Reply to Comment on "Characterization of Sodium Cobalt Oxides Related to P3-Phase Superconductor"

The first comment made by Liu is that the oxidation state of Co may be unchanged upon hydration. The comment is based on an XAF study referred in the comment. However, XAF is not as sensitive as chemical analyses including redox titration that we used in our study.

Change in Co K-edge XANES spectra, for example, have been often investigated for $LiCoO_2$. The Co oxidation state increases with lithium deintercalation, that is, increasing x in $Li_{1-x}CoO_2$. However, the XANES spectra remained unchanged in $0 \leq x \leq 0.13$ and $0.65 \leq x \leq 0.9$.[1] That is, changing the oxidation state does not always change the XANES spectra.

Also in the article cited in the comment, the difference of the peak positions between $Na_{0.3}CoO_2$ and $Na_{0.74}CoO_2$ is very small, as shown in the inset of Figure 4; that is, the change of the Co oxidation state by 0.44 was hardly observed from the XANES spectra. From our redox titration, the Co oxidation state decreased from $+3.58$ to $+3.48$ during the hydration, and it is natural that the change only by 0.1 was not detected in the XAF.

Accordingly, although the XAF spectra in the reference did not show significant change upon the hydration, it cannot be concluded that the oxidation state was not changed. In addition, it should be noted that a similar low oxidation state of Co in a hydrous phase was also reported in the work by Kappinen et al.,[2] which was determined by cerimetric and iodometric titration; thus, there is little doubt that the oxidation state of Co is lower in the hydrous phase than in the anhydrous one.

Liu's second comment is that the amount of H_3O^+ in water is too small to reach the final composition of the superconducting material that we reported. When the anhydrous phase was immersed in water, it oxidized the water because of the high redox potential of Co in the anhydrous phase. It evolves oxygen gas and increase the H_3O^+ concentration as the counter reaction. Therefore, it is not strange that the amount of the inserted H_3O^+ exceeded that in neutral water.

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(1) Nakai, I.; Takahashi, K.; Shraishi, Y.; Nakagome, T.; Izumi, F.; Ishii, Y.; Nishikawa, F.; Konishi, T. *J. Power Sources* **1997**, *68*, 536−539.

(2) Kappinen, M.; Asako, I.; Motohashi, T.; Yamauchi, H. *Chem. Mater.* **2004**, *16*, 1693−1696.

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