

# HAXPES Study of Surface Films on $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ Positive Electrode Charged/discharged with Different Voltage Ranges

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To understand and control the electrode/electrolyte interface is a key issue for the development of superior positive electrodes for Li-ion batteries. We have reported that the stability of the electrode/electrolyte interface of layered rock-salt positive electrode materials is strongly affected by the range of voltage change rather than the charge cutoff voltage itself.<sup>1</sup> In this study, we have investigated the influence of the voltage range for the surface film of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (NCM) electrode by using hard x-ray photoelectron spectrometry (HAXPES).

Positive electrodes were fabricated from a mixture of NCM powder, acetylene black, and PVDF. The electrochemical characteristics of the samples were examined by coin cells with a Li-metal counter electrode. A 1M solution of  $\text{LiPF}_6$  in EC + DEC was used as the electrolyte. The cells were cycled at 2.5–4.6 and 4.2–4.6 V at 1 C. The Li-ion transfer characteristics were measured at the electrode potential of 4.2 V by using AC impedance spectroscopy. The electronic structures of the NCM in the surface films were investigated by HAXPES (Ag  $L\alpha$ , 2.984 keV). The energy resolution of the monochromatized Ag  $L\alpha$  X-ray source was 0.7 eV.

Figure 1 shows charge transfer resistance ( $R_{ct}$ ) versus cycle number of the cells. The increase in  $R_{ct}$  during the cycle tests was significantly suppressed in the range of 4.2–4.6 V compared to that of 2.5–4.6 V. Figure 2 shows P 1s HAXPES spectra of the positive electrode charged to 4.6 V after 12 cycles of 2.5–4.6 V and 4.2–4.6 V. The chemical states of the surface films varied in the voltage range during the cycle-test even at the same charge voltage. The change of the electronic structures in the surface films during the charge/discharge and the degradation mechanism of the electrode/electrolyte interface will be discussed.

## Acknowledgement

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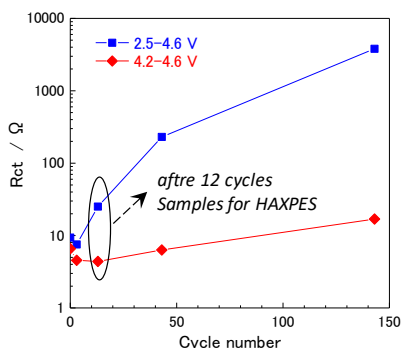


Fig. 1.  $R_{ct}$  vs. cycle number

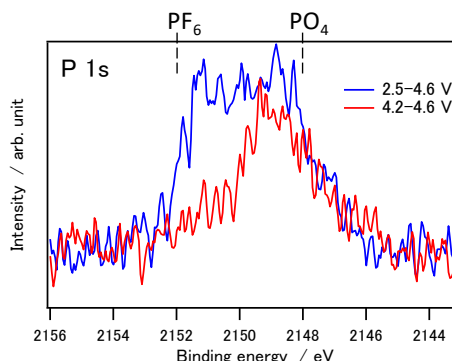


Fig. 2. P 1s HAXPES spectra of NCM charged to 4.6 V.

## References:

[1] A. Yano, M. Shikano, H. Kanzaki, K. Yamanaka, H. Kageyama, T. Ohta, J. Electrochem. Soc., **164** (2017) A3848-A3857.