Charge Compensation and Oxidation in $Na_xCoO_{2-\delta}$ and $Li_xCoO_{2-\delta}$ Studied by XANES

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Layered alkali-metal cobalt oxides, $A_xCoO_{2-\delta}$ (A = Na, Li; $0 \le x \le 1$; $0 \le \delta \le 0.3$), have been extensively studied since the 1950s. In particular,Li_xCoO_2 has attracted attention as an effective cathode material, Na_xCoO_2 as an excellent thermoelectrics, and $Na_xCoO_2 \cdot y\ H_2O$ ($x \approx 0.35$, $y \approx 1.3$) as a superconductor which contains water molecules. After successful preparation of $CoO_{2-\delta}$, i.e. $x = 0$, by electrochemical or chemical deintercalation methods, there has been significant interest in obtaining more information on the electronic structure and properties of the $A_xCoO_{2-\delta}$ system over the whole range of x. Hence, it is interesting to learn the extenet (if any) to which the alkali metal influences the Co^{III}–Co^{IV} balance. Since XAS probes the unoccupied part of the electronic structure and thus gives information on the electronic states of Co and O in $A_xCoO_{2-\delta}$, it is a useful tool in order to study the aforementioned questions. We collected O 1s and Co 2p X-ray absorption spectra for $A_xCoO_{2-\delta}$ (A = Na, Li) samples, and analyzed them in the X-ray absorption near edge structure (XANES) region as a function of alkali metal content, x = 0.75, 0.47, 0.36, 0.12 for A = Na and 1, 0.49, 0.05 for A = Li).

The XAS measurements were performed on BL20A high-energy spherical grating monochromator beamline at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The spectra were recorded in X-ray fluorescence-yield (If) mode for O 1s absorption, and electron-yield (Ie) mode for Co 2p absorption.

Pre-edge regions for the both series are shown in Fig. 1. To numerically evaluate the changes in the spectral weight, plot of O 1s pre-edge peak centroid energy vs. alkali metal content for $Na_xCoO_{2-\delta}$and $Li_xCoO_{2-\delta}$ samples is shown in Fig. 2. The centroid energy for $Na_xCoO_{2-\delta}$ samples remains almost constant for all values of x, whereas there is a clear shift for the $Li_xCoO_{2-\delta}$ samples. Thus, based on both the pre-edge (onset) position and the spectral weight, O 1s XANES indicates that valance of cobalt increases in $Li_xCoO_{2-\delta}$ but not significantly in $Na_xCoO_{2-\delta}$ samples, as x decreases. Moreover, in the case of $Li_xCoO_{2-\delta}$, there is a small decrease in the slope below x = 0.49, which indicates less increase in V(Co).

Plots of centroid energy vs. alkali metal content for $Na_xCoO_{2-\delta}$ and $Li_xCoO_{2-\delta}$ samples are shown in Fig. 3. In the case of Co $2p_{1/2}$ edge (upper part) the plot agrees very well with the above discussion on peak positions. The data points from the Co $2p_{3/2}$-edge, although more spread, do also show increasing separation between the centroid energies for A = Na and A = Li series, as x decreases. Moreover, in the case of A = Li, there is a small decrease in the slope below x = 0.49, which indicates less increase for V(Co). Thus, like the O 1s XANES, Co 2p XANES results also indicate that upon decreasing x, cobalt valence continues to increase in the Li series but not in the Na-series.

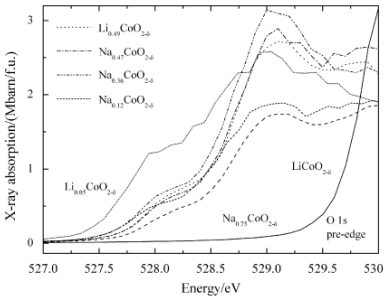

Figure 1. A detail of the O 1s XANES pre-edge region for the $A_xCoO_{2-\delta}$ (A = Na, Li) series.

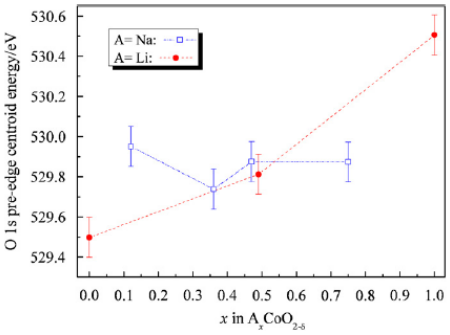

Figure 2. O 1s XANES pre-edge energy vs. x in $A_xCoO_{2-\delta}$ using centroid and first derivative to determine the positions.

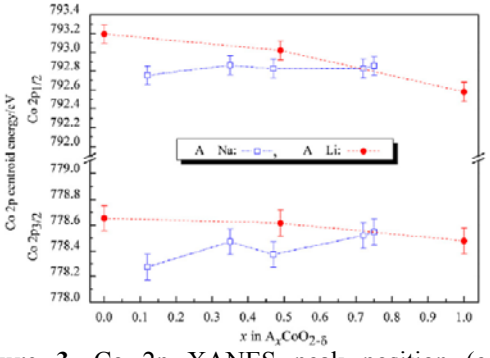

Figure 3. Co 2p XANES peak position (centroid's abscissa) vs. x in $A_xCoO_{2-\delta}$.