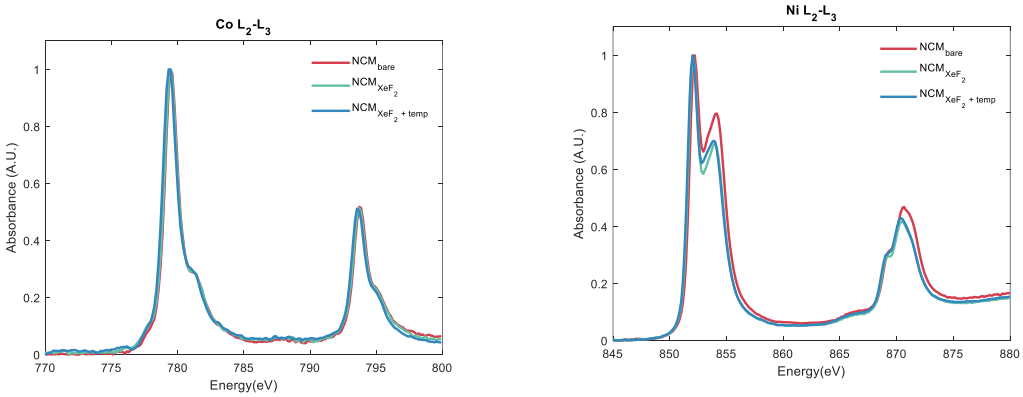

Fig 1 – Left: Co L_2 and L_3 edges in bare samples and with different XeF_2 treatments. Right: Idem Ni L_2 and L_3 edges.

4. 参考文献

1. J. van Elp, G. Peng, B. G. Searle, S. Mitra-Kirtley, Y. H. Huang, M. K. Johnson, Z. H. Zhou, M. W. W. Adams, M. J. Maroney, and S. P. Cramer ”Electronic Structure and Symmetry in Nickel L Edge X-ray Absorption Spectroscopy: Application to a Nickel Protein.” Journal of the American Chemical Society 1994 116 (5), 1918-1923